FLASH PHOTOLYSIS OF THE OXIDES OF CHLORINE

by

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ABSTRACT

The production of vibrationally excited oxygen, O_2^*, following the isothermal flash photolysis of ClO_2, Cl_2O and of the ClO free radical has shown to be due to the reactions of oxygen atom with ClO_2 and ClO (1, 2). In both reactions, the energy distribution in the products is markedly non-equilibrated with a large fraction of the energy liberated in the form of vibrational excitation of the oxygen molecule. The highest level of O_2^* produced corresponds to the exothermicity of the reactions. The rate constants for the production of O_2^* in levels v'' = 6 → v'' = 13 are approximately equal. The relaxation of O_2^* by ClO_2, ClO and by Cl and O atoms has been studied and the exceptional efficiency of the atoms demonstrated.

The rate constant for the bimolecular reaction of ClO radicals (10) was measured using ClO_2, Cl_2/O_2, Cl_2O, Cl_2O/Cl_2 as sources of the radicals. The constancy of the value of $2.7 \pm 0.3 \times 10^7$ l mole^{-1} sec^{-1} obtained from all systems contrasts with the literature values of 6.2×10^7 l mole^{-1} sec^{-1}, 4.8×10^7 l mole^{-1} sec^{-1} and 2.4×10^7 l mole^{-1} sec^{-1}, obtained from the first three systems.

The chlorine and bromine photosensitised decomposition of ClO_2 and Cl_2O have been studied and the extinction coefficient of ClO and BrO free radicals measured. Mechanisms have

been proposed for all systems and all relevant rate constants have been measured. The results are listed below.

	Reaction	$k(1\ mole^{-1}\ sec^{-1})$
1.	$O + ClO_2 \rightarrow ClO + O_2^*(v'' \leq 15)$	3.0×10^{10}
2.	$O + ClO \rightarrow Cl + O_2^*(v'' \leq 14)$	7.0×10^{9}
3.	$O + Cl_2O \rightarrow 2ClO$	5.2×10^{9}
4.	$O + Cl_2O \rightarrow Cl_2 + O_2$	$<<5.2 \times 10^{9}$
5.	$Cl + Cl_2O \rightarrow ClO + Cl_2$	4.0×10^{8}
6.	$Cl + ClO_2 \rightarrow 2ClO$	5.1×10^{9}
7.	$Cl + ClO_2 \rightarrow Cl_2 + O_2$	$<<5.1 \times 10^{9}$
8.	$Br + ClO_2 \rightarrow BrO + ClO$	7.2×10^{9}
9.	$Br + Cl_2O \rightarrow BrCl + ClO$	6.1×10^{8}
10.	$ClO + Cl_2O \rightarrow ClO_2 + Cl_2$	2.7×10^{5}
11.	$ClO + Cl_2O \rightarrow Cl + O_2 + Cl_2$	6.5×10^{5}
12.	$ClO + ClO \rightarrow Cl_2 + O_2$	2.7×10^{7}
13.	$ClO + BrO \rightarrow BrCl + O_2$	1.5×10^{9}
14.	$BrO + BrO \rightarrow Br_2 + O_2$	1.3×10^{9}
15.	$O + O_2^*(v''=12) \rightarrow O + O_2^*(v''<12)$	2×10^{10}
16.	$O + O_2^*(v''=6) \rightarrow O + O_2^*(v''<6)$	9×10^{9}
17.	$Cl + O_2^*(v''=12) \rightarrow Cl + O_2^*(v''<12)$	7×10^{9}
18.	$Cl + O_2^*(v''=6) \rightarrow Cl + O_2^*(v''<6)$	2×10^{9}
19.	$ClO(ClO_2) + O_2^*(v''=12) \rightarrow ClO(ClO_2) + O_2^*(v''<12)$	2×10^{8}
20.	$ClO(ClO_2) + O_2^*(v''=6) \rightarrow ClO(ClO_2) + O_2^*(v''<6)$	8×10^{7}
21.	Extinction coefficient of ClO(2772 Å)	$1.7 \times 10^{3} l\ mole^{-1} cm^{-1}$
22.	Extinction coefficient of BrO(3208 Å)	$2.4 \times 10^{3} l\ mole^{-1} cm^{-1}$

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CHAPTER I

INTRODUCTION

Flash photolysis is a technique of photochemistry in which free radicals or other transients can be produced by a high intensity light source. The concentrations of the species produced is so high that they can be detected in the far infra-red to vacuum ultra violet by absorption spectroscopy. Also at these concentrations in addition to reactions of atoms or radicals with stable molecules, radical-radical reactions or atomic recombination reactions become more important. Thus if spectroscopic methods are used to study their kinetic behaviour after flash photolysis, the technique is known as kinetic spectroscopy. Detailed reviews of the technique of flash photolysis and kinetic spectroscopy and their application to the study of these fast reactions are given by Porter[1,2,3], Norrish[4,5,6], Norrish and Thrush[7] and Thrush.[3] This technique has been used to study energy transfer reactions and this aspect has been reviewed by Callear.[3,8] Above all, the electronic spectra of many new transients have been observed and information about their geometric structure has been obtained from the rotational fine structure studied under high resolution.

A. Reactions of ClO Radical

Since the late twenties, the ClO radical has been proposed as an intermediate in reactions involving chlorine and oxygen, especially in chlorine sensitised oxidation and in the

photolysis of oxides of chlorine. Many papers and review articles have been published about the reactions of ClO radicals studied by flash photolysis and other techniques. The main sources of production of ClO are:

1) Chlorine sensitised oxidation and flash photolysis of chlorine and oxygen.

2) Chlorine sensitised decomposition of ozone.

3) Photolysis and flash photolysis of chlorine dioxide and chlorine monoxide.

Each method will be mentioned but (3) will be discussed in detail because these two systems have been studied extensively, both by the direct photolysis as well as sensitised by halogens (i.e. chlorine and bromine).

1) In 1929, Bodenstein, Lenher and Wagner suggested ClO as a chain carrier in the chlorine sensitised oxidation of carbon monoxide (i.e.):

$$Cl_2 \rightarrow 2Cl$$
$$Cl + CO \rightarrow COCl$$
$$COCl + O_2 \rightarrow CO_2 + ClO$$
$$ClO + CO \rightarrow CO_2 + Cl$$

Though the reaction has not been studied in great detail it becomes difficult to explain the oxidation without having ClO as an intermediate. Similarly, there are other examples, e.g. conversion of chloroform to carbonyl chloride, studied by Schumacher and Wolf, and other examples which have been reviewed by

Edgecombe, Norrish and Thrush.[9]

2) The reaction of chlorine atoms with ozone has been studied thermally as well as photochemically. Bodenstein, Padelt and Schumacher[10] studied the thermal reaction of chlorine atoms with ozone and proposed the following mechanism.

$$Cl_2 + O_3 \rightarrow ClO + ClO_2$$

$$ClO_2 + O_3 \rightarrow ClO_3 + O_2$$

$$ClO_3 + O_3 \rightarrow ClO_2 + 2O_2$$

$$ClO_3 + ClO_3 \rightarrow Cl_2 + 3O_2$$

$$ClO + ClO \rightarrow Cl_2 + O_2$$

$$ClO + O_3 \rightarrow Cl + 2O_2$$

They thought ClO_3 was a chain carrier and neglected the reaction of ClO with ozone, thinking that it has a high activation energy. Later on Norrish and Neville[11] studied the photosensitised decomposition of O_3 by chlorine atoms and postulated the following mechanism.

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O_3 \rightarrow Cl + 2O_2$$

$$ClO + ClO \rightarrow Cl_2 + O_2$$

$$Cl + O_3 + Cl_2 \rightarrow ClO_3 + Cl_2$$

$$Cl + O_3 + O_2 \rightarrow ClO_3 + O_2$$

Though this reaction is photosensitised, it can be compared with the above mentioned scheme. The main difference between the two is that Bodenstein et al.[10] thought ClO_3 was the chain carrier whereas Norrish et al.[11] thought it to be ClO. The latter scheme seems to be more appropriate and more in keeping with the reactivity of ClO radical observed later on in the flash work.

This radical has been further observed spectroscopically when McGrath and Norrish[12,13] flashed halogens in the presence of ozone. They observed both ClO and BrO vibrationally excited:

$$X_2 + h\nu \rightarrow 2X$$

$$X + O_3 \rightarrow XO^* + O_2$$

where X = chlorine and bromine and XO* is the ground state vibrationally excited. This reaction gave an additional weight to their postulate that most of the exothermicity of the reactions of type

$$A + BCD \rightarrow AB + CD$$

goes to the newly formed bond in the form of vibrational energy.

3) Chlorine and Oxygen System

Porter[1] was the first to observe the absorption spectrum of ClO when he flashed a mixture of $Cl_2/O_2/H_2$. Later he did the vibrational analysis.[14] Durie and Ramsay[16] did a more detailed vibrational analysis and studied the rotational struc-

ture. Porter and Wright[15] studied the kinetics of the formation and decay of ClO by flashing Cl_2/O_2 and also in the presence of excess of inert gas (N_2). They found that the system is completely reversible, i.e. Cl_2 and O_2 are the end products, and they could not detect any other oxide of chlorine. In order to study the formation of ClO, they varied the pressure of oxygen and found that chlorine atoms combine 46 times faster in the presence of oxygen than in the presence of nitrogen. They concluded that ClO is formed by the reaction

$$Cl + O_2 \rightarrow Cl\text{-}O\text{-}O \qquad (1)$$

$$Cl\text{-}O\text{-}O + Cl \rightarrow 2ClO \qquad (2)$$

where Cl-O-O was thought to be an unstable transitory intermediate and is quite different from the stable O-Cl-O molecule. ClO is not formed directly in the reaction

$$Cl + O_2 \rightarrow ClO + O \qquad (3)$$

as it is 55 Kcal endothermic. Later on this radical (Cl-O-O) was proposed by Benson and Anderson[17] in their study of trapping of chlorine oxide free radicals. Morris and Johnston[18] have found the absorption spectrum of ClOOin far U.V. by their molecular modulation technique.

Porter and Wright[15] could not determine the rate constant of reaction (1) due to the limitation of the long life time of their flash lamp but recently, Norrish and Nicholas[19] have found that

$$Cl + O_2 + M \rightarrow Cl\text{-}O\text{-}O + M \qquad (1)$$

$$Cl\text{-}O\text{-}O + Cl \rightarrow 2ClO \qquad (2)$$

$$Cl\text{-}O\text{-}O + Cl \rightarrow Cl_2 + O_2 \qquad (4)$$

$k_1 = 6.2 \pm 1.1 \times 10^8$ mole^{-2} l^2 sec^{-1} and $k_4/k_2 \sim 15$ or 7.7 depending on the extinction coefficient of ClO.

The decay of ClO was found to be unaffected by the presence of chlorine, oxygen, nitrogen or carbon dioxide and to be independent of temperature in the range 293 to 433°K. They could not measure the absolute rate constant of the reaction

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (5)$$

since the extinction coefficient of ClO was not known and they could not measure it from the decrease in the chlorine concentration. They found the rate constant in terms of k_5/ε equal to 7.2×10^4 cm sec^{-1} (where ε is the extinction coefficient of ClO at 2577 Å). Thus the value of 4.8×10^7 or 7.6×10^7 l mole^{-1} sec^{-1} could be assigned to k_5 depending upon the extinction efficient.

4) ClO_2 System

More information about the kinetics was found by Lipscomb, Norrish and Thrush[20,21] in the flash photolysis of ClO_2. ClO was the major product of the photolysis at high flash energy. They found that a second order plot of the decay of ClO gives a straight line at all the flash energies used. The

slope increased with increase of flash energy but the intercept was constant. The lower limit calculated for k_5 was 1.9×10^7 l mole^{-1} sec^{-1} at flash energy 240 J and highest 6.2×10^7 l mole^{-1} sec^{-1} for flash energy greater than 1600 J.

Similar behaviour was observed in the determination of the extinction coefficient. This was obtained by the assumption that each molecule of ClO_2 decomposed will give one molecule of ClO. The absorbance of ClO was calculated by extrapolation of the second order plot of ClO. At low flash energy a correction was applied to the ClO_2 decomposed due to the appearance of ClO_3 spectrum. The extinction coefficient at 2577 Å varied from 1.4 to 0.68×10^3 l mole^{-1} cm^{-1} at flash energy 240 to 1600 J respectively. In all their quantitative measurements a soda glass filter was used in order to avoid direct photolysis of ClO.

5) Cl_2O System

Edgecombe, Norrish and Thrush[9,22] carried out the study of ClO further by flashing Cl_2O. Since the continuous spectrum of Cl_2O extends over the whole range of ClO bands, they carried out measurements at 2920 Å (7,0) for ClO and 2912 Å for Cl_2O measurements. Though ClO does take part in the chain propagation of Cl_2O decomposition, these processes are slow as compared to bimolecular decay of ClO. They obtained a value of k_5 of $(2.4 \pm 0.4) \times 10^7$ l mole^{-1} sec^{-1} and were satisfied on finding that their value lay within the range of that found

by Lipscomb et al.[21] Although their values of ε and k_5/ε are not given explicitly, from fig. (2) of their paper, the slope can be calculated to be 4.9×10^4 cm sec^{-1} and thus the extinction coefficient ε_{2920} was calculated as 490 l $mole^{-1}$ cm^{-1}. Clyne and Coxan[23] have found k_5/ε from their plot as 3.1×10^4 cm sec^{-1} at 2577 Å, by means of known relative extinction coefficients at 2577 Å, 2824 Å and 2920 Å and thus 760 l $mole^{-1}$ cm^{-1} could be assigned to the extinction coefficient at 2577 Å. However, no direct correlation was drawn because of the different systems and different wavelengths used.

6) Flow System

Information regarding the reactions and kinetics of ClO was given by Clyne and Coxan[23,24,25] from their study in a flow system. The ClO radicals were generated by the reaction of chlorine atoms with chlorine dioxide. They calculated the extinction coefficient of ClO either by titration with oxygen atoms or with nitric oxide. The value of $1.9 \pm .06 \times 10^3$ l $mole^{-1}$ cm^{-1} was given to the extinction coefficient at 2772 Å, or $1.27 \pm 0.04 \times 10^3$ l $mole^{-1}$ cm^{-1} at 2577 Å, and thus agrees with the upper limit calculated by Lipscomb and others.[21] The lower values obtained at high energies were explained by Clyne and Coxan[23] to be caused by the reaction

$$O + ClO \rightarrow O_2 + Cl \qquad (6)$$

k_6 has been calculated by Clyne and Coxan[23] and the lower limit found to be 6×10^9 l $mole^{-1}$ sec^{-1}, where k_7/k_6 was found to be ~ 4.

$$O + ClO_2 \rightarrow ClO + O_2 \qquad (7)$$

The bimolecular decay of ClO was plotted by them and k_5 found to be $1.4 \pm .1 \times 10^7$ l mole^{-1}sec^{-1} which agrees with the lower limit of Lipscomb et al.[21]

Two types of mechanisms are proposed for the ClO decay:

1) Porter and Wright,[15] Lipscomb et al.[21] and Edgecombe et al.[22] have proposed a molecular mechanism for the observed second order decay of ClO radicals which can be summarized by the reactions

$$ClO + ClO(+M) \rightarrow Cl_2O_2(+M)$$

$$Cl_2O_2(+M) \rightarrow Cl_2 + O_2(+M)$$

2) Benson and Buss[26] have alternatively proposed for this reaction a free radical reaction involving a chlorine atom and the short lived ClOO, peroxy radical, i.e.,

$$ClO + ClO \rightarrow Cl\text{-}O\text{-}O + Cl$$

$$Cl\text{-}O\text{-}O + Cl \rightarrow Cl_2 + O_2$$

$$Cl\text{-}O\text{-}O + M \rightarrow Cl + O_2 + M$$

They pointed out that slow decay of ClO observed by Lipscomb et al.[21] at low flash energy can be explained with this mechanism by including reaction (8)

$$Cl + ClO_2 \rightarrow 2ClO \qquad (8)$$

They also made it clear that, since the rapid reaction

$$Cl + ClOO \rightarrow ClO + ClO$$

is evidently responsible for ClO formation in the flash photolysis of chlorine/oxygen mixture (Burns and Norrish,[27] Norrish and Nicholas[19]) the nearly thermoneutral reverse reaction might be possible to be the rate determining step for ClO removal. They also explained the results of the chlorine sensitised decomposition of nitrous oxide (Kaufman et al.[28]) by a similar mechanism.

Clyne and Coxon[25] have considered both mechanisms but preferred the second, proposed by Benson and Buss.[26] They put forward following evidence:

1) They detected the red chlorine afterglow spectrum (Bader and Ogryzlo,[29] Clyne and Coxon[45]) though it is relatively red shifted.

2) They found a decrease in the chlorine dioxide concentration during the Clo decay. The ClO concentration does remain constant in the presence of chlorine dioxide and follows second order decay kinetics after the chlorine dioxide is used up.

3) Complete replacement of the chlorine afterglow spectrum by a deeper red emission occurred when bromine was added during the ClO decay. The latter spectrum is due to the emission of BrCl ($^3\pi_o^+$).[45]

4) The rate of decay of ClO increased when H_2 was added to the system.

All these results could only be explained if chlorine atoms are present in the system during the ClO decay as explained by Clyne and Coxon[25] and also the reaction of chlorine atoms with chlorine dioxide[25] ($>5 \times 10^8$ l mole^{-1} sec^{-1}) and with molecular bromine[32] are very fast.

B. Photolysis of Chlorine Dioxide

1) Chlorine Dioxide System

The decomposition of chlorine dioxide has been studied both thermally and photochemically, which includes flash and

steady state. Schumacher and Steiger,[33] from their study of thermal decomposition suggested that decomposition is a small chain process and the primary step is

$$ClO_2 \rightarrow ClO + O$$

The steady state photolysis has been studied by a number of workers in the gas phase,[33,34] and in solution[35] using CCl_4 as a solvent. All of them have stressed the formation of higher oxides of chlorine, e.g. chlorine trioxide and chlorine hexaoxide, although the primary step is the same. The first spectroscopic evidence was found by Goodeve and Stein[36] in their study of the chlorine dioxide spectrum. They observed predissociation in the band spectrum of chlorine dioxide, corresponding to dissociation into

$$ClO_2 + h\nu \rightarrow ClO + O$$

thus giving the lower limit of 45 Kcal per mole for the dissociation energy of ClO, although recently it was found to be 63 Kcal/mole, calculated from the absorption spectrum of ClO.[14,16]

In 1931, Finkelberg and Schumacher,[37] in their investigation of spectrum and photochemical decomposition of chlorine dioxide observed that the process

$$ClO_2 + h\nu \rightarrow ClO + O(^3P)$$

occurred by predissociation at wavelengths shorter than 3753 Å. They also suggested that the wavelength approaching the band

convergence (2560 Å) would decompose the chlorine dioxide molecule by the reaction

$$ClO_2 + h\nu \rightarrow ClO + O(^1D)$$

Spinks and Porter[38] carried out the photolysis studies further both dry and in the presence of water. The results obtained by steady state photolysis can be summed up as

$$ClO_2 + h\nu \rightarrow ClO + O$$
$$ClO_2 + O + M \rightarrow ClO_3 + M$$
$$ClO + ClO_2 \rightarrow Cl_2O_3$$
$$ClO + ClO \rightarrow Cl_2 + O_2$$
$$2ClO_3 \rightarrow Cl_2O_6$$

and

$$H_2O + Cl_2O_6 \rightarrow HClO_3 + HClO_4$$
$$2Cl_2O_3 + 2H_2O \rightarrow 2HClO_2 + HClO + HClO_3$$

Though the ClO radical has been predicted and some of the reactions have been discussed, a greater role has been played by the higher oxides of chlorine.

The flash photolysis of chlorine dioxide was carried out by Lipscomb et al.[21] They found that the major product of the photolysis is ClO. They also observed the spectrum of ClO_3 whose production was found to be independent of total pressure for a fixed pressure of chlorine dioxide. The intensity of ClO_3 spectrum increased with the decrease of flash energy and absorption was measured by using Goodeve and

Richardson's data.[39] However, the maximum amount of ClO_3 produced in their work was not more than 10%, calculated from Table 1 of their paper, if 0.5 torr of chlorine dioxide is accepted as the initial concentration. This is quite different from the steady state work where ClO_3 is the major product. They explained this difference in terms of following competing reactions

$$O + ClO_2 \rightarrow ClO_3 \qquad (9)$$

$$O + ClO \rightarrow ClO_2 \qquad (10)$$

$$O + O + M \rightarrow O_2 + M \qquad (11)$$

Since the ratio of the concentration of atomic oxygen plus ClO to the ClO_2 is many times greater in the flash experiments, the probability of reaction (9) relative to (10) and (11) will correspondingly be reduced. Though this explanation is reasonable, the reactions (6) and (7) seem more likely than reaction (9).

Lipscomb et al.[21] also observed the reappearance of ClO_2 spectrum which they explained by the following type of equilibrium

$$ClO_2 + ClO \rightleftharpoons Cl_2O_3$$

Thus as the ClO concentration decreases the equilibrium shifts to the left and ClO_2 spectrum starts appearing. No spectroscopic evidence for this compound has been given but recently Mchale and Elbe[40,41] have established the existence of this compound from their study of ClO_2.

2) Halogen Photosensitised Decomposition of ClO_2

The chlorine photosensitised decomposition of ClO_2 has not been studied in a steady state system. The main trouble in chlorine sensitisation is that the spectrum of chlorine also lies in the same region where the dissociative spectrum of ClO_2 exists. So it becomes difficult to decompose chlorine alone without decomposing ClO_2. However in a flow system, reaction of chlorine atoms (generated by means of r.f. discharge) with ClO_2 was used as a source of ClO radicals. Clyne and Coxon[25] have found the rate constant of this reaction to be greater than 5×10^8 l mole^{-1} sec^{-1} and the stoichiometry of the reaction

$$Cl + ClO_2 \rightarrow 2ClO \qquad (8)$$

to be 1.9 ± 0.1 as compared to the reaction

$$Cl + ClO_2 \rightarrow Cl_2 + O_2 \qquad (12)$$

which is more exothermic than the reaction (8).

The photosensitised decomposition of ClO_2 by bromine in principle is more easily studied than that sensitised by chlorine. The spectrum of bromine lies much above the predissociation limit of ClO_2 so that bromine atoms can be generated without decomposing ClO_2. Schumacher[42] first proposed the mechanism of its decomposition as

$$Br_2 + h\nu \rightarrow 2Br \qquad (13)$$

$$Br + ClO_2 \rightarrow BrCl + O_2 \qquad (14)$$

$$2BrCl \rightarrow Br_2 + Cl_2 \qquad (15)$$

Spinks and Porter[38] studied the same reaction using 5460 Å radiation and suggested that the excited bromine molecules are responsible for the activation of ClO_2 molecules on collision and thus the reaction is started. But later they[43] also found that the quantum yield and the course of the reaction is similar at 3650 Å and 5460 Å, indicating that reaction at 5460 Å probably also proceeds by means of bromine atoms and not by means of an excited molecule. Further, the quantum yield for the sensitised and unsensitised reaction is equal, indicating that, apart from the primary act of light absorption, the mechanism of the two reactions is similar. Since Schumacher's[42] mechanism could not explain the formation of ClO_3 and higher oxides of chlorine, they postulated a new mechanism:

$$Br_2 + h\nu \rightarrow 2\ Br \qquad (13)$$

$$Br + ClO_2 \rightarrow ClO + BrO \qquad (16)$$

$$BrO + ClO_2 \rightarrow ClO_3 + Br \qquad (17)$$

which would give the same products as the direct photochemical reaction.

Clyne and Coxon[44,45] also studied the reaction of bromine atoms with ClO_2 in order to correlate it with the reaction of chlorine atoms with ClO_2. They could not observe the BrO and ClO spectrum, however, instead of these radicals, they observed the emission spectrum of $BrCl(^3\pi_o^+ \leftarrow {}^1\Sigma_g^+)$ which was very similar to that obtained by the direct recombination of bromine and

chlorine atoms:

$$Br + Cl + M \rightarrow BrCl\ (^3\pi_o^+) + M$$

They thus concluded that reaction (14) occurred. Reaction (16) was rejected on the grounds that it is endothermic by 3 Kcal and they did not observe ClO or BrO. Reaction (14) is sufficiently exothermic to account for their results.

Recently,[25] in their reinvestigation of the above reaction, they could identify ClO but could not detect BrO. Since they found that rate of decay of BrO is nearly 50 times faster than ClO, this may be the reason that they could not see the BrO spectrum, so they are still doubtful about the occurrence of reaction (16).

C. Photochemical Decomposition of Cl_2O

Like ClO_2, Cl_2O has also been studied extensively by steady state and flash photolysis. Earlier workers like Bowen[46] and Bodenstein and Kistiakowsky[47] found that decomposition was proportional to the light absorbed and the observed quantum yield was two. The reaction was not affected by the air or oxygen and chlorine dioxide was shown spectroscopically to be present in increasing amounts as the reaction proceeded. However, Bodenstein and Kistiakowsky[47] and Goodeve and Wallace[48] showed that the absorption spectrum of Cl_2O was continuous between 6200 Å and 2300 Å. Thus in order to explain the yield

of two, Schumacher and Wagner[49] suggested the following reaction mechanism.

$$Cl_2O + h\nu \rightarrow ClO + Cl \quad (18)$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \quad (19)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (20)$$

It was not until 1932 when Finkelberg, Schumacher and Steiger,[50] in their reinvestigation of gaseous reaction of Cl_2O, found that the quantum yield of the photochemical decomposition is 3.5 at wavelengths 4360, 3650 and 3130 Å. ClO_2 and higher unknown oxides were shown to be present. Subsequently Schumacher and Towned[51] studied this system in the region where Cl_2O decomposes into atoms and found that quantum yield at 2500 Å was 4.5. In order to explain the higher quantum yield and the formation of ClO_2, the following reactions were suggested, apart from those mentioned above:

$$ClO + Cl_2O \rightarrow ClO_2 + Cl_2 \quad (20)$$

$$ClO + Cl_2O \rightarrow Cl + O_2 + Cl_2 \quad (21)$$

whereas at 2500 Å the primary process was

$$Cl_2O + h\nu \rightarrow 2Cl + O \quad (22)$$

Schumacher and Towned[51] proposed that oxygen atoms do not react with Cl_2O in order to explain their quantum yield.

The thermal decomposition of Cl_2O has been studied by Hinshelwood and Prichard,[52] Hinshelwood and Hughes.[53] They found that apart from the primary process, the mechanism of

the photo and thermal reactions are very similar.

Edgecombe, Norrish and Thrush[22] investigated the photolysis of Cl_2O by the flash technique. They observed a similar behaviour to that observed by the earlier workers in the steady state. However, they pointed out that reaction of oxygen atoms with Cl_2O is quite important, which is analogous to the reaction (7), i.e.

$$O + ClO_2 \rightarrow ClO + O_2 \qquad (7)$$
$$O + Cl_2O \rightarrow 2ClO$$

They divided their study into three parts. The first, lasting for 100 μsec, corresponds to the duration of photolytic flash. During this period, Cl_2O concentration drops sharply and ClO reaches its maximum concentration. In the next 10 msec, the second stage of the reaction, ClO decays very slowly. ClO_2 starts appearing approximately at 1 msec, reaches its maximum value in about 30 sec, after that decreases slowly. This is the third stage of the reaction.

2) Halogen Sensitised Decomposition of Cl_2O

Although the continuum spectrum of Cl_2O extends from 2300 Å to 6200 Å,[48] the extinction coefficient falls so rapidly that the decomposition due the wavelengths above 3300 Å is negligible. The chlorine sensitised reaction could, therefore, be studied. In the steady state photolysis, the earlier workers found that the quantum yield of Cl_2O decomposition with and without the chlorine were the same, i.e. two. Later on,

in the flash photolysis, the course of reaction was found to be similar to that without the chlorine and also similar to that discussed by Finkelnberg et al.[50] So the primary step can be

$$Cl_2 + h\nu \rightarrow 2Cl$$

followed by reactions (19), (20), (21) and (5). Edgecombe et al.[22] also found the lower limit of 4×10^8 l mole^{-1} sec^{-1} for the reaction (19).

Brown and Spinks[54] investigated the bromine sensitised decomposition of Cl_2O using 5460 Å. They found that the course of the reaction is similar to that sensitised and unsensitised by chlorine. The final products were similar and the quantum yield thus evaluated was also equal to that found by Finkelnberg et al.[50] From their results thus they gave the mechanism as

$$Br_2 + h\nu \rightarrow Br_2^* \qquad (23)$$

$$Br_2^* + M \rightarrow 2Br + M \qquad (24)$$

$$Br + Cl_2O \rightarrow BrCl + ClO \qquad (25)$$

or

$$Br_2^* + Cl_2O \rightarrow Br_2 + Cl + ClO \qquad (26)$$

$$Cl + Cl_2O \rightarrow ClO + Cl_2$$

After these primary reactions, the other reactions are similar to those discussed in the case of chlorine sensitised reaction, in order to explain the overall quantum yield and the rest of the final products.

D. Formation and Decay of Vibrationally Excited Oxygen

In the study of the flash photolysis of ClO_2, Lipscomb et al.[21] also observed vibrationally excited oxygen with up to eight quanta, corresponding to an energy of 34 Kcal, in the ground electronic state. They found[9] that the amount of oxygen produced decreases if the primary photolysis is more than fifty percent because there was not enough ClO_2 left to react with oxygen atoms after the primary process. The mechanism proposed for formation of excited oxygen was simple:

$$ClO_2 + h\nu \rightarrow ClO + O$$
$$O + ClO_2 \rightarrow ClO + O_2^* + 59 \text{ Kcal}$$
$$O + ClO_2 \rightarrow ClO_3$$
$$ClO_3 + h\nu \rightarrow ClO + O_2^*$$

where O_2^* is vibrationally excited oxygen.

From their work on ClO_2 and NO_2 as well as from McKinley, Garvin and Boudart,[55] who observed infrared emission from OH produced from the H/O_3 reaction, it was clear that the energy distribution is not equilibrated. A large amount of energy is found as vibration in the newly formed bond. The study of ClO_2 reaction as well as a number of similar reactions studied by flash photolysis, led McGrath and Norrish,[12,58] to the following generalization: "When an exothermic reaction of the general form A + BCD → AB + CD occurs, the molecule AB with newly formed bond takes a high proportion of exothermic energy of the reaction in the form of unequilibrated vibrational energy."

Since the vibrational transitions within the ground state are only allowed as magnetic dipole or quadrupole radiation, collisional deactivation in the ground state must be considered. Collisional deactivation of O_2^* was found to be very ineffective for argon and nitrogen (1 in 10^7 effective). They[21] also observed that the half life of O_2^* (v"=6) varies between approximately 200 to 700 μsec and was inversely proportional to the initial pressure of ClO_2. It was thus concluded that ClO_2 and ClO are approximately equally effective in deactivation O_2^* (one in 2000 effective) and that a value of $k = 1.0 \times 10^8$ l mole^{-1} sec^{-1} could be assigned to the rate constant for the process

$$O_2^*(v"=6) + ClO(\text{or } ClO_2) \rightarrow O_2^*(v"=5) + ClO(\text{or } ClO_2)$$

Again due to the time resolution of the apparatus and pressure of ClO_2 and argon used, they believed that the energy distribution they observed at shortest delays was very close to the initial distribution produced from the reaction. They estimated that at the shortest delay the v"=5,6 and 7 levels of oxygen were equally populated while the v"=8 was populated to a lesser extent.

E. Present Investigation

Although extensive work has been done on the direct photolysis of the oxides of chlorine by various techniques, it can still be seen from the results that there is large variation in the extinction coefficient and rate constant for the

decay of ClO. Clyne and Coxon's[25] values and those of Lipscomb et al.,[21] Edgecombe et al.[22] and Porter and Wright[15] and the present flash photolysis results themselves vary significantly. One reason for the present work was, therefore, to solve the discrepancies which exist between various workers since the ClO radical has played an important role in the explanation of many reaction mechanisms.

The earlier flash photolysis studies of the decomposition of ClO_2 and Cl_2O and of Cl_2/O_2 systems have been, therefore, repeated and the previous inconsistencies resolved. Several new features have been revealed and it has been possible to measure the rate constants for nearly all the elementary reactions involved in the photolysis and chlorine photosensitised decomposition of both ClO_2 and Cl_2O. Reactions of bromine atoms with ClO_2 and Cl_2O have also been studied and the extinction coefficient for the BrO radical measured.

A second reason for this work was to study the energy distribution in the reaction between oxygen and ClO_2, as such information may provide a deeper insight into the detailed mechanism of a reaction than can be obtained for a knowledge of rate constant alone. The exothermicity of the reaction (59 Kcal/mole) is much more than the energy of the highest level observed by Lipscomb et al.[21] In the reaction between oxygen atoms and NO_2 the same situation exists; the highest level observed by Lipscomb et al.[21] being again only the 8th whereas 47 Kcal are available. Later studies by Basco and

Norrish[56] and Basco and Morse[57] have shown that O_2 with vibrational energy up to maximum energetically possible is produced in this case. The present work has also shown this to be true for the ClO_2 reaction. The relative rates of production of O_2^* into the levels observed have also been measured and new information on the relaxation has been obtained.

Thus the present work has been divided into the following sections.

In Chapter three the extinction coefficient of ClO is measured from ClO_2 and supported from Cl_2O and Cl_2O/Cl_2 systems. This chapter also includes the rate of recombination of ClO radicals.

The reaction of oxygen atoms with ClO, Cl_2O and ClO_2 have been reported in chapter four and the values of the rate constants are determined.

Halogen (Cl_2 and Br_2) photosensitised decomposition of ClO_2 and Cl_2O and the determination of the rate constants have been discussed in chapter five.

In the last chapter (VI), the formation, energy distribution and relaxation of O_2^* from ClO_2, Cl_2O and ClO will be discussed.

CHAPTER II

EXPERIMENTAL

A. Apparatus

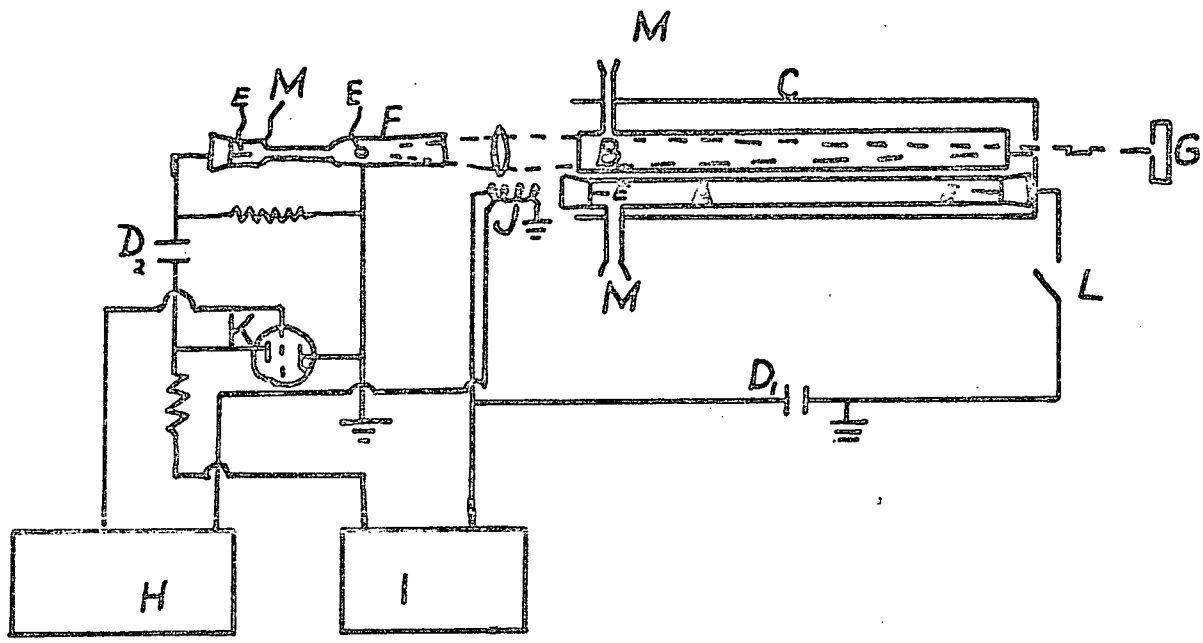
1) The term flash photolysis is applied to high intensity irradiation for an extremely short time. The principles of the method have been described by Porter[1] in detail.

There are two techniques, the photographic and the photoelectric, used to detect the products and transient intermediates produced by flash photolysis and the subsequent chemical reactions.

a) In the photographic technique, the absorption spectrum of the transients is taken at predetermined times after the photolytic flash by means of a second flash lamp and recorded on photographic plates through a spectrograph. The main advantage of this technique is that a large wavelength region can be studied in one experiment, the price being that each delay time requires a separate experiment.

b) In the photoelectric technique the situation is reversed, the complete time behaviour of a narrow region of the spectrum is followed by one experiment by means of a photomultiplier and monochromator.

The photographic technique was used throughout this investigation. The apparatus used in this investigation is essentially the same as that used by Basco and Norrish[59] and Yee.[60] The main features of the apparatus are shown in fig.(1).



LEGEND

A	- Photolysis Lamp	G	- Spectrograph Slit
B	- Reaction Vessel	H	- Electronic Delay Unit
C	- Brass Container	I	- High Voltage Charging Unit
D_1, D_2	- 33 and 2μF	J	- Induction Coil Pick-up
E	- Tungsten Electrodes	K	- Hydrogen Thyratron
F	- Spectroscopic Lamp	L	- High Voltage Switch
		M	- Gas Inlets from Vaccum System

Figure 1. Schematic Diagram of a Conventional Flash Photolysis Apparatus.

The only difference is the use of manual firing instead of with a Tesla coil, i.e., one electrode was connected to the condensor, the other to one end of the firing switch. The other end of the switch was grounded. The firing was done by closing the switch. The advantage of this manual switch over triggering with a pulse from a Tesla coil was that spontaneous breakdown of the lamps , was avoided. The pressure of argon in the lamp was only 10 torr, at which pressure the lamp always fired immediately on closing the switch.

The flash energy used in the present work varies from 150 to 1300 J. It was observed that characteristic profile of the flash lamp remains approximately constant at each flash energy used. The half lifetime of the high energy pulse, i.e. the time taken to decay half of its peak height was found to be 20 μsecs. The flash energy used in the spectroscopic lamp was ∿100 J. The half life of spectroscopic lamp was found to be 5 μsec.

The mixtures of the gases being studied was subjected to the high energy, short duration pulse of light which is produced by discharging the condensors through the flash lamp containing argon. A pulse, picked by the coil wrapped around the ground lead, is fed into a delay unit and, after a predetermined time delay, the spectroscopic lamp fires. Thus the light from this lamp, which monitors the transient species produced by main flash lamp, passes through the reaction

vessel and is focused on the spectrograph slit by quartz lenses. The absorption spectrum of the species present in the reaction vessel was photographed.

2) Double Lamp System

Similar to the conventional flash photolysis apparatus a double flash system was developed which allowed the photolysis of transient species. The arrangement for this system over and above what is required for the conventional apparatus is shown in fig.(2). A second photolysis lamp (auxiliary), which can be electronically delayed in the same manner as the spectroscopic lamp, is placed parallel to the first photolysis lamp (main) on the opposite side of the reaction vessel. The spectroscopic lamp is then triggered from the auxiliary lamp.

The triggering circuit used to fire the auxiliary lamp is similar to that used to fire the spectroscopic lamp in the conventional flash photolysis apparatus, i.e., a pulse picked up from an induction coil (J) wound around the high voltage lead is fed into an electronic delay unit (H_1) consisting of a collection of calibrated R.C. circuits. The delay pulse is strengthened by a small thyratron-capacitor circuit and is delivered to the grid of a large hydrogen thyratron which in turn discharges the capacitor through the auxiliary lamp.

Since accurate time delays of the auxiliary lamp were required, traces of the light output of the lamps were checked for each double lamp experiment on the screen of an oscilloscope. The delay times quoted are measured from the

peak of the first flash to the peak of the second.

3) Vacuum System

The usual type of vacuum system was used, with a two stage mercury diffusion pump and a one stage rotary oil pump. The stop cocks were greased with silicon grease supplied by Dow Corning. This grease was used in order to avoid the decomposition of oxides of chlorine because these gases were sensitive to organic greases like Apiezon. With the use of this grease, it was still possible to pump the system to less than 10^{-5} torr. Most of the gases used were corrosive to mercury so the pressure of the gases was measured with two spiral gauges of ratios 1:4 and 1:2. These spiral gauges were calibrated with a mercury manometer. The total pressure or cooling gas pressure was measured with a mercury manometer.

4) Spectrographs

Most of the work described here was done on the Jarrell Ash spectrograph but a few runs were done on the medium Hilger. The Jarrell Ash is a 3.4 meter Ebert mounting type spectrograph with the following characteristics:

1) interchangeable plane grating mounting;
2) two plane gratings each with 15,000 lines per inch, one blazed for 3300 Å and the other for 6000 Å;
3) reciprocal linear dispersion of 5.1 Å per mm. in the first order;
4) 2500 Å range in first order by two 10 × 4 inch photographic plates.

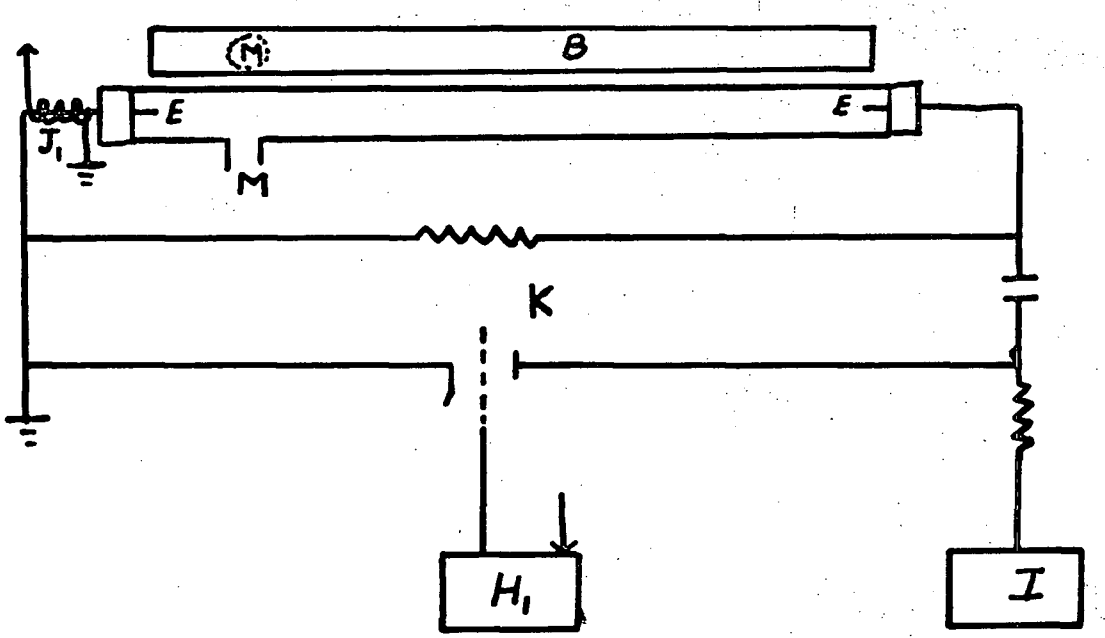


Figure 2. Auxiliary Lamp Triggering Circuit. Components with Subscripts are the duplicate components of the conventional system, otherwise the labeling is the same as in figure 1.

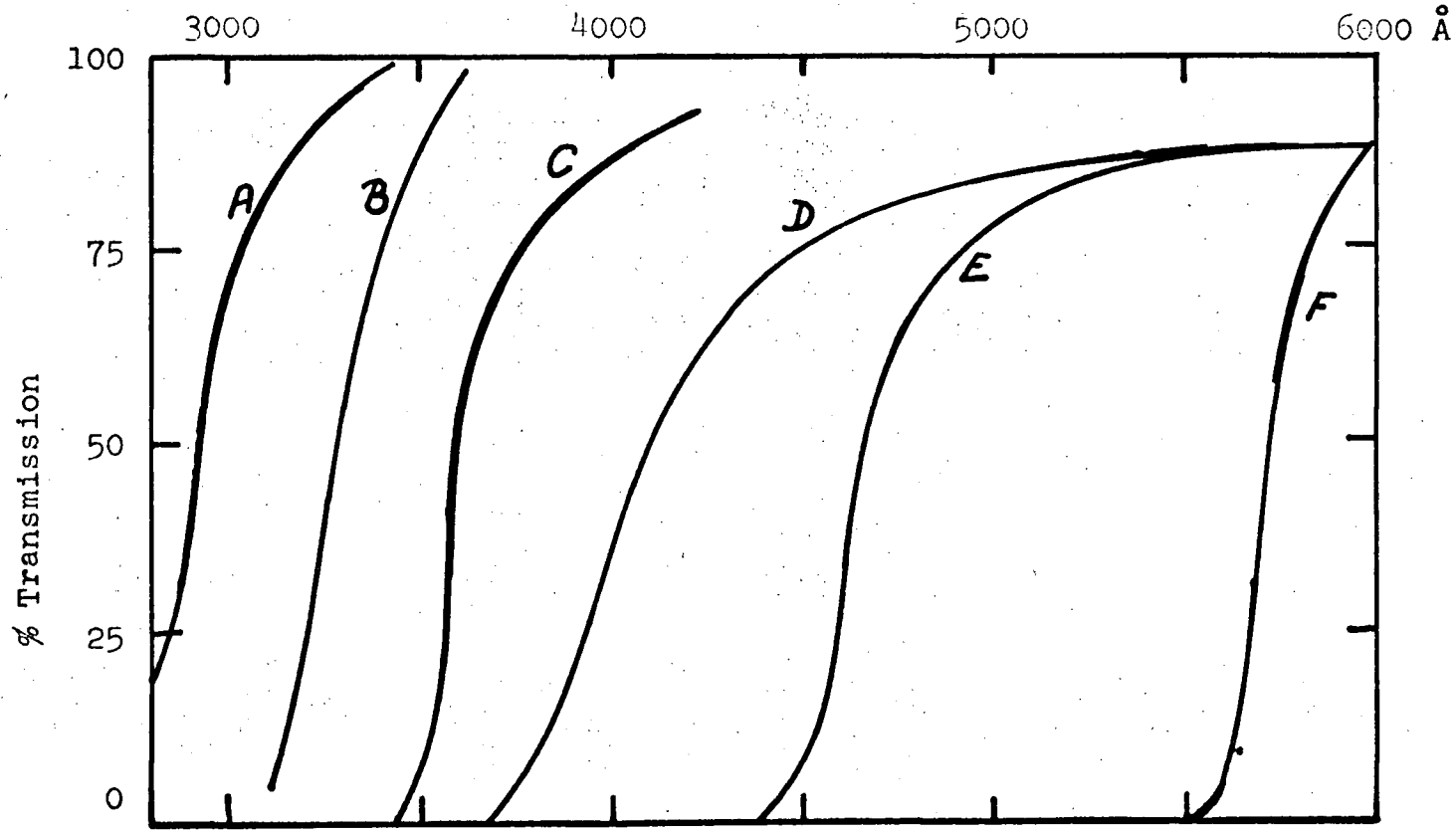
The second spectrograph was a medium Hilger prism instrument using quartz optics. It was used only for comparing the extinction coefficient and rate constant for the decay of ClO with those of Lipscomb et al.[21] The spectrum obtained from this instrument extends from 2000 Å to 10,000 Å and is 221 cm. long, enabling it to be recorded on a single plate. The reciprocal linear dispersion at 2200 Å is approximately 5 Å per mm. whereas at 6000 Å it is about 150 Å per mm. This instrument is most useful for exploratory work or work involving continuous spectra because of the wide range covered at the expense of dispersion and resolution and also because of its speed.

B. Filters

Almost all the work mentioned here required the selective photolysis of either ClO_2, Cl_2O or halogens. This was achieved by placing 3 mm thick corning glass filters between the photolysis lamp and the reaction vessel. The type of filters used will be mentioned in the respective section. One of the filters used was prepared from photographic plates after removing the gelatine completely; this is called glass filter A. The transmission properties of the filters used are given in fig.(3). The curves are reproduced from the Corning Glass Works Circular[61] except for the filter which was prepared from photographic plates and pyrex reaction vessel.

Figure 3. Transmission Characteristics of the Filters.

A = Pyrex reaction vessel, B = Glass filter A, C = 0-52, D = 3-75, E = 3-72, F = 3-66 Corning Filters.



Their transmission was measured on Cary 14. The transmission of the filters was unchanged after many flashes. The nominally zero transmission regions of the filters had a measured optical density of greater than five.

C. Photography and Photometery

In the present work, only Ilford plates were used to photograph the spectra of different species. HP^3 were used for wavelengths greater than 2300 Å and Q2 for wavelengths below 2300 Å. The slit width of the spectrograph was 30μ in all of the experiments except for Q2 where it was 100μ . Since Q2 plates were used only to monitor NOCl, which has a continuous spectrum, the slit width does not affect the apparent shape of the band.

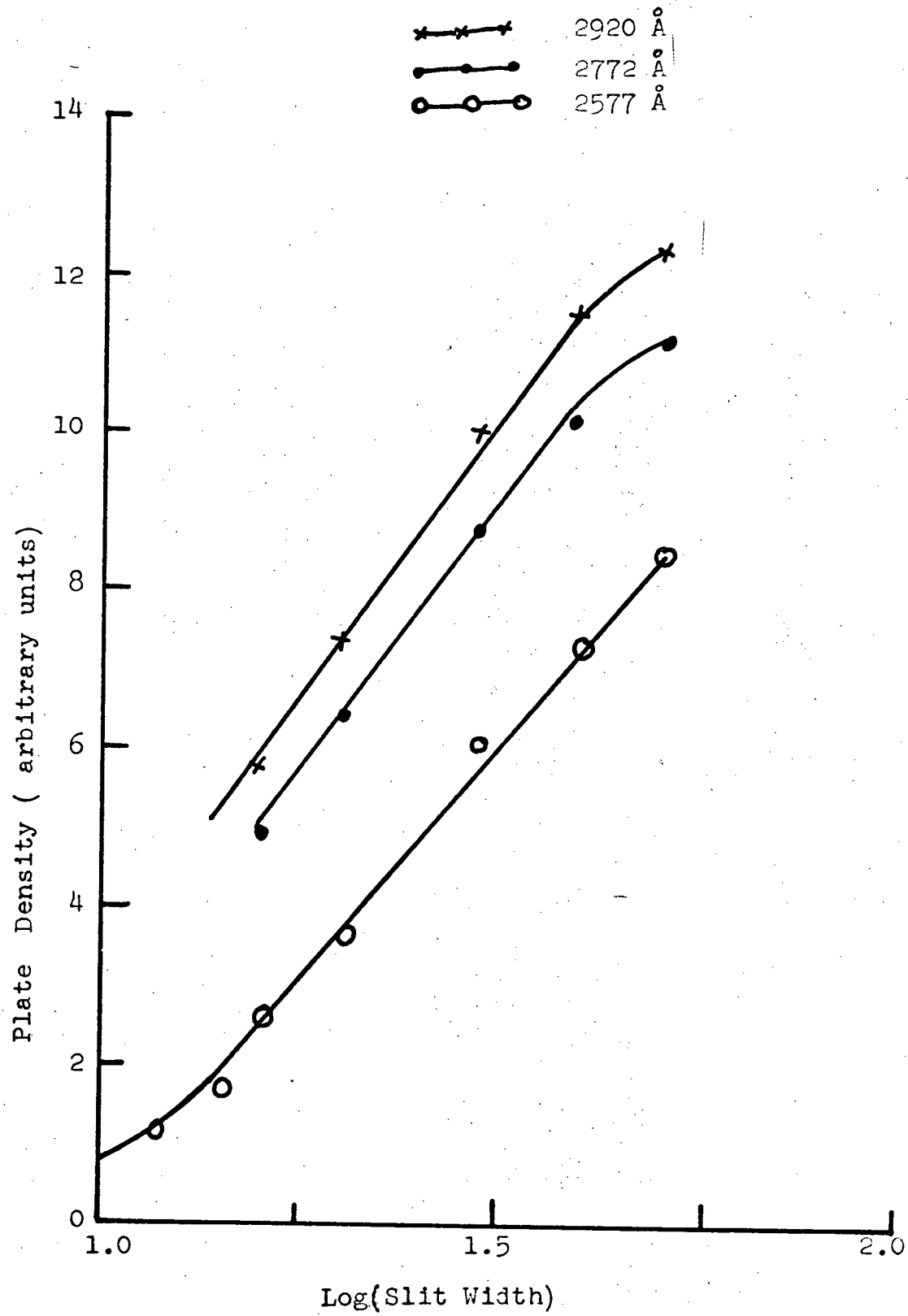
The photographic plates were developed in Kodak D19 developer for 5 min. with continuous agitation. The temperature of the developer was kept at 20°C. The plates were dipped in a stop bath (3% acetic acid) for 30 sec. and then fixed for two minutes in the Kodak rapid fixer. The plates were washed in running water for half an hour, rinsed with distilled water and dried with a stream of air at room temperature.

The photographic prints shown in the next chapters were made using a standard photographic enlarger and Agfa BNI print paper, the development of which is the same as the plates except Agfa Deutol was used for developing the paper.

The density of each plate was measured on a Joyce-Loebel double beam recording microdensitometer Model III, using an accurately calibrated neutral density wedge. In most of the measurements, especially ClO, ClO_2 and Cl_2O, the 0 to 2 wedge was used but for vibrationally excited oxygen or other weak spectra, 0 to 1 was used. The calibration of the wedge was supplied by the makers of the instrument and it was also checked by using two neutral density filters of optical density 1.0 and 1.5. The value thus obtained for calibration was within experimental error of that was supplied. So the value given by the makers was used, i.e., 0.087 per cm (while our experimental value was 0.09 ± 0.01).

The quantitative measurements studied with the help of photography does depend upon the physical properties of emulsions, e.g., contrast, speed, latitude or useful range of exposure, graininess and spectral sensitivity. Of these, the first three are the main ones which can be obtained from the characteristic curve of emulsion, which shows the relationship between the light exposure (on a logarithmic scale) received by the emulsion and the resultant density of the developed image. The variation in the exposure for the plots was obtained by varying the slit width since the area illuminated is proportional to the exposure if everything else is kept constant. Thus the characteristic curves were drawn for each wavelength wherever the measurements were done. It can be seen from fig.(4) that the curves show a linear relationship

Figure 4. Characteristic Curves for the HP3 plate for selected wave lengths.



between the plate density and exposure for the 0.2 to 0.8 plate density region. All intensity measurements were confined to this region. From these curves the slope of the linear portion, which is known as the contrast (γ), i.e., the development factor of the emulsion, was calculated and is listed in Table I. It was found that γ changes with time of development and the temperature of the developing bath, so for all the plates which were used for quantitative measurements, similar conditions were used with fresh developing solution each time.

Table I

(Å)	2577	2772	2920	3208	3383	3515
γ	1.02	1.17	1.21	--	--	1.30
	--	1.74	1.74	2.18	2.35	2.61

The γ of the plates was checked from time to time in order to confirm that it does remain constant. In the present study two types of plates were used. The batch of plates which came in the later part of the study was found to have greater contrast than the plates used earlier.

Similar characteristic curves were drawn for Ilford Q2 plates but here it was found that γ is very sensitive to the physical conditions than Ilford HP 3 plate. So more care was taken here, although they were used very rarely.

D. Measurements of Absolute Concentrations

In order to calculate the absolute concentration of any species, it is necessary to know whether Beer-Lambert's law is obeyed by it. This has been checked by the two path length method as described by Norrish et al.[63] The regular mixture was flashed and the spectrum was taken. Then half of the reaction vessel was covered with black paper and the fresh mixture was flashed with the same energy and the spectrum was taken under the same conditions as with full reaction vessel. A number of strips were taken using different delay times, different pressures of ClO_2 and Cl_2O with same total pressure, different flash energies and covering a different half of the reaction vessel with black paper, but care was taken that the strips taken with half reaction vessel were under the same conditions as full reaction vessel. Plates were photometered and the peak heights h(with full reaction vessel) were plotted against the peak heights $h_{1/2}$ (with half the reaction vessel) and the best possible straight line was drawn. It is an assumption in the two path method that the power to which both the concentration and the length must be raised in describing the optical density, i.e.,

$$D = \varepsilon (cl)^n$$

$$D_{1/2} = \varepsilon \left(\frac{cl}{2}\right)^n$$

so $$D/D_{1/2} = h/h_{1/2} = 2^n$$

This power 'n' can be determined from the ratio of $h/h_{1/2}$ from fig. (5) in case of ClO and fig. (6) in case of (0-12) band of O_2^*. For a curve, the power would vary over a range of observations, for a straight line it would be constant and for an absorption obeying the Beer-Lambert law, the ratio $h/h_{1/2}$ would be equal to 2 and thus the resulting power 'n' would be one. It is thus possible to calculate analytically the dependence of h on concentration.

1) ClO

In case of ClO this power 'n' is found to be $0.9 \pm .02$ for 12,0 band and thus the densitometric height should be raised to the power $1.1 \pm .02$ in order to determine the absolute concentration of ClO. Since the value of 'n' obtained is 1.0, within the experimental error, it was assumed that ClO obeys the Beer-Lambert law. This was also checked in another way. The ratio of the absorption at 2772 Å (12,0) to the absorption at 2577 Å (continuum) was calculated to be $1.52 \pm .04$, which agrees with the value obtained by Porter and Wright[15] and also by Clyne and Coxon[23] and remains constant over a large range of concentration and under other conditions. Since the Beer-Lambert law is obeyed by the continuum, constancy of the ratio shows that it should be obeyed by 12,0 band as well as by 7,0 band (diffuse band, 2920 Å). Thus the concentration of ClO was calculated

$$C = D/\varepsilon l$$

where ε = extinction coefficient of ClO; l = path length.

Figure 5. A plot of h(ClO) against $h_{\frac{1}{2}}$(ClO).

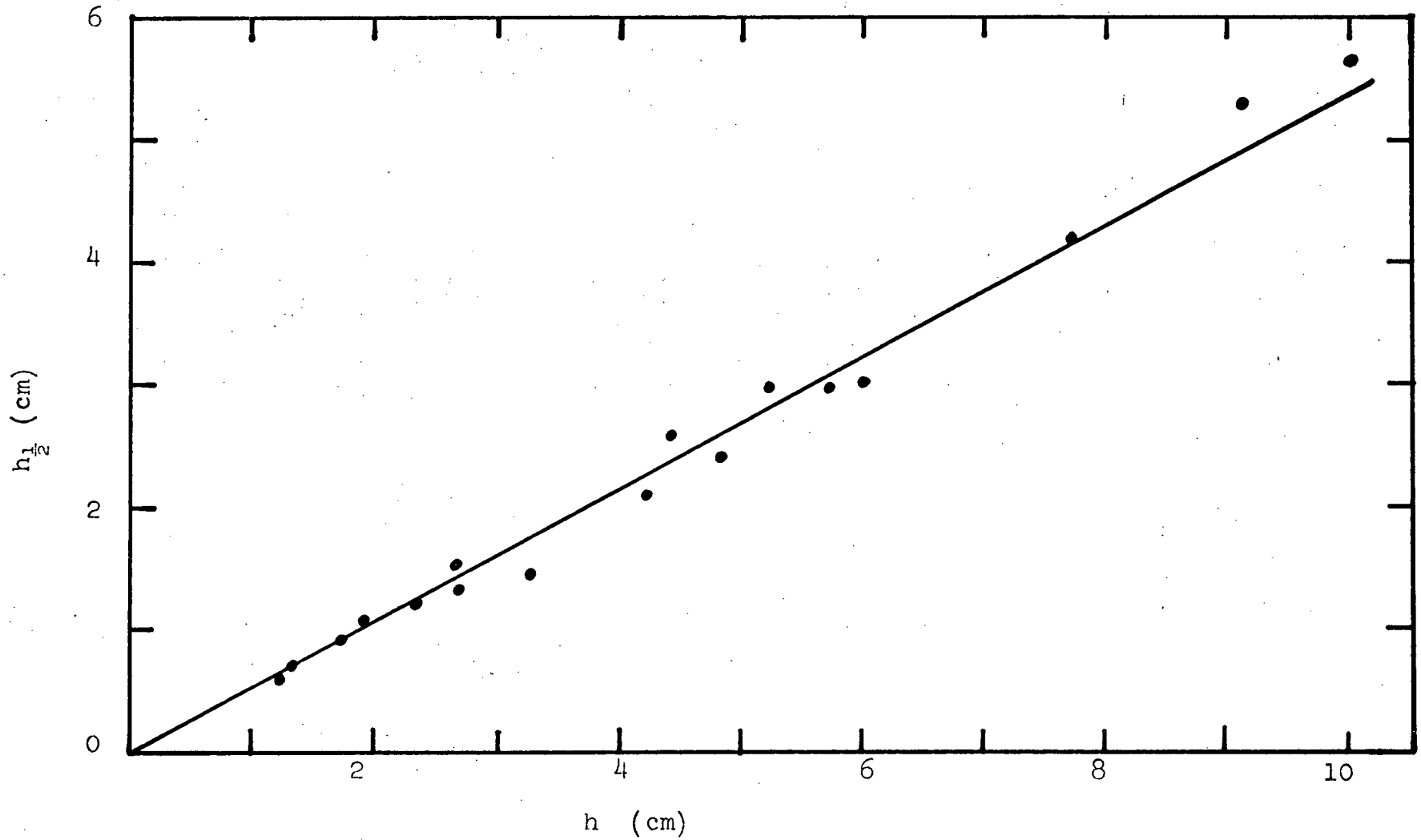
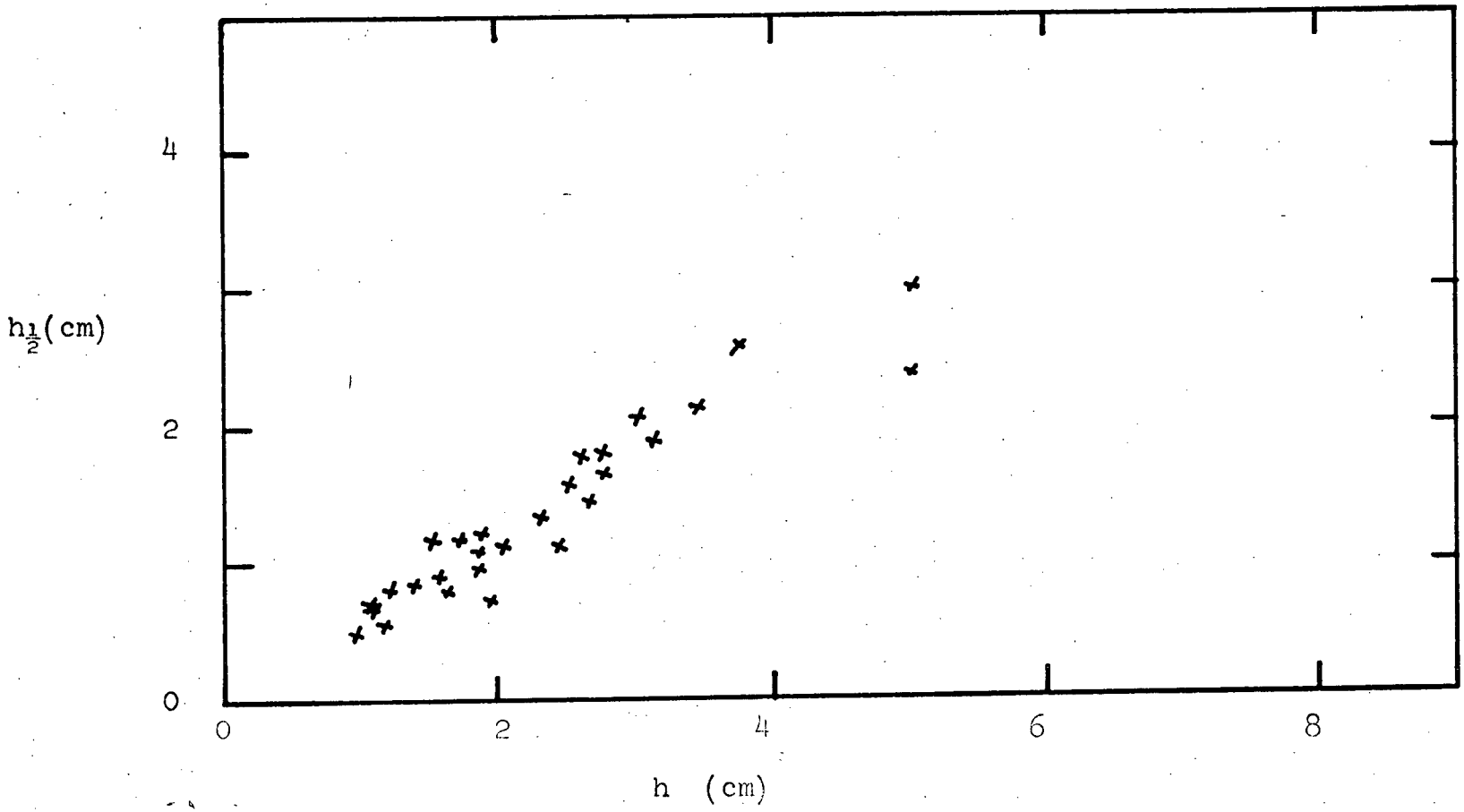


Figure 6. A plot of h (0_2^*) against $h_{\frac{1}{2}}(0_2^*)$.



2) Vibrationally Excited Oxygen

The same procedure as that described for ClO measurements was used to measure excited oxygen in different bands. The difficulty with excited oxygen was that nearly all the bands were either mixed up with ClO_2 spectrum, ClO spectrum (banded and continuous) or the dispersion was not large enough to resolve the lower bands of oxygen. The bands (0,12) and (3,6) were the best out of the whole range of bands. It was found that the power 'n' for (0,12) is not constant and it does depend upon the amount of interference with ClO_2 (only the band head and a few rotational lines could be detected before the band of ClO_2). The average value found from four different sets of experiments showed that the power to which h should be raised has a value $1.5 \pm .25$. As it will be seen later on, the relative population of excited oxygen was calculated using the power as 1.0 and 1.75. In the case of NO_2,[64] similar behaviour is observed in our laboratory, i.e., wherever the O_2^* is not interfered by NO or NO_2, it obeys Beer-Lambert law, whereas otherwise departure from the Beer-Lambert law is observed.

E. Preparation and Purification of Materials

Chlorine dioxide. ClO_2 was prepared as described by Derby and Hutchinson.[65] Chlorine and air, after bubbling through concentrated sulphuric acid, were mixed together. The mixture was passed through a column loosely packed with crystalline $NaClO_2$. The gases are then collected in a trap kept

at acetone/dry ice temperature (i.e. -78°C). The ClO_2 is then pumped vigorously at liquid nitrogen temperature, dried by passing over P_2O_5 in a trap and finally it was distilled from acetone/dry ice to liquid nitrogen temperature. The sample at liquid nitrogen was disposed of and material left at acetone/dry ice temperature was pumped at this temperature. The purity of the compound was tested by its vapour pressure.[67] The sample thus obtained was always kept at liquid N_2 temperature.

Chlorine monoxide. Cl_2O was prepared by the method suggested by Cady.[66] A mixture of chlorine and air, after passing through concentrated sulphuric acid, was passed through a column containing a mixture of mercuric oxide and glass chips. The glass chips were added to allow the passage of gases. The gases were collected at -78°C. Purification was carried out in the same manner as above with the difference that methanol/liquid nitrogen slush was used for pumping the last traces of chlorine present. The Cl_2O was stored at liquid nitrogen temperature whenever it was not being used.

Nitrosyl chloride. NOCl was prepared by allowing a mixture of pure dry chlorine and excess nitric oxide to stand for three days. The products were condensed in a liquid nitrogen trap with the excess nitric oxide and the latter was pumped off. After distillation, the nitrosyl chloride was stored at -196°C until required.

Chlorine. Cl_2 (Liquid Air Ltd.), was degassed at -196°C, dried by passing over P_2O_5 and finally distilled from -78°C to -196°C. The gas was stored at room temperature.

Bromine. Br_2 (Allied Chems.) was purified as chlorine except that it was distilled from an ice/common salt mixture and stored at -78°C until required.

Oxygen, Nitrogen(98%), Argon (99.999%) and Carbon Dioxide were supplied by Liquid Air Ltd. These gases were used as such without further purification except that they were passed through a trap containing glass wool and kept at -78°C.

The purification of all the gases except inert gases was done under vacuum.

F. Preparation of a Mixture and Procedure

Mixture of the reactant species and argon or other inert gas was done at least three hours before commencing the run to ensure homogeneous mixing. The mixture was made in a large bulb at the same argon: reactant ratio to be used in the experiments but in sufficient higher total pressure to allow the experiments to be completed. Since oxides of chlorine are sensitive to light, all the bulbs were blackened, also the feeding lines to reaction vessel were covered with black paper. All the experiments were done in a dark room. Pressures less than one mm were measured by expanding from a high pressure in a small volume to an evacuated bulb. The

expansion ratios of these lines to the bulbs were measured beforehand. There are some experiments where the mixing time is less than that mentioned above (in order to avoid dark reaction) but that will be mentioned at the specified place.

There are twenty three strips available on each plate which allows at least 18 to 19 of these to be time experiments. At least two of the other strips were used for blanks to confirm the constancy of the output of the spectroscopic lamp throughout the experiment. The other exposures are the "before," which is the absorption spectrum of the reaction mixture in the cell before the photolysis and "after", an absorption spectrum of products and reactants remaining at relatively long time (30 seconds) after the photolysis flash. Each of these exposures is necessary on every plate to act as a standard for the particular conditions used.

CHAPTER III

EXTINCTION COEFFICIENT OF ClO AND DECAY OF ClO

A. Extinction Coefficient of ClO

1) From ClO_2 Photolysis

The assumption involved in the measurement of extinction coefficient of ClO in the following experiment is that one ClO radical is produced from each molecule of ClO_2 decomposed and that the total concentration of ClO produced initially may be measured by extrapolation back to zero time.

ClO_2 was flashed using four different flash energies in the presence of excess inert gas. The ratio of ClO_2 to inert gas was varied from 1:750 to 1:3300, at which ratios the photolysis is isothermal. Since the pyrex reaction vessel (used in our system) transmits some light below 3000 Å, in all the experiments 2 to 3 mm of glass filter A was used. This filter absorbs all the radiation below 3000 Å (fig.3) and thus the direct photolysis of ClO was avoided. Because of the strong absorption of ClO and ClO_2, the concentration of ClO_2 used for the measurements of extinction coefficient of ClO varied between 0.06 to 0.12 torr. Some experiments were done using 0.25 torr of ClO_2 but it has been found that the results were not very accurate due to the saturation of the photographic plate. Since there could be a small error in making the ClO_2 mixture by the expansion method, though less

than 10% even at the lowest ClO_2 pressure, the ClO_2 pressure was checked by measuring its concentration from its absorption spectrum. From accurately measured pressures, the extinction coefficient at 3515 Å was measured and found to be in excellent agreement with the literature value[25] of (3000 ℓ mole^{-1} cm^{-1}).

At low flash energy where the primary photolysis is less than 25%, only three processes need to be considered, e.g.

$$ClO_2 + h\nu \rightarrow ClO + O \qquad (27)$$

$$ClO_2 + O \rightarrow ClO + O_2 \qquad (7)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (5)$$

Convincing reasons for believing that (27) is the only significant primary process will be given in connection with the mechanism of the production of vibrationally excited oxygen. The rate of decay of ClO is very slow compared to the rate of its production and the second order plot for the decay is strictly linear over the range of delay times used. The accuracy of the short linear extrapolation to zero time is then limited only by a small uncertainty in the definition of zero time due to finite lifetime of the photo-flash. This uncertainty of $\leq$ 10 μsec leads to a possible error of only $\pm$ 5% in the extinction coefficient.

At high flash energies, the second order plot for the ClO (as can be seen from fig. 8, p. 59), becomes markedly non-

linear at delay times below ∿200 μsec, but, since the initial rapid decay can be followed over most of the period, the extrapolation is still valid. Because of the curvature and the steepness at high flash energies, the extrapolation is more difficult and an error of 10 μsec in zero time would give ∿20% error in the extinction coefficient. From the closeness of the agreement between the values of extinction coefficient obtained at high and low flash energies, it would appear that the zero time is known within ± 5 μsec.

Taking into consideration that there is no other reaction competing with the above mentioned, then

$$\Delta[ClO_2] = [ClO]_o = \varepsilon cl = D$$

where

$\Delta[ClO_2]$ = decrease in the $[ClO_2]$

D = optical density

ε = extinction coefficient of ClO

l = length of the reaction vessel

and the extinction coefficient of ClO can be calculated from

$$\varepsilon = D/l[ClO]_o = D/l\Delta[ClO_2]$$

The values of extinction coefficient of ClO were calculated by measuring the concentration of ClO formed at three different wavelengths and under the various conditions. The data thus obtained are given in Table II. Values with * show the effect of working in the non-linear region of the plate characteristic curve and are not included in the average. The average value of ε(ClO) at 2577 Å, 2772 Å and 2920 Å are

found to be $1.15 \pm 0.06 \times 10^3$, $1.7 \pm 0.07 \times 10^3$ and $1.05 \pm 0.04 \times 10^3$ mole^{-1} cm^{-1} respectively. The error limits are the standard deviations.

Table II

Extinction Coefficient of ClO from ClO_2 Photolysis

Plate no.	ClO_2 (torr)	Argon (torr)	Energy J	$\varepsilon \times 10^{-3}$ (l mole^{-1} cm^{-1}) 2577 Å	2772 Å	2920 Å
104	0.25	200	1060	0.8*	0.86*	0.8*
105	0.06	200	1060	1.17	1.78	--
107	0.08	75	1060	--	1.66	1.10
114	0.12	200	1060	--	1.74	1.02
105	0.06	200	600	1.17	1.72	--
154	0.1	200	600	--	1.7	1.04
118	0.25	200	260	1.04	1.28*	1.0
120	0.1	75	260	1.14	1.76	1.02
156	0.1	200	260	1.16	1.71	1.04
164	0.25	200	260	1.25	1.65	1.10
118	0.25	200	160	1.16	1.55	1.05
156	0.1	200	160	1.12	1.71	1.10
		Average		1.15 ± 0.06	1.70 ± 0.07	1.05 ± 0.04

* These values are neglected due to saturation of plate

From these results the ratio of ε(2577 Å) : ε(2772 Å) : ε(2920 Å) is found to be 1.09 : 1.61 : 1.0. The relative values of ε(ClO) for these wavelengths were also calculated from 100 measurements of ClO absorption at different time delays. These

gave an average value for ε(2577 Å) : ε(2772 Å) : ε(2920 Å) = 1.07 : 1.60 : 1.0, thus in exact agreement with that obtained by extrapolation. The ratio of ε(2577 Å) : ε(2772 Å) = 1.0 : 1.48, is also in good agreement with the ratio calculated by Porter and Wright[15] (1.0:1.5) and Clyne and Coxon[23] (1.0:1.54).

The value of 1.15×10^3 l mole^{-1} cm^{-1} for ε(ClO) at 2577 Å is in excellent agreement with that obtained at low flash energy values by Lipscomb et al.[21] but the value at 2920 Å is approximately twice that which can be obtained from the work of Edgecombe et al.[22] to be discussed in the next section.

2) Calculation of Extinction Coefficient of ClO from the Direct Photolysis of Cl_2O and Chlorine Photosensitised Decomposition of Cl_2O

As it can be seen from the absorption spectrum of Cl_2O,[48] the light absorbed by Cl_2O above 3000 Å will lead to the following reactions:

$$Cl_2O + h\nu \rightarrow ClO + Cl$$
$$Cl_2O + Cl \rightarrow ClO + Cl_2$$
$$ClO + ClO \rightarrow Cl_2 + O_2$$

There are other reactions following these but they are quite slow and will be considered in Chapter V of this work.

Considering these three simple reactions as with ClO_2 photolysis, Cl_2O was flashed at three flash energies and two

pressures, keeping a total inert gas pressure of 200 torr. The assumption that one molecule of Cl_2O decomposed will give rise to one ClO radical still holds in the above reaction scheme as well as in the chlorine sensitised photolysis of Cl_2O, i.e.

$$Cl_2 + h\nu \rightarrow 2\ Cl$$

$$Cl + Cl_2O \rightarrow ClO + Cl_2$$

Therefore Cl_2O was also flashed in the presence of chlorine. The ratios vary approximately from 1:1 to 1:4 at three flash energies. The chlorine atom concentration at each flash energy was calculated from the titration of chlorine atoms with nitrosyl chloride, i.e., by measuring the decrease in the amount of nitrosyl chloride by the reaction

$$Cl + NOCl \rightarrow NO + Cl_2$$

This was achieved by flashing $NOCl/Cl_2/Ar$ mixture under the same conditions as $Cl_2O/Cl_2/Ar$.

A difficulty noticed in the measurement was that the spectrum of Cl_2O is spread over the whole region of that of ClO. Even at 2350 Å ClO has an extinction coefficient approximately 50 to 80 l mole^{-1} cm^{-1} whereas Cl_2O has ~100 l mole^{-1} cm^{-1}. Although with the eye the ClO spectrum looks discrete, with a densitometer trace, all the bands are mixed with each other. This will be discussed later on. Thus to find the Cl_2O decrease or ClO produced, the ratio of the peak height measured from the actual base line to the peak height measured from the base line (obtained by joining the two successive

bands), was measured from the flash photolysis of ClO_2. It was found that actual peak height of ClO band is approximately 20% more than the apparent one. Thus, in this case

$$D_t = D\ (Cl_2O) + D\ (ClO) \qquad (a)$$

$$= D\ (Cl_2O) + D\ (ClO)_{app.} + 20\%\ D\ (ClO)_{app.}$$

Total peak height (D_t) and apparent peak heights were measured. The actual peak height of ClO was thus calculated by adding 20% of the apparent peak height to it and hence the decrease in the Cl_2O was calculated from the expression (a). A similar procedure was applied to the chlorine sensitised decomposition of Cl_2O. Thus the extinction coefficients at two wavelengths were calculated with the results listed in Table III. The averages of ε(2772 Å) and ε(2920 Å) were found to be $1.61 \pm 0.05 \times 10^3$ and $0.99 \pm 0.05 \times 10^3$ l mole^{-1} cm^{-1} respectively. Though this procedure is not very accurate due to the interference of two spectra, the values obtained are approximately of the same order as calculated from ClO_2 photolysis.

Discussion

It can be seen from Table II that our value of ε(ClO) at 2577 Å agrees very well with those obtained by Lipscomb et al.,[21] at low flash energies but at high flash energy our value is twice that obtained by them.[21] We also found the same behaviour as noticed by them, i.e., if the extinction

Table III

Extinction Coefficient of ClO from Cl_2O and Cl_2O/Cl_2 Photolysis

Plate no.	$Cl_2O \times 10^{+6}$ (mole/ℓ)	$Cl_2 \times 10^{+6}$ (mole/ℓ)	Ar torr	Energy J	$\varepsilon \times 10^{-3}$ (l mole^{-1}cm^{-1} 2772 Å	2920 Å
167	34.1	137.5	200	260	1.69	--
169	63.0	68.0	200	600	1.58	--
170	35.6	137.5	200	600	1.57	0.97
171	63.3	137.5	200	600	--	1.0
173	36.5	137.5	200	1060	--	0.90
184	57.8	--	200	830	1.60	1.10
191	52.3	--	200	1060	1.58	--
193*	33.0	--	200	1325	1.65	0.96
			Average		1.61 ± 0.05	$0.99 \pm .0$%

N.B. In all the experiments 2mm of glass filter A was used except with * .

coefficient is calculated from the linear extrapolation of second order plot at all flash energies, the value obtained decreased with increasing flash energy. From our measurements, values of ε at 2577 Å as low as 400 l mole^{-1} cm^{-1} would have been obtained using this procedure. It, therefore, seems very probable that the difference between our results and those reported by Lipscomb et al.[21] may be explained by the fact that they did not observe the initial rapid decay of ClO. It will be shown later that the reason for this rapid decay is

the reaction

$$O + ClO \rightarrow Cl + O_2 \qquad (6)$$

In this treatment, no account of the presence of ClO_3 has been taken, the formation of which is the reaction

$$O + ClO_2 \rightarrow ClO_3 \qquad (9)$$

proposed by Lipscomb et al.[21] and by the steady state workers. They found a weak continuous absorption (mainly below 3000 Å), apparently due to ClO_3 which is formed during the flash and which disappeared slowly over a period of one minute. By measuring the concentration of ClO_3 at 2948 Å (using $\varepsilon(ClO_3)$ found by Goodeve et al.[39]), a correction was applied to the absorption at 2577 Å, the wavelength used as a measure of the ClO concentration. The correction of ClO_3 produced was greatest at low flash energies between 240 and 400 J (at these flash energies the decomposition of ClO_2 was between 73% and 91%). At energies of 1280 J and 1620 J where the ClO_2 decomposition was 98-99%, the proportion of ClO_3 produced was only 3% and 2%.

If the existence of ClO_3 is admitted, then

$$D = D(ClO) + D(ClO_3)$$

and

$$\Delta[ClO_2] = [ClO]_o + [ClO_3]$$

where D and $\Delta[ClO_2]$ have the same meaning as before. The value of $\varepsilon(ClO)$ in the present work denies the existence of ClO_3 so that the extinction coefficient of ClO was measured simply from

$$\varepsilon = \frac{D}{l[ClO]_o} = \frac{D}{l\Delta[Cl_2O]}$$

Since our value of $\varepsilon(ClO)$ at 2577 Å (1150 l mole^{-1} cm^{-1}) is very close to $\varepsilon(ClO_3)$[39] at this wavelength (∿1100 l mole^{-1}cm^{-1}), the correction is negligible (less than 1%) and even at 2772 Å the maximum error would have been only ∿3%. If the value of 690 l mole^{-1}cm^{-1} given by Lipscomb et al.[21] is used, the maximum error would be only 15% but the evidence presented here and the results of Clyne and Coxon[21] make the higher value more probable.

Although the presence of ClO_3 is irrelevant to the discussion on $\varepsilon(ClO)$, it is convenient to consider the evidence for its formation here. To detect the underlying continuous absorption in the presence of discrete bands, it is necessary either that the latter is completely resolved or that successive bands of the discrete spectrum should be free from overlap. Although, visually, this latter condition appears to be fulfilled for the ClO spectrum recorded on medium quartz spectrograph (e.g. fig.(2) of L.N.T.[21]), a microdensitometer tracing shows that this impression is false and overlap is still apparent on our spectra obtained at two to three times greater dispersion where the rotational structure appears, virtually, to be largely resolved. In spectra taken in the fourth order of a 21 ft. grating spectrograph[16] the rotational structure is described as sharp but complex owing to the overlapping of successive vibrational bands. A tracing of a spectrum taken

in second order of 3.4 meter grating spectrograph under conditions reported favourable to the formation of ClO_3, no indication of an underlying continuum spectra is apparent. Spectra taken at high flash energy are similar. At long delays (from 5 seconds to 5 minutes) where the ClO concentration is negligible, the spectra show again no indication of continuous absorption, although according to L.N.T.[21] the ClO_3 spectrum should still be present at these times (fig.7).

Further reasons for denying the presence of detectable concentration of ClO_3 in the present work are that the ClO spectrum is unchanged when it is produced from other sources (Cl_2/O_2 system) where the production of ClO_3 is less likely and the rate constants for the decay of ClO produced in the various ways (Cl_2O, Cl_2O/Cl_2 and Cl_2/O_2 systems) are in good agreement. We conclude that there is no evidence of ClO_3 or that if it is produced, it is very likely rapidly removed by the following reactions:

$$O + ClO_3 \rightarrow ClO_2 + O_2 \qquad (28)$$

$$ClO + ClO_3 \rightarrow 2ClO_2 \qquad (29)$$

$$Cl + ClO_3 \rightarrow ClO + ClO_2 \qquad (30)$$

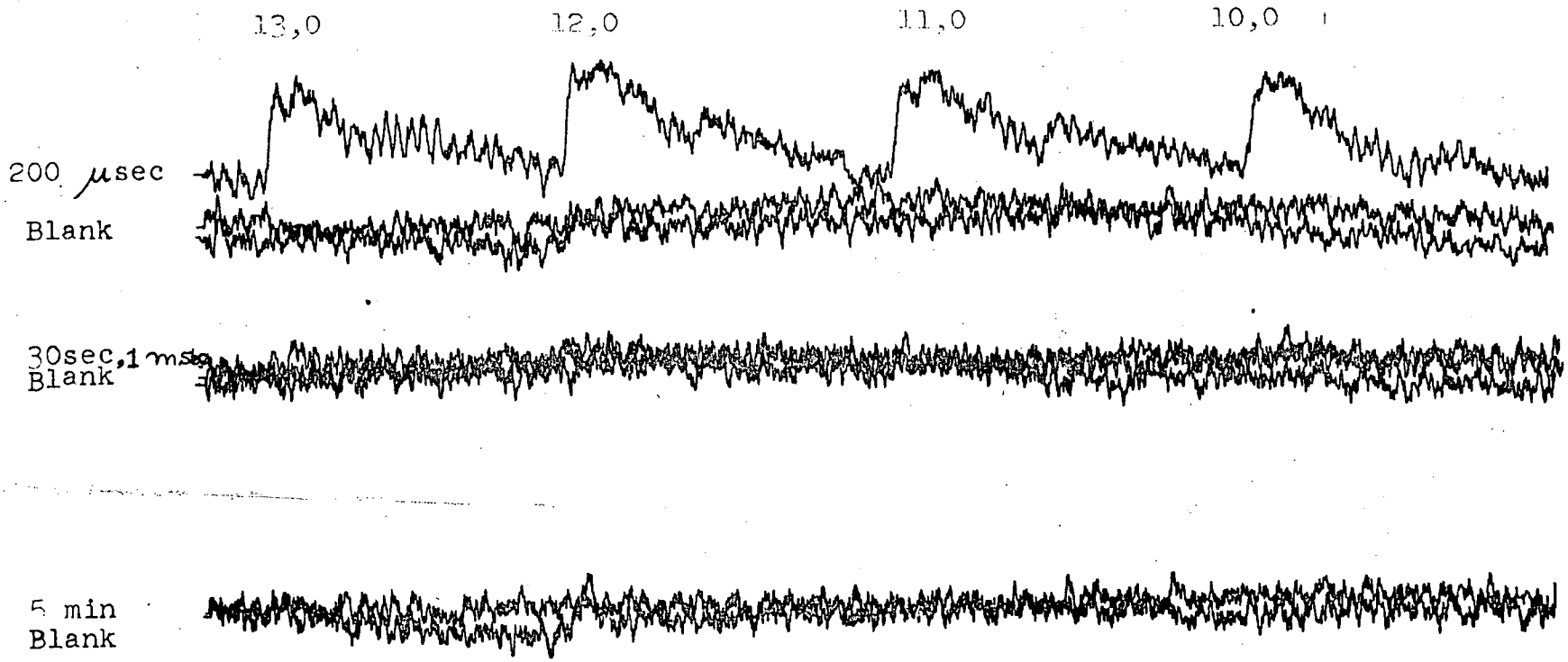
The possibility of production of O_2^* in the reaction (28) or as proposed by L.N.T.[21] in the photolysis of ClO_3

$$ClO_3 + h\nu \rightarrow ClO + O_2^* \qquad (31)$$

will be considered in a later section.

Fifure 7. Densitometer tracing of ClO bands taken in second order of 3.4 meter grating spectrograph under conditions reported favourable of ClO_3 formation.

ClO_2 = 0.2 torr, Argon = 200 torr, E = 260 J.



Although our values of ratio of ε(ClO) at 2772 Å to ε(ClO) at 2577 Å agree well with that found by Clyne and Coxon,[25] our values at these wavelengths are ~10% less than those of Clyne and Coxon.[25] Although this difference is within experimental error, the possibility that it arose from instrumental, thermal or nonequilibrium effects were considered.

The possibility of instrumental effects was tested by measuring the extinction coefficient using a medium quartz spectrograph as well as the 3.4 meter grating spectrograph with various slit widths but no difference was noted. Since 2920 Å refers to the equilibrium concentration of ClO ($^2\pi_{3/2}$, v" = 0) at the temperature of the system, only a small temperature change is needed to account for the discrepancy. However, since the values obtained were the same with a 800 fold dilution of ClO_2 with inert gas as with a 3300 fold dilution, it would appear that in both cases the system was strictly isothermal or that the effective temperature coefficient of ε is small. It remains possible that the population of ClO ($^2\pi_{3/2}$, v" = 0) produced either by photolysis or by chemical reaction was not strictly equilibrated, but as there is no independent evidence for this, we conclude that the small discrepancy between our results and those of Clyne and Coxon[25] is caused by experimental error.

B. Bimolecular Decay of the ClO Radical

ClO radical, as already mentioned in the introduction, can be generated by different methods and thus its bimolecular decay can be studied by different methods, so long as other reactions of ClO do not interfere during its decay. We have generated ClO radical by five different methods and the results obtained are discussed below.

1) From ClO_2 Photolysis

As mentioned in the last section on the determination of extinction coefficient of ClO radical, ClO_2 was flashed using four flash energies (mentioned in Table IV). ClO_2 pressure used was varying from 0.06 to 0.25 torr and two argon pressures were used, 75 torr and 200 torr. Thus the ratio of ClO_2 to inert gas (argon) was between 300 to 3300. In all the experiments used to determine the rate constant of bimolecular decay, 2mm glass filter A was placed between the reaction vessel and flash lamp in order to avoid the direct photolysis of ClO.

It was found that at all flash energies, the decay of ClO produced from the above sets of experiments was strictly second order for the delay times above 100 to 250 μsec (fig.8). The reaction involved is taken to be

$$2ClO \rightarrow Cl_2 + O_2 \qquad (5)$$

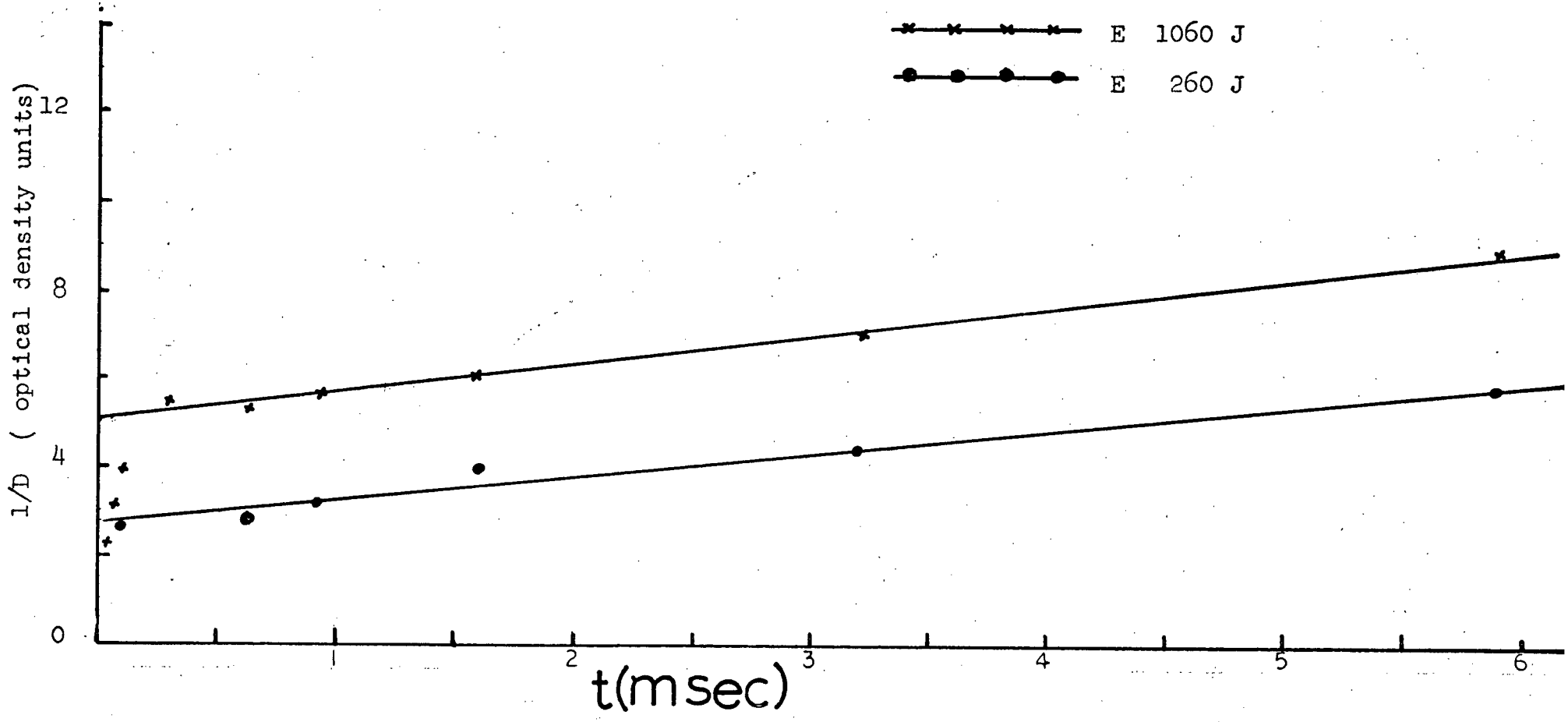
The rate constant, k_5, defined by the equation

Table IV

Plate no.	$[ClO_2]$ (torr)	Argon (torr)	Energy J	$k_5 \times 10^{-7}$ (l mole^{-1} sec^{-1}) 2577 Å	2772 Å	2920 Å
104	0.25	200	1060	2.97	2.96	2.60
105	0.06	200	1060	2.90	2.20	--
106	0.25	75	1060	2.97	2.65	3.25
107	0.08	75	1060	--	2.3	2.98
114	0.12	200	1060	2.99	2.96	2.45
115	0.25	200	1060	--	2.69	2.28
152	0.25	200	1060	2.62	2.10	--
104	0.25	200	600	2.77	2.49	2.43
105	0.06	200	600	2.69	2.49	--
106	0.25	75	600	3.36	2.41	2.43
107	0.08	75	600	2.62	--	--
119	0.25	75	600	2.03	2.20	--
120	0.1	75	600	2.93	3.04	--
154	0.1	200	600	--	2.20	2.53
118	0.25	200	260	2.60	2.52	2.4
119	0.25	75	260	2.13	2.52	--
120	0.1	75	260	3.07	2.70	2.98
121	0.25	200	260	2.8	2.3	2.95
156	0.1	200	260	2.75	2.52	3.10
164	0.25	200	260	2.25	2.72	2.80
110	0.25	200	160	--	2.65	2.67
156	0.1	200	160	2.52	2.6	2.73
121	0.25	200	160	2.62	2.77	2.64

Average $k_5 = 2.65 \pm 0.29 \times 10^7$ ℓ mole^{-1}sec^{-1}

Figure 8. A plot of 1/ [ClO] against time following the flash photolysis of ClO_2. ClO_2= 0.25 torr, Argon = 200 torr.



$$-\frac{1}{[ClO]^2}\frac{d[ClO]}{dt} = k_5$$

can be integrated to give the form:

$$\frac{1}{[ClO]} = \frac{1}{[ClO]_o} + k_5 t \ .$$

This can be transformed into

$$\frac{1}{D} = \frac{1}{D_o} + \frac{k_5 t}{\varepsilon \ell}$$

where D = optical density at any time $t = \varepsilon [ClO]_t l$

$D_o = \varepsilon [ClO]_o l$ = optical density at time t = 0.

1/D was plotted against time t and the data were found to follow straight lines after 200 μsec at all flash energies. From the slopes of the plot and the extinction coefficient determined as described in the last section, k_5 was calculated. The ClO concentration was measured at three wavelengths and the decay followed at all flash energies, ClO_2 pressures and total pressures mentioned above. The results are listed in Table IV.

From Table IV, it is clear that k_5 is independent of flash energy, total pressure and ClO_2 pressure. The agreement between the results obtained at three wavelengths is good. The average value of all fifty seven determinations of k_5 is $(2.65 \pm 0.29) \times 10^7$ l mole^{-1} sec^{-1}. The average of five determinations using medium quartz spectrograph was identical. The value of k_5 obtained is in satisfactory agreement with that of $(2.4 \pm 0.4) \times 10^7$ l mole^{-1} sec^{-1}, obtained by Edgecombe et al.[22] from the flash photolysis of Cl_2O and it is similar to the values

obtained by L.N.T.[21] at the two lowest flash energies used. The results given here, however, differ significantly from those reported by Porter and Wright[15] and Clyne and Coxon.[25] From the flash photolysis of Cl_2/O_2 mixtures, Porter and Wright[15] found $k_5/\varepsilon = 7.2 \times 10^4$ cm sec^{-1} at 2577 Å, which, combined with our value of ε at 2577 Å, gives $k_5 = 8.3 \times 10^7$ l $mole^{-1}$ sec^{-1}. Clyne and Coxon[25] from their flow system in which ClO radicals were generated by the reaction of chlorine atoms with ClO_2, got average values of k_5 as $(1.4 \pm 0.1) \times 10^7$ l $mole^{-1}sec^{-1}$.

2) Production of ClO Radicals by Flashing a Mixture of Chlorine and Oxygen

Considering the great difference between the value of k_5 determined by us from ClO_2 photolysis and that of k_5 found by Porter and Wright[15] from the chlorine and oxygen system, we therefore reinvestigated this system. Cl_2 with pressure 5 torr and 7.5 torr, and oxygen 50 or 66 torr was flashed with a total pressure of 200 torr using inert gas (nitrogen or argon). The above mixtures were flashed with only one flash energy (1325 J), using both pyrex and quartz reaction vessels. In two of the runs, the same mixture was flashed again and again to see if there was any variation in the results obtained by reflashing the mixture or taking fresh one each time. The spectrum thus obtained is similar to that obtained by Porter,[14] is shown in fig. 9 (plate 208). The ClO concentration was measured at two wavelengths, i.e., 2772 Å and 2577 Å to follow its decay.

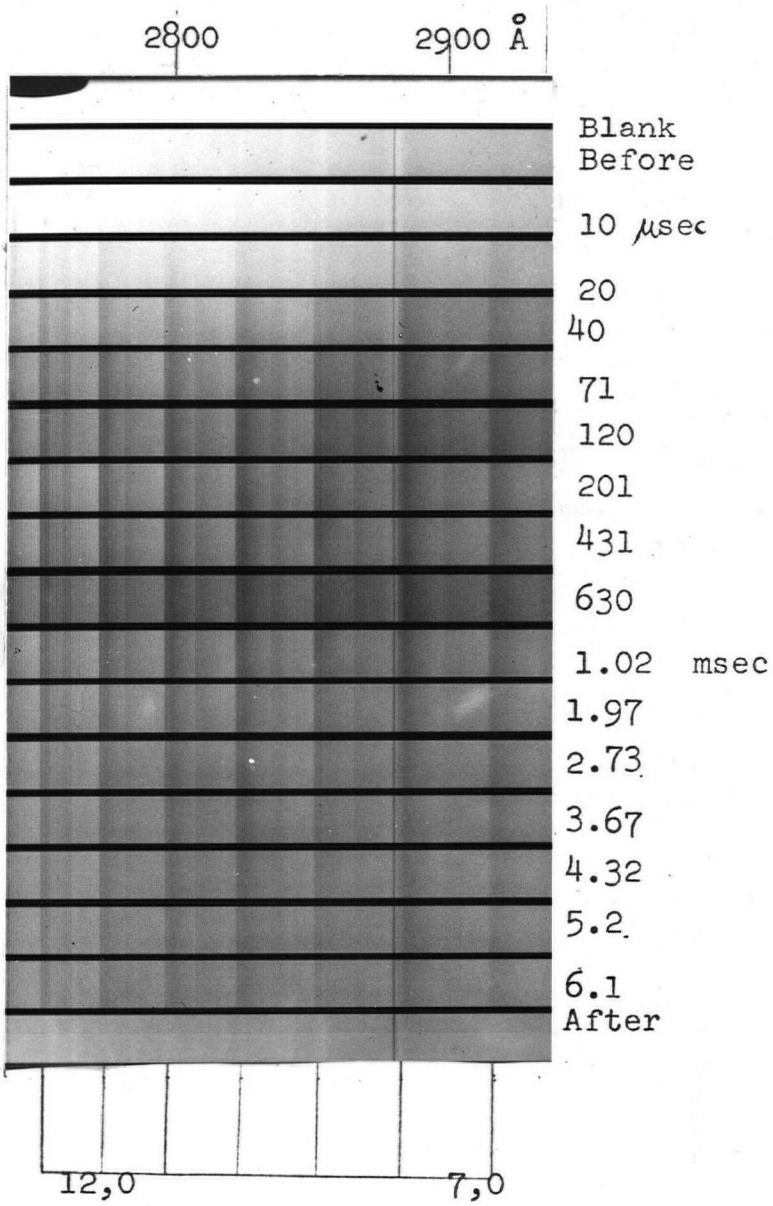


Figure 9. Rise and Decay of ClO.

Cl_2=5.0 torr, O_2=50 torr, Argon = 145 torr, E=1325J

The measurements at 2920 Å were neglected due to the interference of continuum of chlorine absorption. The results were treated in the same manner as in ClO_2 photolysis and the results are listed in Table V. The average of fourteen determinations of k_5 was $2.77 \pm 0.26 \times 10^7$ l mole^{-1}sec^{-1} and thus in excellent agreement with the value obtained in the previous system. The same results were obtained with nitrogen and argon as inert gas and with quartz and pyrex reaction vessels. It can also be seen from Table V, results were the same in the experiments where the same mixture of $Cl_2/O_2/Ar$ was used for all delays and those where a fresh mixture was used for each delay time. The value of k_5 obtained is much lower than that obtained by Porter and Wright[15] but no explanation is offered for the difference between the two results.

3) Production of ClO Radicals from Cl_2O and Chlorine Sensitised Photolysis of Cl_2O

In view of the possible complexity of the ClO_2 system (in particular the proposed formation of ClO_3 and Cl_2O_3) and also as there was no obvious reason for the higher values obtained by Porter and Wright,[15] we studied the decay of ClO radicals produced in the photolysis of Cl_2O and in the chlorine sensitised decomposition of Cl_2O.

The Cl_2O at two pressures but with the same total pressure of argon was flashed at three flash energies. In two of the

Table V

Plate no.	$[Cl_2]$ (torr)	$[O_2]$ (torr)	R.V.	$k_5 \times 10^{-7}$ (1 mole^{-1} sec^{-1}) 2577 Å	2772 Å
201	5.0	56	P	2.65	3.05
202	5.0	56	Q	2.95	2.94
203	5.0	50	Q	2.70	--
204	7.5	50	Q	2.99	(1.90)
205*	7.5	50	Q	3.10	2.70
206*	7.5	50	P	3.0	2.60
207	7.5	50	P	--	2.53
208	7.5	50	P	2.62	2.15
			Average	2.86 ± 0.18	2.66 ± 0.26

Mean $k_5 = (2.77 \pm 0.26) \times 10^7$ l mole^{-1}sec^{-1}

* Nitrogen was used as inert gas
P = pyrex
Q = quartz

experiments two mm glass filter A was placed between the photolysis lamp and the reaction vessel to see if there is any difference in the results. The measurements of ClO were carried out at the 12,0 (2772 Å) and 7,0 (2920 Å) bands in the same manner as has been described in the calculation of extinction coefficient of ClO.

It was found that the concentration of ClO produced or Cl_2O decomposed was greater when no filter was used. This was quite expected, firstly due to the increase in the extinction

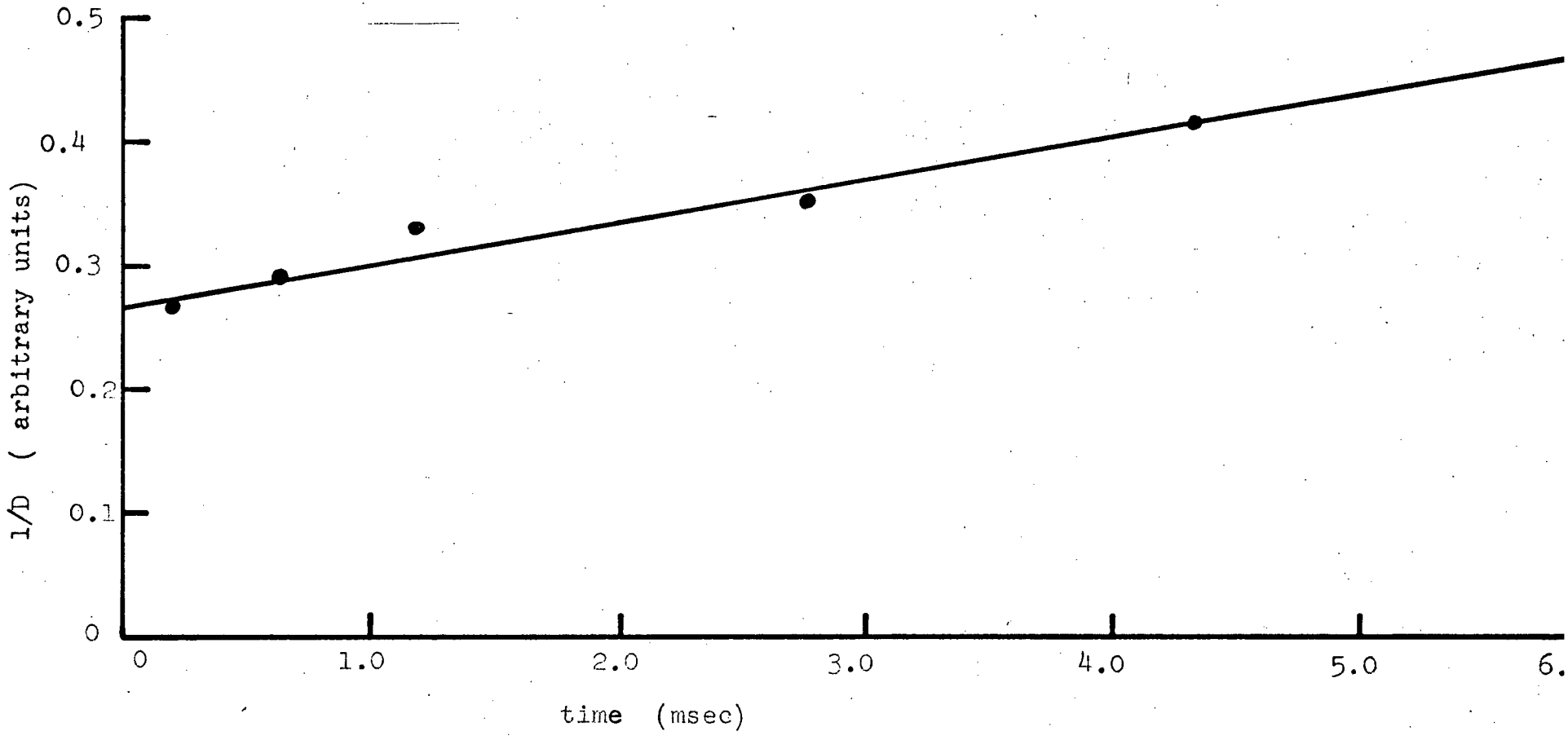
coefficient of Cl_2O towards the lower wavelengths and secondly due to decomposition of Cl_2O into atoms (which will be discussed in Chapter V), followed by their reactions. Except for this no difference in the decay of ClO was noted.

In a similar way as with the ClO_2 photolysis, 1/D was plotted against time and a reasonably good straightline was observed as shown in fig.(10), indicating that other processes during the ClO decay are slow. These will be discussed in more detail in Chapter V. Combining the slopesof the straight lines with the extinction coefficient k_5 was calculated and values are listed in Table VI. The average of seven runs was found to be $2.77 \pm 0.22 \times 10^7$ l $mole^{-1}sec^{-1}$.

The ClO radical was also generated by flashing Cl_2 in the presence of Cl_2O in the pyrex reaction vessel and two mm of glass filter A was placed between the flash lamp and reaction vessel. Two flash energies viz. 600 and 1060 J, two Cl_2O concentrations (3.65×10^{-5} and 5.8×10^{-5} mole/l) and one chlorine pressure was used. Details of the reaction of the chlorine atom with Cl_2O and other secondary processes will be discussed in Chapter V. A similar procedure was used to calculate the rate constant for ClO decay and the results are listed in Table VI. The average of four results was found to be $(2.88 \pm 0.3) \times 10^7$ l $mole^{-1}$ sec^{-1}.

It can be seen from the results of Table VI that there is a satisfactory agreement between our value and that of Edgecombe et al.[22] The agreement may, however, be coincidental

Figure 10. A plot of 1/ [ClO] against time following the flash photolysis of Cl_2O. Cl_2O = 0.6 torr, Argon = 200 torr, E = 1325 J.



in that the value of ε(ClO) measured by them at 2920 Å (the wavelength used to follow the ClO decay) is not explicitly stated. Clyne and Coxon[25] have calculated from the relative extinction coefficients of ClO at 2577 Å and 2824 Å (10,0) given by Porter and Wright[15] and from the relative intensities of 10,0 and 7,0 bands given by Porter,[14] that Edgecombe, Norrish and Thrush,[22] would have obtained a value of ε at 2577 Å of 760 l mole^{-1} cm^{-1} with $k_5/\varepsilon = 3.1 \times 10^4$ cm sec^{-1} at this wavelength. From the data given by E.N.T.,[22] we calculated $k_5/\varepsilon \sim 4.8 \times 10^4$ cm sec^{-1} and ε = 500 l mole^{-1} cm^{-1} at 2920 Å. In both cases a significant discrepancy is apparent.

Table VI

Plate no.	$[Cl_2O]$ (mole/l	$[Cl_2]$ $\times 10^{-6}$)	Filter	Energy J	$k_5 \times 10^{-7}$ (l mole^{-1}sec^{-1}) 2772 Å	2920 Å
170	35.6	137.5	A	600	2.82	--
171	63.3	137.5	A	600	2.92	2.59
173	36.5	137.5	A	1060	--	3.18
					2.88 ± 0.3	
184	57.8	--	A	830	2.8	2.45
191	52.3	--	A	1060	3.1	--
192	55.0	--	-	1325	2.62	2.8
193	33.0	---	-	1325	3.1	2.55
				Average	2.77 ± 0.22	

4) Flash Photolysis of a Mixture of ClO_2 and Cl_2O

Though main reasons for flashing mixtures of Cl_2O and ClO_2 at flash energies 1060 and 1325 J were to compare the rate constants for the reaction of oxygen atoms with ClO radicals and Cl_2O and ClO_2 as will be discussed in the next chapter, a study of the bimolecular decay of ClO was also carried out after the preliminary reactions of atoms are over (approx. 200 to 300 μsec). The different mixtures (as mentioned in Table VII) of Cl_2O and ClO_2 were flashed using 3400 Å filter. This filter was used to prevent the decomposition of Cl_2O. It was found that rapid decay of ClO in the early part with high flash energy was reduced and replaced by a steady increase in its concentration depending upon the ratio of ClO_2 to Cl_2O as can be seen from fig. 19 (page 100). After the early reactions, the ClO concentration was monitored at 2772 Å and the 1/D was plotted against time which was found to be a straight line. The values of k_5 calculated from the slopes of the straight lines, combined with extinction coefficients are listed in Table VII. The average of two (without Cl_2O) and six runs (with Cl_2O) was found to be $(2.4 \pm 0.2) \times 10^7$ l mole^{-1}sec^{-1} which is in good agreement with the value of k_5 obtained by previous methods.

Mechanism of the Decay of ClO

In view of the consistency of the results of k_5 obtained by five different flash photolysis methods, it appears probable

Table VII

Plate no.	$[ClO_2]$ (10^{-6} mole/l)	$[Cl_2O]$ (10^{-6} mole/l)	Energy J	$k_5 \times 10^{-7}$ (l $mole^{-1} sec^{-1}$)
186	4.4	--	1060	2.6
186	4.4	6.9	1060	2.4
187	4.4	2.75	1060	2.5
187	4.4	5.5	1060	2.4
188	4.4	--	1325	2.4
188	4.4	9.6	1325	2.1
189	4.4	4.1	1325	2.4
189	4.4	6.9	1325	2.2

Average = $(2.4 \pm 0.2) \times 10^7$ l $mole^{-1}$ sec^{-1}

that the difference between Clyne and Coxon's[25] value $(1.4 \pm 0.01) \times 10^7$ l $mole^{-1} sec^{-1}$ and ours arises from because the mechanism of the reaction changes at low pressure (~1mm) used in the discharge flow experiments of Clyne and Coxon.[25] Thus they adopted the free radical mechanism proposed by Benson and Buss[26] and their k_5 is identified with k_{20},

$$2ClO \underset{k_{-20}}{\overset{k_{20}}{\rightleftharpoons}} Cl\text{-}O\text{-}O + Cl$$

This interpretation was supported by the effects produced when chlorine atom scavengers (ClO_2, O_3, Br_2) were added to the ClO system. A rapid removal of both ClO_2 and O_3 was observed in chain reactions whose rates were closely related to that of the ClO recombination rate. Br_2 is effective in suppressing the chain reaction of H_2 with ClO.

The mechanism of Porter and Wright[15] involves the intermediate Cl_2O_2 and perhaps the simplest solution is to combine the two mechanisms using Cl_2O_2 as the common intermediate.

$$2ClO \rightleftarrows Cl_2O_2$$

$$Cl_2O_2 \rightarrow Cl\text{-}O\text{-}O + Cl$$

$$Cl_2O_2 + M \rightarrow Cl_2 + O_2 + M$$

$$Cl + Cl\text{-}O\text{-}O \rightarrow Cl_2 + O_2$$

This leads to the same limiting high and low pressure behaviour as the similar mechanism proposed by Clyne and Coxon,[25] i.e., their mechanism:

$$2ClO + M \underset{k_{-90}}{\overset{k_{90}}{\rightleftarrows}} Cl_2O_2 + M$$

$$Cl_2O_2 \xrightarrow{k_{100}} Cl_2 + O_2$$

identifies k_5 with $k_{90} \times k_{100} / k_{-90}$ (where k_{90} and k_{100} correspond to k_9 and k_{10} of Clyne and Coxon's[25] respectively).

Evidence that the Benson and Buss [26] mechanism is not important at high pressure is provided by the following obser-

vations. The decay of ClO produced from ClO_2 at high flash energies where an appreciable concentration of chlorine atoms is produced in reaction (6) is the same as at low flash energies. At low flash energies, where an appreciable concentration of ClO_2 is present during the decay of ClO, no decrease of ClO_2 concentration was observed as can be seen from fig. (10-a), unlike results at low pressure of Clyne and Coxon,[25] although the reaction of chlorine atoms with ClO_2 is very fast ($k_8 > 5 \times 10^8$ l mole^{-1} sec^{-1}[25] or $k_8 = 5 \times 10^9$ l mole^{-1}sec^{-1}).[31] This observation was confirmed during the photosensitised decomposition of ClO_2 by chlorine atoms, in which the ClO_2 concentration decreases in the beginning (due to the reaction of chlorine and oxygen atoms with ClO_2) and the ClO concentration increases. After this ClO_2 remains constant and the rate of ClO decay is likewise not decreased in the presence of ClO_2.

Finally, when ClO is produced from Cl_2O or from Cl_2O/Cl_2, there is a large excess of Cl atoms. Subsequently, the Cl_2O behaves as an efficient chlorine atom scavenger ($k_{19} > 4 \times 10^8$ l mole^{-1}sec^{-1} by E.N.T.[22] and $k_{19} = 4 \times 10^8$ l mole^{-1}sec^{-1} in the present work) yet the same value for the rate constant k_5 was observed in all the systems studied.

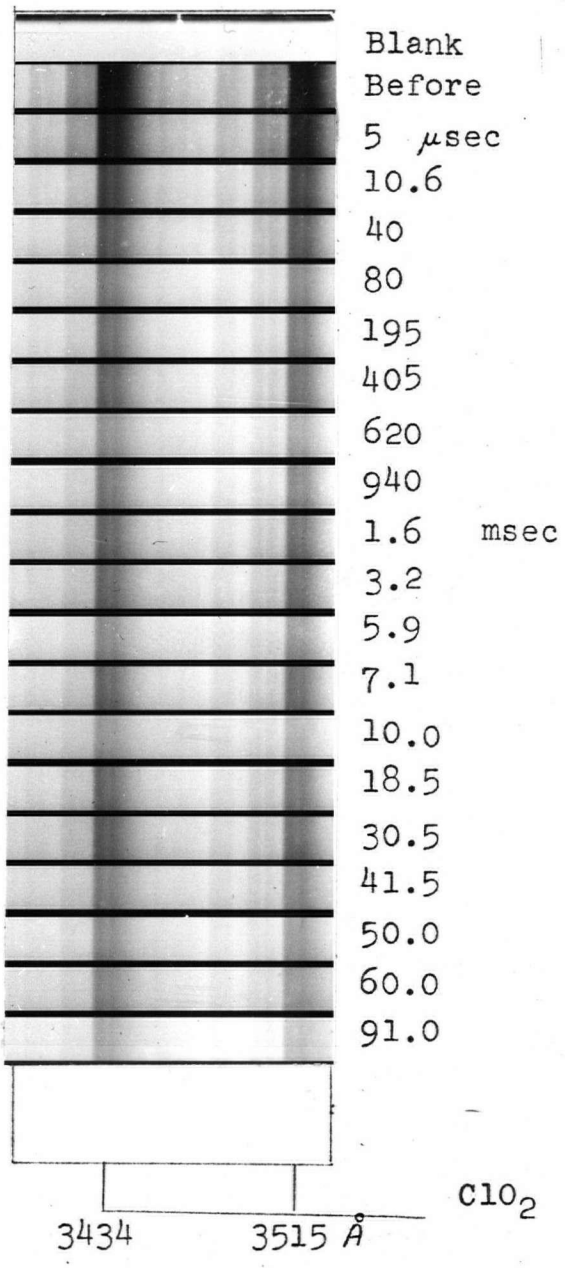


Figure 10-a. Behaviour of ClO_2 during the decay of ClO.

ClO_2= 0.1 torr, Argon= 200 torr, E=160 J

After the thesis was written, Johnston, Morris and Van den Bogaerde[99] reported their results of a detailed kinetic study of photolysis of chlorine in the presence of oxygen with square wave excited UV lamps at frequencies of 0.25 - 32 Hz. Using a new molecular modulation technique, the UV and IR spectra attributed to the ClOO radical were found in the regions 2300 Å - 2600 Å and 1430 - 1460 cm^{-1} and the UV spectrum of ClO was also observed.

A most significant feature of their results was an almost linear dependence of the rate constant for the decay of ClO on total pressure in the range studied (50 - 760 mm). This complete mechanism, preserving their nomenclature, is

$$Cl_2 + h\nu \xrightarrow{a} 2\,Cl$$

$$Cl + O_2 + M \underset{c}{\overset{b}{\rightleftarrows}} ClOO + M$$

$$Cl + ClOO \underset{e}{\overset{d}{\rightleftarrows}} 2\,ClO$$

$$Cl + ClOO \xrightarrow{f} Cl_2 + O_2$$

$$2\,ClO + M \underset{h}{\overset{g}{\rightleftarrows}} Cl_2O_2 + M$$

$$Cl_2O_2 + M \xrightarrow{i} Cl_2 + O_2 + M$$

$$2\,Cl + M \xrightarrow{j} Cl_2$$

and they find $e = 3.8 \times 10^{6}$ litre $mole^{-1}$ sec^{-1}

$$\frac{ig}{h} = 1.2 \times 10^{10} \text{ litre}^2 \text{ mole}^{-2} \text{ sec}^{-1} \text{ (Argon)}$$

For the time dependence of $C\ell O$, they derive the equation

$$\frac{d[C\ell O]}{dt} = \frac{2cd[C\ell OO]^2}{b[O_2]} - 2(e + \frac{ig[M]}{h})\,[C\ell O]^2$$

so that

$$K_2 = 2(e + \frac{ig[M]}{h})$$

At pressures of $\sim$ 2 mm, the first term is more important and the value of K_2 obtained from this equation is in good agreement with that found experimentally by Clyne and Coxon.[25] Above 60 mm $\frac{ig[M]}{h} > 10$ e and the reaction is essentially third order

$$2\,C\ell O + Ar \rightarrow C\ell_2 + O_2 + Ar$$

with a calculated rate constant K_2 at 200 mm of 2.6×10^8 litre $mole^{-1}$ sec^{-1}. The reported pressure dependence of K_2 is in complete disagreement with our results and with the work of Porter and Wright [15], who showed that the rate was independent of total pressure over the range 55-610 mm. Moreover, the calculated value of the rate constant K_2 of 2.6×10^8 litre $mole^{-1}$ sec^{-1} at 200 mm total pressure is higher than our value by a factor of $\sim$ 10. Johnston, Morris and Van den Bogaerde[99] draw attention to the activation energy of 2.5 kcal $mole^{-1}$ found by Clyne and Coxon [25] for the reaction and to their own observation of a pressure dependence. They state there was a large adiabatic temperature rise in Porter's system so that a reduction in total pressure would tend both to increase the rate because of the resulting increase in temperature and to lower it because of the pressure effect. "Thus the near cancellation of these two effects may have caused Porter to miss both of them." This explanation of

the difference between their results and those of Porter is however unconvincing. First, the activation energy found by Clyne and Coxon [25] surely applies to reaction e which is of negligible importance at the pressures used except at impossibly high temperatures. For example at 300 mm total pressure, $e = \frac{ig[Ar]}{h}$ only at $\sim 3700°$ h. Accidental cancellation of the two effects of pressure would not be possible over the range of pressures studied by Porter. Secondly, if any significant temperature rise did occur in Porter's system and if the reaction does have a positive temperature coefficient, his value for K_2 would have been higher than those of Johnston et al [99], whereas the reverse is the case.

Our results show that K_2 is independent of pressure and that the small temperature rises which may occur in the systems studied have no measureable effect on the rate constant. In the $C\ell O_2$ system, for example, the two factors which largely determine the temperature rise viz. flash energy and the ratio $[C\ell O_2]$ [Ar] have both been varied at the same total pressure without changing the value of K_2 obtained (table IV).

The conflicts between the results of Johnston et al [99], Porter [15] and those presented in this thesis remain to encourage further studies of this reaction.

CHAPTER IV

REACTIONS OF OXYGEN ATOMS WITH ClO, Cl_2O AND ClO_2

In this chapter the reactions of oxygen atoms with ClO, ClO_2 and Cl_2O will be discussed. The reaction of oxygen atoms with ClO and ClO_2 in the ClO_2 system and with Cl_2O and ClO in the Cl_2O system take place simultaneously, depending upon the extent of decomposition of the parent compound in the primary process. So it is quite complicated to find the rate constant of the individual reactions. But ClO_2 has two advantages over the Cl_2O system.

1) Using glass filter A, there is only one primary process, i.e.

$$ClO_2 + h\nu \rightarrow ClO + O \qquad (27)$$

followed by

$$ClO_2 + O \rightarrow ClO + O_2 \qquad (7)$$

2) ClO_2 absorbs very strongly as compared to Cl_2O and hence the complete removal of ClO_2 can be achieved with comparatively low flash energy.

Thus the ClO_2 was used to find the rate constants of the reactions of oxygen atoms with ClO and the mixture of Cl_2O and ClO_2 was used to compare the rate constants of oxygen atoms with ClO to ClO_2 or to Cl_2O depending upon the flash energy and the ratio of ClO_2 to Cl_2O.

In the first section, the reaction of oxygen atoms with ClO studied in two ways will be discussed and confirmatory evidence obtained by one method will be presented. This will

be followed by an account of the reaction of oxygen atoms with Cl_2O and ClO_2, respectively.

A. Reaction of Oxygen Atoms with ClO

1) Using ClO_2 as the Parent Compound

As mentioned before, ClO_2 absorbs very strongly and virtually complete decomposition of pressures in the range 0.05 to 0.25 torr can be achieved by relatively low flash energies (400 to 800 J) depending upon the type of the reaction vessel and flash lamp enclosure used. At any high flash energy, if more than half of the ClO_2 is photolysed and there must be an excess of oxygen atoms over that necessary to complete the removal of ClO_2 in the reaction

$$O + ClO_2 \rightarrow ClO + O_2 \qquad (7)$$

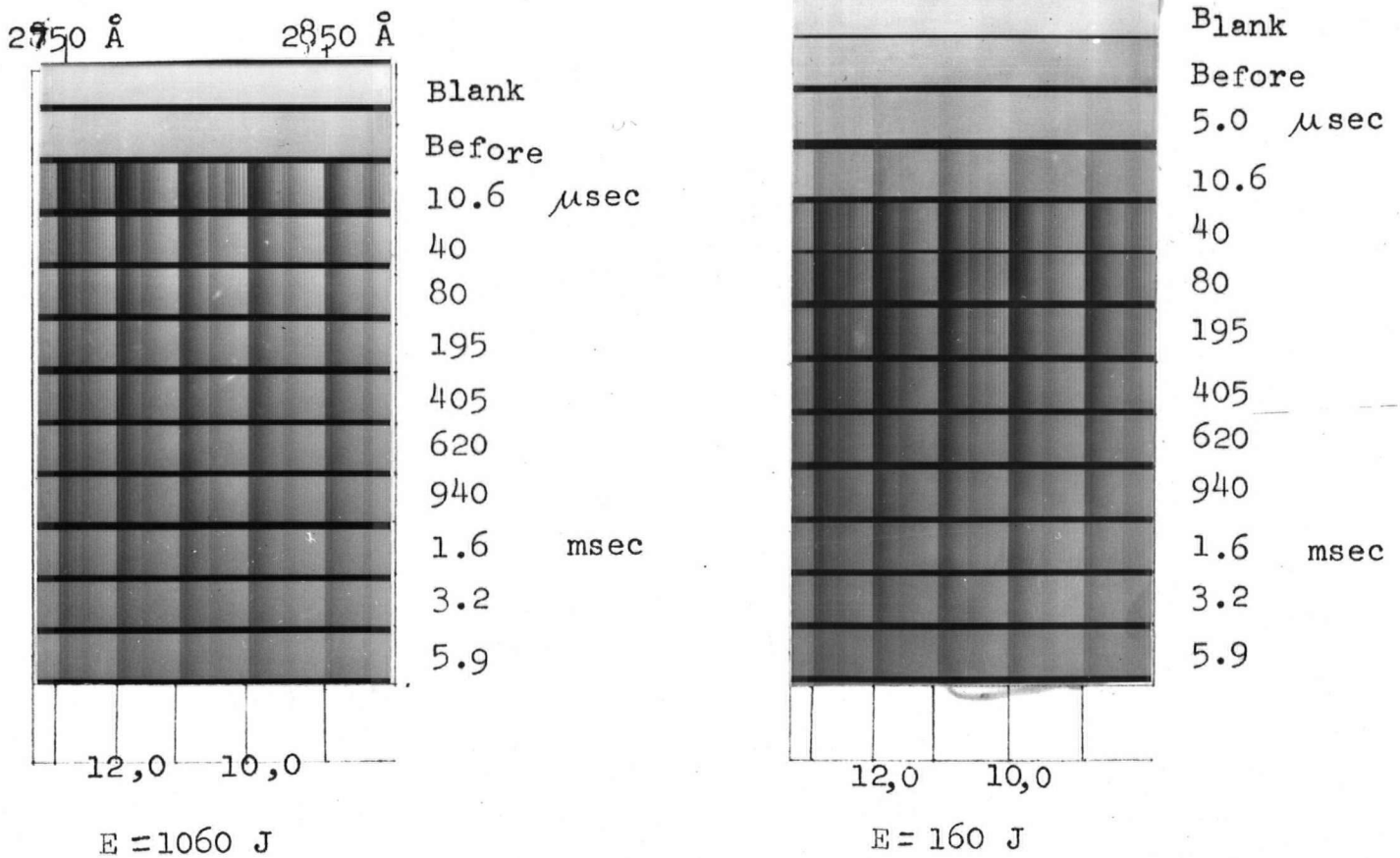
The likely fate of the excess oxygen atoms is the reaction

$$O + ClO \rightarrow Cl + O_2 \qquad (6)$$

and we propose that this reaction is fast and that it is responsible for the initial fast decay of ClO observed at high flash energies. This can be seen from the second order plot of ClO vs time (fig. 8, page 59). At low flash energies the plot is linear from the peak of ClO whereas at high flash energies the plot departs from linearity though the peak can be reached within 10 μsec. The decay of ClO at flash energies 1060J and 160J are compared in fig.(11)(plates 106 and 110).

Figure 11. Comparison of the decay of ClO following the flash photolysis of ClO_2 at high(1060 J) and low(160 J) energies.

ClO_2= 0.25 torr, Argon = 200 torr.



The importance of reaction (6) at low energies depends upon the relative values of k_6 and k_7. Clyne and Coxon[23] found k_7/k_6 to be approximately 4, so the reaction (6) must be taken into account where the primary process exceeds ∿30%. The overall production of ClO is, however, not affected unless the primary photolysis exceeds 50% and total decomposition of ClO_2 is achieved, since the chlorine atoms produced in reaction (6) will react rapidly with any ClO_2 left in the reaction

$$Cl + ClO_2 \rightarrow 2ClO \qquad (8)$$

The rate constant for this reaction has been given by Clyne and Coxon[25] as $>5 \times 10^8$ l mole^{-1} sec^{-1} and we have found $k_8 = 5 \times 10^9$ l mole^{-1} sec^{-1}.

Evidence that reaction (6) is occurring to a significant extent in the experiments of Lipscomb, Norrish and Thrush[21] has already been presented in the discussion on the extinction coefficient of ClO. Support for this view is provided by Table I of their paper in which it is seen that the percentage decomposition of ClO_2 achieved is remarkably insensitive to the flash energy. For example, increasing the energy from 400 to 1620 J, raises the decomposition from 91% to 99% while it only falls to ∿73% at 240 J.

The same experimental procedure was used in studying reaction (6) as in the determination of bimolecular decay of ClO except that only the early part of the second order plot

was used for one energy, 1060 J. This beginning portion of the plot of 1/D (representation of ClO concentration) has been replotted in fig. (12) on a larger scale. It can be seen very clearly that this portion is markedly non-linear.

At high flash energies then, the decay of ClO is represented by the equation

$$\frac{-d[ClO]}{dt} = k_5[ClO]^2 + k_6[ClO][O] \qquad (b)$$

with the reasonable assumption that the effect of chlorine atoms on the decay of ClO may be neglected. The rate constant k_6 was measured as follows from fig.(12).

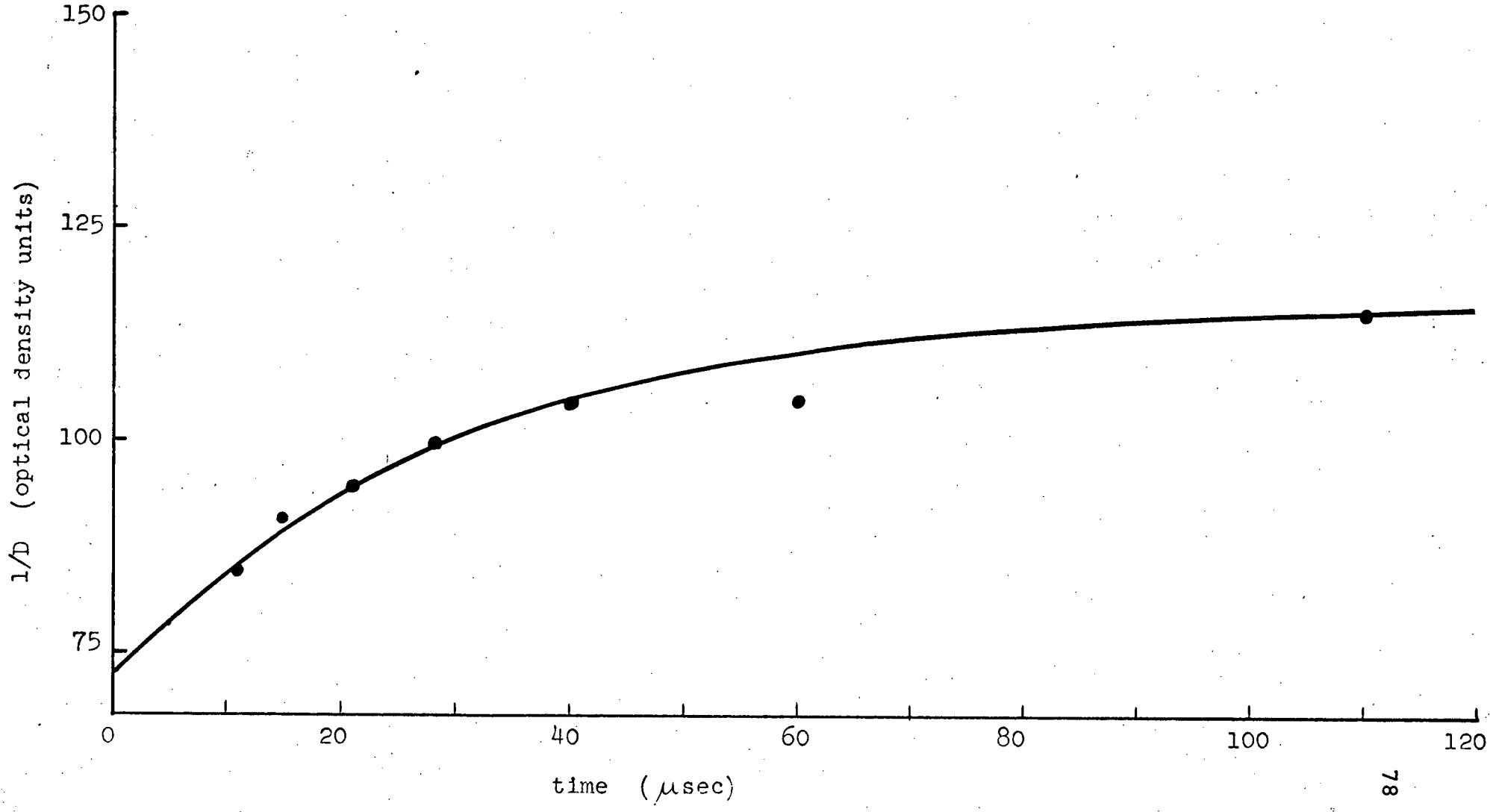
The ClO concentration, measured from the curve passing through the experimental points at very short delays (∿5 to 8 μsec), was extrapolated to zero time. The value at zero time $[ClO]_o$ is the total [ClO] produced and since 100% decomposition of ClO_2 was achieved, a check on the accuracy of the extrapolation is provided by the condition $[ClO]_o = [ClO_2]_o$. The linear part of the second order plot is extrapolated to zero time, this line representing the bimolecular decay of ClO for an initial concentration $[ClO]'_o$. The concentration of ClO removed by reaction (6) and hence the initial oxygen atom concentration which is left after reacting with ClO_2 is given by

$$[O]_o = [ClO]_o - [ClO]'_o$$

At any time the oxygen atom concentration is obtained from the equation

$$[O] = [ClO] - [ClO]' \qquad (b')$$

Figure 12. A plot of 1/ [ClO] against time at short time delays.
ClO_2 = 0.25 torr, Argon = 200 torr, E = 1060 J.



where [ClO] is the measured ClO concentration and [ClO]' is the value obtained from the linear extrapolation.

The results were treated in two ways:

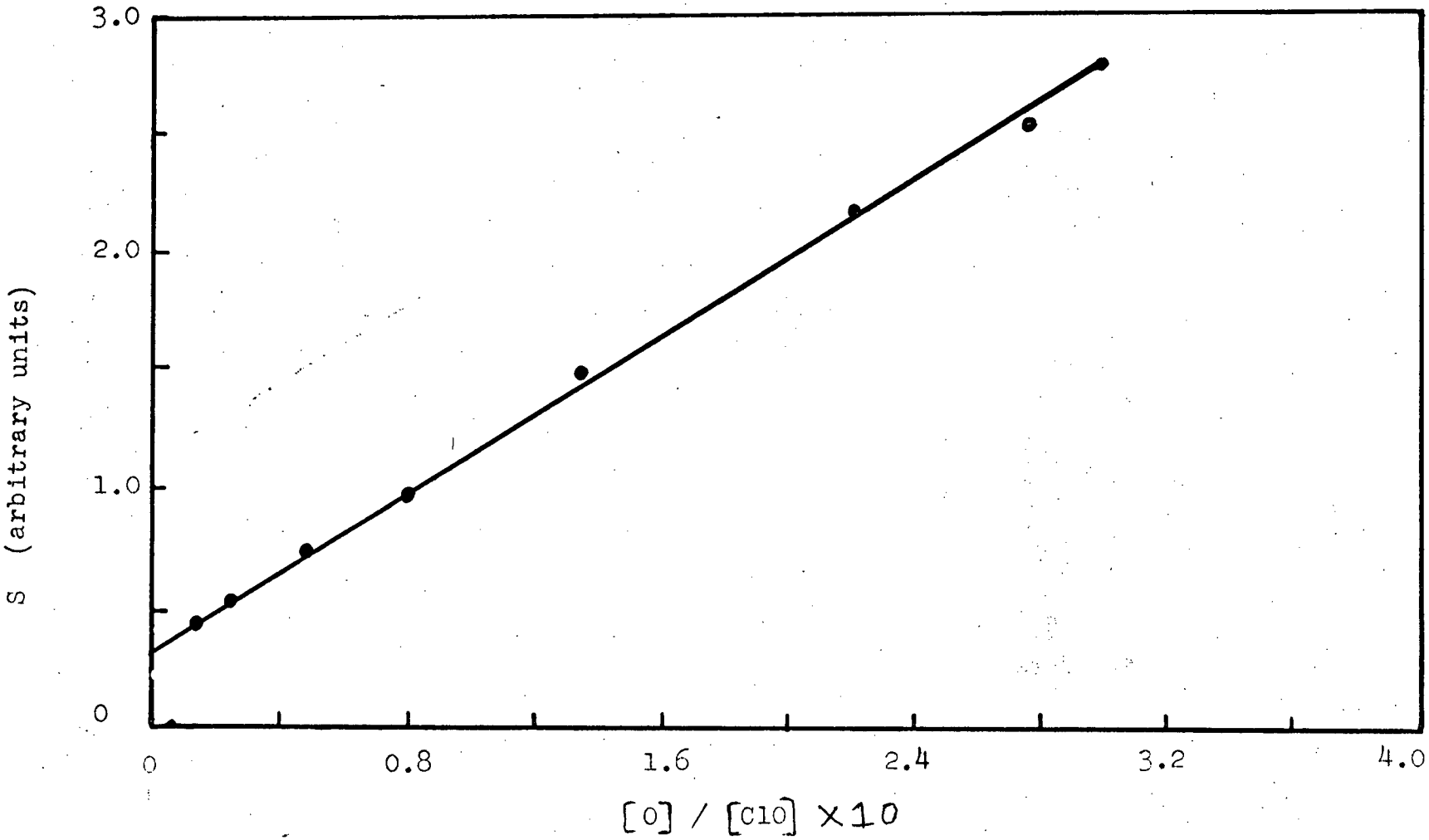
i) Equation (b) can be converted into

$$\frac{-1}{[ClO]^2}\frac{d[ClO]}{dt} = k_5 + k_6\frac{[O]}{[ClO]} \qquad (c)$$

from fig.(12) slopes of the second order plot were measured and at the same time the ratio of oxygen atoms to ClO radicals were calculated. Thus the slopes calculated in this way were plotted against the ratio of oxygen to ClO radicals. As expected from the above equation this plot was linear (fig. 13) and the values of k_6 thus obtained are listed in Table VIII. The average of five experiments is $(7.05 \pm 0.42) \times 10^9$ l mole^{-1} sec^{-1}. From equation (c) it is also clear that the intercept of this plot should give the rate constant for the bimolecular decay of ClO but it was found that the intercept is too small to be measured accurately. Still it is of the order of the value of k_5 previously determined.

ii) As has been seen from procedure (i) the intercept is too small to be determined accurately and also it can be seen from the linear extrapolation that [ClO]' is nearly constant over the period 200μsec, to the first approximation the first term in the equation (b) can be neglected and thus equation (b) reduces to

Figure 13. A plot of slopes calculated at different times from fig. 12 against [O] / [ClO] at the same time.



$$-\frac{d[ClO]}{dt} = k_6[O][ClO]$$
$$= k_6[ClO]\left([ClO] - [ClO]'\right)$$

after substituting for oxygen atoms at any time. Writing x for ClO, the above equation becomes

$$-\frac{dx}{dt} = k_6 x\,(x - a)$$

or
$$\ln\frac{x}{x-a} = a\,k_6 t + c$$

where c is constant of integration.

When $t = 0$, $x = x_o$ so,

$$c = \ln\frac{x_o}{x_o - a}$$

i.e. $$\ln\frac{x}{x-a} = a\,k_6 t + \ln\frac{x_o}{x_o - a}$$

or $$\log\frac{[ClO]}{[ClO]-[ClO]'} = \frac{a\,k_6}{2.303} + \log\frac{[ClO]_o}{[ClO]_o-[ClO]'} \qquad (d)$$

$\log\frac{x}{x-a}$ was plotted against time (fig.14) and found to be linear as expected from equation (d). The results are shown in Table IX and the average of five found to be $6.9 \pm 0.44 \times 10^9$ l mole^{-1} sec^{-1}. The overall average value $7.0 \pm 0.44 \times 10^9$ l mole^{-1} sec^{-1} is consistant with the lower limit of 6×10^9 l mole^{-1} sec^{-1} given by Clyne and Coxon[23] for this rate constant.

Figure 14. A plot of log([ClO] / [O]) against time.

ClO_2 = 0.25 torr, Argon = 200 torr, E = 1060 J.

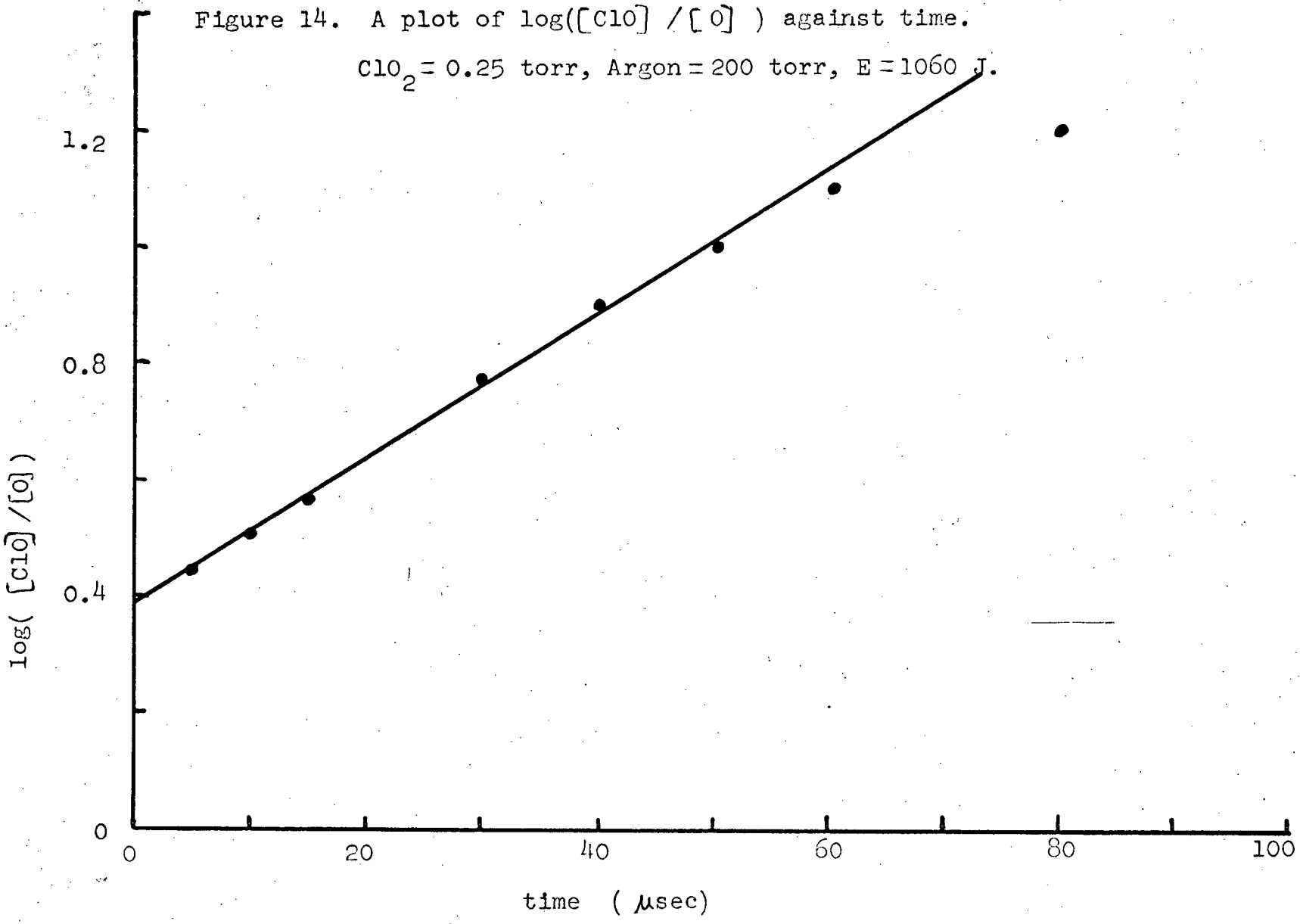


Table VIII

Calculation of the Rate Constant of Reaction O + ClO

Plate no.	$[ClO_2]$ (torr)	Argon (torr)	Energy J	$k_6 \times 10^{-9}$ (l mole^{-1} sec^{-1}) Method I	Method II
104	0.25	200	1060	6.7	6.4
152	0.25	200	1060	7.2	6.8
107	0.08	200	1060	7.2	7.3
105	0.06	200	1060	7.7	7.6
106	0.25	75	1060	6.4	6.4
			Average	7.04 ± 0.42	6.9 ± 0.44
				$(7.00 \pm 0.44) \times 10^9$ l mole^{-1} sec^{-1}	

Table IX

Plate no.	$[ClO_2]$ (torr)	Argon (torr)	Delay time μsec	ClO $\times 10^{+6}$ (mole/l)	$k_6 \times 10^{-9}$ (l mole^{-1}sec^{-1}
214	2.0	360	200	5.3	8.1
215	2.0	360	100	7.2	8.3
219*	2.0	188	100	8.75	6.8
219*	2.0	188	166	7.3	6.7
			Average		7.5 ± 0.8

*These two experiments contain 10 torr of CO_2.

2) Flash Photolysis of ClO Radicals

Flash photolysis has been used for producing the transient species so far but in this work we have also used a flash photolysis technique to photolyse the transients. This has been achieved by firing one flash lamp (known as the main lamp) to generate the transients, followed by a firing of second lamp (auxiliary lamp) at a known delay (0 to 214 μsec) after the main lamp. The other details of this circuit have been mentioned in the experimental section. This technique has been used here to flash the transient, ClO, in order to find the rate constant of the reaction of oxygen atoms with ClO and to see if we can get a vibrationally excited oxygen in its ground electronic state. The former will be discussed here whereas the latter will be in Chapter VI.

As usual, ClO radicals were generated by flashing ClO_2 at pressure varying from 0.5 to 2.0 torr with 360 torr of argon or nitrogen in quartz or pyrex reaction vessel. The flash energy used in the main lamp was 1060 J. The behaviour of ClO_2 and ClO in the quartz reaction vessel was similar to that with pyrex having two mm of extra glass filter, i.e. very fast decay of ClO radicals in the beginning followed by the usual bimolecular decay.

Then the mixture was flashed with the auxiliary lamp at various flash energies and at different time delays after all the ClO_2 had decomposed. At these times, the mixture contains ClO, Cl_2 and O_2 (from the secondary reactions) and some

chlorine atoms from reaction (6). The spectra were recorded at different delay times after the firing of auxiliary flash. The trace of the main, auxiliary and spectroscopic lamps were observed on the screen of oscilloscope every time in order to assure that auxiliary lamp was firing at the proper delay.

The decay of ClO, as can be seen from fig.(15) (plate 214) and (16), is faster after the auxiliary flash lamp than that observed without the auxiliary lamp. After the initial fast decay, the ClO decays slowly as has been observed in the ClO_2 when flashed with high flash energy. This fast decay can be explained by the primary process (6-1) or (6-2) followed by (6-5) because the pressure of argon or nitrogen used was enough to have (6-4) faster than (6-3), i.e.,

$$ClO + h\nu \quad \text{(predissociation)} \rightarrow \quad Cl + O(^3P) \qquad (6\text{-}1)$$

$$ClO + h\nu \quad (< 2800\ \mathring{A}) \quad \rightarrow \quad Cl + O(^1D) \qquad (6\text{-}2)$$

followed by

$$O(^1D) + ClO(^2\pi) \rightarrow Cl(^2P) + O_2(^3\Sigma_g^-) \qquad (6\text{-}3)$$

$$O(^1D) + M \rightarrow O(^3P) + M \qquad (6\text{-}4)$$

$$O(^3P) + ClO(^2\pi) \rightarrow Cl(^2P) + O_2(^3\Sigma_g^-) \qquad (6\text{-}5)$$

The details of the preference of (6-5) over (6-3) will be discussed in Chapter VI. At the moment, we will consider only (6-5). The slow decay in the latter part is explained by reaction (5).

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (5)$$

Figure 15. Decay of ClO with and without flashing with auxiliary lamp.

ClO_2 = 2.0 torr, Argon = 360 torr, Reaction Vessel = Quartz, E_m = 1060 J

$E_{aux.}$ = 1325 J.

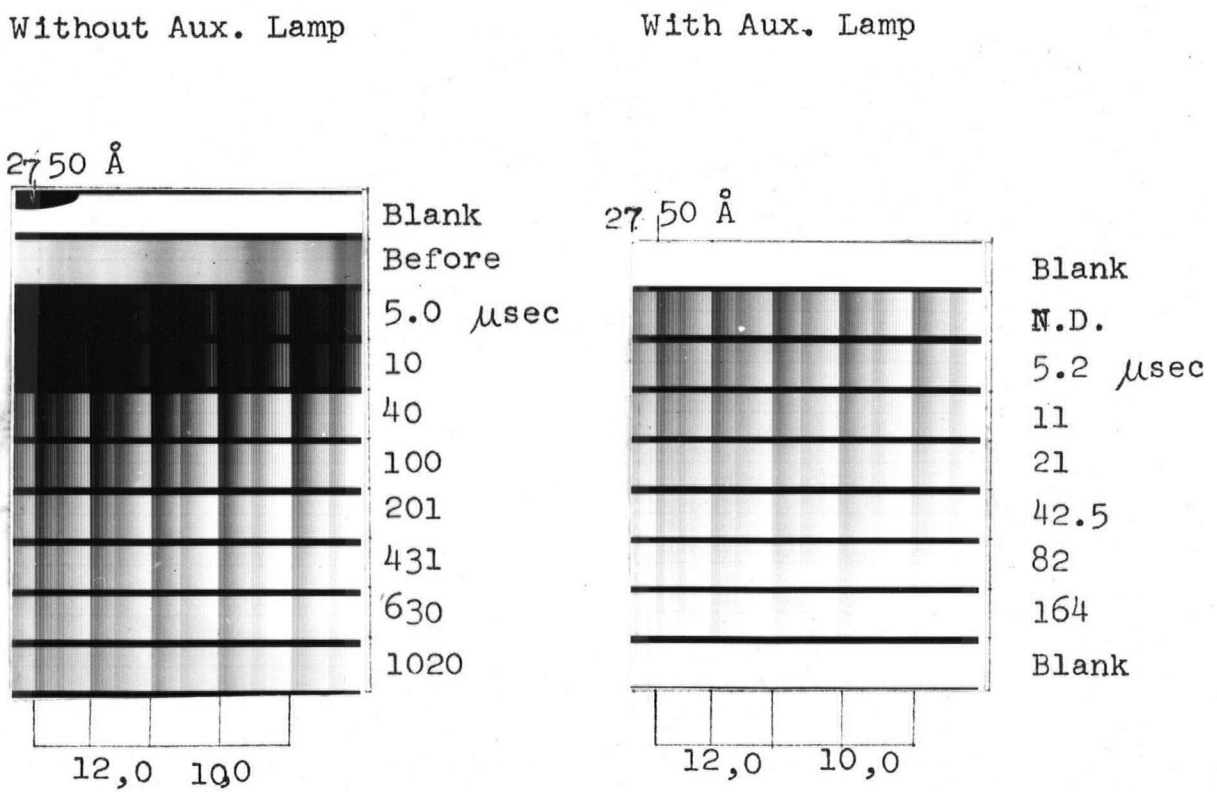
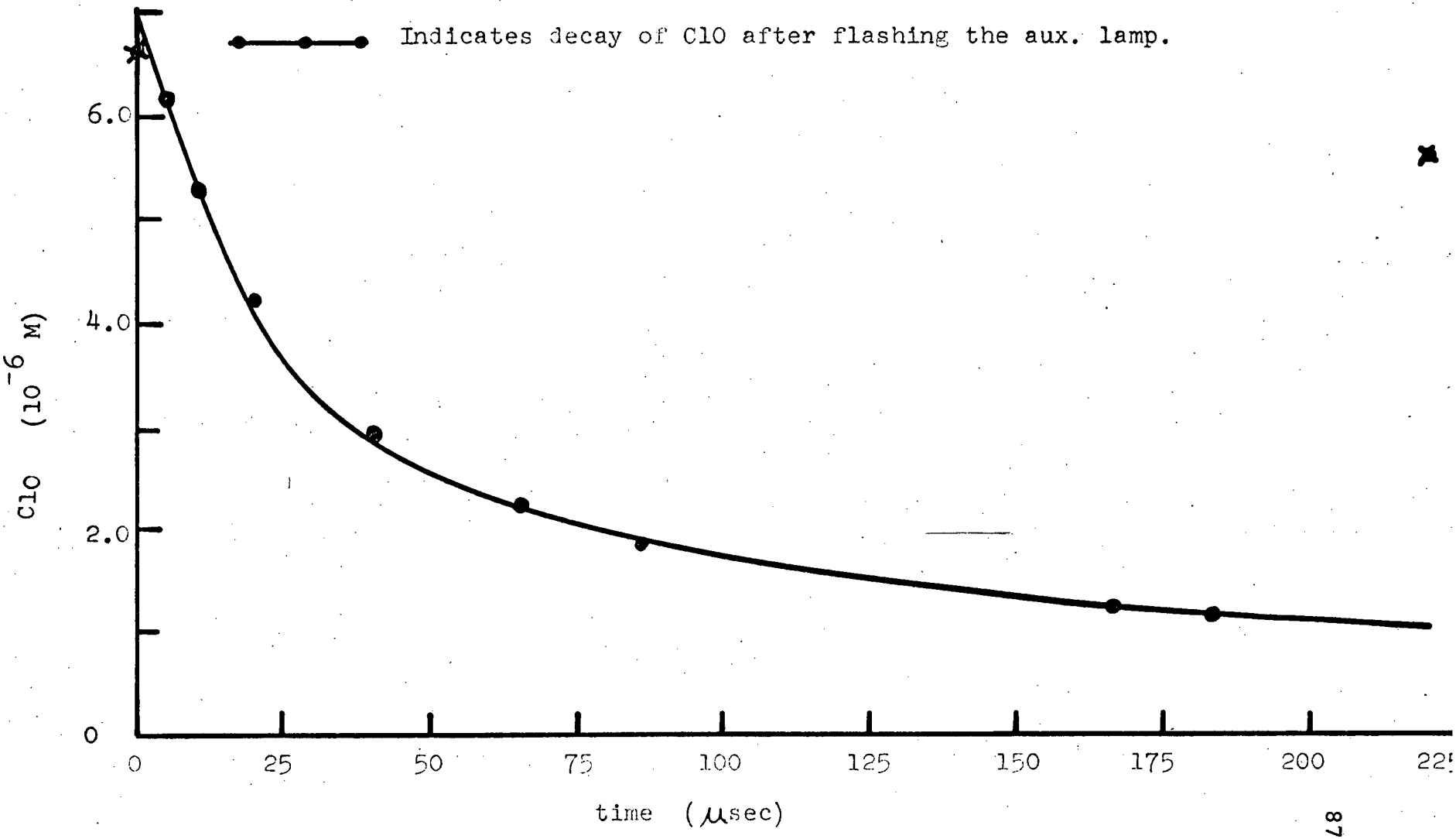


Figure 16. Comparison of decay of ClO with and without flashing the auxiliary lamp.

ClO_2 = 2.0 torr, Argon = 360 torr, E_m = 1060 J, E_{aux} = 1325 J, Delay time = 200 μsec.

Indicates ClO without flashing aux. lamp.

Indicates decay of ClO after flashing the aux. lamp.



The rate constant of reaction (6-5) was calculated as follows. The oxygen atom concentration is given by $\frac{1}{2}(a-b)$ where $a = [ClO]_o$ before the auxiliary flash; $b = (ClO)_\infty$ where all the oxygen atoms have reacted with ClO, found by extrapolating the slow decay part of ClO curve. It has been assumed that reaction (5) can be neglected as slow compared to (6-5). The $[O]_t$ at any time is given by $[O]_t = x-b$ where x is the concentration of ClO at any time t.

Thus the decay of ClO can be represented by

$$-\frac{d[ClO]}{dt} = k_6[O][ClO]$$

or

$$-\frac{dx}{dt} = k_6\, x\,(x-b)$$

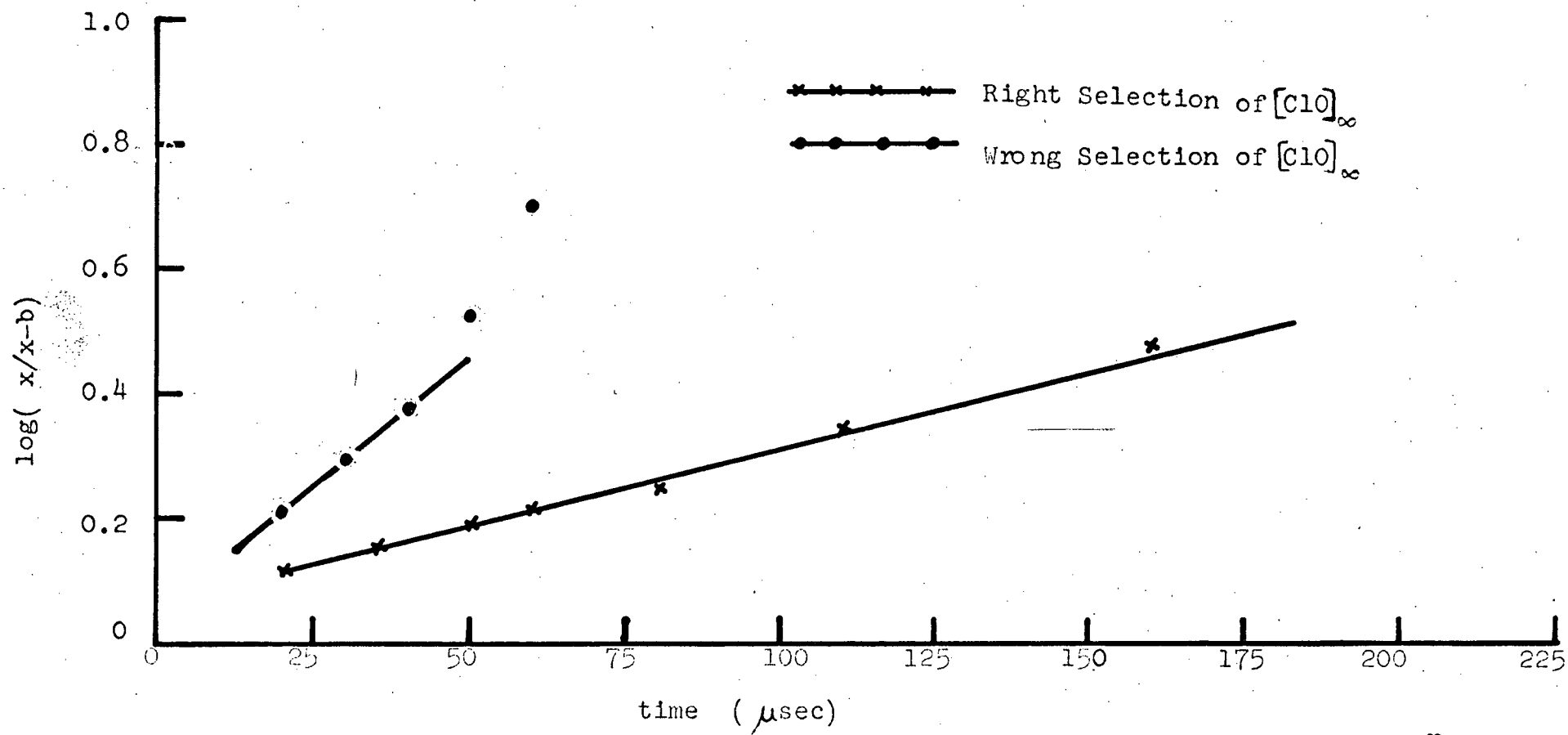
or

$$\log\frac{x}{x-b} = \frac{k\,b}{2.303}\,t + \log\frac{B}{B-b} \qquad (e)$$

where B = [ClO] just after the auxiliary flash = $a - \frac{1}{2}(a-b) = \frac{1}{2}(a+b)$. Thus $\log\frac{x}{x-b}$, plotted against time, was linear as shown in fig.(17). The values of k_6 are listed in Table IX. The average of four are found to be $7.5\pm0.8 \times 10^{+9}$ 1 $mole^{-1}$ sec^{-1}, which is in satisfactory agreement with that obtained previously.

This method has certain limitations. Firstly, as it can be seen from equation (e) that value of k_6 obtained is dependent on the selection of b, the amount of $[ClO]_\infty$. The various values of b were selected and it was found that any value of b taken before 150 μsec does not give a linear plot in the whole region and the plot behaves as shown in fig.(17).

Figure 17. A plot of log(x/x-b) against time. $b = [ClO]_\infty$, $x = [ClO]_t$.
ClO_2 = 2.0 torr, Argon = 360 torr, E_m = 1060 J, E_{aux} = 1325 J, Delay time = 200 μsec.



The values of k_6 calculated in this manner were found to vary by a factor of 2. This indicates that reaction (6-5) is not complete within this period. Whereas between 150 and 200 μsec, any value of b selected would change the value of k_6 by only 10% which is within the experimental error. But after 200 μsec k_6 decreases rapidly, as well, as the plot departs from linearity, thus indicating that in this region reaction (5) is more significant than (6-5).

The other error can be due to the finite life time of the flash, i.e., oxygen atoms are consumed by the reaction (6-5) as well as produced by (6-1) or (6-2). The curve was drawn first with the assumption that only the photolysis is taking place during the flash but it was modified by taking into account the amount of ClO actually present. It was found that less than 5% of the total photolysis takes place after the times that were used to find k_6. These curves were drawn with the assumption that decomposition is linearly proportional to the flash energy.

Thus taking into consideration these limitations, the variations in the individual values as mentioned in Table IX are not bad and give a satisfactory agreement with that calculated previously.

3) Photolysis of ClO_2 in Presence of Oxygen

The ClO_2 was flashed in the presence of oxygen with ratios varying from 1:5 to 1:3000. The experiments in which

the total pressure was less than 200 torr, was made 200 torr by adding argon. The flash energies used were 1060 and 1325 J and the reaction vessel used was pyrex with and without the presence of 2 mm of glass filter A. The results obtained are mostly qualitative although some approximate quantitative results are obtained.

When the ClO_2 to O_2 ratio is low (1:5), the behaviour of each species is similar to that when no oxygen was added to the system, i.e., ClO and excited oxygen (in chapter VI) decay very fast as usual. As the ratio is increased ($\sim$500), the rate of decay of ClO is reduced and at the same time a continuous spectrum having a maxima around 2500 Å appears. The intensity of the continuous spectrum depends upon the pressure of oxygen used. At the highest ratio used (1:2800), the ClO_2 spectrum does not disappear completely and even seems to have increased at long times.

Similar results in the decay of ClO were observed when two mm of glass filter A was used. In this case the oxygen pressure was so adjusted that the ClO_2 was completely reacted since these results were used quantitatively. This has been shown in fig.(18) (plate 293).

The possible reactions are

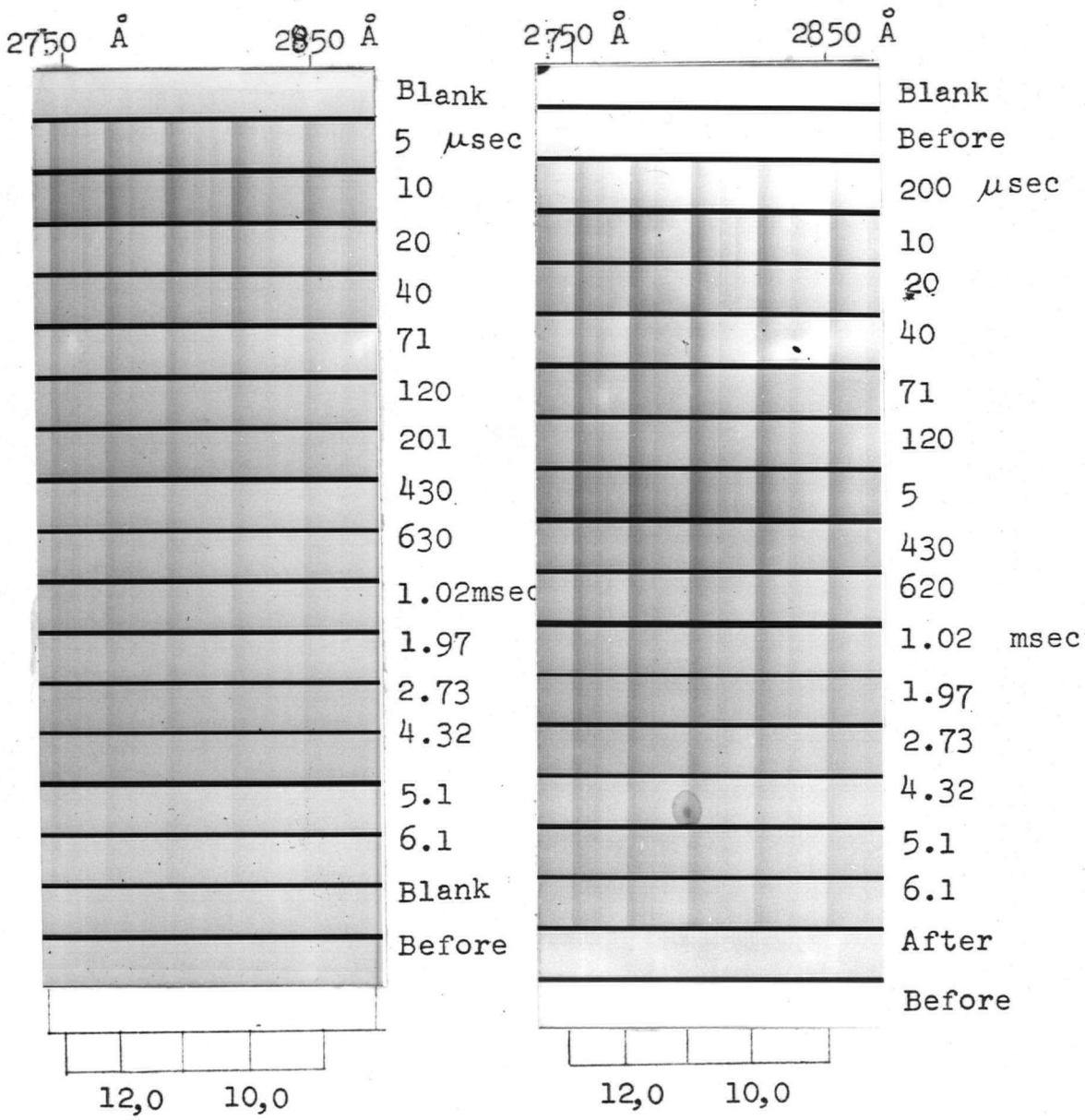
$$ClO_2 + h\nu \rightarrow ClO + O \quad (80\%) \qquad (27)$$

$$ClO_2 + O \rightarrow ClO + O_2 \quad \text{(complete)} \qquad (7)$$

Figure 18. Decay of ClO in the presence and absence of O_2.

ClO_2 = 0.05 torr
Argon = 200 torr

ClO_2 = 0.05 torr
O_2 = 50 torr
Argon = 150 torr



$$O + ClO \rightarrow Cl + O_2 \quad (6)$$

$$O + O_2 + O_2 \rightarrow O_3 + O_2 \quad (32)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (33)$$

$$Cl + O_2 + O_2 \rightarrow Cl\text{-}O\text{-}O + O_2 \quad (1)$$

$$Cl + Cl\text{-}O\text{-}O \rightarrow Cl_2 + O_2 \quad (4)$$

$$Cl + Cl\text{-}O\text{-}O \rightarrow 2\ ClO \quad (2)$$

$$O + O_3 \rightarrow O_2 + O_2 \quad (34)$$

There can be two explanations for the slow decay of ClO in the presence of oxygen.

1) Chlorine atoms produced in the reaction (6) react with oxygen via reaction (1) to form the intermediate Cl-O-O (peroxy radical), followed by reaction (4) or (2). Nicholas and Norrish[19] have calculated the rate constant of reaction (1) to be $6.2 \pm 1.1 \times 10^8$ $l^2 mole^{-2} sec^{-1}$ and also found that reaction (4) is 14 times faster than reaction (2). Hence reaction (1) will be followed by step (4) preferentially and thus cannot account very much for the slow decay of ClO.

Though there can be some doubt about the continuum around 2500 Å since the ClO continuum also extends over this region, the intensity of this continuum was greater than the intensity due to ClO continuum calculated by comparing it with that at 2772 Å. This suggests that the continuum is due to ozone which has its maximum absorption around 2500 Å. Thus reactions (1), (4) and (2) cannot explain the slow decay of ClO completely though they may be taking part in the reaction scheme.

2) The most likely explanation seems to be competition between reactions (6) and (32). As has been seen, the slow decay of ClO and the increase in the intensity of the continuum with increase of oxygen pressure favours reaction (32) over (6).

Although the decay of ozone in this experiment was not measured, it does seem to be slow. The reaction (34) can be neglected because it is very slow ($k_{34} = 1.5 \times 10^6$ l mole^{-1} sec^{-1}, or 4.0×10^6 l mole^{-1} sec^{-1})[69,70,71] compared to that of oxygen atoms with ClO. Also, the concentration of ozone present will be less than the concentration of ClO. Thus it seems that ozone either reacts with chlorine atoms whose half life is found to be at least 400 μsec, taking the minimum value of k_{33} as 4×10^8 l mole^{-1} sec^{-1} found by Clyne and Coxon,[25] or by slow reaction with ClO as also suggested by Clyne and Coxon.[25]

If we neglect the reactions considered above and also the reaction of chlorine atoms with ozone, the decay of ClO and oxygen atoms can be represented as

$$-\frac{d[ClO]}{dt} = k_6[O][ClO]$$

where there is no oxygen, and

$$-\frac{d[O]}{dt} = k_6[O][ClO] + k_{32}[O][O_2]^2$$

when there is oxygen present in the system.

Dividing the two equations

$$\frac{d[O]}{d[ClO]} = \frac{k_6[O][ClO] + k_{32}[O][O_2]^2}{k_6[O][ClO]} = 1 + \frac{k_{32}}{k_6}\frac{[O_2]^2}{[ClO]}$$

$$= 1 + \alpha\frac{1}{[ClO]}$$

where $\alpha = \frac{k_{32}}{k_6}[O_2]^2$ or $\frac{k_{32}}{k_6}[O_2][M]$ where M= Total Pressure

as the amount of oxygen is so large that it can be considered as constant. Integrating the above equation

$$[O] = [ClO] + \alpha \ln[ClO] + c$$

when t = 0. $[O] = [O]_o$ and $[ClO] = [ClO]_o$

$$c = [O]_o - [ClO]_o - \alpha \ln[ClO]_o$$

substituting the value of constant c in the above equation we have

$$[O] - [O]_o = [ClO] - [ClO]_o + \alpha \ln \frac{[ClO]}{[ClO]_o} \qquad (e')$$

when $t = \infty$, i.e., all the oxygen atoms have reacted with ClO or oxygen

$$[O] = 0$$

equation (e′) reduces to

$$[O]_o = [ClO]_o - [ClO] + \alpha \ln \frac{[ClO]_o}{[ClO]}$$

$$[O]_o = \Delta[ClO] + \alpha \ln \frac{[ClO]_o}{[ClO]}$$

$[O]_o$ can be measured as described in the section (1), i.e. $[ClO]_o - [ClO]'_o$ and $\Delta[ClO]$ represents the amount of oxygen atoms that have reacted with ClO in presence of oxygen. The results of three experiments gave the ratio of k_6/k_{32} to be 75, 60 and 36 when the oxygen pressure used was 75 torr, 100 torr and 200 torr, respectively. Thus depending upon the value of k_{32}[79] selected (as k_{32} varies from 7×10^7 l^2 $mole^{-2}$ sec^{-1} to 2×10^8 l^2 $mole^{-2}$ sec^{-1}), the value of k_6 varies from2.6

to 1.5×10^{10} l mole^{-1} sec^{-1}. It was further found that even an error of 5% in the calculation of [ClO] can cause an error of 25 to 50% in the final value of k_6. Though there is thus a large degree of uncertainty in the value of k_6 obtained in this way, but the agreement is sufficiently good to suggest that the early fast decay of ClO is due to its reaction with oxygen atoms and that this is reduced because of the competition for oxygen atoms in reaction (6) and (32).

If we include reaction (33) in the reaction scheme the decay of each species can be represented as

$$-\frac{d[ClO]}{dt} = k_6[O][ClO] - k_{33}[Cl][O_3]$$

$$-\frac{d[O]}{dt} = k_6[O][ClO] + k_{32}[O][O_2]^2$$

$$\frac{d[Cl]}{dt} = k_6[O][ClO] - k_{33}[Cl][O_3] = -\frac{d[ClO]}{dt}$$

Though the reaction of chlorine atoms with ozone is quite fast (>4 × 10^8 l mole^{-1} sec^{-1}),[25] it is slow as compared to reaction (6) and (32). Solving these equations will lead us to the following results with the assumption that C_{ClO}= constant

$$\frac{\Delta[ClO]'}{\Delta[ClO]} = \frac{[ClO] + \alpha}{[ClO] - \alpha}$$

where $\Delta[ClO]^1$ = oxygen atoms reacted with ClO in the absence of oxygen;

$\Delta[ClO]$ = oxygen atoms reacted with ClO in presence of oxygen;

[ClO] = concentration of ClO obtained by extrapolating the linear part of the plot

$\alpha = \frac{k_{32}}{k_6} [O_2]^2$ or $\frac{k_{32}}{k_6} [O_2] [M]$ where M= Total Pressure

Substituting the experimental data of the three experiments, the ratio of k_6/k_{32} was found to be 252, 224 and 173 mole/l oxygen pressure was 75 torr, 100 torr and 200 torr, respectively. It seems from these three results that either reaction of chlorine with ozone is too slow to observe any change in ClO concentration or that there is no reaction with ozone. The first argument seems to be more reasonable though our results are not accurate enough to prove this point.

B. Reaction of Oxygen Atoms with ClO_2 and Cl_2O

As already mentioned in the beginning of this chapter, the rate constant of oxygen atoms with Cl_2O and ClO_2 can only be compared with that of oxygen atoms with ClO, when a mixture of ClO_2 and Cl_2O is flashed. In this section general details of the experimental procedure will be discussed. The calculation of rate constants of reactions of oxygen atoms with Cl_2O and ClO_2 will be covered separately.

ClO_2 was flash photolysed in the range of 260 to 1300 J. The concentration of ClO_2 was varied from 2.4 to 4.75×10^{-6} mole/liter and that of Cl_2O from 5.5×10^{-7} to 6.1×10^{-5} mole/liter. In these experiments, photolysis of Cl_2O was avoided

by means of a Corning 0-52 filter. The pressure of ClO_2 and Cl_2O were so adjusted that the plate saturation was avoided. The results of these experiments are given in figs. (19), (20), (21), (22) and (23) (plate 177) and Tables X, XI and XII.

It has been found that at low flash energies, the decomposition of ClO_2 was decreased in the presence of Cl_2O (fig. 21 and 20) and at the same time, the concentration of ClO was increased (fig. 23). There is a decrease in the amount of excited oxygen produced and using a ratio of ClO_2 to Cl_2O = 1:20, the vibrationally excited oxygen is hardly visible (fig. 24, page 113). The rate of decay of O_2^* is, however, significantly reduced. These effects increase as the ratio of Cl_2O to ClO_2 is increased.

At high flash energies, the effect of Cl_2O is much more marked. The initial rapid decay of ClO which is a feature of the high flash energy photolysis of ClO_2, is reduced (fig. 19) and the half life of O_2^* which is very short at these flash energies is dramatically increased. A convenient measure of the effect of Cl_2O on ClO decay is provided by extrapolating the linear part of the portion of the second order plot of ClO $\left([ClO]^{-1} \text{ vs. time}\right)$ to zero time. The values of $[ClO]'_o$ thus obtained with and without Cl_2O and their ratios are listed in Table XII (page 115).

These assumptions may be explained by the reactions

$$O + ClO_2 \rightarrow ClO + O_2^* \qquad (7)$$

$$O + ClO \rightarrow Cl + O_2^* \qquad (6)$$

$$O + Cl_2O \rightarrow 2ClO \qquad (35)$$

At low flash energies, ClO_2 and Cl_2O compete for oxygen atoms and this accounts for the reduction in the amount of ClO_2 decomposed and O_2^* produced and for the increase in the ClO concentration produced. At high flash energies, ClO and Cl_2O compete for the excess oxygen atoms and the extent of the initial rapid decay of ClO caused by the reaction (6), is reduced by the reaction (35). At sufficiently high ratios of Cl_2O to ClO_2, reaction (35) will cause the ClO concentration to increase initially and this effect has been observed (fig.19).

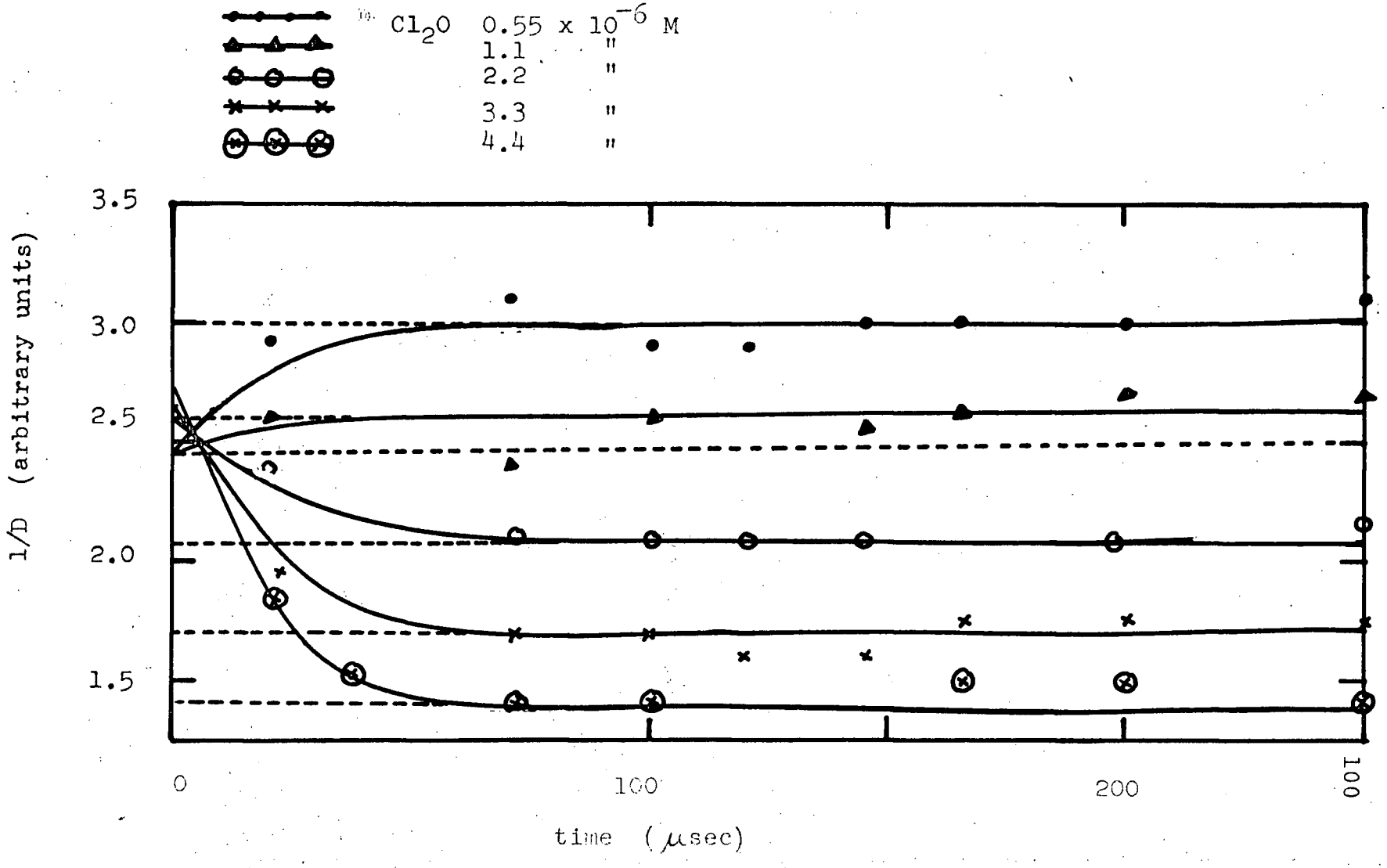
A detailed discussion of the behaviour of O_2^* will be provided in Chapter VI. The conclusion reached there is that the rapid decay of O_2^* at high flash energies is due to the exceptionally high efficiency of chlorine and oxygen atoms in the vibrational relaxation. On this basis, the effect of Cl_2O on the decay of O_2^* is readily understood in terms of the reduction in the oxygen atom concentration by reaction (35) and in the production of chlorine atoms by reaction (6). A secondary effect of Cl_2O is to increase the rate of decay of those chlorine atoms which are formed in reaction (6).

With a rate constant k_{19} of 4×10^8 l mole^{-1} sec^{-1} for the reaction

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \qquad (19)$$

the half life is reduced to 64 μsec for a Cl_2O pressure of 0.5 torr. In most of the experiments, this pressure is sufficiently

Figure 19. A plot of 1/[ClO] against time in the presence of Cl_2O.
$ClO_2 = 2.44 \times 10^{-6}$ M, Argon = 200 torr, E = 1060 J.



large to suppress the formation of chlorine atoms and this secondary effect is usually much less important than reaction (35).

Thus the quantitative effect of Cl_2O on the formation and decay of ClO allows the relative values of $k_7:k_6:k_{35}$ to be measured. First $k_6:k_{35}$ will be discussed and then $k_7:k_{35}$.

1) The Reaction of Oxygen Atoms with Cl_2O

At high flash energies (1060 and 1325 J), where more than 50% primary photolysis of ClO_2 is achieved, we may consider that the photolysis is essentially instantaneous and that the small amount of ClO_2 remaining is very readily removed by the reaction with oxygen atoms. The excess oxygen atoms then react with ClO and Cl_2O and the decay is given by the equation

$$-\frac{d[ClO]}{dt} = k_5[ClO]^2 + k_6[O][ClO] - 2\,k_{35}[O][Cl_2O] \quad (f)$$

The reactions

$$ClO + Cl_2O \rightarrow ClO_2 + Cl_2 \quad (20)$$

$$ClO + Cl_2O \rightarrow Cl + Cl_2 + O_2 \quad (21)$$

may be omitted since $(k_{20} + k_{21}) < 10^6$ l mole^{-1}sec^{-1} so that

$$(k_{20} + k_{21})\,[ClO] \ll k_6\,[ClO] \ll k_{35}\,[Cl_2O]$$

except at very long times. These reactions will be considered in detail in Chapter V.

Since reaction (6) is the only source of chlorine atoms and since $k_{19} << k_{35}$, the reactions (8) and (19), i.e.

$$Cl + ClO_2 \rightarrow 2\ ClO \qquad (8)$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \qquad (19)$$

can likewise be omitted.

If, therefore, the relationship

$$k_6[ClO] = 2\ K_{35}\ [Cl_2O]$$

can be satisfied, the equation (f) reduces to

$$-\frac{d[ClO]}{dt} = k_5\ [ClO]^2$$

and the initial rapid decay of ClO can be eliminated. The second order plot then remains linear even at short delays and extrapolates back to give $[ClO]_o = [ClO_2]_o$. Various ratios of ClO_2 to Cl_2O were tried in order to achieve this condition as closely as possible. In practice there was always a small initial increase or decrease in the rate of decay of ClO (fig. 19) and extrapolating the subsequent second order plot linearly to zero time gave $[ClO]'_o \neq [ClO]_o$. The difference $[ClO]'_o - [ClO]_o$ was calculated. A small correction in this calculation was applied by taking into consideration that $[ClO_2]_o$ is the concentration of ClO_2 that has been decomposed in the presence of Cl_2O rather than the initial concentration of ClO_2 used. Experimentally only 4 to 10% ClO_2 was left depending upon the pressure of Cl_2O and flash energy. Thus the difference $[ClO]'_o - [ClO]_o$ was plotted against $[Cl_2O]$ as

shown in fig.(20) and the concentration of Cl_2O was found which will give zero difference. The average of four sets of experiments gave $k_{35}/k_6 = 0.75 \pm 0.05$ (Table X). Each set of experiments consists of one experiment without Cl_2O and three to five with Cl_2O of different concentration. The concentration of Cl_2O was selected to have minimum difference so that the further error in plotting could be reduced.

Using the value of k_6, determined previously, we find that $k_{35} = 5.3 \times 10^9$ l mole^{-1} sec^{-1}.

The validity of the assumptions made in this determination of k_{35} has been checked by detailed calculation of their effect on the production of ClO. Various values for the ratios of the constants, $k_7:k_6:k_{35}:k_{19}$ were used for various percentages of the primary decomposition and the depletion of Cl_2O was taken into account. The assumption that the photolysis was instantaneous (i.e. photolysis was much faster than the subsequent chemical reactions) is known to be reasonable from the flash profile and also can be seen from the primary photolysis of ClO_2. The detailed calculations were also done by assuming that photolysis and chemical reactions are occurring simultaneously. It was found that only $\sim$ 5% more ClO would have been produced according to later calculations. The assumption that all ClO_2 was decomposed before the excess oxygen atoms start reacting with ClO and Cl_2O was tested by calculating the effect of allowing all three reactions of oxygen atoms to occur

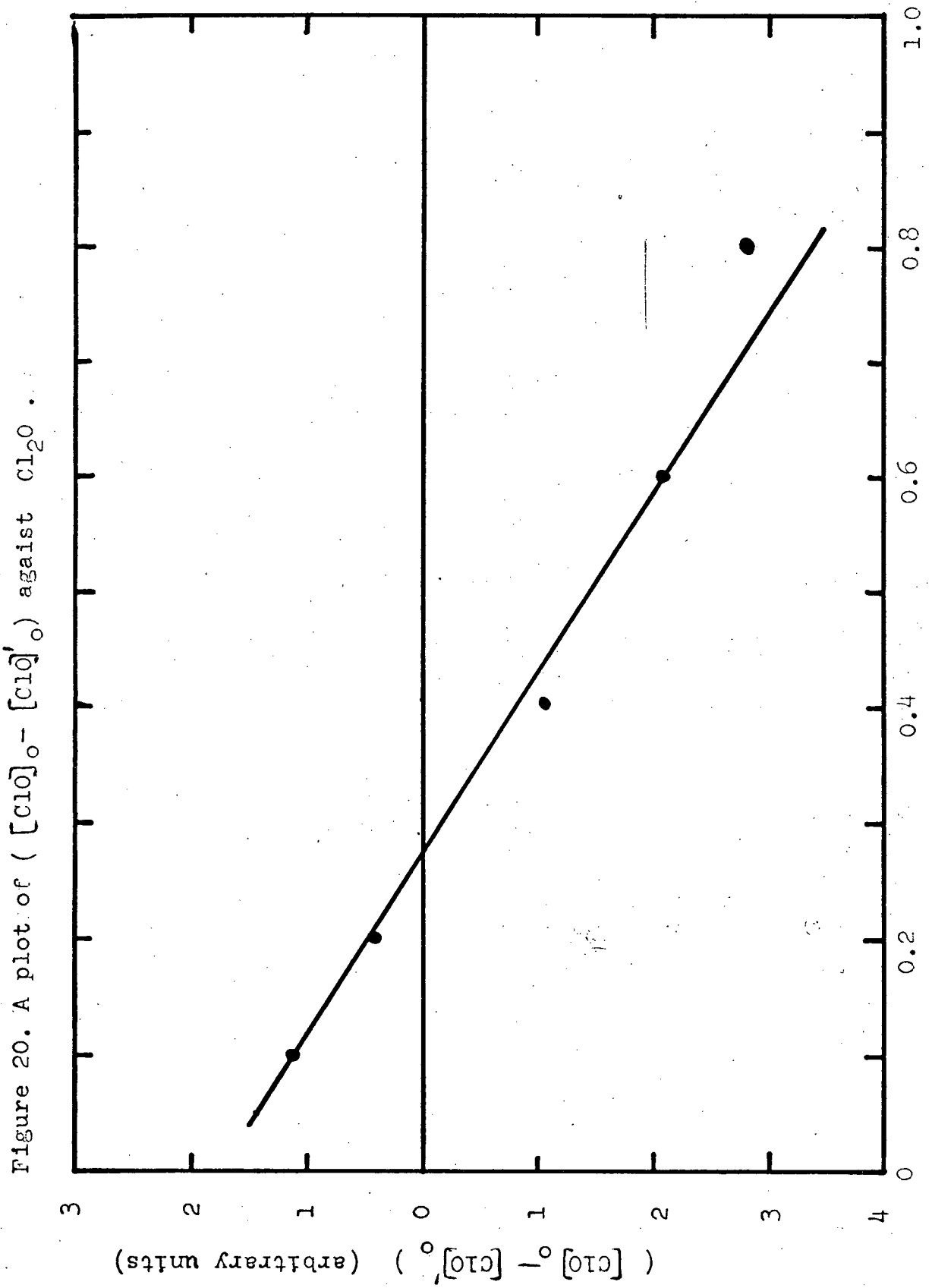


Figure 20. A plot of ($[ClO]_o - [ClO]'_o$) against Cl_2O .

simultaneously as well as the reactions of chlorine atoms with ClO_2. These calculations showed that the amount of ClO produced would be reduced by ∿5% and that a small amount (∿2 to 8%) of ClO_2 would remain undecomposed even for 75% primary process. Experimentally, this calculation was confirmed by the observation that between 4 to 10% of the ClO_2 did in fact remain unreacted.

We thus conclude that no significant error arises from the assumption used. The value of k_{35} obtained is in fair agreement with the value of 8.3×10^9 l mole^{-1} sec^{-1} given by Phillips[73] from the fast flow mass spectrometer study.

Table X

$[ClO_2] \times 10^6$ (mole/l)	Argon (torr)	Energy J	p_{Cl_2O} required (torr)	k_{35}/k_6
4.4	200	1060	0.057	0.67
4.4	200	1325	0.049	0.78
2.44	200	1060	0.032	0.72
2.44	200	1325	0.028	0.80

Average $k_{35}/k_6 = 0.74 \pm 0.06$

$k_{35} = 0.74 \times 7.0 \times 10^9 = 5.2 \times 10^9$ l mole^{-1} sec^{-1}

2) Reaction of Oxygen Atoms with ClO_2

At low flash energies, only a small fraction of the oxygen atoms produced in the photolysis of ClO_2 react with ClO. In the presence of a Cl_2O concentration sufficient to compete with ClO_2 for oxygen atoms, reaction (6) may be neglected. Three effects have been noted when ClO_2 is flashed in excess of Cl_2O. First, it has been found that there is a reduction in the decomposition of ClO_2 figs.(21) and (22). Secondly, reduction in the amount of O_2^* produced, fig. 24 (page 113) and thirdly, the increase in the ClO concentrations have been noticed as shown in figs. (23) and (19). The first two of the three have been used to determine the values of the ratios of the rate constants $k_7:k_{35}$. The third one has been used to predict the amount of ClO produced by using this ratio of k_7/k_{35}. The values obtained are listed in Table XII (page 115) and are compared with those obtained experimentally.

Method 1

In the absence of Cl_2O and for less than 50% photolysis, the overall decomposition of ClO_2, Δ_1 (mole/liter), is simply twice the concentration photolysed, i.e.,

$$\Delta_1 = 2\alpha$$

where α = the amount of ClO_2 photolysed and because of reaction (8) this is independent of reaction (6).

If, then, in the presence of Cl_2O, a fraction β of the oxygen atoms have reacted with ClO_2, the overall decomposition of ClO_2 (Δ_2) is given by

Figure 21. Disappearance of ClO_2 when it is flashed with and without Cl_2O. $ClO_2 = 4.0 \times 10^{-6}$ M, Argon = 200 torr, E = 600 J

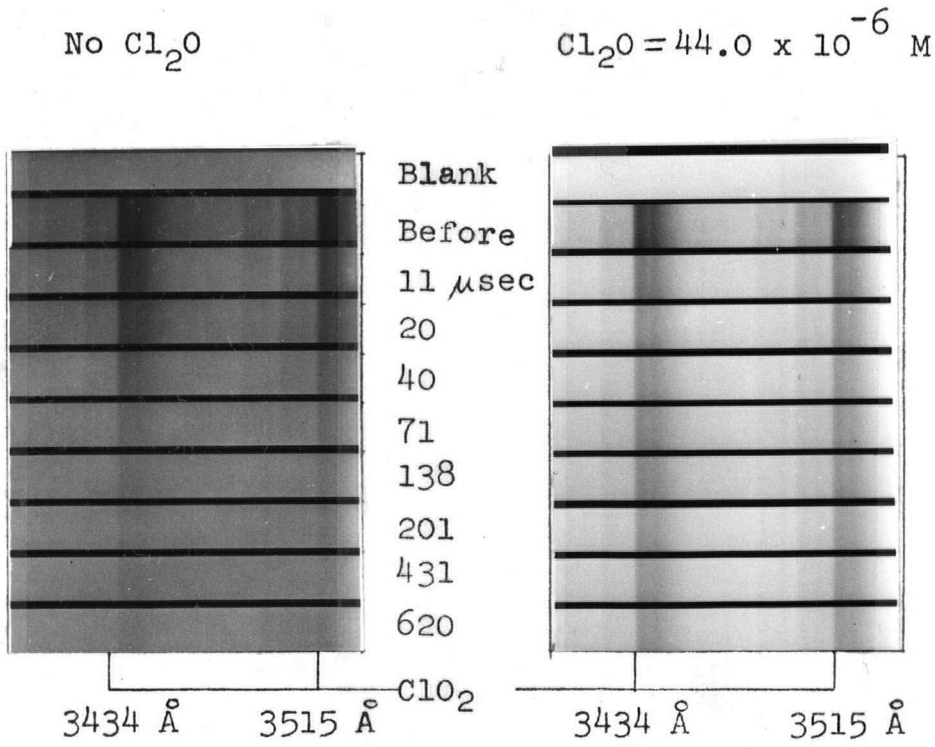


Figure 22. A plot of ClO_2 against time in the presence and absence of Cl_2O. $ClO_2 = 4.75 \times 10^{-6}$ M, $Cl_2O = 36.2 \times 10^{-6}$ M, Argon = 200 torr, E = 260 J.

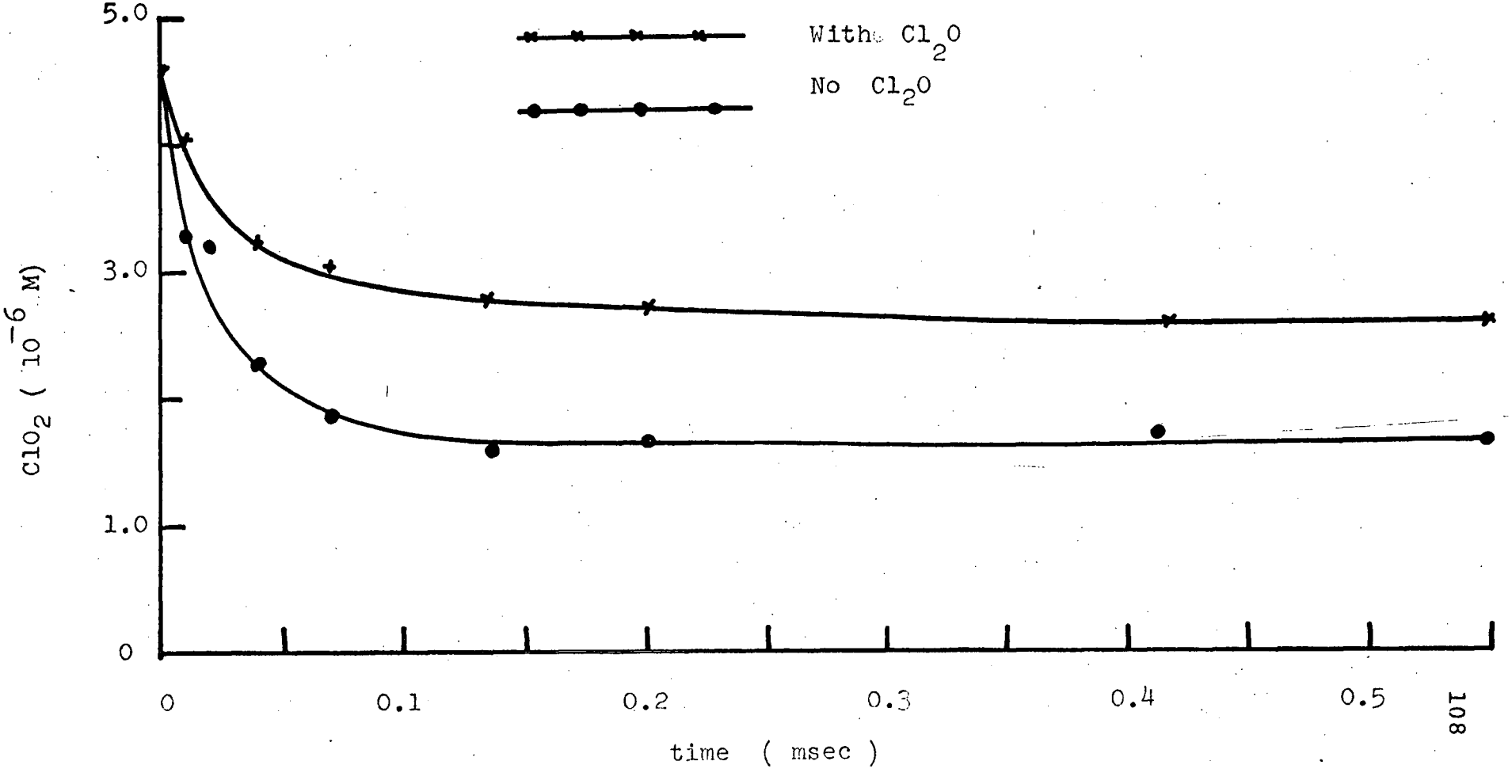
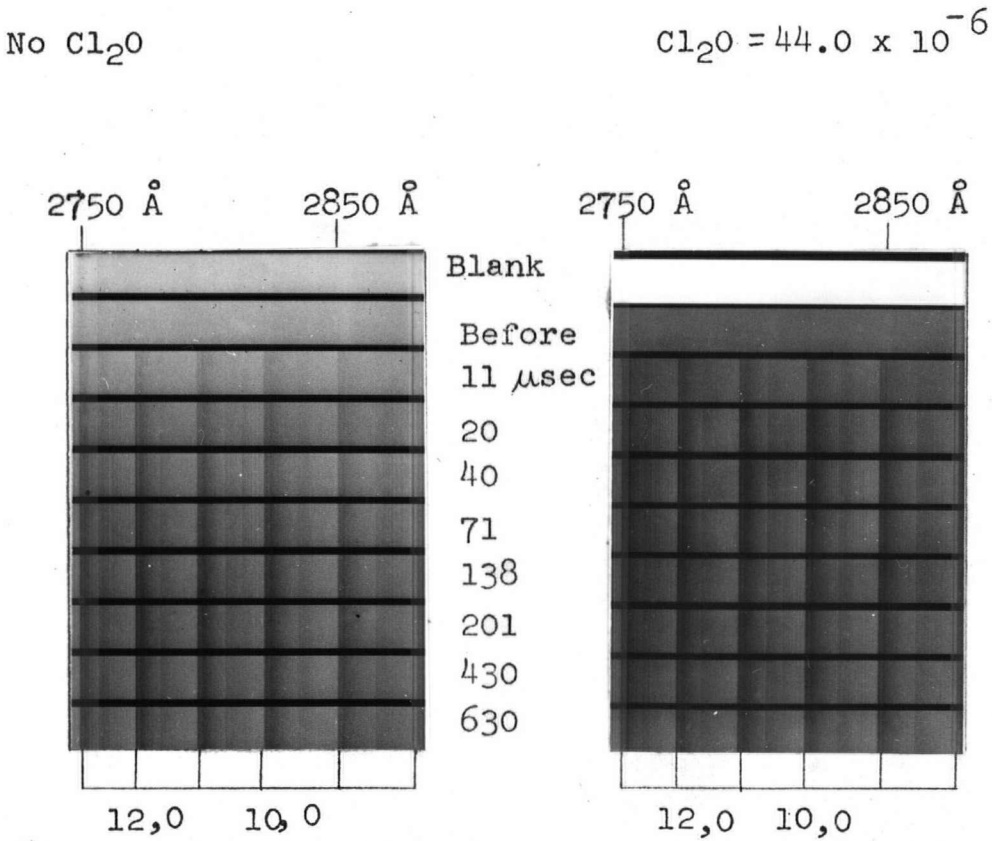


Figure 23. Comparison of ClO when ClO_2 is flashed with and without Cl_2O. $ClO_2 = 4.0 \times 10^{-6}$ M, Argon = 200 torr, E = 600 J



$$\Delta_2 = \alpha(1+\beta) = \frac{\Delta_1(1+\beta)}{2} \qquad (g)$$

if reaction (6) is omitted. The values of β are obtained from the measured values of Δ_1 and Δ_2 for various ratios of $[Cl_2O]$: $[ClO_2]$ with low energies.

At the flash energies and the Cl_2O pressure used for the determination of $k_7:k_{35}$, the overall decomposition of ClO_2 is sufficiently small for the ClO_2 concentration to be taken as constant at its average value $[ClO_2]_{av}$. The concentration of Cl_2O, to an even better approximation, is likewise taken as constant (within 10%). Then

$$\beta = \frac{k_7\,[ClO_2]_{av}}{k_7[ClO_2]_{av} + k_{35}[Cl_2O]_{av}}$$

From equation (g), the value of β is

$$\beta = \frac{2\,\Delta_2 - \Delta_1}{\Delta_1}$$

Thus $$\frac{k_7\,[ClO_2]_{av}}{k_7[ClO_2]_{av} + k_{35}[Cl_2O]_{av}} = \frac{2\,\Delta_2 - \Delta_1}{\Delta_1}$$

or this can be reduced to

$$\frac{k_7}{k_{35}} = \frac{2\,\Delta_2 - \Delta_1}{2(\Delta_1 - \Delta_2)} \cdot \frac{[Cl_2O]_{av}}{[ClO_2]_{av}}$$

Thus from the measured values of Δ_1 and Δ_2 at different flash energies and various ratios of $[Cl_2O]$: $[ClO_2]$, the average value of k_7/k_{35} equal to 5.8 ± 0.1 was obtained by using the above equation. The other values are listed in Table XI.

The validity of this formula was tested by calculating $\frac{\Delta_2}{\Delta_1}$ as a function of k_7/k_{35} for various values of k_7/k_6, initial $[Cl_2O]$: $[ClO_2]$ ratios, and percentage primary photolysis. Allowance was made for the change in ClO_2 and Cl_2O concentrations as both photolysis and chemical reactions proceeded and reaction of chlorine atoms with ClO_2 and Cl_2O was also taken into account.

It was found that for our experiments, the error in the equation

$$\Delta_2 = \frac{\Delta_1(1+\beta)}{2}$$

which arises from the neglect of reaction (6) was small and almost equal to that arising from the neglect of the use of $[ClO_2]_{av}$ in the calculation of β. Fortunately, these errors were ofopposite sign and we conclude that negligible error is introduced by the use of the simple formula given for k_7/k_{35}.

Method 2

The concentration of O_2^* produced is reduced by a factor β by Cl_2O. Measurements using the extrapolated values of O_2^* at zero time yielded the average value of k_7/k_{35} = 5.8 ± 0.4. The other values are listed in Table XI. The approximations introduced by neglecting reaction (6) and using $[ClO_2]_{av}$ to calculate β are rather less satisfactory in this case since the error cancellation is less complete. Evidence has been obtained[31] that the oxygen molecules pro-

duced in reaction (6) are vibrationally excited as in reaction (7), but the relative populations of the excited levels are not known to be the same as in the case of ClO_2. Even so, the error of less than 10% is probably exceeded by the experimental error in measuring O_2^* concentrations. The agreement between the methods of calculating k_7/k_{35} is better than might have been expected.

From the previously determined value of k_{35} we thus obtain $k_7 = 3.0 \times 10^{10}$ l mole^{-1} sec^{-1} and $k_7/k_6 = 4.3$. These results are in satisfactory agreement with those of Clyne and Coxon,[23] i.e., $k_7 > 2.4 \times 10^{10}$ l mole^{-1} sec^{-1} and $k_7/k_6 \sim 4$.

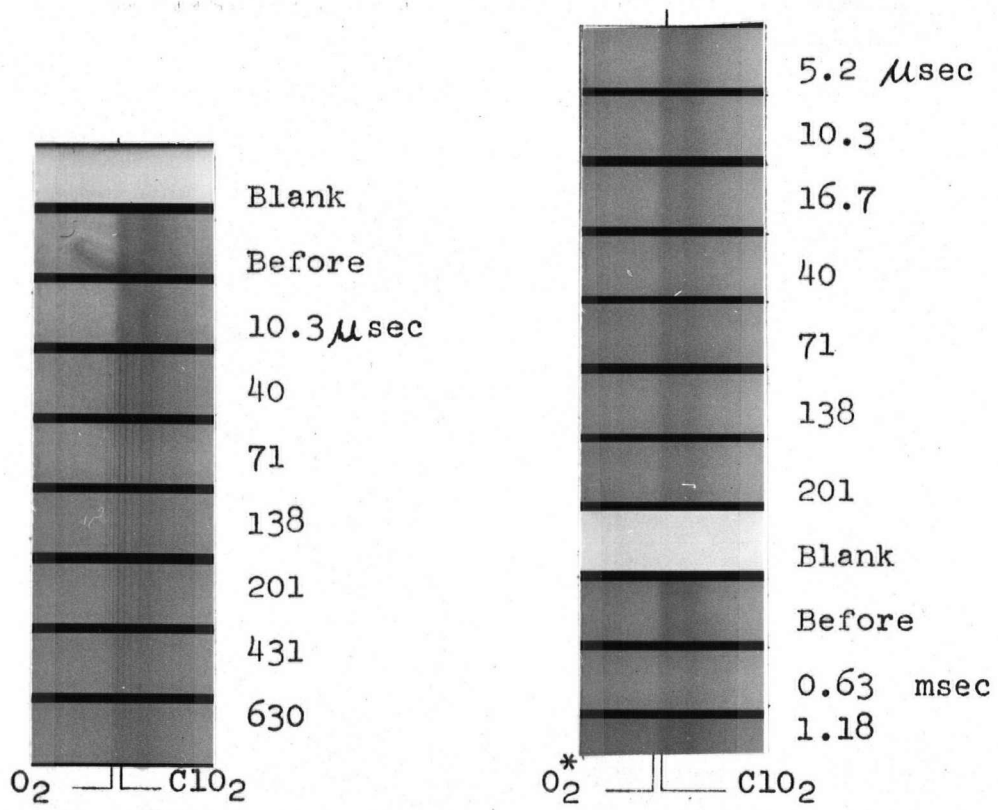
Table XI

Plate no.	$[ClO_2] \times 10^{+6}$ (mole/l)	$[Cl_2O] \times 10^{+6}$ (mole/l)	Argon (torr)	Energy J	k_7/k_{35} from ClO_2	k_7/k_{35} from O_2^*
176	4.06	57.0	200	260	5.8	--
177	4.0	44.0	200	600	5.9	5.6
179	4.75	36.2	200	260	5.7	6.3
180	4.70	36.2	200	600	5.9	5.6
			Average		5.8 $\pm$ 0.1	5.8

Mean $k_7/k_{35} = 5.8$

$k_7 = 3.0 \times 10^{10}$ l mole^{-1} sec^{-1}

Figure 24. Formation of O_2^* when ClO_2 is flashed with and without Cl_2O.
ClO_2 = 0.05 torr, Argon = 200 torr, E = 260 J



Method 3

At low flash energies the total concentration of ClO produced in the presence of Cl_2O is given by

$$[ClO]_o' = (3 - \beta)\frac{\Delta 1}{2}$$

while in its absence

$$[ClO]_o = \Delta_1$$

if reaction (6) is neglected in both the cases. The values of $\frac{3 - \beta}{2}$ are compared with the experimental values of $\frac{[ClO]_o'}{[ClO]_o}$. The agreement is not bad, but it should be noted that, since all the values of $\frac{3 - \beta}{2}$ must lie in the range of 1.25 ± 0.25, this is not the strongest test of the accuracy of the ratio $k_7:k_{35}$. The more detailed calculations used to test the validity of the approximations made in the determination of the ratio $k_7:k_{35}$, yielded the theoretical values of $[ClO]_o'/[ClO]_o$ in better agreement with experiment (Table XII).

The most significant fact is that the ratio $\frac{[ClO]_o'}{[ClO]_o}$ is greater than one and approaches 1.5. This provides strong evidence that the inherently unlikely reaction

$$O + Cl_2O \rightarrow Cl_2 + O_2 \qquad (36)$$

which was ignored in the determination of ratio k_6 to k_{35} is negligible compared to reaction (35):

$$O + Cl_2O \rightarrow 2ClO \qquad (35)$$

Further evidence for this conclusion has been obtained from the measurement of the vibrationally excited oxygen discussed in Chapter VI.

Table XII

Comparison of the Ratios of ClO formed in the Cl_2O/ClO_2 and in the ClO_2 Systems.

Plate no.	Energy J	$[ClO_2]$	$[Cl_2O]$	% Photo. (Prim.)	Experimental A	Experimental B	Ratio	Calculated Ratio C	
187	1060	4.4	2.75	70	2.89	4.39	1.52	4.18	1.45
187	1060	4.4	5.5	70	2.89	4.65	1.61	4.98	1.72
186	1060	4.4	6.9	70	2.89	5.54	1.92	5.28	1.83
189	1325	4.4	4.1	83	1.52	4.56	3.00	4.75	3.1
189	1325	4.4	6.9	83	1.52	5.10	3.36	5.72	3.76
188	1325	4.4	9.6	83	1.52	6.4	4.04	6.38	4.2
291	1060	2.44	0.55	75	1.22	1.86	1.52	1.74	1.43
290	1060	2.44	1.1	75	1.22	2.2	1.80	2.09	1.71
287	1060	2.44	2.2	75	1.22	2.9	2.37	2.58	2.11
288	1060	2.44	3.3	75	1.22	3.45	2.83	3.48	2.85
289	1060	2.44	4.4	75	1.22	4.11	3.36	3.76	3.0
291	1325	2.44	0.55	85	0.73	1.56	2.13	1.49	2.04
290	1325	2.44	1.1	85	0.73	1.93	2.64	2.00	2.74
287	1325	2.44	2.2	85	0.73	2.64	3.61	2.58	3.53
288	1325	2.44	3.3	85	0.73	3.27	4.48	3.06	4.19
289	1325	2.44	4.4	85	0.73	4.11	5.63	4.02	5.5

N.B. A=[ClO] without Cl_2O, B = [ClO] with Cl_2O, C= [ClO] with Cl_2O.

All the concentrations have the units 10^{-6} mole/litre.

At high flash energies, the effect of Cl_2O can be expressed as the ratio of ClO concentration at zero time obtained by linear extrapolation of the second order decay plot in the presence of Cl_2O to that in its absence. In this case,

$$[ClO]_o \leq \Delta_1$$

and hence the ratio of $\frac{[ClO]_o}{[ClO]_o}$ would be greater than 1.5, depending upon the ratio of Cl_2O to ClO_2 and increases with the increase of flash energy and hence the primary photolysis of ClO_2.

Table XII-a

Comparison of the Ratios of ClO formed in the Cl_2O/ClO_2 and in the ClO_2 systems.

Plate no.	E (J)	$[ClO_2]$	$[Cl_2O]$	Experimental A	Experimental B	Ratio	Calculated C	Calculated D	C/A	D/A
179	260	4.75	36.2	2.9	3.5	1.21	3.88	3.68	1.34	1.29
176	260	4.06	57.0	1.79	2.39	1.34	2.49	2.43	1.39	1.36
178	260	4.06	61.0	1.92	2.5	1.30	2.51	2.67	1.3	1.36
180	600	4.7	36.2	3.74	5.1	1.37	5.2	4.88	1.4	1.3
177	600	4.0	44.0	3.22	4.4	1.37	4.6	4.3	1.37	1.34

N.B. All the concentrations have the units 10^{-6} mole/liter.

A= [ClO] without Cl_2O

B=[ClO] with Cl_2O

C= [ClO] calculated with approx. calculation. with Cl_2O.

D= [ClO] calculated with detailed calculations in the presence of Cl_2O

CHAPTER V

REACTIONS OF HALOGEN ATOMS (Cl AND Br) WITH Cl_2O AND ClO_2

A. Photolysis of Cl_2O

The photolysis of Cl_2O was reinvestigated in order to correlate the results that were obtained from ClO_2 photolysis, discussed in Chapter III, IV, and VI. Some new results were obtained which are relevant to the mechanism of the photolysis and of the Cl_2 photo-sensitised decomposition of Cl_2O. Cl_2O was flashed at three flash energies with both pyrex and quartz reaction vessels, as well as with a glass filter A, but at only two pressures of Cl_2O as mentioned in Table XV and one total pressure (200 torr) of argon.

The results obtained (as can be seen from fig. 25) when a two mm filter A was used are similar to those obtained by E.N.T.[22] and fit their reaction scheme very well with few modifications. The three stages noted by them and by us are:

1) Primary photolysis of Cl_2O(depending upon the wavelength of excitation) followed by rapid decrease of the Cl_2O concentration and then by an increase in the ClO concentration:

$$Cl_2O + h\nu(\lesssim 3000\ \text{Å}) \rightarrow ClO + Cl \qquad (18)$$

$$Cl_2O + h\nu(< 3000\ \text{Å}) \rightarrow 2Cl + O \qquad (22)$$

$$Cl_2O + Cl \rightarrow ClO + Cl_2 \qquad (19)$$

$$Cl_2O + O \rightarrow 2ClO \quad (35)$$

$$ClO + O \rightarrow O_2^* + Cl \quad (6)$$

2) Bimolecular decay of ClO and decrease in the Cl_2O concentration very slowly

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (5)$$

3) Slow appearance of ClO_2 (which starts in the end of the second stage), attaining maximum concentration at nearly 30 seconds and remaining constant for at least 1 minute. The reactions involved are

$$Cl_2O + ClO \rightarrow ClO_2 + Cl_2 \quad (20)$$

$$Cl_2O + ClO \rightarrow Cl + Cl_2 + O_2 \quad (21)$$

The second stage has been discussed in Chapter III-B. The reactions of oxygen atoms with Cl_2O has been mentioned in Chapter IV-B and production of vibrationally excited oxygen will be discussed in Chapter VI. Only reaction of chlorine atoms and the third stage will be described here.

1) Chlorine Sensitised Photo-decomposition of Cl_2O

After the primary process with light above 3000 Å, the immediate reaction is that of chlorine atoms with Cl_2O to give ClO (reaction 19). In order to calculate the rate constant k_{19}, a mixture of Cl_2O and Cl_2 in the ratio of 1:1 to 1:5 was flash photolysed at three flash energies using light above 3000 Å. Though the Cl_2O has an absorption in this region, the extinction

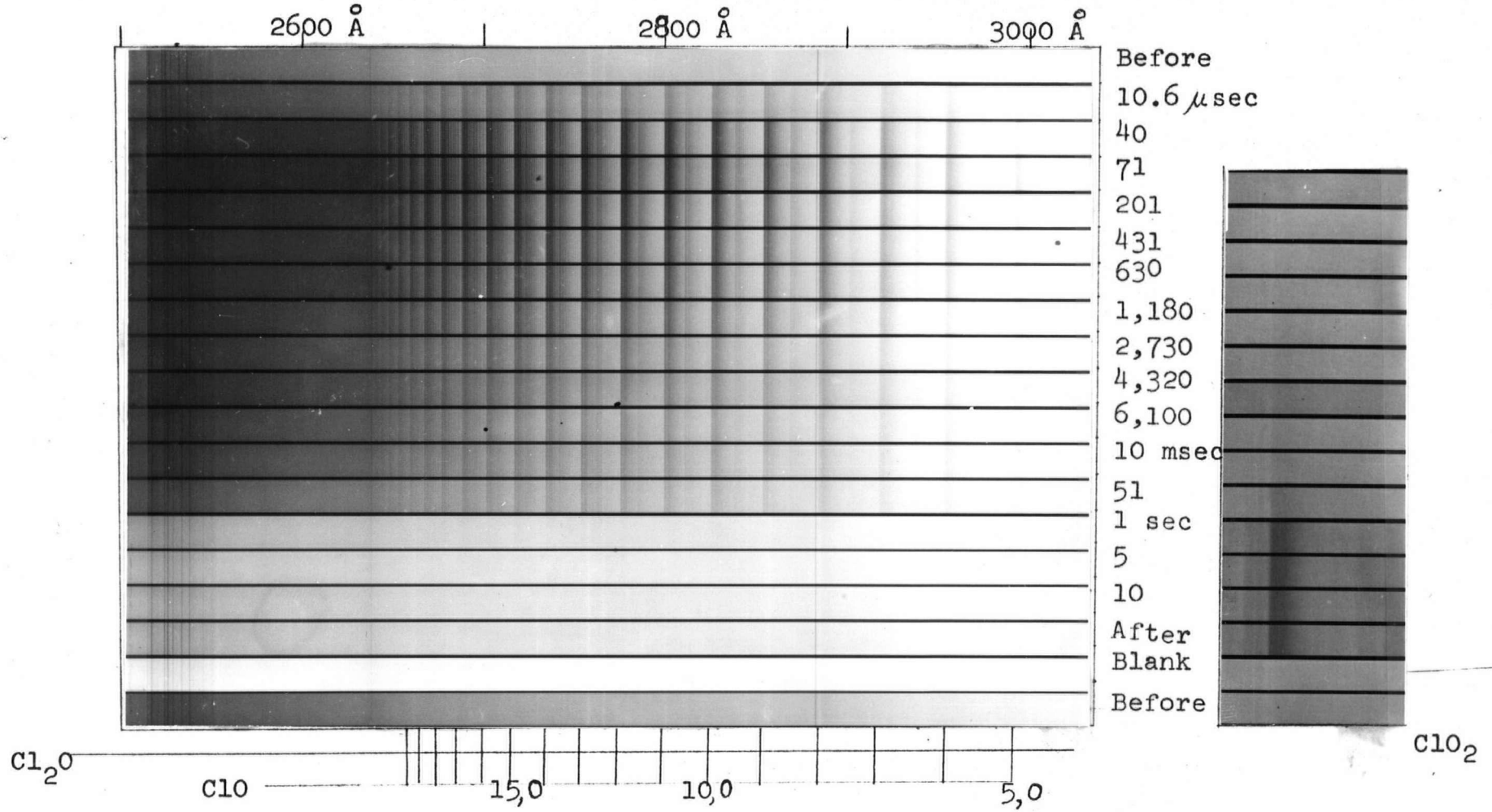


Figure 25. Flash Photolysis of Cl_2O. Cl_2O = 0.6 torr, Argon = 200 torr, E = 1325 J.

coefficient is quite small. A small correction was made to calculate the decrease in the Cl_2O or formation of ClO by comparing it with that when Cl_2O was flashed alone at the same conditions (see fig. 26).

The measurement of ClO was carried out in the same manner as described in Chapter III, section 2. Since the rate of recombination of chlorine atoms is quite small during this period, all of the chlorine atoms produced will react with Cl_2O by the reaction (19) and the rate constant can be obtained from the equation

$$\frac{d[ClO]}{dt} = -\frac{d[Cl_2O]}{dt} = k_{19}[Cl][Cl_2O] \qquad (j)$$

It was difficult to calculate k_{19} directly from the Cl_2O measurements since less than 20% of the Cl_2O is decomposed and measurements of the ClO concentration are much more accurate than that of Cl_2O. Thus k_{19} was calculated as follows.

$$[Cl]_o = [ClO]_o = a$$

$$[Cl]_t = [ClO]_o - [ClO]_t = a-x$$

$$[Cl_2O]_t = [Cl_2O]_o - [ClO]_t = b-x$$

where x is the amount of [ClO] present at time t and b the amount of Cl_2O to start with. Equation (j) can be reduced to

$$\frac{dx}{dt} = k_{19}(a-x)(b-x)$$

or

$$\log\frac{b-x}{a-x} = \frac{(b-a)\,k_{19}}{2.303}\,t + \log b/a \qquad (k)$$

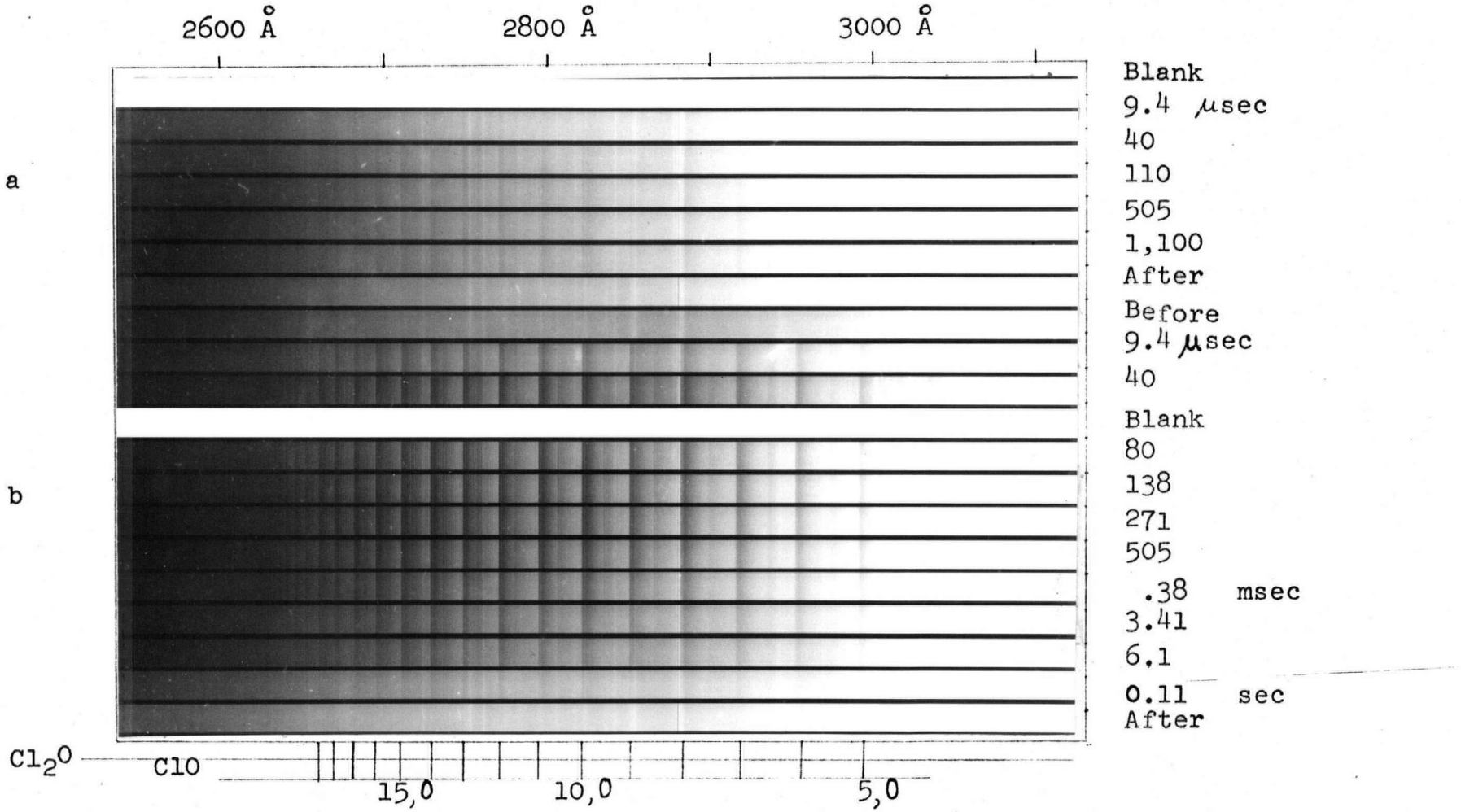


Figure 26. Flash Photolysis of Cl_2O/Cl_2. a) $Cl_2O = 6.3 \times 10^{-6}$ M, Argon=200 torr, E = 600 J. b) $Cl_2O = 6\ 3 \times 10^{-6}$ M, $Cl_2 = 137.5 \times 10^{-6}$ M, Argon=200 torr, E= 600 J.

$\log \frac{b-x}{a-x}$ was plotted against time as shown in fig.(27) and a straight line was obtained as expected from equation (k). From the slope of the linear plot, k_{19} was calculated and is listed in the Table XIII. The ClO concentration was measured at two wavelengths. Blanks are left in Table XIII for data in the non-linear part of the photographic plate or when the ClO formed is too small to be accurately measured. The average value of six measurements was found to be $4.1 \pm 0.4 \times 10^8$ l mole^{-1} sec^{-1} which agrees with the lower limit of 4×10^8 l mole^{-1} sec^{-1} calculated by E.N.T.[22] from the fact that the decomposition of Cl_2O was virtually complete in approximately 200 μsec.

Table XIII

Calculation of k_{19} of Reaction of Chlorine Atoms with Cl_2O

Plate no.	$[Cl_2O]$ (10^{-6} M)	$[Cl_2]$ (10^{-6} M)	Energy J	$k_{19} \times 10^{-8}$ (l mole^{-1}sec^{-1}) 2772 Å	2920 Å
167	34.1	137.5	260	5.0	--
169	63.0	68.0	600	4.0	--
170	35.6	137.5	600	3.9	3.7
171	63.3	137.5	600	--	4.3
173	36.5	137.5	1060	--	3.8

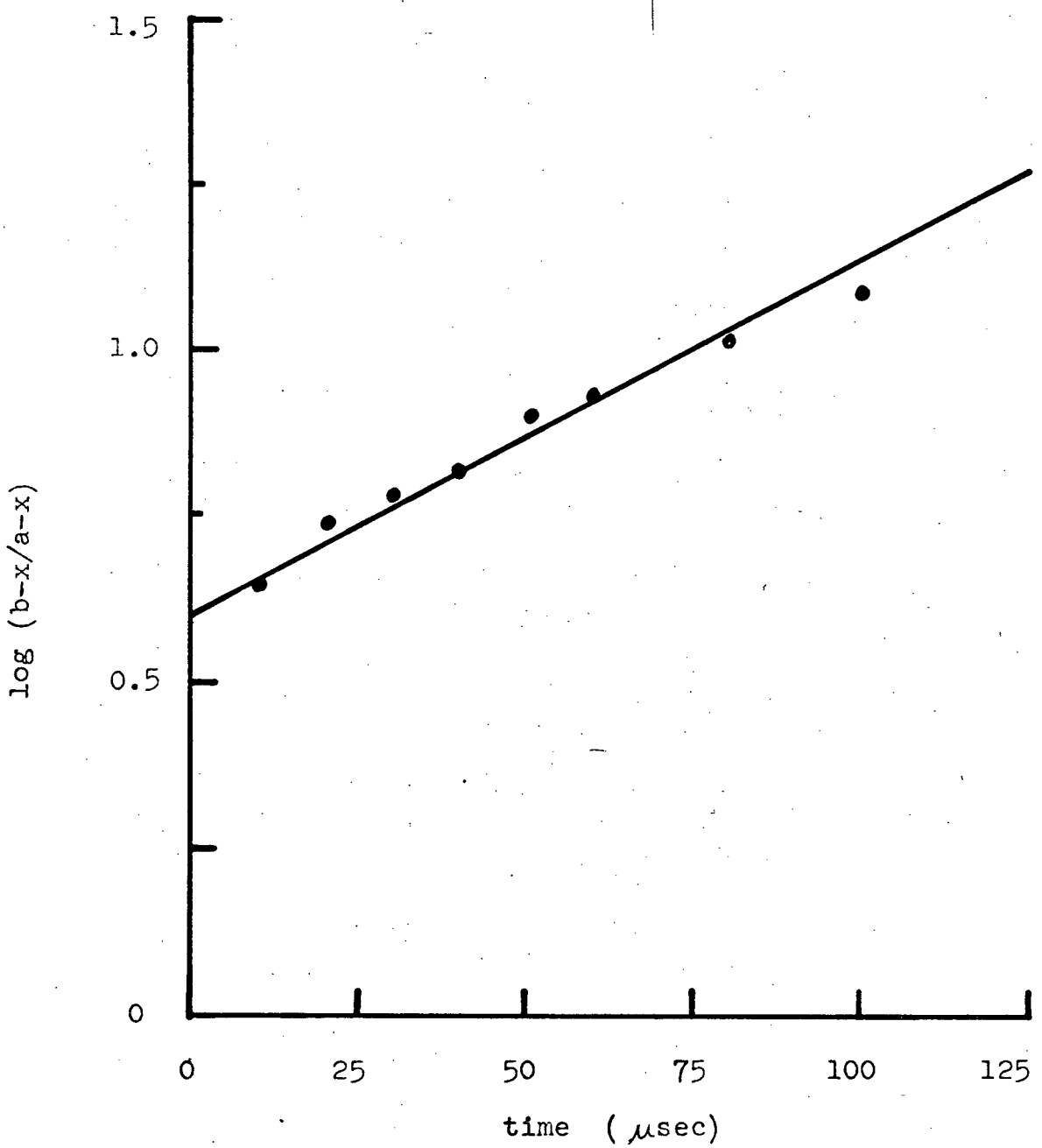
Average $k_{19} = 4.1 \pm 0.4 \times 10^8$ l mole^{-1} sec^{-1}

Figure 27. A plot of log(b-x/a-x) against time.

$b = [Cl_2O]_o$, $a = [ClO]_o$ $x = [ClO]_t$.

$Cl_2O = 63.3 \times 10^{-6}$ M, $Cl_2 = 137.5 \times 10^{-6}$,

Argon = 200 torr, E = 600 J.



2) Stage 3

This section will be divided into two parts. The first will deal with the formation of ClO_2 and the second will be about the calculation of the quantum yield.

a) Formation of ClO_2

The formation of ClO_2 was observed in agreement with the results obtained in the steady state[49,50] as well in the flash photolysis of Cl_2O.[22] The ClO_2 spectrum starts appearing at roughly 1 msec, attains a maximum intensity around one second, and remains virtually constant for at least one minute. The amount of ClO_2 formed depends upon the primary photolysis of Cl_2O. For example using a quartz reaction vessel and high flash energy (1060 J), when nearly all the Cl_2O has been decomposed within 200 to 300 μsec, no ClO_2 was detected. Also with a 3000 Å cut off filter at low flash energy, when only a very small amount of decomposition occurs, the concentration of ClO_2 is also less. This suggests that it must be a reaction between Cl_2O and ClO which is responsible for the ClO_2 production. The reaction proposed by E.N.T.[22] accounts satisfactorily for the formation of ClO_2.

$$Cl_2O + ClO \rightarrow ClO_2 + Cl_2 \qquad (20)$$

This is not the only reaction of ClO radicals with Cl_2O because it has been observed that the rate of formation of ClO_2 is

slower than the decay of ClO and Cl_2O. Thus the Cl_2O must be reacting with ClO by some reaction other than reaction (20) and we agree with the reaction suggested by E.N.T.[22]:

$$Cl_2O + ClO \rightarrow Cl + Cl_2 + O_2 \qquad (21)$$

followed by:

$$Cl + Cl_2O \rightarrow ClO + Cl_2$$

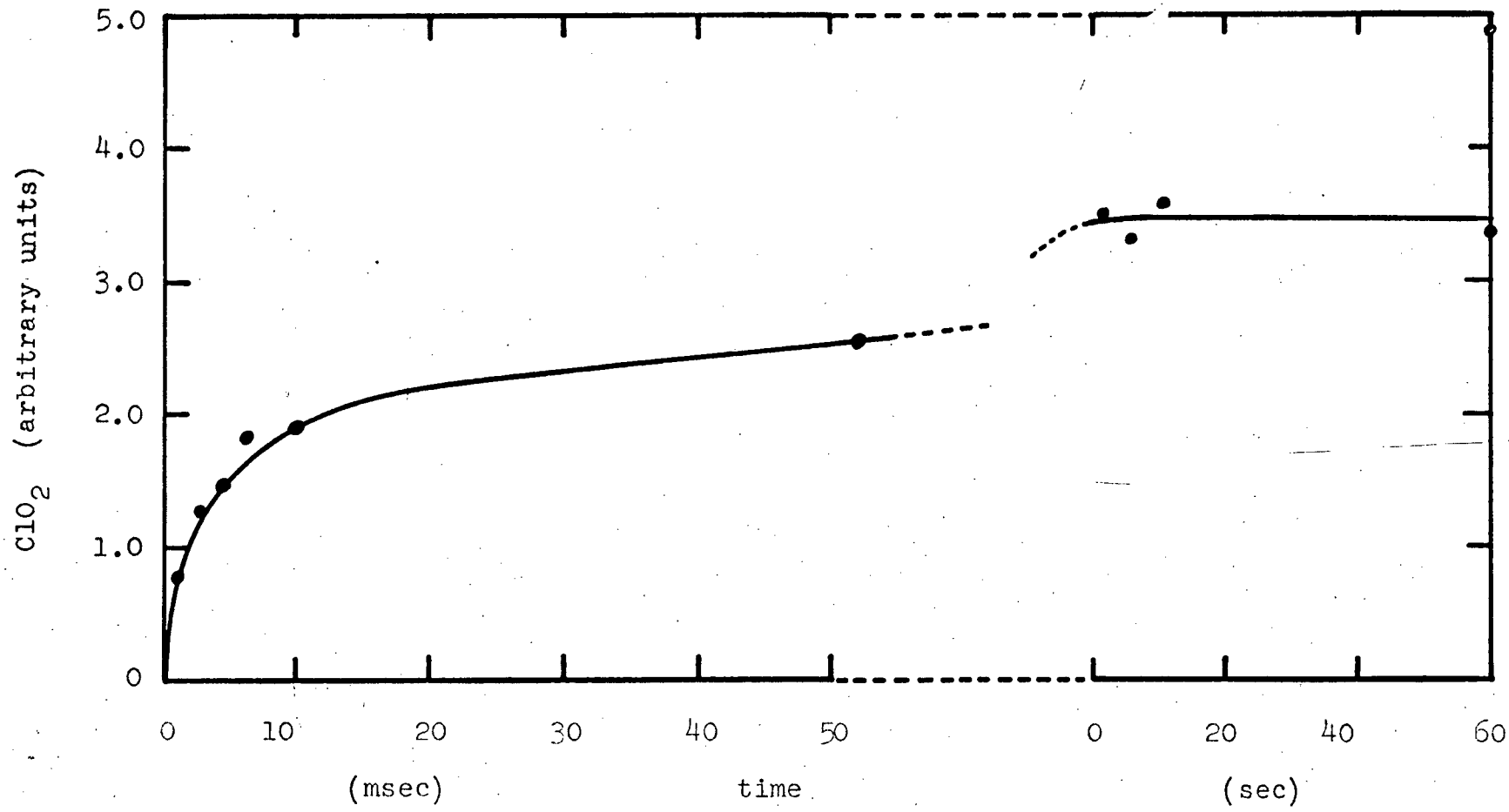
The results obtained thus agree qualitatively with those of E.N.T.[22] They mentioned the possibility that the late appearance of ClO_2 might be due to the following equilibrium:

$$ClO + ClO_2 \rightleftarrows Cl_2O_3$$

This equilibrium was also suggested by L.N.T.[21] in order to explain the reappearance of ClO_2 in their photolysis of ClO_2. Recently Mchale and Elbe[40,41] have also found the new oxide of chlorine with the formula Cl_2O_3 in their study of ClO_2 explosions but we have not observed this in our system. They also rejected the possibility that the late appearance of ClO_2 was due to its removal at short times by oxygen atoms produced in the second primary process. Our measurement of the rate constant confirms that oxygen atoms can be neglected at short times. We did not try to look for the ClO_3 spectrum because the continuum spectrum of Cl_2O is in the same region as ClO_3 and because of the overlap of the successive ClO bands.

The rise of ClO_2 concentration is shown in fig.(25-a) and the rate constant for its formation has been calculated with

Figure 27-a. Formation of ClO_2 following the flash photolysis of Cl_2O.
Cl_2O = 1.0 torr, Argon = 200 torr, E = 1325 J.



the equation derived by E.N.T.[22] and also by finding slopes at various points. Details of this calculation will be given later. The average value of k_{20} was found to be $2.8 \pm 0.6 \times 10^5$ l mole^{-1} sec^{-1}, nearly three times larger than that calculated by E.N.T.[22]

The slow decay of ClO_2 observed by E.N.T.[22] was explained by the reaction

$$ClO_2 + Cl_2O \rightarrow Cl_2 + O_2 + ClO \qquad (20\text{-a})$$

Since in our system the ClO_2 concentration does not decrease, at least for one minute, we neglect this reaction. It can also be rejected from the following experiments. Mixtures of Cl_2O and ClO_2 were prepared in the ratio 1:1, 1:1.5 and 1:2 with a total pressure of 200 mm of argon in the black bulbs. The spectrum of each mixture was taken after 2, 8, 9.5, 15 and 33 hours and were compared with that taken of ClO_2. It was found that there is no decrease in the ClO_2 and Cl_2O concentration. Mixtures with larger ratios (i.e. up to 1:20) were also flashed and the concentrations of ClO_2 and Cl_2O were measured between three to five hours later and similar results were observed. Thus it appears that if there is a decay of ClO_2, it will be by the reaction of chlorine atoms with ClO_2 and not by reaction (20-a).

The above qualitative results can be put into differential equations with the same assumptions as made by E.N.T.[22] because they also hold here too. They are:

1) k_{19} is greater than k_5 and much greater than k_{20} and k_{21}. Under these conditions, the chlorine atom concentration can be neglected and equation (19) can be added to equation (21).

2) The reaction of chlorine atoms with ClO_2 can be neglected.

3) The percentage change in the Cl_2O concentration during this time is small.

Thus from the decay of ClO and Cl_2O, the formation of ClO_2 can be represented as follows:

$$-\frac{d[ClO]}{dt} = k_5[ClO]^2 + k_{20}[ClO][Cl_2O] \qquad (l)$$

$$-\frac{d[Cl_2O]}{dt} = k_{20}[ClO][Cl_2O] + 2\,k_{21}[ClO][Cl_2O] \qquad (m)$$

$$\frac{d[ClO_2]}{dt} = k_{20}[ClO][Cl_2O] \qquad (n)$$

From equation (l) the concentration of ClO at any time can be given by

$$[ClO] = \frac{e^{-k_{20}[Cl_2O]\,t}}{1/[ClO]_o + \frac{k_7}{k_8[Cl_2O]}\,(1 - e^{-[Cl_2O]k_{20}t})}$$

substituting the concentration of ClO into equation (n), the equation can be integrated into the following form:

$$[ClO_2] = \frac{k_{20}}{k_5}[Cl_2O]\ \ln\left[1 + \frac{k_5[ClO]_o}{k_{20}[Cl_2O]}\,(1-e^{-k_{20}[Cl_2O]t})\right] \qquad (A)$$

where $[ClO]_o$ is the amount of ClO present immediately after the flash. k_{20} was calculated by substituting the amount of ClO_2 formed at 1 sec and making successive approximations of k_{20}.

The average value of k_{20} from three experiments found to be $2.8 \pm 0.7 \times 10^5$ l mole^{-1} sec^{-1} as listed in Table XIV.

The equation (n) was also solved by finding the slope at different times (fig. 25-a) and substituting the amount of ClO and Cl_2O present at the same time. The values are listed in Table XIV and average of five found to be $2.64 \pm 0.3 \times 10^5$ l mole^{-1} sec^{-1}, which is in excellent agreement with the value found from the integrated expression.

b) Decay of Cl_2O

The rate constant of the second reaction of Cl_2O with ClO can be calculated from equation (m) by two methods.

1) The slopes of decay of Cl_2O (S_2) and rise of ClO_2 (S_1) were measured at the same time and subtracting equation (n) from (m)

$$S_2 - S_1 = 2\, k_{21}[ClO][Cl_2O]$$

k_{21} was calculated by substituting the amount of ClO and Cl_2O present at that time. The average value obtained for k_{21} was found to be $6.2 \pm 1.5 \times 10^5$ l mole^{-1} sec^{-1} (Table XIV).

2) The two equations were divided to get

$$S_2 / S_1 = 1 + 2\, k_{21}/k_{20}$$

thus $k_{21} = 1/2(S_2/S_1 - 1)\, k_{20}$.

The values of the slopes S_2 and S_1 (calculated in method 1) were substituted and the values of k_{21} thus obtained are listed in Table XIV. The average value of k_{21} thus obtained was

found to be 6.8 ± 0.9 10^5 l $mole^{-1}$ sec^{-1} which agrees with the above value within experimental error. The overall value of k_{21} = 6.5 ± 1.3 10^5 l $mole^{-1}$ sec^{-1}.

The value of k_{21} found by us is 10 to 12 times greater than that calculated by E.N.T.[22]. From fig. (3) of their paper, the slopes of decay of Cl_2O and rise of ClO_2 were measured. The ratio of the two slopes thus found was substituted in their equations and the value of k_{21} found to be 7 to 10 times greater than k_{20} but they found k_{21} to be half of k_{20}. In calculating this ratio from their paper, it was assumed by us that fig.(3) represents the absolute concentration. Similar results will be derived from the calculation of quantum yield mentioned in the next section.

Table XIV

Plate no.	$[Cl_2O] \times 10^{+6}$ (mole/l)	Energy J	$k_{20} \times 10^{-5}$ (l $mole^{-1} sec^{-1}$) by Eq.A.	$k_{21} \times 10^{-5}$ (l $mole^{-1} sec^{-1}$) Method I	Method II
192	55.0	1325	3.0	2.9	8.0	8.0
				2.3	5.0	6.2
193	33.0	1325	3.5	3.0	8.2	7.8
				2.3	4.9	5.8
				2.7	5.0	6.0
191*	52.3	1325	2.0	--	--	--
		Average		2.64 ± 0.3	6.2 ±1.5	6.8 ±0.9
					6.5±1.3	

*Two mm of glass filter A was placed between the reaction vessel and flash lamp.

3) Quantum Yields in Both Sensitised and Nonsensitised Decomposition of Cl_2O

It is quite difficult in our system to find quantum yield at different wavelengths as it is difficult to filter the radiation. Since the extinction coefficient of Cl_2O decreases sharply above 3400 Å and using two mm of glass filter A, the radiation which can cause decomposition in our system is mostly within 300 Å of 3000 Å. The overall quantum yield was calculated for these wavelengths and found to be 3.6 ± 0.2 which agrees with that found by Finkelnberg et al.,[50] i.e., 3.5 at 10°C. If we apply the correction for the temperature coefficient, their value will become ∿4.0 at room temperature, even then the agreement is satisfactory.

It can be seen from the reaction scheme that if reaction (18) is the primary step followed rapidly by reaction (19), the change in the Cl_2O concentration produced is the same as in the case of chlorine photosensitised decomposition of Cl_2O having (18-a) as the primary step and both the chlorine atoms reacting with Cl_2O. Thus the quantum yield in both systems should be the same and it can be seen from Table XV that average value of the quantum yield obtained by chlorine photosensitisation is 3.5 ± 0.2 which agrees with the above results.

The overall quantum yield for the wavelengths between 2300 to 2750 Å was calculated by Schumacher et al.[51] to be 4.5.

They explained it by assuming that oxygen atoms do not react with Cl_2O. But it was found by us[31] and by Phillips et al.[73] that oxygen atoms react via reaction (35) with $k_{35} = 5.3 \times 10^9$ l mole^{-1} sec^{-1} or 8.3×10^9 l mole^{-1} sec^{-1}, respectively. If reaction (22) is the primary step followed by (19), (35), or (36) rapidly and followed by reactions (20) and (21), the quantum yield should have been 5.5. In our system it is quite difficult to separate the reactions (18) and (22), followed by the competition between (35) and (6), although the overall change would have been the same even if reaction (6) is taking place. Thus it seems more reasonable to explain the small increase in quantum yield towards shorter wavelengths, found by Schumacher et al.,[51] to be due to a limited occurrence of reaction (22) followed by (19), (35) or (6).

It can be seen, also, that after the first stage of reactions are over, the quantum yield of the decomposition of Cl_2O should be the same in both chlorine sensitised and direct photolysis. The formula can be derived as follows (details can be seen in Appendix I):

$$\phi_{Cl_2O} = \frac{[Cl_2O]_o}{[ClO]_o} \left[1 - \left(1 + \frac{c}{b} \frac{[ClO]_o}{[Cl_2O]_o} \right)^{-1/c} \right]$$

where $b = \dfrac{k_{20}}{k_{20} + 2\,k_{21}}$

$$c = \frac{k_5}{k_{20} + 2\,k_{21}} - 1$$

$$\frac{c}{b} = \frac{k_5 - 2k_{21}}{k_{20}} - 1$$

$[Cl_2O]_o$ = $[Cl_2O]$ left after flash and Cl + Cl_2O reaction is finished. $[ClO]_o$=[ClO] after the flash and Cl + Cl_2O reaction is finished.

The quantum yield (ϕ) of Cl_2O decomposition was calculated by substituting k_5, k_{20} and k_{21} determined by us, ϕ^1 using our value of k_5 and k_{20} but E.N.T.'s value of k_{21}, ϕ^{11} using our value of k_5 but E.N.T.'s value of k_{20} and k_{21} and the values obtained are listed in Table XV and also the ϕ_e (experimental) are included in Table XV. It can be seen from Table XV that by using the values of k_{20} and k_{21}, determined by E.N.T.,[22] very low values of ϕ are obtained and hence the overall quantym yield would be 2.3 $\pm$ 0.1, but if we use our values, the overall quantum yield is found to be 3.24 $\pm$ 0.22, which is low but in satisfactory agreement with the experiment. This is further evidence that the value of k_{20} and k_{21} calculated by us is more reasonable than those calculated by E.N.T.[22]

Table XV

Calculation of Quantum Yield of Cl_2O Photolysis

Plate no.	$[Cl_2O]\times10^{+6}$ (mole/l)	$[Cl_2]\times10^{+6}$ (mole/l)	Energy J	Filter	ϕ	ϕ_e	ϕ^1	ϕ^{11}
170	35.6	137.5	600	A	3.3	3.6	2.3	2.2
171	63.3	137.5	600	A	3.5	3.5	2.4	2.3
172	63.3	137.5	1060	A	3.1	3.8	2.2	2.1
173	36.5	137.5	1060	A	2.9	3.3	2.2	2.1
184	57.8	--	830	A	3.2	3.5	2.3	2.2
191	52.3	--	1060	A	3.2	3.5	2.3	2.4
192	55.0	--	1325	-	3.0	3.7	2.7	2.2
193	33.0	--	1325	-	3.6	3.6	2.3	2.2
		Average			3.24 $\pm$0.22	3.6 $\pm$0.15	2.3 $\pm$0.2	2.2 $\pm$0.1

A = glass filter A

ϕ = calculated by using our value of rate constants

ϕ_e = calculated experimentally

ϕ^1 = calculated by using our value of k_5 and k_{20} but E.N.T.'s value of k_{21}

ϕ^{11} = calculated by using our value of k_5 but E.N.T.'s value of k_{20} and k_{21}.

B. Bromine Photosensitised Decomposition of Cl_2O

Brown and Spinks[54] in their study of bromine photosensitised decomposition of Cl_2O found that this system behaves in the same manner as chlorine photosensitised or direct photolysis. They found that the quantum yield is 4.3 and that ClO_2 is formed. The reactions suggested by them are simply:

$$Br + Cl_2O \rightarrow ClO + BrCl \qquad (25)$$

with subsequent reactions of ClO and Cl_2O identical to those occurring in the Cl_2/Cl_2O system. Thus the rate constant k_{25} can be measured in a similar way to that used for the $Cl + Cl_2O$ reaction. A further important application of this reaction is its use as a method for estimating bromine atom concentration which is more accurate than measurements of the decrease of Br_2 concentration.

Br_2 and Cl_2O mixtures in the ratio of nearly 1:1 and 1:4 were flashed at two flash energies. Two light filters 4400 Å and 5600 Å were used and thus only Br_2 was photolysed. The total pressure used was 200 mm of argon in all the cases. The results obtained were similar to those obtained in the Cl_2 photosensitised and in the nonsensitised photolysis of Cl_2O. A typical run is shown in the fig. (28).

The measurement of ClO was carried out in the same manner as described in ChapterIII, section A-2. It is found that ClO concentration attains its maximum value within 200 μsec and then starts decaying slowly. No other spectra in the

range of 2300 Å to 4500 Å were observed during the first 500 μsec, in particular no BrO spectrum. The ClO_2 spectrum starts appearing at approximately 1 msec, attains its maximum value at 1 sec and then decreases slowly.

It appears from the results that a reaction scheme similar to Cl_2/Cl_2O can be written in this case too.

$$Br_2 + h\nu \rightarrow 2\ Br \qquad (23\text{-a})$$

$$Br + Cl_2O \rightarrow ClO + BrCl \qquad (25)$$

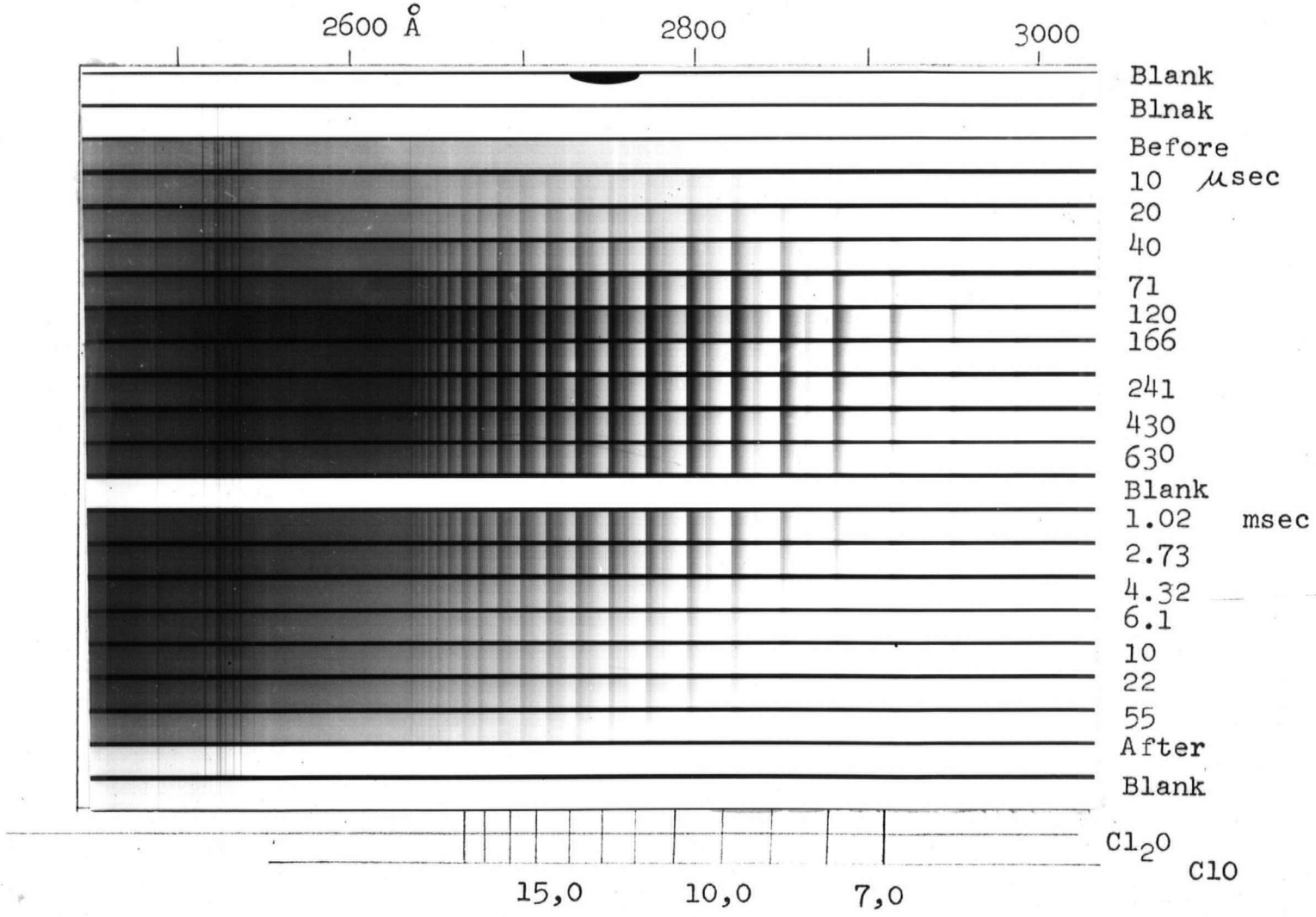
The subsequent reactions of ClO and Cl_2O are the same as discussed before in the direct photolysis.

The bromine atoms involved in this reaction are presumably ground state because the pressure of argon and bromine used are enough for the quenching of excited atoms. Quenching rates of excited bromine atoms, calculated by Donovan and Hussain[80] are used. The subsequent reactions of ClO and Cl_2O are the same as discussed before in the direct photolysis. This is confirmed from the following results.

1) The behaviour of ClO_2 is similar to that observed in the case of nonsensitised experiments though a detailed study was not carried out.

2) $\frac{1}{[ClO]}$ was plotted against time and the slopes were calculated. Combining them with the extinction coefficient (calculated previously), k_5 was calculated and the average found to be $3.0 \pm 0.5 \times 10^7$ l mole^{-1} sec^{-1}. Although this value is higher than that found in case of ClO_2 photolysis

Figure 28. Flash Photolysis of bromine in the presence of Cl_2O.
$Cl_2O = 24.4 \times 10^{-6}$, Argon = 200 torr, $Br_2 = 27.5 \times 10^{-6}$ M, E = 1060 J, Filter 4400 Å.



($2.65 \pm 0.29 \times 10^{7}$ l mole^{-1} sec^{-1}), the difference is not enough to require the inclusion of the following reaction

$$BrCl + ClO \rightarrow BrO + Cl_2$$

which is only one Kcal endothermic.

3) Similar to the chlorine photosensitised photolysis of Cl_2O, the overall quantum yields for the decomposition of Cl_2O by bromine atoms were calculated. The average of six measurements was 3.7 ± 0.3, regardless of the radiation used. This value is in satisfactory agreement with the value found by Brown and Spinks,[54] and also that calculated from the Cl_2 sensitised and the non-sensitised photolysis of Cl_2O.

The above results show that the reaction mechanism is similar to that sensitised by chlorine and the only extra species, BrCl, present in this system does not interfere with the reaction scheme.

Calculation of Rate Constant of Bromine Atoms with Cl_2O

The rate constant of bromine atoms with Cl_2O was measured in a similar way as that for the reaction of chlorine atoms with Cl_2O, i.e., from the rate of formation of ClO radicals. The rate equation can be written as

$$-\frac{d[Cl_2O]}{dt} = \frac{d[ClO]}{dt} = k_{25}[Br][Cl_2O]$$

If $[Br]_o = [ClO]_o = a$

$[Br]_t = [ClO]_o - [ClO]_t = a - x$

$$[Cl_2O]_t = [Cl_2O]_o - [ClO]_t = b - x$$

thus

$$\frac{d[ClO]}{dt} = \frac{dx}{dt} = k_{25}(a - x)(b - x)$$

or $$\log \frac{b - x}{a - x} = \frac{(b - a)k_{25}}{2.303} t + \log \frac{b}{a}$$

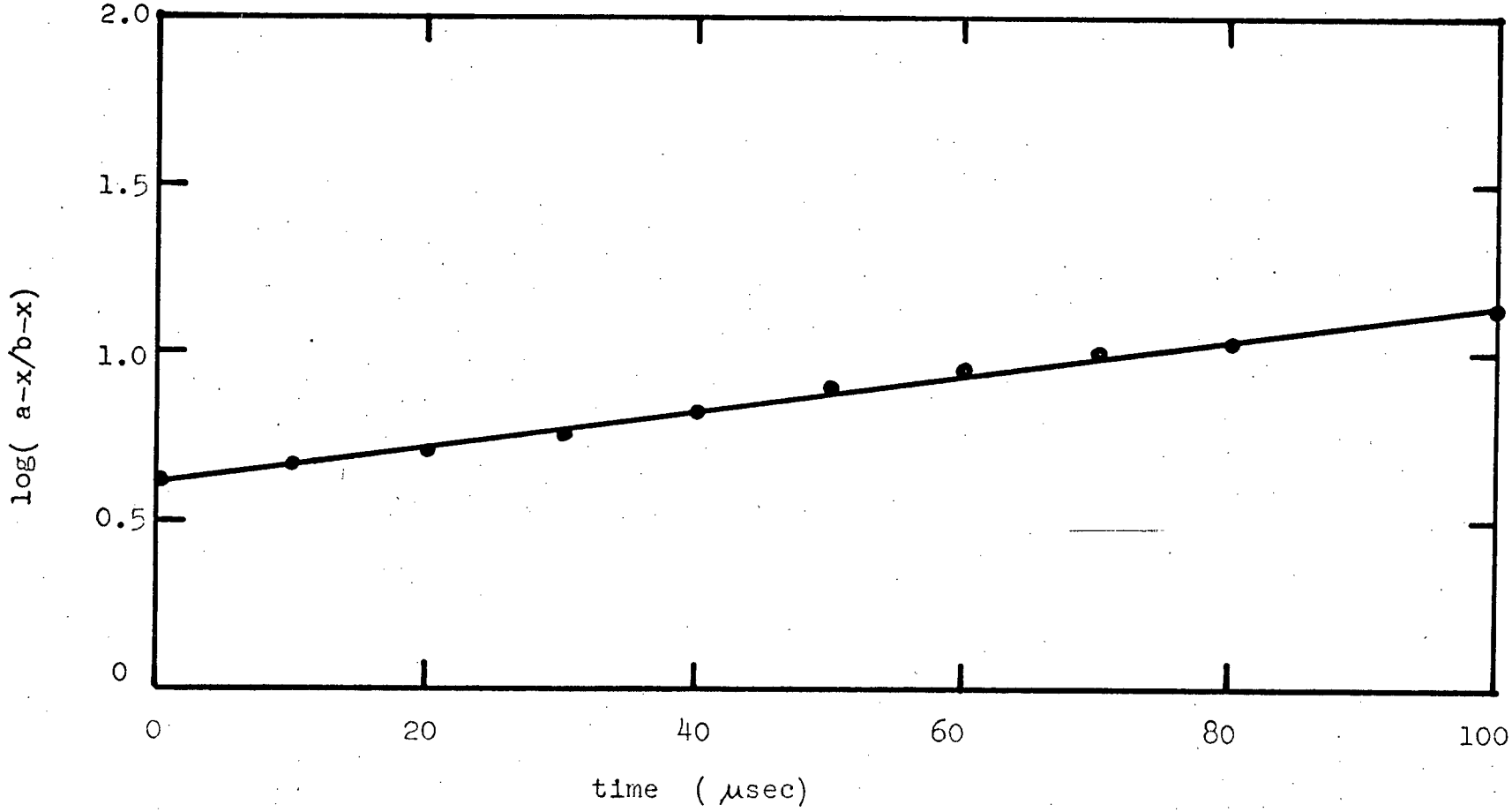
$\log \frac{b - x}{a - x}$ was plotted against time as shown in fig.(29) and from the slope of the straight line as expected from the equation, the value of k_{25} was calculated and is listed in Table XVI. The ClO concentration was measured at two wavelengths (2772 Å and 2920 Å). The average of eleven measurements was found to be $6.1 \pm 0.6 \times 10^8$ l mole^{-1} sec^{-1}.

Table XVI

Plate no.	Energy J	$[Cl_2O] \times 10^{+6}$ (mole/l)	$[Br_2] \times 10^{+6}$ (mole/l)	Filter Å	$k_{25} \times 10^{-8}$ (l mole^{-1} sec^{-1}) 2772 Å	2920 Å
257	1060	25.7	20.6	4400	6.7	6.1
258	1060	24.4	27.5	4400	6.5	6.2
259	1060	39.6	41.3	4400	--	6.2
260	600	36.3	41.3	4400	6.3	5.5
261	600	23.4	20.6	4400	6.6	6.4
296	1060	39.2	137.5	5600	5.4	5.0

Average $k_{35} = 6.1 \pm 0.6 \times 10^8$ l mole^{-1} sec^{-1}

Figure 29. A plot of log(a-x/b-x) against time. $b=[ClO]_o$, $a=[Cl_2O]_o$, $x=[ClO]_t$. $Cl_2O = 24.4 \times 10^{-6}$ M, $Br_2 = 27.5 \times 10^{-6}$, Argon = 200 torr, E = 1060 J, Filter 4400 Å.



C. Chlorine Photosensitised Decomposition of ClO_2

Mixtures of ClO_2 and Cl_2 in ratios varying from 1:15 to 1:35 were flash photolysed using energies 160 and 260 J. The argon pressure was 200 torr in all the experiments and 2 mm of glass filter A was used to prevent the photolysis of ClO. The purpose of using low flash energies was to reduce the primary photolysis of ClO_2 and thus to avoid the reaction

$$O + ClO \rightarrow Cl + O_2 \qquad (6)$$

The ratio of Cl_2 to ClO_2 was kept high in order to have enough chlorine atoms to produce a reasonable decrease in ClO_2 concentration by the reaction

$$Cl + ClO_2 \rightarrow 2\ ClO \qquad (8)$$

because the extinction coefficient of chlorine is much smaller than ClO_2. The main difficulty in this system is that both ClO_2 and Cl_2 absorb in the same region and hence both will be photolysed. Thus in order to find the amount of ClO_2 decomposed by chlorine atoms, the results of the photolysis of ClO_2 with and without chlorine were compared.

The decay of ClO_2 with and without chlorine is shown in fig. (30)(plate 196) and fig. (31). It can be seen from fig. (31) that after approximately 200 to 300 μsec, the ClO_2 remains constant over the period of our reaction time (20 msec), indicating that all the reactions involving ClO_2 are over within this period. The decrease in the ClO_2 concentration or the

Figure 30. Comparison of the behaviour of ClO_2 in the absence and presence of Cl_2.

a) $ClO_2 = 4.0 \times 10^{-6}$ M, Argon = 200 torr, E=260 J.

b) $ClO_2 = 4.0 \times 10^{-6}$ M, $Cl_2 = 66.0 \times 10^{-6}$ M, Argon = 200 torr, E = 260 J.

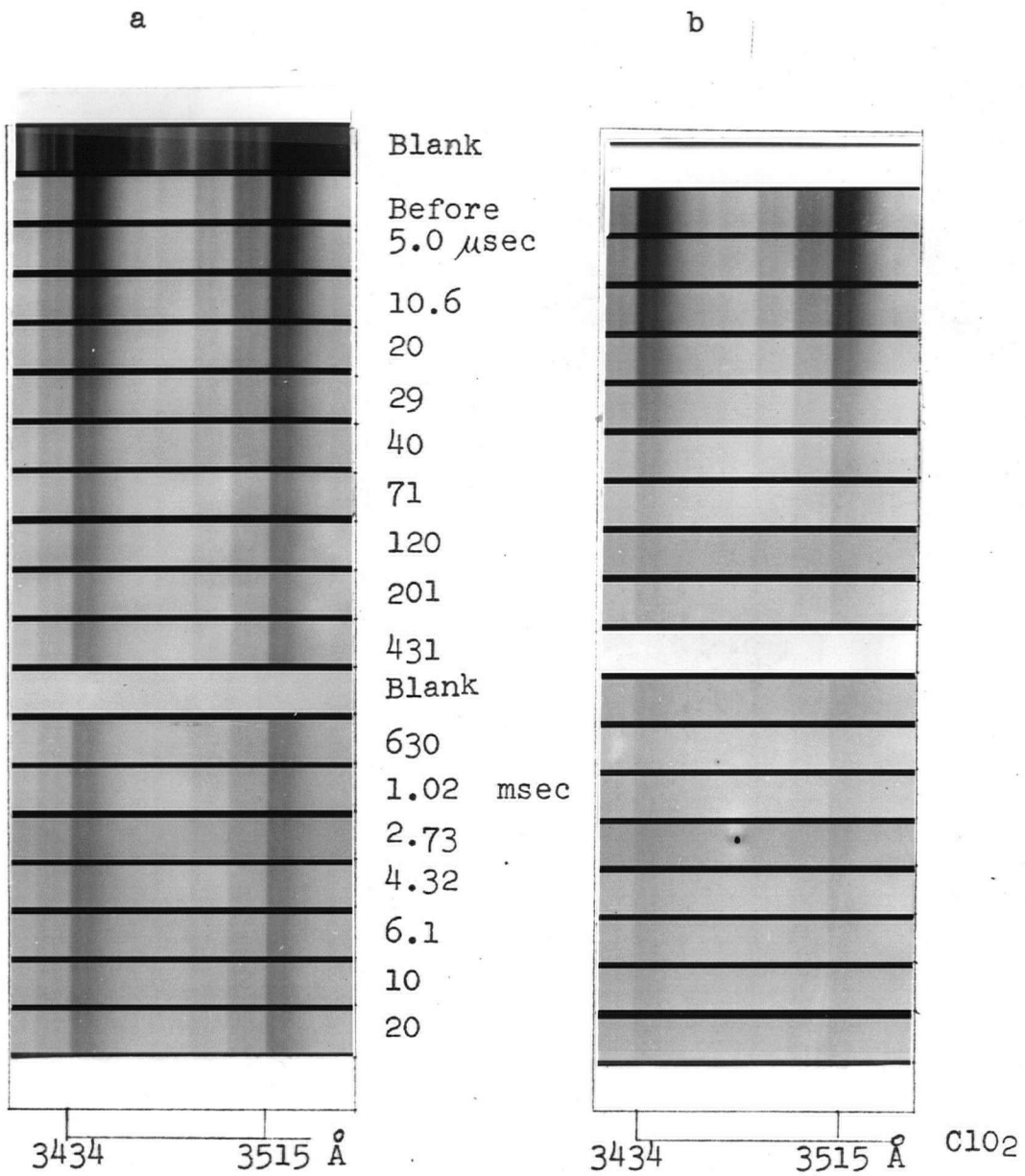
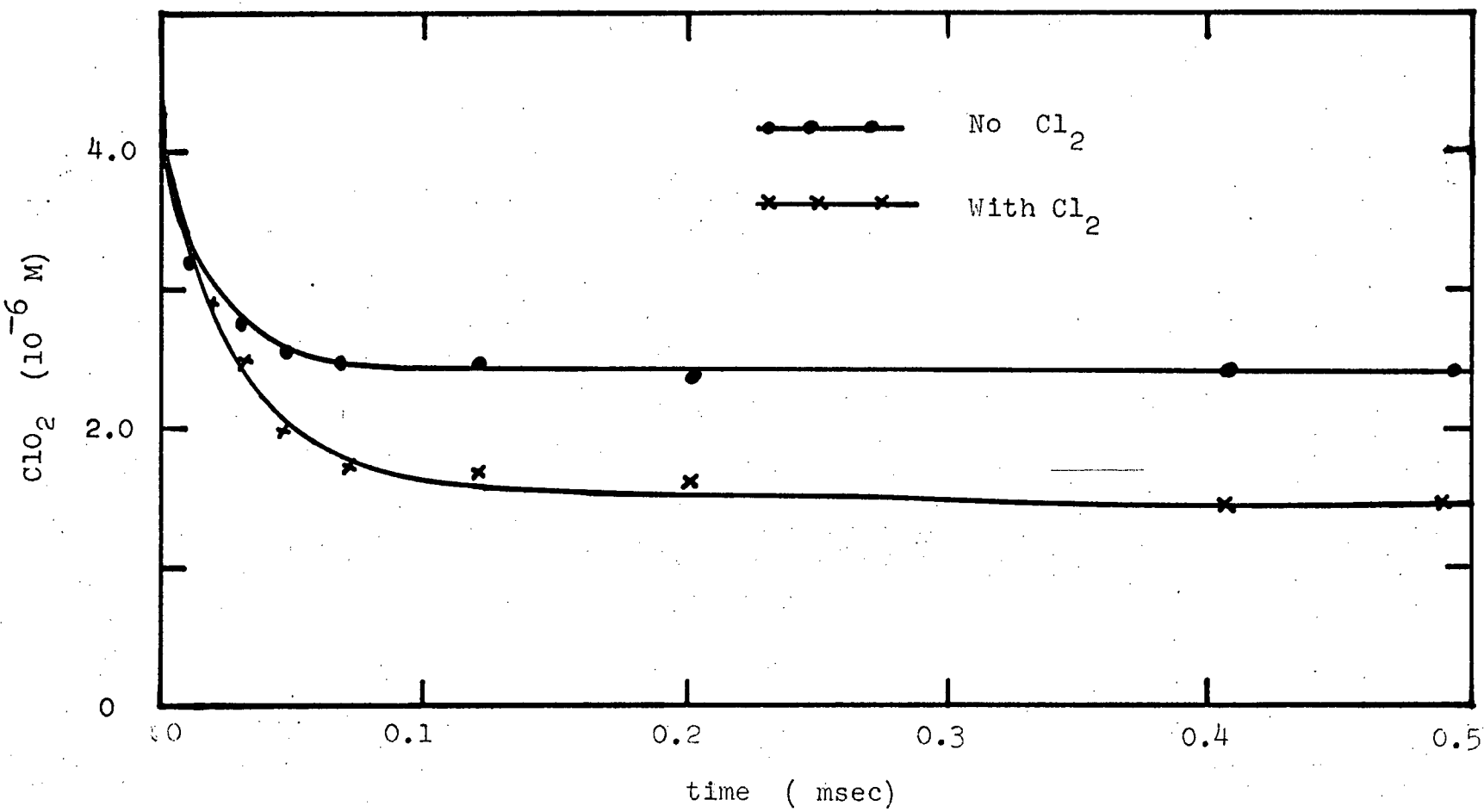


Figure 31. Decay of ClO_2 in the absence and presence of Cl_2.
$ClO_2 = 4.0 \times 10^{-6}$ M, $Cl_2 = 66.0 \times 10^{-6}$ M, Argon = 200 torr, E = 260 J.



concentration of chlorine atoms formed, was calculated from fig.(31) and compared with the concentration of chlorine atoms formed calculated by the titration of chlorine atoms with NOCl. The agreement between the two values was satisfactory (∿10 to 15%).

The decomposition of ClO_2 or amount of chlorine formed was also checked by measuring the concentration of ClO, with and without Cl_2 present. These values were compared with the values obtained from the decrease in the ClO_2 concentration. The values are listed in Table XVII and the agreement is quite good. A comparison of ClO formed with and without Cl_2 is given in figs. (32) and (33).

1) Stoichiometry of the Reaction

The results of the above experiments can be explained in terms of the following reactions.

In the absence of chlorine

$$ClO_2 + h\nu \rightarrow ClO + O \qquad (27)$$

$$O + ClO_2 \rightarrow ClO + O_2 \qquad (7)$$

$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad (5)$$

The reactions

$$O + ClO \rightarrow Cl + O_2 \qquad (6)$$

$$Cl + ClO_2 \rightarrow 2ClO \qquad (8)$$

Figure 32. Rise and Decay of ClO when ClO_2 is flashed with and without Cl_2.

a) $ClO_2 = 4.0 \times 10^{-6}$ M, Argon = 200 torr, E = 260 J.

b) $ClO_2 = 4.0 \times 10^{-6}$ M, $Cl_2 = 66.0 \times 10^{-6}$ M, Argon = 200 torr, E = 260 J.

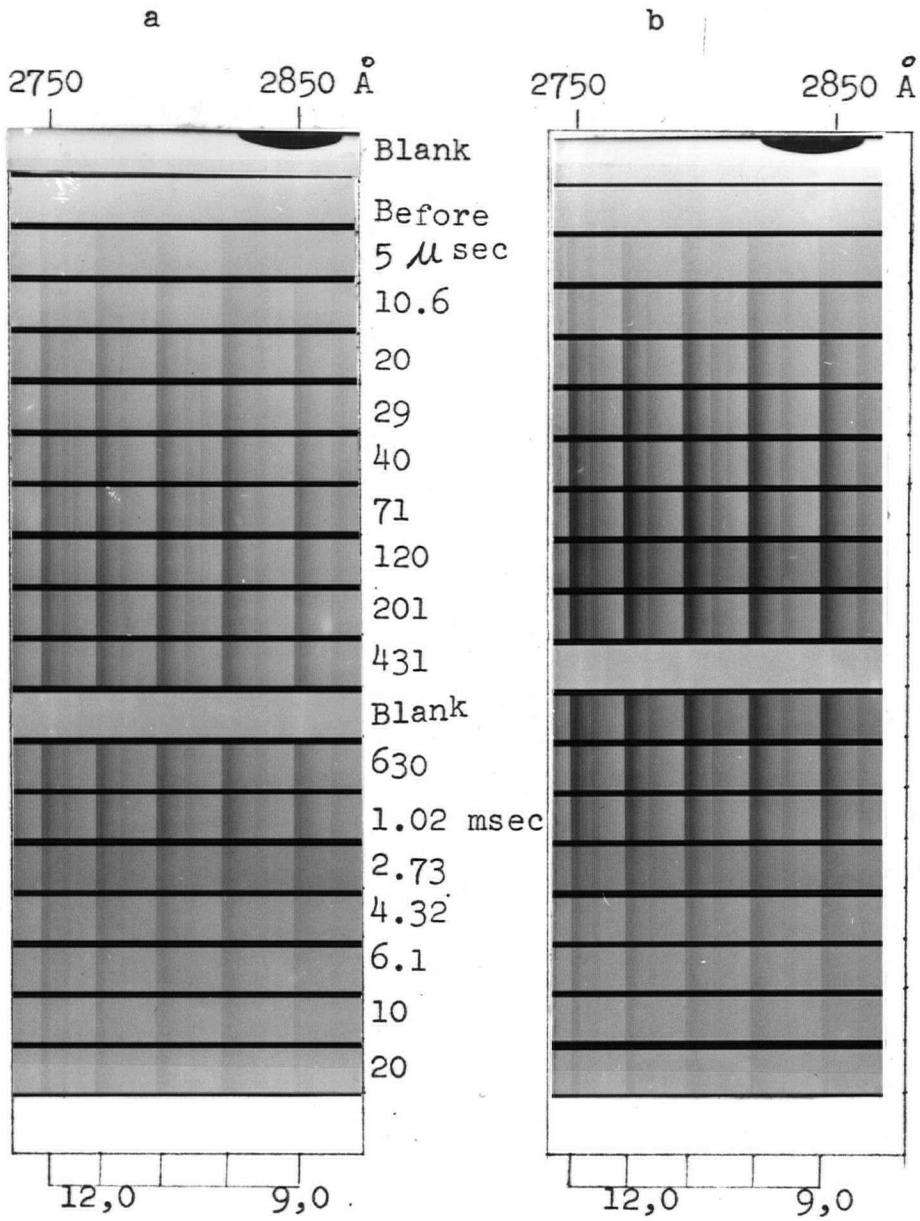
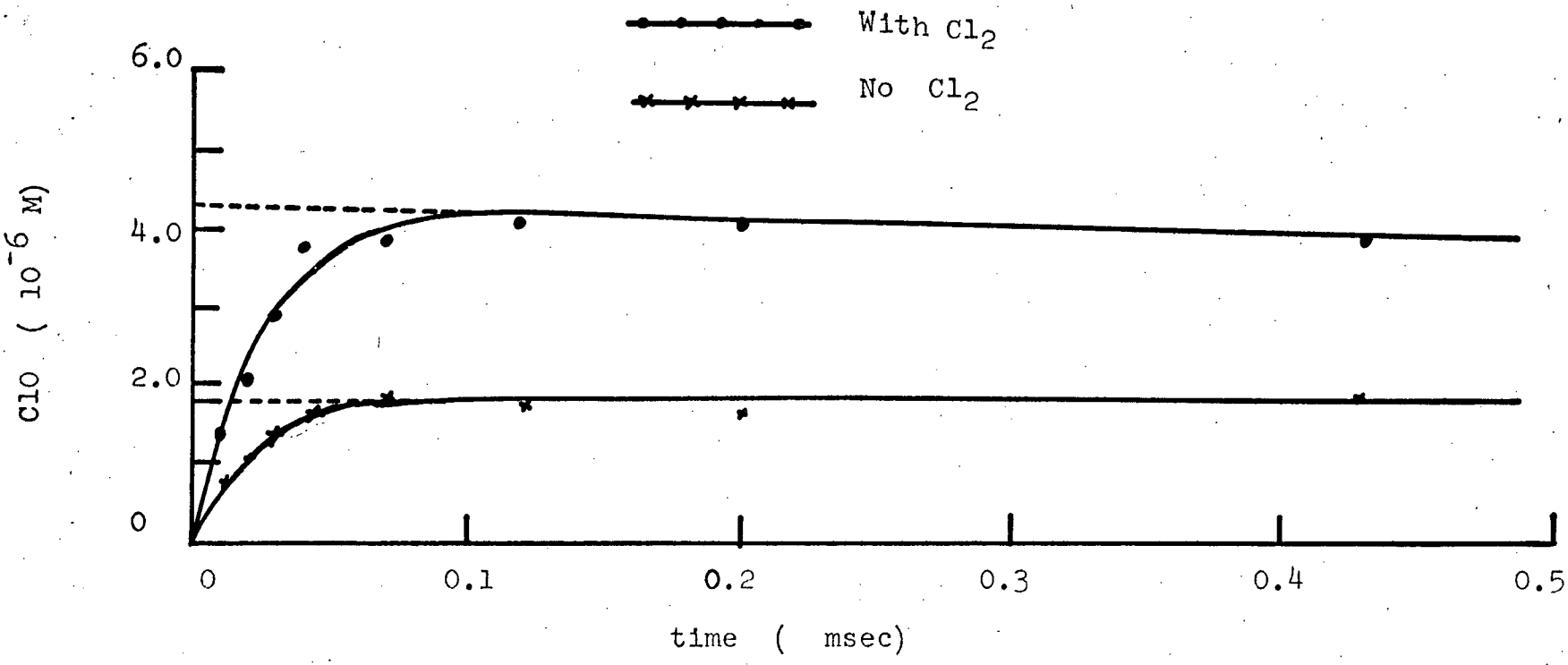


Figure 33. Formation of ClO in the presence and absence of Cl_2.
$ClO_2 = 4.0 \times 10^{-6}$ M, $Cl_2 = 66.0 \times 10^{-6}$ M, Argon = 200 torr, E = 260 J.



contribute less than 5% to the overall decay of oxygen atoms.

In the presence of chlorine, the following reactions may occur:

$$Cl_2 + h\nu \rightarrow 2\ Cl$$

$$Cl + ClO_2 \rightarrow 2\ ClO \qquad (8)$$

$$Cl + ClO_2 \rightarrow Cl_2 + O_2 \qquad (8\text{-a})$$

$$O + Cl_2 \rightarrow ClO + Cl \qquad (38)$$

The recombination of chlorine atoms can be neglected because it is too slow if the rate constant given by Bader et al.[29,30] and Linnet et al.,[79] is used.

If chlorine atoms react with ClO_2 via reaction (8-a), there would not be any increase in the ClO concentration when it is flashed in the presence of chlorine. If reaction (8) is predominant, there will be 2 ClO formed for each molecule of ClO_2 decomposed. Otherwise, the amount of ClO formed would vary between 0 to 2 times the change in the ClO_2 concentration, depending upon the reaction which is dominant. It can be seen from Table XVII that the amount of ClO formed due to the reaction of chlorine atoms is approximately 10% more than the amount that would have been obtained by reaction (8). Taking this as an experimental error, it is clear that the stoichiometry of the reaction is two. Clyne and Coxon[25] have found the stoichiometry to be 1.9 ± 0.1 and the agreement is satisfactory between the two values. On these grounds, reaction (8-a) can be neglected, the contribution probably being less

than 5% of reaction (8).

Although a 10% difference in the concentration of ClO can be regarded as within experimental error much of it can be explained by taking into consideration the reaction (38), i.e., each oxygen atom reacting with a Cl_2 molecule will give two extra ClO radicals. Taking $k_{38} = 5.0 \times 10^7$ l mole^{-1} sec^{-1}, calculated by Clyne and Coxon[25] and by Niki and Weinstock,[84] the difference was reduced to 5%. It seems likely that reaction (38) does occur to some extent though it is not very important in our system.

Table XVII

Amount of ClO Formed with and Without Chlorine

Plate no.	Energy J	$[ClO_2]$	$[Cl_2]$	[ClO] without A	$[Cl_2]$ B	[ClO] with C	Cl_2 D
196	260	4.0	66.0	2.48	2.62	4.46	4.65
197	260	2.65	41.3	1.58	1.66	2.82	3.07
198	160	4.0	137.5	1.68	1.75	3.96	4.47
198′	160	4.0	137.5	1.68	1.75	3.96	4.3
200	160	4.0	87.5	1.68	1.75	3.02	3.24

Note: All concentrations are measured in 10^{-6} mole/l

ClO concentration in columns A and C are calculated from the decrease in the ClO_2 and in columns B and D from the direct measurement of ClO.

2) Calculation of k_8

The rate constant k_8 can be calculated either by following the decay of ClO_2 or by the increase in the ClO concentration. It will be seen that in both the methods certain approximations have to be used because the differential equations obtained are difficult to solve.

From the ClO_2 Measurement

The rate of the reactions after the photolysis can be written as

$$-\frac{d[ClO_2]}{dt} = k_7[O][ClO_2]$$

without chlorine and with chlorine

$$-\frac{d[ClO_2]}{dt} = k_7[O][ClO_2] + k_8[Cl][ClO_2]$$

neglecting reaction (6) in both cases. Since 98 % of oxygen at atoms have been reacted with ClO_2 within 60 μsec, when ClO_2 is flashed alone, the difference in the $k_7[O][ClO_2]$ term of the two equations becomes small after that time. Thus to the first approximation by subracting first equation from the second

$$-\frac{d[\Delta ClO_2]}{dt} = k_8[Cl][ClO_2] \qquad (o)$$

where $\Delta[ClO_2]$ is the difference of ClO_2 concentration decomposed with and without chlorine atoms.

The chlorine atom concentration can be calculated as follows

$$[Cl]_o = \left([ClO_2]_a - [ClO_2]_b\right)_\infty = \Delta[ClO_2]_\infty$$

where $[ClO_2]_a$ = amount of ClO_2 present at ∞ without Cl_2

$[ClO_2]_b$ = amount of ClO_2 present at ∞ with Cl_2

and $[Cl]_t = \Delta[ClO_2]_\infty - \Delta[ClO_2]_t$

Thus equation (o) can be written as

$$-\frac{d[\Delta ClO_2]}{dt} = k_8 \left(\Delta[ClO_2]_\infty - \Delta[ClO_2]_t\right)[ClO_2] \quad (p)$$

This equation was solved as follows. The decay curve of ClO_2 was divided into small segments of 10 μsec intervals. Taking the average value of ClO_2 between the two successive intervals and assuming this to be a constant, the equation (p) was integrated.

$$-\ln(\Delta[ClO_2]_\infty - \Delta[ClO_2]_t) = k_8[ClO_2]_{av}t - \ln(\Delta[ClO_2]_\infty) \quad (q)$$

In this way k_8 was calculated by computing the value of each species after time interval of 10 μsec after the initial 60 μsec when the reaction of oxygen atoms with ClO_2 was almost complete. The values thus obtained are listed in Table XVIII and average of $k_8 = 5.1 \pm 0.81 \times 10^9$ l mole^{-1} sec^{-1} was obtained. Although the use of this equation restricts the period over which the reaction is followed to one where measurements are difficult, the standard deviation of 20 determinations is quite small.

k_8 was also calculated by using the simple procedure of measuring the half life of reaction (8). $\Delta[ClO_2]_\infty$ was measured and the time to reach $\frac{1}{2}\Delta[ClO_2]_\infty$ was found from fig.(31). Using the simple relation

$$k_8 = \frac{.69}{t_{1/2}\,[ClO_2]_{av}} \qquad (r)$$

k_8 was calculated. $[ClO_2]_{av}$ was the concentration of ClO_2 between the t = 0 and t = $t_{1/2}$. The values of k_8 obtained in this way are listed in Table XVIII and the average found to be $5.1 \pm 0.6 \times 10^9$ l mole^{-1} sec^{-1}, is in agreement with that obtained above.

From the Measurement of ClO

A similar procedure was used for calculating k_8 by measuring the ClO concentration.

1) By Measuring Half Life. A similar method was used for calculating the time taken to reach half of the concentration of ClO produced by reaction (8). Using equation (r), k_8 was calculated and the average of k_8 was found to be $4.5 \pm 0.4 \times 10^9$ l mole^{-1} sec^{-1}. The other values are listed in Table XVIII and the value obtained agrees with that calculated previously.

2) The rate of the equation (8) can be written in terms of ClO as follows.

$$\frac{d[\Delta ClO]}{dt} = 2\,k_9[ClO_2][Cl]$$

where Δ[ClO] is concentration produced by chlorine atoms. The chlorine atom concentration can be calculated as

$$[Cl]_o = \tfrac{1}{2}([ClO]_b - [ClO]_a)_o = \tfrac{1}{2}\Delta[ClO]_o$$

$[ClO]_b$ = total amount of ClO produced in presence of Cl_2.

$[ClO]_a$ = total amount of ClO produced without Cl_2

and

$$[Cl]_t = \tfrac{1}{2}(\Delta[ClO]_o - \Delta[ClO]_t)$$

thus the above equation can be written as

$$\frac{d[\Delta ClO]}{dt} = k_8 (\Delta[ClO]_o - \Delta[ClO]_t)[ClO_2]$$

This equation was treated in the similar manner as equation (p), i.e., by taking small intervals of time and also using the average value $[ClO_2]$ at the beginning and end of the interval. Thus it can be integrated to

$$-\ln (\Delta[ClO]_o - \Delta[ClO]_t) = k_8[ClO_2]_{av}t - \ln(\Delta[ClO]_o) \qquad (s)$$

Thus k_8 was calculated from the ClO concentration measurements and the average value found to be $5.2 \pm 0.7 \times 10^9$ l mole^{-1} sec^{-1}, agrees with the values obtained previously. The average of all the values was found to be $5.0 \pm 0.7 \times 10^9$ l mole^{-1} sec^{-1}. This value is nearly 10 times greater than the lower limit found by Clyne and Coxon.[25]

Table XVIII

Calculation of k_8 of the Reaction $Cl + ClO_2 = 2\ ClO$

Plate no.	Energy J	$[ClO_2]$ $(10^{-6}M)$	$[Cl_2]$ $(10^{-6}M)$	$k_8 \times 10^{-9}$ (1 mole^{-1} sec^{-1}) From ClO = n(r)	= n(s)	From ClO_2 = n(r)	= n(q)
196	260	4.0	66.0	4.0	4.9(4)	4.7	5.0(4)
197	260	2.65	41.3	4.6	5.3(3)	5.0	4.8(4)
198	160	4.0	137.5	4.5	5.1(3)	4.5	5.4(4)
198'	160	4.0	137.5	--	4.9(5)	5.5	5.1(5)
199	160	2.65	66.0	--	--	5.8	4.7(5)
200	160	4.0	87.5	4.9	5.7(5)	5.5	5.6(5)
			Average		5.18±.33		5.1±.35

Mean $k_8 = 5.1 \pm 0.7 \times 10^9$ l mole^{-1} sec^{-1}

Note: Numbers in parentheses show the nos. of measurements used in obtaining the average of each experiment.

D. Bromine and Oxygen System

It has been observed that BrO radicals are produced when O_2/Br_2 is flash photolysed,[16] but no measurements have been reported on its decay. McGrath and Norrish[12] showed that BrO is also produced when Br_2 is flashed in the presence of ozone:

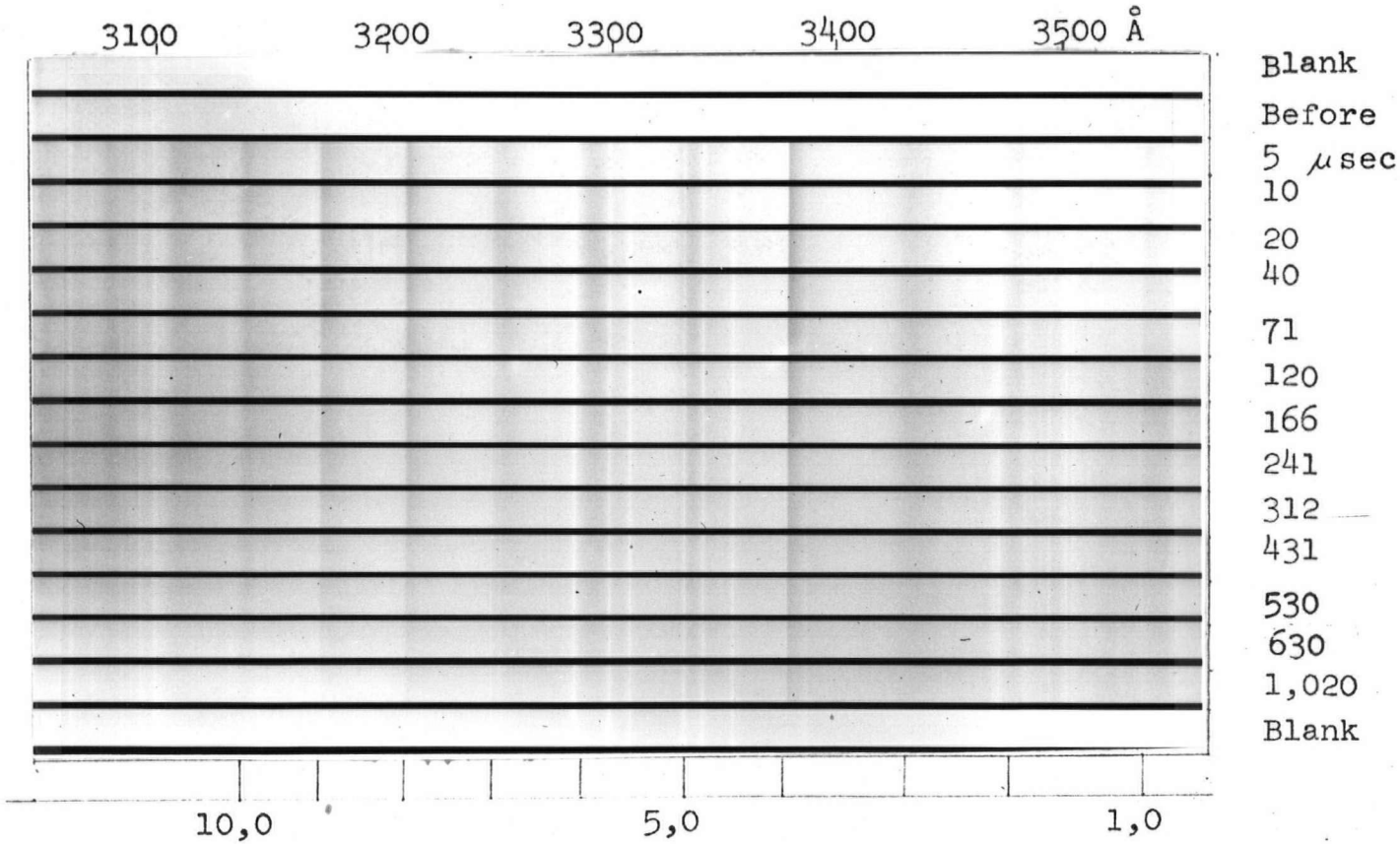
$$Br + O_3 \rightarrow BrO + O_2$$

This reaction has also been studied by Clyne and Coxon[25] in the flow system. They generated bromine atoms by the reaction of chlorine atoms with Br_2. They also found that a second order decay with a value for k_{39}/ε at 3383 Å of $4.5 \pm 0.5 \times 10^5$ cm sec^{-1}. Therefore bromine and oxygen mixtures in the ratio varying from 1:80 to 1:180 were flashed with flash energy 1325 J, using a quartz reaction vessel, as this system looks simpler than the one studied above. The oxygen pressure was varied from 400 to 780 torr, so no other inert gas was added as a dilutent. Experiments were done using the fresh mixture each time and also flashing the same mixture repeatedly.

The spectrum observed is the same as observed by Durie and Ramsay,[16] as shown in fig. (34) and no other spectrum was seen in the region 3000 Å to 4000 Å. The spectrum of BrO was observed at the shortest delays used, reaches a maximum at approximately 40 to 50 μsec and decays faster than ClO, as has been seen by Clyne and Coxon.[25] The BrO concentration was measured at two wavelengths, i.e., at 3208 Å and at 3383 Å. The concentration in terms of optical density is given in Table XIX. It can be seen that the amount of BrO formed increases with the increase of oxygen pressure, whereas it remains constant if the concentration of bromine is changed. This indicates that it is the oxygen which is more important in the formation of BrO and not bromine.

Figure 34. Rise and Decay of BrO.

$Br_2 = 5.0$ torr, $O_2 = 400$ torr, E = 1325 J.



1/[BrO] in terms of optical density was plotted against time as shown in fig. (35) and plots were found to be good straight lines. The slope was measured and the k_{39}/ε thus calculated are listed in Table XIX. The average values of nine measurements at 3208 Å was found to be $(5.4 \pm 0.9) \times 10^5$ cm sec^{-1} and the average value of eight at 3383 Å was $(4.3 \pm 0.2) \times 10^5$ cm sec^{-1}. The value obtained at 3383 Å is in reasonable agreement with that found by Clyne and Coxon[25] $(4.5 \pm 0.5 \times 10^5$ cm $sec^{-1})$. Combining this value with the extinction coefficient of BrO calculated from the reaction of bromine atoms with ClO_2 (discussed in the next section), k_{39} was found to be 1.25×10^9 l $mole^{-1}$ sec^{-1}, which is nearly three times greater than that obtained by Clyne and Coxon.[25] They calculated the extinction coefficient of BrO from the measured absorption due to BrO by saying the following: "It appeared that the extinction coefficients of BrO at the intense band heads at 3289 and 3383 Å are similar to ε(ClO) at 2772 Å," and obtained k_{39} to be 4×10^8 l $mole^{-1}$ sec^{-1}.

From the results we have, it appears that k_{39} does not depend on bromine, oxygen or total pressure. It is also independent of whether the fresh mixture is used or the same mixture is flashed repeatedly. Thus the decay of BrO resembles the decay of ClO and hence a similar mechanism for its decay may be proposed.

$$BrO + BrO \rightarrow (BrO)_2$$

$$(BrO)_2 \rightarrow Br_2 + O_2$$

Figure 35. A plot of 1/[BrO] against time.

Br_2 = 5.0 torr, O_2 = 400 torr, E = 1325 J.

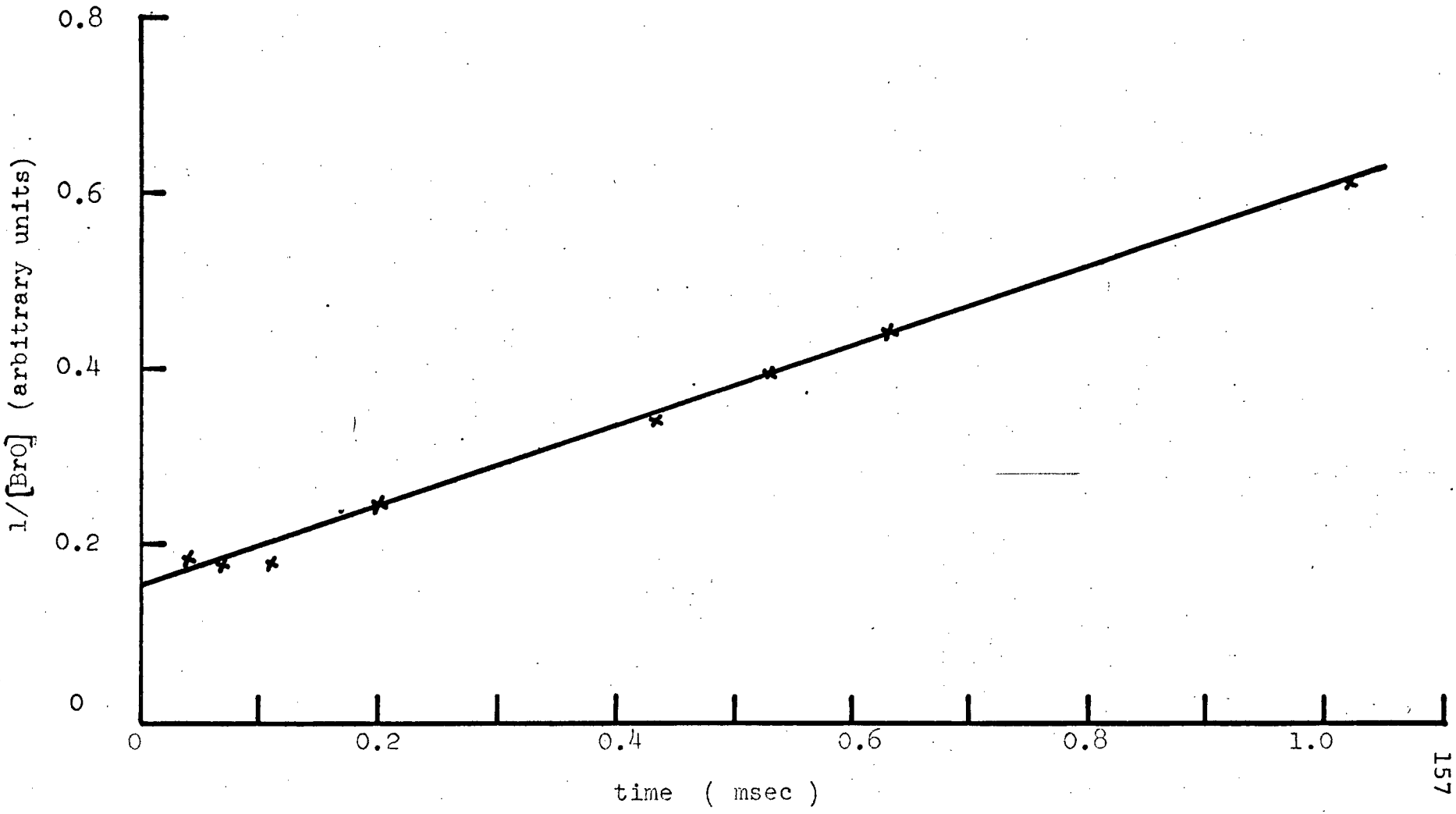


Table XIX

Plate no.	$[Br_2]$ (torr)	$[O_2]$ (torr)	O.D. 4,0	O.D. 8,0	$D_{4,0}/D_{8,0}$ A	$D_{4,0}/D_{8,0}$ B	k_{39}/ε (10^5cm sec^{-1}) 4,0	k_{39}/ε (10^5cm sec^{-1}) 8,0
241	5.0	400	0.117	0.103	1.2	1.13	4.1	5.0
243	5.0	500	0.107	0.1	1.05	1.07	4.5	7.5 neglected
244	5.0	500	0.14	0.11	1.3	1.27	4.5	6.3
246	5.0	600	0.14	0.127	1.13	1.10	4.3	5.5
245	5.0	690	0.137	0.136	1.06	1.0	4.5	4.8
245	5.0	780	0.185	0.15	1.28	1.22	3.4	5.0
242	5.0	400	0.132	0.11	--	1.2	4.4	6.2
242	4.2	500	--	0.12	--	--	--	4.6
244	2.8	500	0.115	0.095	1.26	1.21	4.2	6.0
		Average			1.18 $\pm$.09	1.22 $\pm$.07	4.4 $\pm$0.2	5.4 $\pm$0.9

Note: In column A ratios of $D_{4,0}/D_{8,0}$ are calculated by method (1) and in column B by method (2).

Ratios of Optical Densities at 3383 and 3208 Å

The ratio of the optical densities at two wavelengths was calculated by two methods.

1) The optical density was calculated from the linear extrapolation of the second order plot at t=0 and thus the ratios obtained are listed in Table XIX and the average of eight found to be 1.18 $\pm$ 0.09.

2) The optical densities were measured at each delay and the ratios were calculated. The average of each experiment was calculated and listed in Table XIX. In this way the average of 70 measurements, made at different delays and different concentrations of BrO gave the value to be 1.22 ± 0.07 which is in good agreement with that calculated by procedure (1).

The average of these two methods was compared with ratios of k_{39}/ε which was found to be 1.26 . The agreement is satisfactory and $\varepsilon_{3383}/\varepsilon_{3207} = 1.2$ was adopted.

E. The Bromine Photo-sensitised Decomposition of ClO_2

Spinks and Porter[38] found Cl_2O_6 as the main product of the bromine photo-sensitised decomposition of ClO_2 at 15°C, chlorine and oxygen being formed at 30°C. For this reason, Spinks et al.[38] rejected the mechanism proposed by Schumacher.[42]

$$Br + ClO_2 \rightarrow BrCl + O_2$$

$$2\ BrCl \rightarrow Br_2 + Cl_2$$

and suggested that the primary reaction is

$$Br + ClO_2 \rightarrow BrO + ClO$$

followed by $$BrO + ClO_2 \rightarrow Br + ClO_3$$

In either case, bromine atoms rather than excited bromine molecules[43] are involved since the quantum yields at 3650 Å and 5460 Å were found to be equal.

Clyne and Coxon[44,45] studied the reactions of bromine atoms with ClO_2 in a flow system at low (1 to 3 torr) total pressures. They found a rapid reaction accompanied by emission of a deep red chemiluminescence from the reaction zone which was identified as arising from the transition

$$BrCl(^3\pi_o^+) \rightarrow BrCl(^1\Sigma^+)$$

The same spectrum was observed in the radiative combination of bromine and chlorine atoms, accompanied by some weak bands of the chlorine afterflow spectrum. The absorption spectrum of ClO and BrO could not be detected over a wide range of reactant partial pressures. The possibility that the reason for absence of BrO and ClO was due to a rapid reaction between them was considered but thought unlikely because of the corresponding slow reaction of ClO + ClO, On these grounds and because of its endothermicity, the reaction

$$Br + ClO_2 \rightarrow BrO + ClO - 3 \text{ Kcals}$$

was rejected.

The formation of BrCl ($^3\pi_o^+$) was, therefore, explained by the reaction

$$Br + ClO_2 \rightarrow BrCl + O_2$$

with the transition state being $Br.ClO_2$ rather than OClOBr. The possibility that $BrCl(^3\pi_o^+)$ was formed by radiative combination of chlorine and bromine atoms which might be formed as intermediates in the reaction between bromine atoms and ClO_2 was rejected because of the absence of the chlorine afterglow.

The overall rate constant at 300°K for the reaction

$$Br + ClO_2 \rightarrow BrCl + O_2$$

which includes the formation of both $BrCl(^3\pi_o^+)$ and $BrCl(^1\Sigma^+)$, was measured by following the decay of ClO_2 at 3515 Å under conditions of equal ClO_2 and bromine atom concentrations. Although the second order plot deviated from linearity, the limiting slope at zero time gave the value $k = 3.1 \pm 0.3 \times 10^7$ $l\ mole^{-1}\ sec^{-1}$.

Clyne and Coxon[45] also found that the reaction between bromine atoms and ClO_2, was self propagating after initiation and considered a rapid reaction between $BrCl(^3\pi_o^+)$ and either ClO_2 and Br_2.

$$BrCl(^3\pi_o^+) + ClO_2 \rightarrow BrCl(^1\Sigma^+) + Cl + O_2$$

$$BrCl(^3\pi_o^+) + Br_2 \rightarrow BrCl(^1\Sigma^+) + 2Br$$

In the former case bromine atoms would be regenerated in the subsequent reactions

$$Cl + ClO_2 \rightarrow 2\ ClO$$

$$Cl + Br_2 \rightarrow BrCl + Br$$

$$Cl + BrCl \rightarrow Cl_2 + Br$$

A considerable stationary state concentration of chlorine atoms would be expected. Since no chlorine afterglow was observed, the reaction with bromine was preferred.

In a later paper, Clyne and Coxon[25] reported an experiment in which bromine atoms produced by the reaction

$$Cl + Br_2 \rightarrow BrCl + Br$$

were reacted with ClO_2. In this case the ClO radical was identified as a product, but again no BrO was observed. It was also found that BrO radicals produced in the reaction of bromine atoms with ozone decayed much faster than ClO. They concluded that their earlier interpretation of reaction between bromine atoms and ClO_2 was probably erroneous. Chemiluminescence observed during the decay of ClO in the absence and in the presence of bromine was then explained by the reactions

$$2\ ClO \rightarrow ClOO + Cl$$

$$Cl + Br_2 \rightarrow BrCl + Br$$

$$Cl + ClOO \rightarrow Cl_2(^3\pi_o^+) + O_2 + 46\ Kcals$$

$$Br + ClOO \rightarrow BrCl(^3\pi_o^+) + O_2 + 45\ Kcals$$

It should be noted, however, that the reactions of bromine atoms with both ClO_2 and ClOO are insufficiently exothermic to account for the degree of excitation observed (57 Kcals, v' = 8). Clyne and Coxon[25] noted this for the reaction of bromine atoms with ClO_2, but the rate constant obtained allowed an activation energy of up to 5.5 Kcals, whereas only 4 Kcals were needed to account for the energy of the highest level of $BrCl(^3\pi_o^+)$ observed. If Clyne and Coxon's[25] value for $D_o(ClOO)$ of 7 Kcals is accepted, the discrepancy of 7 Kcals for the reaction (14) is rather harder to believe.

In view of the rather uncertain situation which seems to exist with respect to the reaction of bromine atoms and ClO_2, a preliminary reinvestigation of this reaction was undertaken.

Mixtures of ClO_2 (~0.6 torr) and Br_2 in the ratios of 1:16 to 1:50 with excess argon or nitrogen were flash photolysed with an energy of 1060 J. To prevent the direct photolysis of ClO_2, Corning 3-72 and 3-66 filters were used with cut-off wavelengths of 4400 Å and 5600 Å. Separate experiments without bromine showed that no detectable photolysis of ClO_2 did in fact occur under these conditions. Since mixtures of ClO_2 and Br_2 were found to react on standing, all parts of the apparatus were painted black or covered with black paper and the experiments were performed under subdued lighting. The time allowed for mixing the bromine with inert gas/ClO_2 mixtures was reduced to 20 to 30 minutes from the usual 2 to 3 hours normally allowed in other experiments. Nevertheless the method used ensured that the resulting mixtures were homogeneous. This was tested by repeating certain time delays at the end of the run with identical results. Under these conditions no detectable decomposition of ClO_2 occurred on standing over the period from the original mixing to the end of the run.

On flash photolysis of the Br_2/ClO_2, there was an initial rapid removal of ClO_2 over a period of 200 to 300 μsec. This was followed by a further slow decrease in the ClO_2 concentration extending over ~1 msec and even up to 45 sec. Complete

removal of the ClO_2 was achieved only at the higher bromine pressures and with the 4400 Å filter. Under all conditions the spectra of ClO and BrO were observed in absorption. Both species are produced rapidly, attain maximum concentrations at ∿100 μsec and then decay quite rapidly over a period of ∿1 msec. The concentration of ClO was measured at 2772 Å (12,0), that of BrO at 3208 Å (8,0 band). Both are found free from interference by ClO_2 whose concentration was measured at 3515 Å. The behaviour of all three species is shown in fig. (36).

1) The Stoichiometry and Mechanism of the Fast Reaction

The decrease in ClO_2 concentration in the initial reaction was measured by extrapolation of the slow decay region to zero time. The total concentration of ClO and BrO produced $\left([ClO]_o \text{ and } [Bro]_o\right)$ was measured by extrapolation of their decay plots to zero time. For these the plots of reciprocal optical density against time were most suitable, being linear over a wide range (figs. 37 and 38). Under all conditions it was found that

$$[ClO]_o = \Delta[ClO_2]$$

It can, therefore, reasonably be assumed that the overall reaction is represented by the equation

$$Br + ClO_2 \rightarrow BrO + ClO$$

The optical density at 3208 Å corresponding to $[BrO]_o$, D_o, is related to the extinction coefficient at this wavelength by the

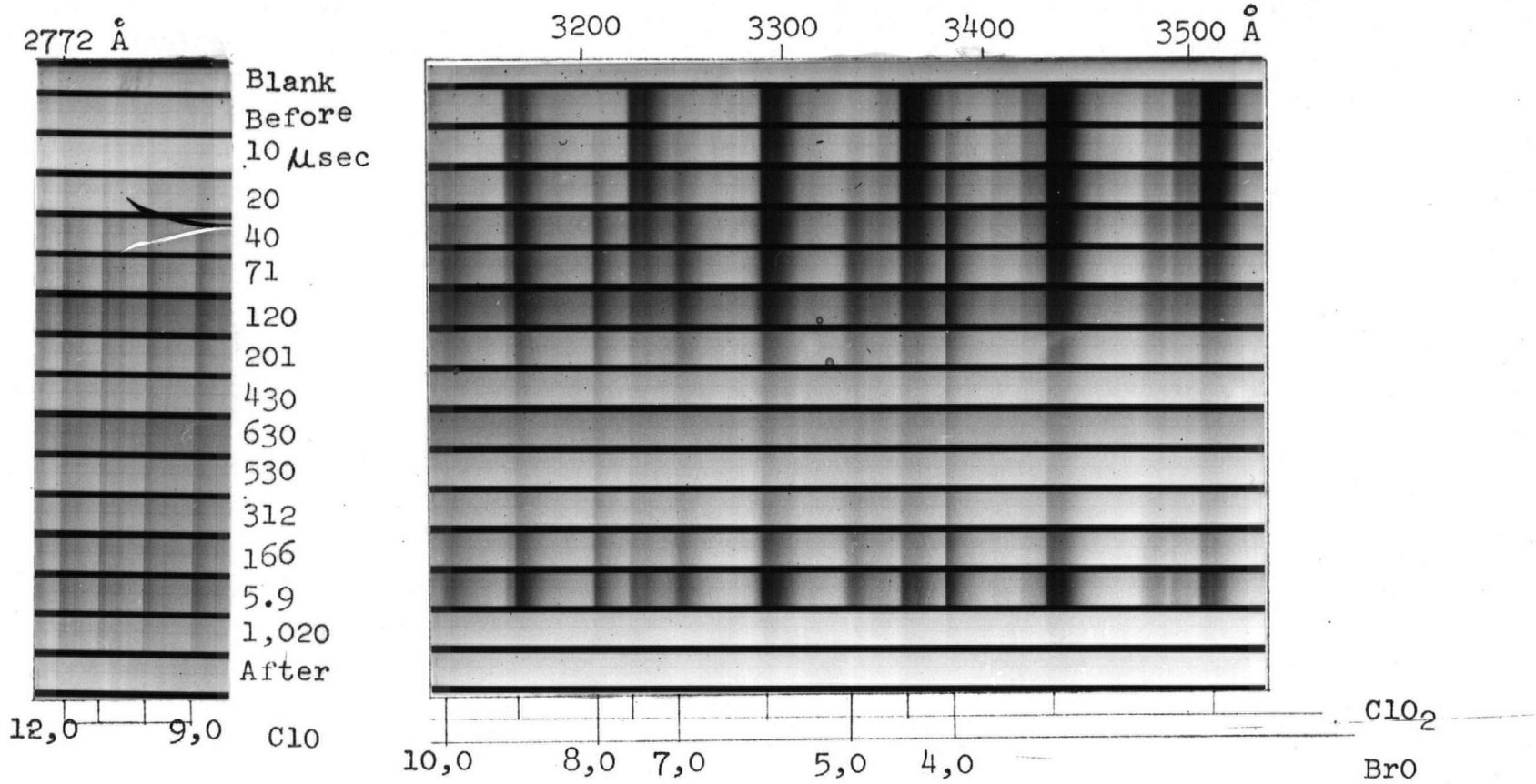


Figure 36. Flash Photolysis of bromine in the presence of ClO_2.
$ClO_2 = 3.16 \times 10^{-6}$ M, $Br_2 = 137.5 \times 10^{-6}$, Argon = 200 torr, E = 1060 J, Filter 4400 Å.

equation

$$\varepsilon_{3208\ \text{Å}} = \frac{D_o}{[BrO]_o l} = \frac{D_o}{[ClO]_o l} = \frac{D_o}{\Delta[ClO_2] l}$$

The values obtained are listed in Table XX, the average of all measurements from ClO_2 was $2.26 \pm 0.2 \times 10^3$ l mole^{-1} cm^{-1} and from the same number using ClO was $2.38 \pm 0.1 \times 10^3$ l mole^{-1} cm^{-1}, is very much higher than the value of 900 l mole^{-1} cm^{-1}, used by Clyne and Coxon.[25] If our value is in error then because of the equality $[ClO]_o = \Delta[ClO_2]$, the true value must be even higher.

The value obtained here has been used to determine the rate constants for the reactions

$$2\ BrO \rightarrow Br_2 + O_2$$

and

$$ClO + BrO \rightarrow BrCl + O_2$$

2) Decay of ClO and BrO

Both ClO and BrO radicals were found to decay more rapidly than would be expected from the known rates of the reactions

$$2\ ClO \rightarrow Cl_2 + O_2 \qquad (5)$$

$$2\ BrO \rightarrow Br_2 + O_2 \qquad (39)$$

The difference in decay rate is particularly marked for ClO and over the first 400 μsec, when the BrO and ClO concentrations are comparable. This behaviour can only be explained by the

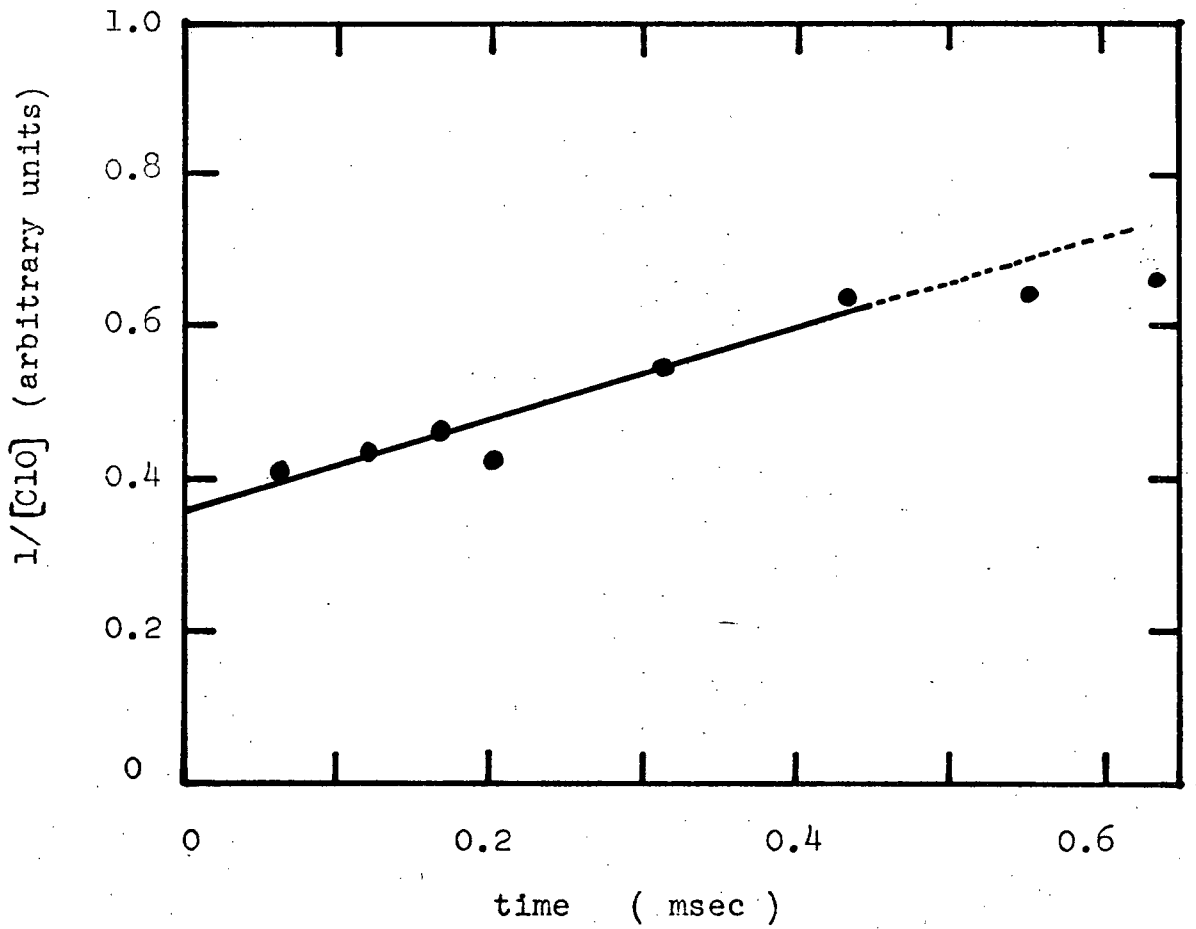
Table XX

Calculation of $\varepsilon(3208)$ of BrO

Plate no.	$[ClO_2]$ (10^{-6}M)	$[Br_2]$ (10^{-6}M)	P_T torr	Filter Å	E J	$\Delta[ClO_2]$ (10^{-6}M)	[ClO]=[BrO] (10^{-6}M)	$\varepsilon \times 10^{-3}$ (l mole^{-1} cm^{-1}) A	B
248	3.21	82.5	200(N_2)	4400	1060	1.51	1.42	2.48	2.35
249a	2.62	137.5	200(N_2)	4400	1060	--	1.44	2.33	--
250	3.16	137.5	200	4400	1060	1.96	1.72	2.42	2.12
251	2.54	41.3	200	4400	1060	0.99	1.06	2.49	2.67
252a	3.00	137.5	100	4400	1060	2.1	1.74	2.34	2.00
252b	2.96	137.5	500	4400	1060	1.4	1.28	2.50	2.29
253	3.7	82.5	200	4400	1060	1.7	1.60	2.45	2.31
254	3.49	137.5	200	5600	1060	1.0	0.92	2.35	2.16
255	3.95	220	200	5600	1060	1.25	1.18	2.30	2.18
256a	3.30	137.5	500	5600	1060	1.0	0.92	2.26	2.10
256b	3.1	137.5	100	5600	1060	1.0	1.04	2.22	2.40
Mean ε_{3208} = $2.32 \pm 0.15 \times 10^3$ l mole^{-1}cm^{-1}							Average	2.38 ± 0.09	2.26 ± 0.2

Note: a = from [ClO] measurements; b = from $[ClO_2]$ measurements.

Figure 37. A plot of 1/[ClO] against time following the flash photolysis of bromine in the presence of ClO_2.
$ClO_2 = 3.16 \times 10^{-6}$ M, $Br_2 = 137.5 \times 10^{-6}$ M,
Argon = 200 torr, E = 1060 J, Filter 4400 Å.



reaction

$$ClO + BrO \rightarrow BrCl + O_2 + 52 \text{ Kcal} \qquad (40)$$

For ClO the other possible reactions are

$$ClO + Br_2 \rightarrow BrO + BrCl \quad -1 \text{ Kcal} \qquad (42)$$

$$ClO + Br \rightarrow BrO + Cl \quad -8 \text{ Kcal} \qquad (41)$$

$$ClO + Br \rightarrow BrCl + O \quad -11 \text{ Kcal} \qquad (41\text{-a})$$

Since the last two reactions of ClO with bromine atoms are too endothermic, they are not considered. Reaction (42) can also be rejected because the rate of ClO decay produced in the bromine photosensitised decomposition of Cl_2O is normal, and no BrO was observed. Further, since $[Br_2] >> [ClO]$, the first order plot for the decay of ClO should be linear with a slope proportional to the bromine concentration. As seen from fig. (37-a), this is not so. Thus the decay of ClO can be represented as

$$-\frac{d[ClO]}{dt} = k_5[ClO]^2 + k_{40}[BrO][ClO]$$

or

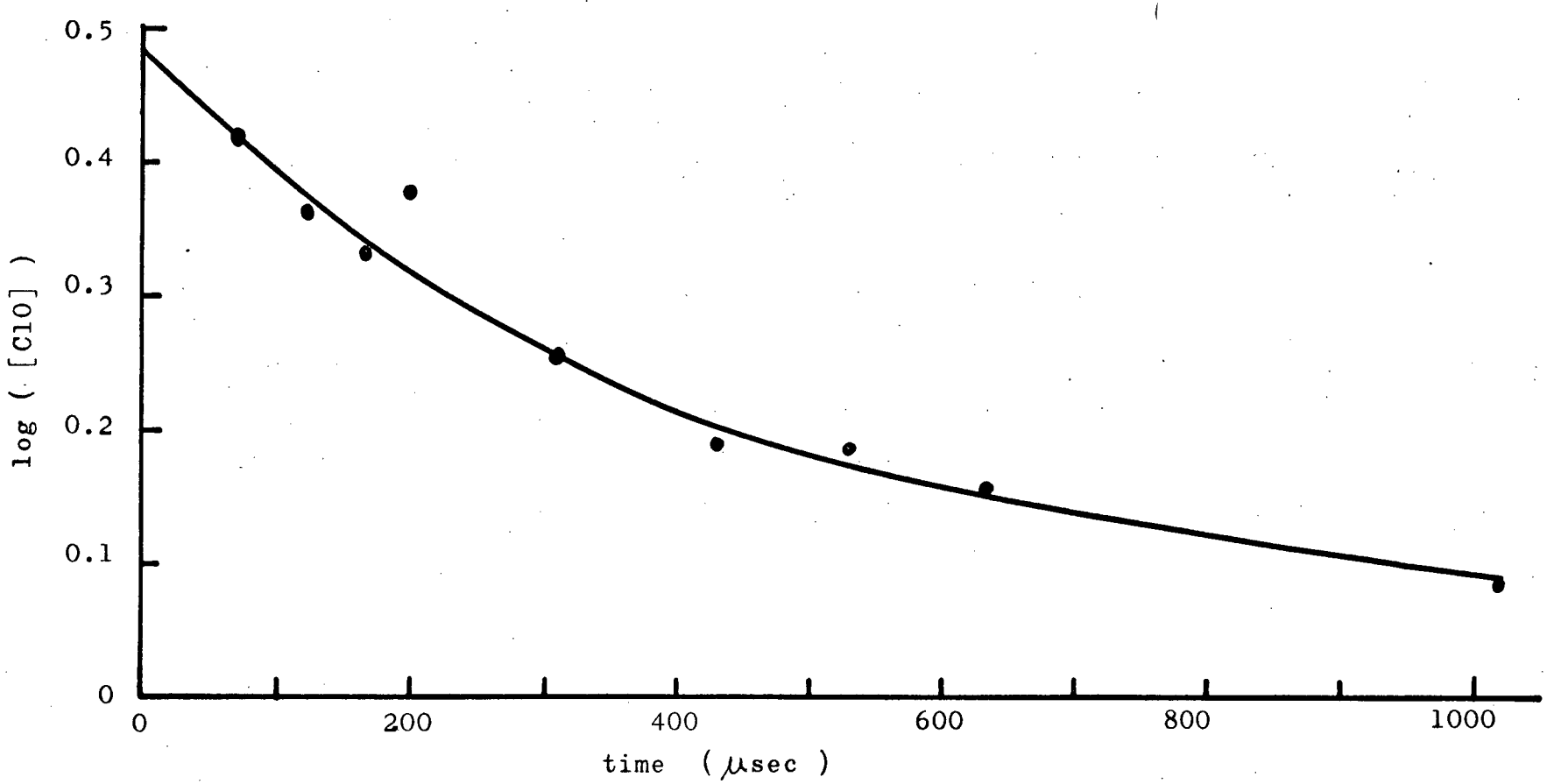
$$\frac{d[ClO]^{-1}}{dt} = k_5 + k_{40}\frac{[BrO]}{[ClO]} \qquad (o)$$

If we assume that [BrO]/[ClO] ratio remains constant (i.e., 1), equation (o) can be written as

$$\frac{d[ClO]^{-1}}{dt} = (k_5 + k'_{40}) = k'$$

Figure 37-a. A first order plot of ClO following the flash photolysis of bromine in the presence of ClO_2.

ClO_2= 3.16 x 10^{-6} M, Br_2= 137.5 x 10^{-6} M, Argon= 200 torr, E= 1060 J, Filter= 4400 Å .



$[ClO]^{-1}$ was plotted against time as shown in fig.(37) and it was found that the plots obey a linear relation up to ∿300 to 400 μsec but then depart from linearity with a smaller slope, as expected from equation (o). It can be clearly seen from fig. (36) that BrO decay is faster than ClO and the ratio [BrO]/[ClO] will decrease from its initial value of unity. This ratio was calculated from the experimental data and found that the average value lies between 0.8 ± 0.2, within the whole period of our study, i.e., 0.630 to 1.02 msec. The slope was measured from the linear part and combined with the extinction coefficient of ClO, k' was calculated and listed in Table XXI. From the relation

$$k' = k_5 + k'_{40}$$

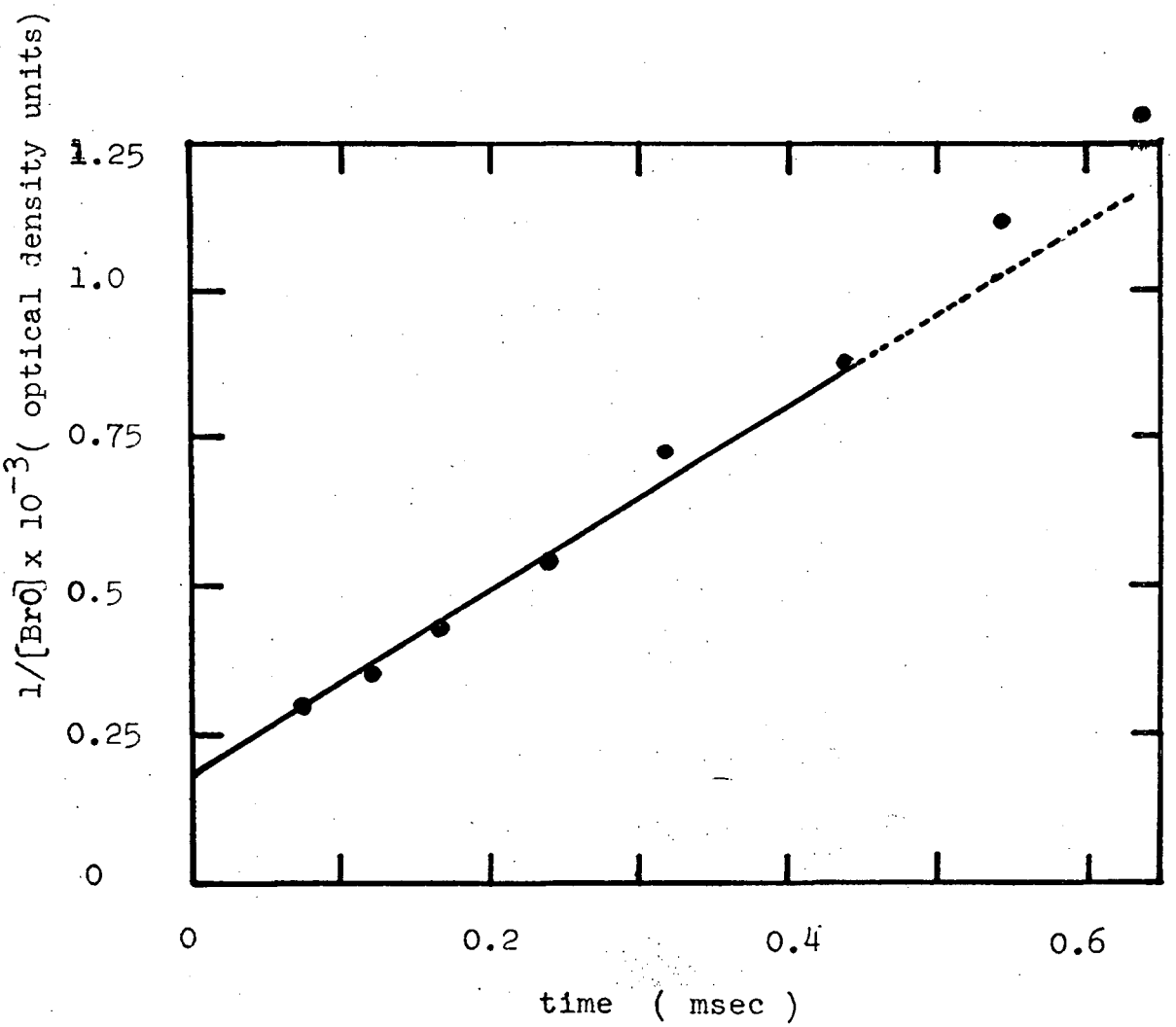
and average value of [BrO]/[ClO] in the respective experiment, k_{40} was calculated and is listed in Table XXI The average of 11 measurements gave $k_{40} = 1.43 \pm 0.1 \times 10^9$ l mole^{-1} sec^{-1}.

The other possible reaction of BrO can be the reverse reaction (16), i.e.,

$$BrO + ClO \rightleftarrows Br + O\text{-}Cl\text{-}O + 3 \text{ Kcal}$$

which is exothermic by 3 Kcals. There are, however, two objections to this reaction. Firstly, the ClO_2 should increase and secondly, as BrO concentration is consumed by reaction (39), the equilibrium should shift to the left and thus the ClO concentration should nearly remain constant as the decay of ClO by reaction (5) is slow. But neither ClO_2 concentration

Figure 38. A plot of $1/[BrO]$ against time following the flash photolysis of bromine in the presence of ClO_2.
$ClO_2 = 3.16 \times 10^{-6}$ M, $Br_2 = 137.5 \times 10^{-6}$ M,
Argon = 200 torr, E = 1060 J, Filter 4400 Å.



increases (rather it decreases slowly) nor the ClO concentration remains constant during the BrO decay. Further, reaction (40) is more suitable to account for the production of BrCl, because the reaction is exothermic exactly to the extent of the energy of the highest level of BrCl[$^3\pi_o^+$] observed by Clyne and Coxon[45] (i.e., 18,153 cm^{-1}), whereas Clyne and Coxon[25] reasonably suggested that the E_a for the reaction (14) was available to make up the 4 Kcal discrepency between the exothermicity and the highest level observed. Thus the BrO decay can be represented by

$$-\frac{d[BrO]}{dt} = k_{39}[BrO]^2 + k_{40}[BrO][ClO]$$

or

$$\frac{d[BrO]^{-1}}{dt} = k_{39} + k_{40}\frac{[ClO]}{[BrO]} \qquad (p)$$

This was treated in the same manner as equation (o) and a 1/[BrO] plot against time gave a straight line in the beginning but departs from linearity with increasing slope as expected from the equation (p) since the $\frac{[ClO]}{[BrO]}$ increases from its initial value of unity. Slopes were measured from the linear part of curves (fig.38) and the value of k_{40} was calculated using $k_{39} = 1.25 \times 10^9$ l $mole^{-1}$ sec^{-1} (calculated from Br_2/O_2 system) and using respective values of $\frac{1}{[ClO]/[BrO]}$ ratio, the average value of which lies between 0.8 ± 0.2. The values are listed in Table XXI and the average of k_{40} was found to be $1.76 \pm 0.35 \times 10^9$ l $mole^{-1}$ sec^{-1}. The agreement with the value calculated previously is very satisfactory. The relatively

Table XXI

Calculation of k_{40} of Reaction ClO + BrO → BrCl + O_2

Plate no.	$[ClO_2]$ (10^{-6}M)	$[Br_2]$ (10^{-6}M)	P_T torr	Filter Å	E J	k'	k''	$k_{40} \times 10^{-9}$ (l mole^{-1}sec^{-1}) from k'	from k''
248	3.21	82.5	200(N_2)	4400	1060	1.06	4.16	1.50	2.02
249a	2.62	137.5	200(N_2)	4400	1060	1.02	4.24	1.52	1.88
250	3.16	137.5	200	4400	1060	1.02	3.70	1.22	2.00
251	2.54	41.3	200	4400	1060	1.28	2.86	1.60	1.25
252a	3.00	137.5	100	4400	1060	1.20	3.90	1.43	2.18
252b	2.96	137.5	500	4400	1060	1.19	4.05	1.43	2.20
253	3.7	82.5	200	4400	1060	1.07	4.00	1.43	2.00
254	3.49	137.5	200	5600	1060	1.07	3.28	1.51	1.40
255	3.95	220.0	200	5600	1060	1.00	3.28	1.35	1.46
256a	3.30	137.5	500	5600	1060	1.07	3.33	1.33	1.61
257b	3.1	137.5	100	5600	1060	--	2.88	--	1.11
				Average				1.43 ±0.1	1.76 ±0.35

large standard deviations reflect that k_{39} and k_{40} are very similar. The value obtained from the ClO measurements is therefore taken to be the more accurate measurement and we adopt the value of 1.5×10^9 l mole^{-1} sec^{-1} for k_{40}.

3) Reaction of Bromine Atoms with ClO_2

If the reaction of bromine atoms with ClO_2 can be written as

$$Br + ClO_2 \rightarrow BrO + ClO \qquad (16)$$

the rate of the reaction can be represented as

$$-\frac{d[ClO_2]}{dt} = -\frac{d[Br]}{dt} = \frac{d[ClO]}{dt} = k_{16}[Br][ClO_2] \qquad (r)$$

To test this simple mechanism k_{16} was determined from the decrease in the ClO_2 concentration and the increase in the ClO and BrO concentrations.

i) From ClO_2

Unlike the ClO_2/Cl_2 system, ClO_2 in the presence of Br_2 goes on decreasing slowly after the first rapid decay for several msec or sec depending upon the Br_2 concentration. This indicated that there are two types of reactions, of which only the first need be considered here. The decay of ClO_2 was plotted against time as shown in fig.(39) and the slow part of the curve was extrapolated back to zero time in order to calculate the amount of ClO_2 reacted with bromine atoms. Thus

$$[Br]_o = [ClO_2]_o - [ClO_2]_\infty = a-b$$

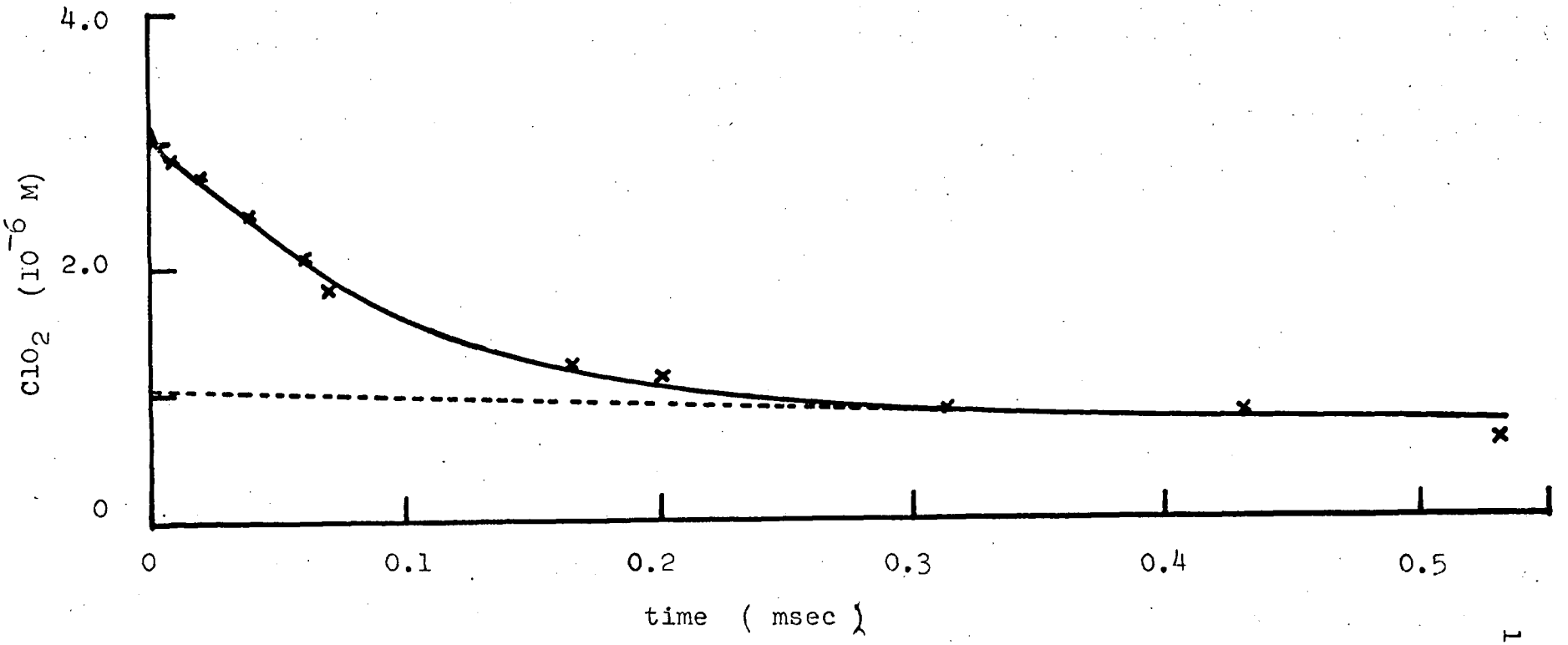
$$[Br]_t = [ClO_2]_t - [ClO_2]_\infty = x-b$$

where $[ClO_2]_o$, $[ClO_2]_t$ and $[ClO_2]_\infty$ are the concentration of ClO_2 at $t = 0$, at time t and $t = \infty$, obtained from the linear extrapolation. Equation (r) can be written

Figure 39. Decay of ClO_2 following the flash photolysis of bromine in the presence of ClO_2.

$ClO_2 = 3.16 \times 10^{-6}$ M, $Br_2 = 137.5 \times 10^{-6}$ M, Argon = 200 torr,

——— E = 1060 J, Filter 4400 Å.



$$-\frac{d[ClO_2]}{dt} = -\frac{dx}{dt} = k_{16}x(x - b)$$

$$\text{or} \quad \log \frac{x}{x-b} = \frac{a\,k_{16}}{2.303}\,t + \log \frac{a}{a-b} \qquad (r')$$

$\log \frac{x}{x-b}$ was plotted against time as shown in fig.(40) and from the slope of the straight line k_{16} was calculated and is listed in Table XXII. The average value of k_{16} obtained is $6.4 \pm 0.9 \times 10^9$ l mole^{-1} sec^{-1}.

ii) From ClO and BrO Measurements

If there is no other reaction of bromine atoms with ClO_2, producing BrO or ClO except reaction (16), the bromine atom concentration, in terms of ClO and BrO can be represented as

$$[Br]_o = [ClO]_o = [BrO]_o = a$$

$$[Br]_t = [ClO]_o - [ClO]_t = [BrO]_o - [BrO]_t = a-x$$

$$[ClO_2]_t = [ClO_2]_o - [ClO]_t = [ClO_2]_o - [BrO]_t = b-x$$

The $[ClO]_o$ or $[BrO]_o$ are obtained from the $\frac{1}{[ClO]}$ or $\frac{1}{[BrO]}$ decay plot against time at t = 0. The equation (r) can be written in terms of ClO and BrO as

$$\frac{dx}{dt} = k_{16}(a - x)(b - x)$$

$$\text{or} \quad \log \frac{b - x}{a - x} = \frac{(b - a)k_{16}}{2.303}\,t + \log \frac{b}{a}$$

$\log \frac{b - x}{a - x}$ was plotted against time for both ClO and BrO as shown in figs. (41) and (42) and k_{16} was calculated from the

Figure 40. A plot of log(x/x-b) against time.

$b = [ClO_2]_\infty$, $x = [ClO_2]_t$.

$ClO_2 = 3.16 \times 10^{-6}$ M, $Br_2 = 137.5 \times 10^{-6}$ M,

Argon = 200 torr, E = 1060 J, Filter 4400 Å.

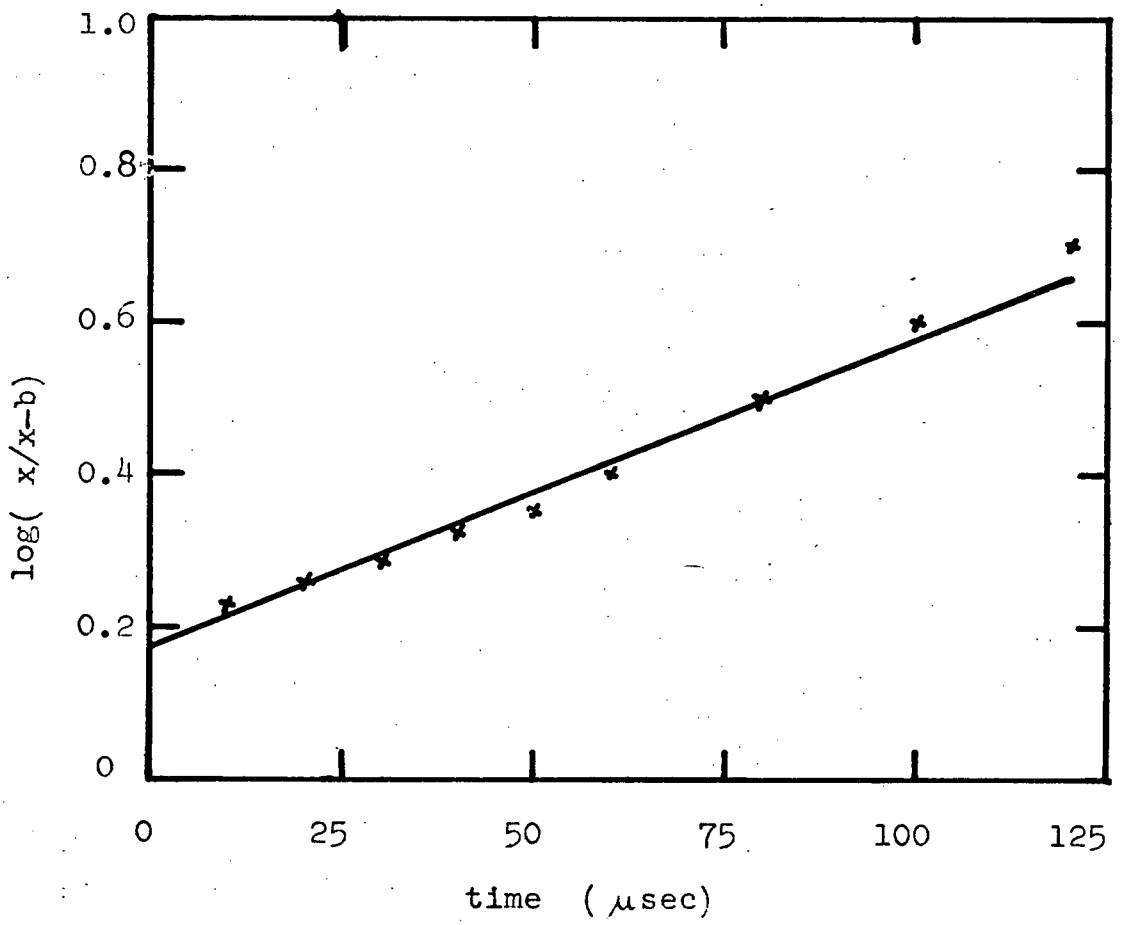


Figure 41. A plot of log(a-x/b-x) against time.
$a = [ClO_2]_o$, $b = [ClO]_o$, $x = [ClO]_t$.
$ClO_2 = 3.16 \times 10^{-6}$ M, $Br_2 = 137.5 \times 10^{-6}$ M,
Argon = 200 torr, E = 1060 J, Filter 4400 Å.

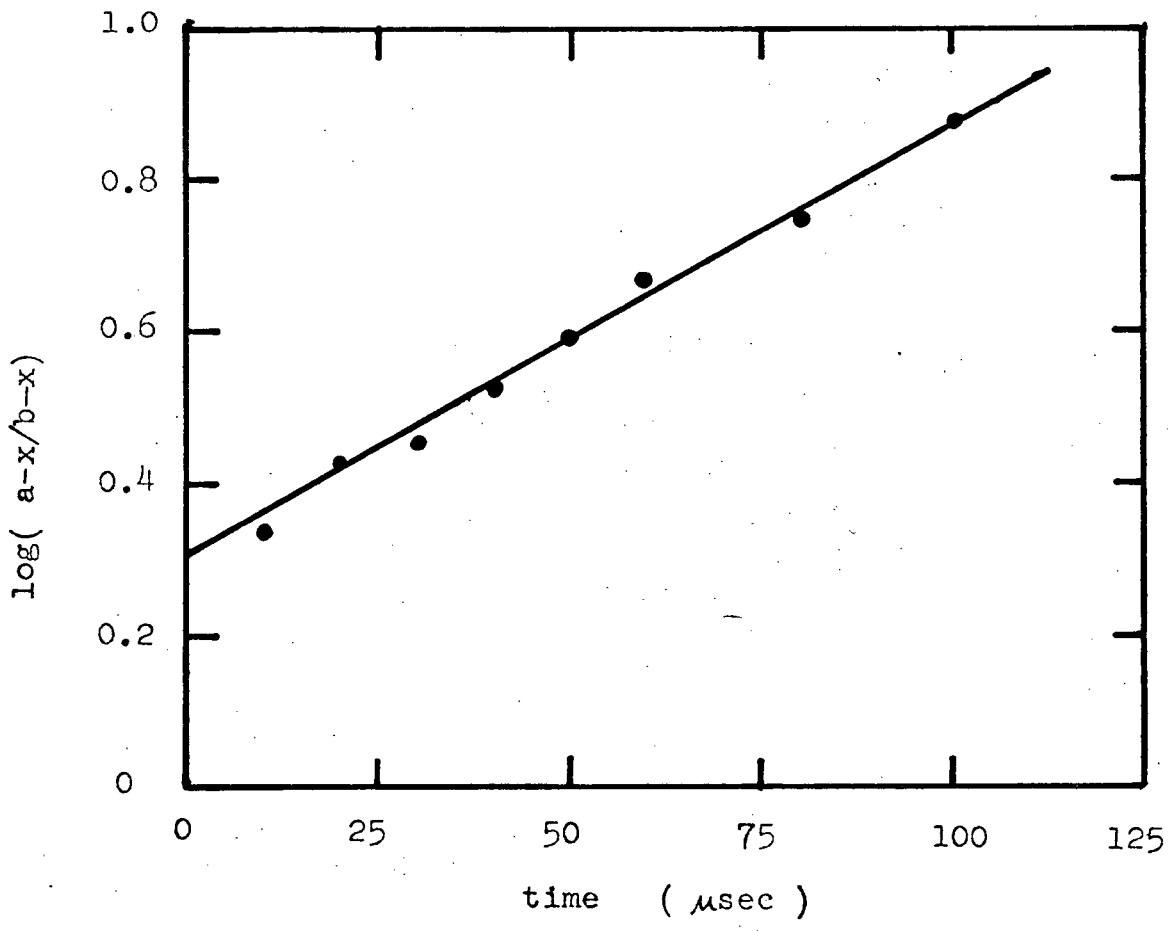
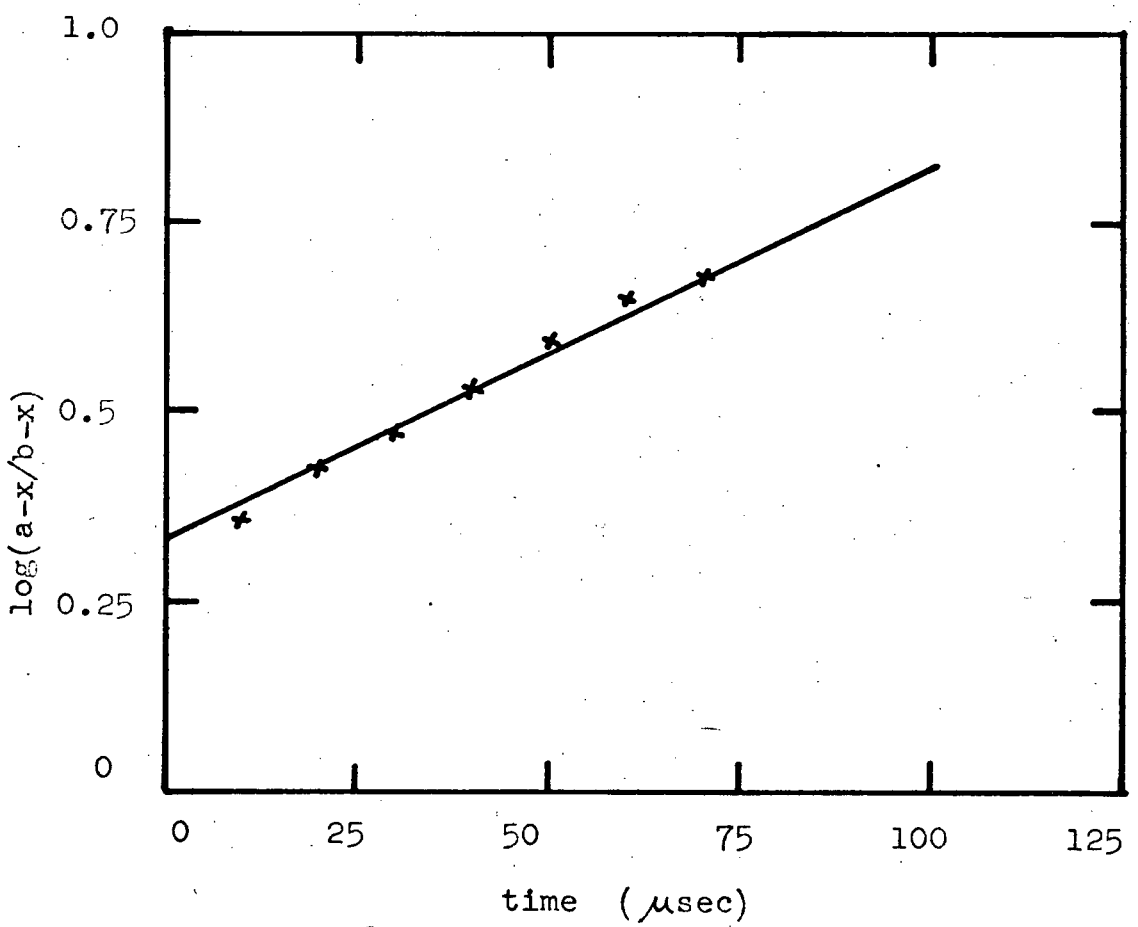


Figure 42. A plot of log(a-x/b-x) against time.

$a = [ClO_2]_o$, $b = [BrO]_o$, $x = [BrO]_t$.

$ClO_2 = 3.16 \times 10^{-6}$ M, $Br_2 = 137.5 \times 10^{-6}$ M,

Argon = 200 torr, E = 1060 J, Filter 4400 Å.



slope of the straight line. The values obtained are listed in Table XXII. The average value for k_{16} was found to be $7.7 \pm 1.3 \times 10^9$ l mole^{-1} sec^{-1} from ClO and $7.7 \pm 1.3 \times 10^9$ l mole^{-1} sec^{-1} from BrO measurements. The values obtained agree with each other and are in satisfactory agreement with that from the ClO_2 measurement. The overall average value was found to be $7.2 \pm 2.0 \times 10^9$ l mole^{-1} sec^{-1}.

The difference between the ClO_2 and (ClO and BrO) values is probably within experimental error. There are, however, two systematic errors. Firstly, the extrapolation of $[ClO_2]$ to zero time assumes that the late slow reaction is also occurring during the first 200 to 300 μsec. If it is not, the value of ClO_2 at, say, 300 μsec is used for $[ClO_2]_\infty$, $k_{16}(ClO_2)$ is increased by ∽15% and the ratio of $\Delta[ClO]/[BrO]$ by ∽10%. Secondly, the error in the calculation of k_{16} from ClO and BrO is the neglect of their decay during the period of formation. Inclusion of correction for this would increase the value obtained from ClO by ∿20 to 30%.

Although this treatment of the results appears to be successful, the value of k_{16} obtained is unacceptably high for a reaction at room temperature endothermic by 3 Kcals. The possibility that excited bromine atoms are involved can be ruled out because, using the rate constant for spin orbit relaxation of $Br(^2P_{1/2})$ by bromine obtained by Donovan and Hussain,[80] the half life of the excited atom is calculated to be ∿2 μsec.

Table XXII

Calculation of k_{16} of the Reaction $Br + ClO_2 \rightarrow BrO + ClO$

Plate no.	$[ClO_2]$ (10^{-6}M)	$[Br_2]$ (10^{-6}M)	P_T torr	Filter Å	E J	$k \times 10^{-9}$ (l mole^{-1}sec^{-1}) From ClO_2	From ClO	From BrO
248	3.21	82.5	200(N_2)	4400	1060	6.24	7.6	7.6
249a	2.62	137.5	200(N_2)	4400	1060	--	8.9	8.5
250	3.16	137.5	200	4400	1060	7.75	8.7	7.8
251	2.54	41.3	200	4400	1060	5.3	8.3	9.0
252a	3.00	137.5	100	4400	1060	8.0	7.5	7.6
252b	2.96	137.5	500	4400	1060	6.3	7.7	8.5
253	3.7	82.5	200	4400	1060	6.4	6.6	6.4
254	3.49	137.5	200	5600	1060	6.3	6.6	6.9
255	3.95	220.0	200	5600	1060	5.1	7.2	6.6
256a	3.30	137.5	500	5600	1060	6.3	7.2	7.6
256b	3.1	137.5	100	5600	1060	5.8	7.6	7.7
				Average		6.35 $\pm$1.2	7.6 $\pm$1.3	7.7 $\pm$1.3

Mean $(7.2 \pm 2.0) \times 10^9$ l mole^{-1}sec^{-1}

Moreover, the same value for k_{16} was found from experiments with the 4400 Å and the 5600 Å filters.

The assumption inherent in the calculation that

$$[Br]_o = \Delta[ClO_2]$$

must therefore be re-examined. The assumption is only valid if the rate of recombination of bromine atoms is much less than

that of reaction (16). Considering argon and bromine as the only third bodies and using the data of Strong et al.[82] Burns,[83] Christie et al.[84] Burns and Horing[85] and Basila and Strong,[86] the minimum half life for bromine atoms in the $ClO_2/Br_2/Ar$ mixtures used is 0.75 msec. It is, therefore, necessary to postulate that a much more rapid removal of bromine atoms can occur through complex formation. This mechanism has been used to explain, for example, the exceptional efficiency of nitric oxide as third body for the recombination of I,[87] Cl,[88] H[89] and O[90] atoms. Spectroscopic evidence for the existence of the intermediate NOI[87] has been obtained. The mechanism proposed is

$$NO + I \rightleftarrows NOI$$

$$NOI + I \rightarrow NO + I_2$$

together with

$$2\ NOI \rightarrow 2\ NO + I_2$$

at high NO pressures. The formation of the complexes CS_3 and COS_2 has been proposed to explain the high recombination rate of sulphur atoms in the presence of CS_2 and COS.[91] For bromine atoms, complexes with ClO, BrO and ClO_2 appear reasonable and could lead to a very rapid recombination.

The precise effect of these reactions on the apparent value of the rate constant k_{16} depends, of course, upon the detailed mechanism which determines the ratio of the rates of

removal of bromine atoms and ClO_2. If this is constant then

$$[Br]_o = n([ClO_2]_o - [ClO_2]_\infty) = n(a - b)$$

$$[Br]_t = n([ClO_2]_t - [ClO_2]_\infty) = n(x - b)$$

$$-\frac{d[ClO_2]}{dt} = \frac{dx}{dt} = n\,k_{16}x(x - b)$$

Thus a straight line would still be obtained from the plot of $\log \frac{x}{x-b}$ and from the plots for ClO and BrO but the slope is now given by $k_{16}\,n$ rather than by k_{16}. The effect then is to reduce the measured rate constant by a factor n.

One mechanism by which a constant value of n is still predicted involves the complex ClO_2Br as the common intermediate for the production of ClO and BrO. Both structures of this complex, $BrCl<^{O}_{O}$ and $Br{-}O{-}Cl<^{O}_{O}$ were considered by Clyne and Coxon[25] as possible transition states in the reaction, the former accounting much more naturally for the formation of BrCl.

$$Br + ClO_2 \rightarrow ClO_2{\cdot}Br \qquad (43)$$

$$Br + ClO_2{\cdot}Br \rightarrow Br_2 + ClO_2 \qquad (44)$$

$$Br + ClO_2{\cdot}Br \rightarrow BrO + ClO{\cdot}Br \qquad (45)$$

$$Br + ClO{\cdot}Br \rightarrow ClO + Br_2 \qquad (46)$$

A steady state treatment yields

$$\frac{d[ClO]}{dt} = \frac{d[BrO]}{dt} = -\frac{d[ClO_2]}{dt} = \frac{k_{43}\cdot k_{45}}{k_{44}+ k_{45}}[ClO_2][Br]$$

and $$\frac{[Br]_o}{\Delta[ClO_2]} = 3 + \frac{2\,k_{44}}{k_{45}} = n$$

One other interesting feature of this type of mechanism is that it allows the possibility that another complex $ClO_2 \cdot Br$ would give BrCl and O_2 at low pressures, although reaction (16) still seems to be a better explanation of BrO formation followed by reaction (40) to give BrCl. For a mechanism by which the recombination of atoms occurs independently of reaction (16), e.g.

$$\begin{aligned} Br + ClO_2 &\rightarrow BrO + ClO \\ Br + ClO_2 &\overset{K}{\rightleftarrows} ClO_2 \cdot Br \\ Br + ClO_2 \cdot Br &\overset{k_{47}}{\rightarrow} ClO_2 + Br_2 \end{aligned} \qquad (47)$$

$$-\frac{d[Br]}{d[ClO_2]} = 1 + \frac{K\, k_{48}\, [Br]}{k_{16}}$$

and the ratio will depend on the initial [Br] and will change with time. Preliminary experiments designed to test the possibility that the bromine atoms are removed by other reactions than reaction (16) have been performed. Mixtures of bromine (at pressures of 0.25 to 0.75 torr when 4400 Å filter and 2.5 torr when 5600 Å filter was used) with Cl_2O and argon have been flash photolysed and at a flash energy 1060 J. The concentration of bromine atoms produced was equal to the ClO concentration extrapolated to zero time. A comparison with the ClO_2/Br_2 system then shows that the bromine atom concentration is much higher than the amount of ClO_2 decomposed. For experiments with different pressures of bromine than those used with Cl_2O,

the bromine atom concentration can be taken as approximately proportional to the pressure. The data so far obtained are not sufficiently precise to help in deducing the mechanism, but there is no doubt that $\frac{[Br]_o}{\Delta[ClO_2]} >> 1$ and the true value for the overall rate constant for reaction (16) is lower (by at least a factor of 10) than that obtained from the first treatment.

CHAPTER VI

VIBRATIONALLY EXCITED OXYGEN

Vibrationally excited oxygen in the ground electronic state has been observed in three different systems, viz., the flash photolysis of ClO_2, of Cl_2O and of the ClO radical. Though the first system has been studied in more detail, the other two have helped very much in elucidating the mechanism for the production of O_2^*, its population distribution and finally, the decay of O_2^*. This chapter has been divided into three sections. First will include the formation, second, the population distribution, and in the last, the decay of O_2^* will be discussed.

A. Production of Vibrationally Excited Oxygen

1) By Flashing ClO_2

The flash photolysis of ClO_2 has been studied at several ClO_2 and total pressures and in the presence of various additives, e.g., Cl_2 and Cl_2O. The ClO_2 pressure was varied from 0.05 to 0.25 torr, total pressure from 30 to 500 torr and the pressure of Cl_2 and Cl_2O as mentioned in the respective tables. Quartz and pyrex reaction vessels were used as well as the light filters restricting radiation above 3100 Å, 3400 Å or 3700 Å. The flash energy was varied within the range corresponding to approximately 25 to 85% primary photolysis of ClO_2. Under all

conditions, the spectrum of vibrationally excited oxygen was observed by its absorption in the Schumann-Runge system ($B\ ^3\Sigma^-_u - X^3\Sigma^-_g$). A typical spectrum is shown in fig.(43). This was observed 10 μsec from the peak of photolysis flash with 0.25 torr of ClO_2 in 200 torr of argon using pyrex reaction vessel and flash energy 1060 J.

The highest level of O_2^* detected was v'' = 15, though only levels up to v'' = 14 were strong enough for positive identification. The presence of O_2^* (v''=15) was confirmed by flash photolysing ClO_2 at high energies in the presence of a small amount of Cl_2O. Under these conditions, for reasons to be discussed later, a strong spectrum of the higher levels is observed and this allowed the positive identification of the (0,15) level of O_2^*. It is significant that no level higher than v'' = 15 was observed under these more favorable conditions. These results confirm Lipscomb, Norrish and Thrush's[21] observation of O_2^* (v'' = 4 to v'' = 8), with the important addition of v'' = 9 to v'' = 15.

The amount of O_2^* formed at each flash energy was measured at O,12 and 3,6 levels. It was found that with the increase in the primary photolysis of ClO_2, the amount of O_2^* produced also increases. This has been shown in fig. (44), where the amount of oxygen formed is plotted against the primary photolysis of ClO_2. This is quite contrary to L.N.T.[21] who observed that the amount of oxygen formed decreases when the primary photolysis of ClO_2 is more than 50%.

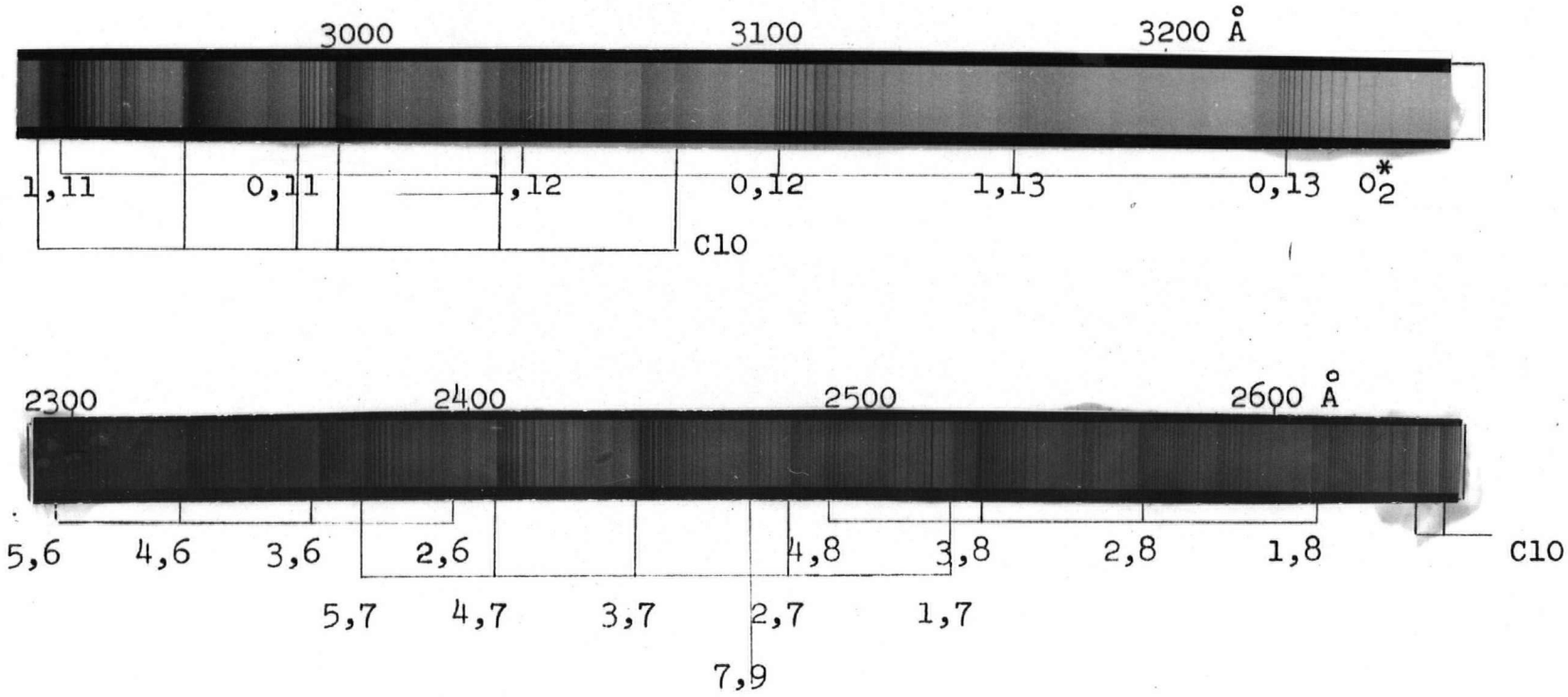


Figure 43. A portion of the Schumann Runge System of $O_2\left({}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-\right)$ observed in the isothermal flash photolysis of ClO_2. ClO_2= 0.25 torr, Argon = 200 torr, E=1060 J.

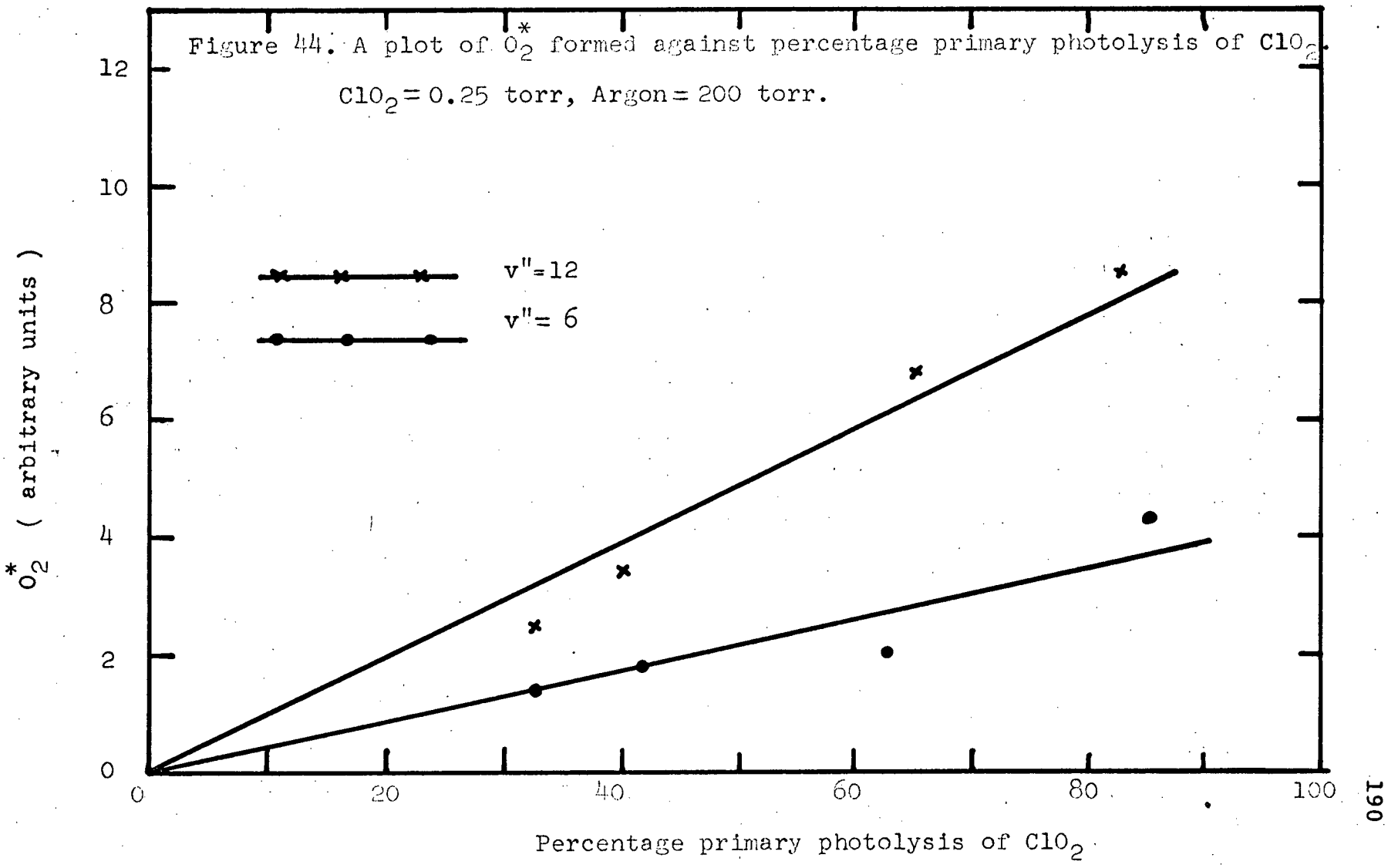


Figure 44. A plot of O_2^* formed against percentage primary photolysis of ClO_2.
ClO_2 = 0.25 torr, Argon = 200 torr.
v" = 12
v" = 6
O_2^* (arbitrary units)
Percentage primary photolysis of ClO_2
0
2
4
6
8
10
12
0
20
40
60
80
100

2) From the Photolysis of Cl_2O

As with ClO_2, Cl_2O was flash photolysed with different flash energies, with Cl_2O and argon pressure varying from 0.25 to 1.0 torr and 75 to 200 torr, respectively. The quartz and pyrex reaction vessels were used as well as a filter to restrict the light radiation above 3100 Å. Chlorine as an additive gas was also used when Cl_2O was flashed using pyrex and quartz reaction vessels. Under the above conditions the following results were obtained:

1) When Cl_2O was flash photolysed restricting the radiation above 3100 Å, no spectrum of vibrationally excited oxygen was observed.

2) Using pyrex and quartz reaction vessels, the spectrum of vibrationally excited oxygen was seen by its absorption in the Schumann-Runge system ($B^3\Sigma^-_u - X^3\Sigma^-_g$). A typical spectrum is shown in fig. (45) with conditions as mentioned there.

The highest level of O_2^* detected was v'' = 14 though the spectrum was very weak as compared to those for levels up to v'' = 13. Observation of levels $\leq$ 8 was hindered by the overlapping continuum of Cl_2O and the levels seen depend on the degree of photolysis. It was observed that the lower levels (v'' = 8) could not be seen when pyrex reaction vessel was used. That is the reason only those levels of O_2^* have been shown in fig. (45), which were quite visible even though the quartz reaction vessel was used. The intensity of all the levels ob-

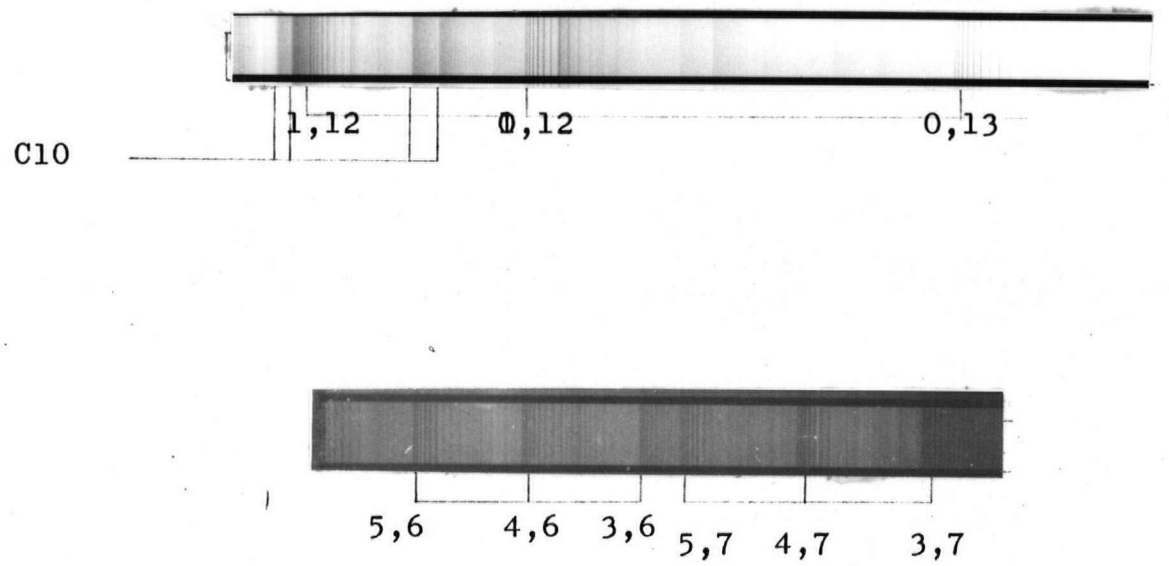


Figure 45. A portion of the Schumann Runge System of O_2 ($^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$) observed in the isothermal flash photolysis of Cl_2O.

Cl_2O= 1.0 torr, Argon= 200 torr, E= 600 J.

served with pyrex reaction vessel was very weak compared to that when quartz reaction vessel was used. The minimum energy necessary for the observation of O_2^* was 600 J when the pyrex reaction vessel was employed. These results are quite different from those of Edgecombe et al.[22] but these have helped to establish the mechanism of the formation of O_2^* from ClO_2.

3) From the Photolysis of ClO

ClO radicals were generated from the photolysis of ClO_2 as has been described in Chapter IV, sec. A-2. The mixture thus obtained containing ClO, Cl_2 and O_2 (from the secondary reactions) and chlorine atoms left from the reaction of oxygen atoms with ClO, was flash photolysed with the auxiliary lamp using two flash energies at different time delays. The delays for the auxiliary lamp were selected in such a manner that all the vibrationally excited oxygen produced in flashing ClO_2 had disappeared and all the ClO_2 had been decomposed. In some experiments a very small amount of ClO_2 remained at the time of the auxiliary flash. Mixtures containing this amount were flashed in separate experiments and no O_2^* was found. Both pyrex and quartz reaction vessels were used.

In all cases, O_2^* was observed with vibrational levels up to v'' = 13 (14 ?). The spectrum of oxygen was very weak in all the levels as compared to that when the same pressure of ClO_2 (between 0.1 to 0.15 torr) was photolysed with primary

photolysis approximately 30%. The reasons for this will be discussed in Section C. The intensity of each band does depend upon the initial pressure of ClO_2 and the amount of ClO present at the time of reflashing. Only the rise and decay of 0,12 level has been shown in fig. (46), when ClO radical was flashed with flash energy 1325 J and delay times 100 and 166 μsec respectively.

Mechanism

The principal mechanism for the production of O_2^* proposed by L.N.T.[21]

$$ClO_2 + h\nu \rightarrow ClO + O \qquad (27)$$

$$ClO_2 + O \rightarrow ClO + O_2^* (X^3\Sigma^-_g) + 59 \text{ Kcals} \qquad (7)$$

receives immediate support from our observation of O_2^* (v'' = 15), the energy of which corresponds exactly to the exothermicity of the reaction (7). However, this mechanism requires that the maximum concentration of O_2^* should be produced when the primary photolysis of ClO_2 is 50%. Whereas we have observed a continued increase up to 85% photolysis (fig. 44) contrary to L.N.T.[21]

The second mechanism proposed involved the production and photolysis of ClO_3,

$$O + ClO_2 \rightarrow ClO_3 \qquad (9)$$

$$ClO_3 + h\nu \rightarrow ClO + O_2^* \qquad (31)$$

and is open to same objection. Unless O_2^* is a very minor product of photolysis of ClO_2, this mechanism requires an extremely high

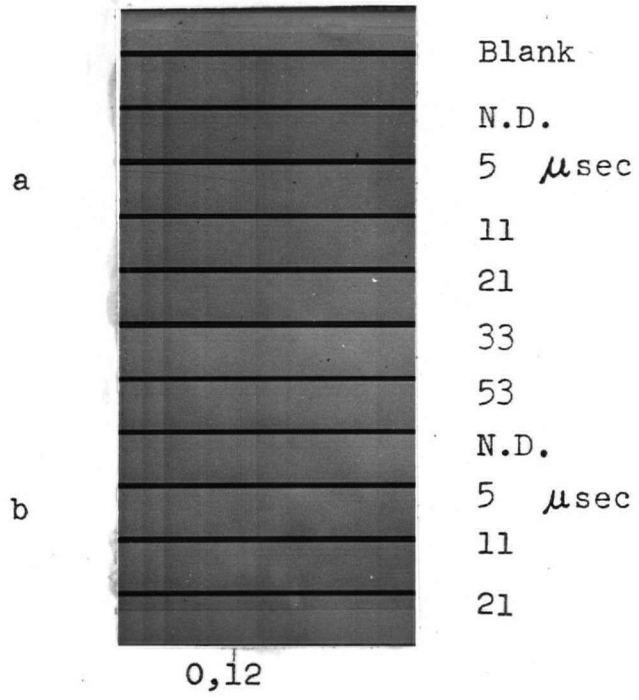


Figure 46. Rise and Decay of O_2^* .

ClO_2 = 1.0 torr, Argon = 200 torr, E_m = 1060 J

$E_{aux.}$ = 1325 J.

a) Delay time = 241 μsec

b) Delay time = 166 μsec

rate constant for the formation of ClO_3 in competition with reaction (7). Unlike the analogous formation of NO_3,[74] no third body could be invoked since the production of O_2^* is independent of total pressure at least in the range of 30 to 500 torr.

This mechanism also requires the integrated absorption of ClO_3 in the wavelength region used to photolyse ClO_2 to be extremely high. The strongest absorption of ClO_3 is, however, in the region 2000 to 3000 Å ($\varepsilon \sim 1200$ l mole^{-1} cm^{-1}), the extinction coefficient then decreases to $\sim$100 l mole^{-1} cm^{-1} near 3600 Å. The amount of O_2^* produced would be then markedly dependent on wavelength and the relative population of different levels and the highest level produced very probably would vary with wavelength. In practice, the production of O_2^* is the same with quartz and pyrex reaction vessels and with 3100 Å, 3400 Å and 3700 Å light filters. The concentration of O_2^* is reduced only by the amount expected from the decrease in the ClO_2 photolysis. We therefore conclude that this mechanism may be neglected.

Although any mechanism involving ClO_3 is unlikely, a better case can be made for the production of O_2^* in the reaction

$$O + ClO_3 \rightarrow ClO_2 + O_2^* \qquad (28)$$

Evidence against this, however, is the absence of levels higher than v'' = 15 and the fact that the presence of chlorine atoms in a flash photolysed mixture of ClO_2 and Cl_2 only seems to

affect the rate of relaxation of O_2^* rather than its production.

Another possibility worth considering is the direct production of O_2^* in the primary process

$$ClO_2 + h\nu \rightarrow Cl + O_2^* \qquad (37)$$

A similar mechanism has been proposed to explain the presence of SO^* following the flash photolysis of SO_3.[75] The formation of ClO in the fast reaction

$$Cl + ClO_2 \rightarrow 2\ ClO \qquad (8)$$

makes the overall yield of both the products the same as that obtained from the first primary process (reaction 27), provided that $\leq$ 50% of the ClO_2 is photolysed. The decreased yield of ClO at higher energies would explain the apparent fall in its extinction coefficient observed by L.N.T.,[21] while the continued linear dependence of O_2^* production on flash energy follows automatically. The effect of Cl_2O in decreasing the amount of ClO_2 decomposed at low flash energies is accounted for by the reaction

$$Cl + Cl_2O \rightarrow ClO + Cl_2 \qquad (19)$$

which competes with the ClO_2 for chlorine atoms. The apparent increase in ClO production (as measured at long delays or by linear extrapolation of the second order plot) caused by Cl_2O at high energies is equally well explained by the same reaction (19) when there is an excess of chlorine atoms over unphotolysed ClO_2. This excess of chlorine atoms causes the rapid relaxation of O_2^* at high flash energies and their removal by Cl_2O produces the required effect, i.e. the rapid relaxation of O_2^* is drama-

tically replaced by a slow decay.

While this mechanism is qualitatively attractive our results provide convincing reasons for believing that ∿10% of total ClO is in fact produced in the reaction (8). Firstly, the same value of the extinction coefficient of ClO has been obtained at low and high flash energies and this value is very close to those obtained from Cl_2O and Cl_2O/Cl_2 and to the (non-photolytic) value of Clyne and Coxon.[25] Secondly, the initial rapid decay of ClO cannot reasonably be explained by this mechanism. Thirdly, the total concentration of ClO produced at high flash energies in the presence of Cl_2O exceeds the initial ClO_2 concentration (fig. 19). This can only be explained by the reaction of oxygen atoms with Cl_2O as has been suggested in the comparison of the rate constants of oxygen atoms with ClO and Cl_2O (Chapter IV, Section B), i.e.,

$$O + ClO_2 \rightarrow ClO + O_2^* \qquad (7)$$

$$O + Cl_2O \rightarrow 2\ ClO \qquad (35)$$

Fourthly, the decrease in ClO_2 decomposition in presence of Cl_2O can be explained by the competition of ClO_2 and Cl_2O for chlorine atoms. But if we accept this explanation, there should be, consequently, a decrease in the ClO production too. On the other hand, our results suggest a corresponding increase in the ClO production but a decrease in the ClO_2 decomposition. This can nicely be explained if we assume a competition of ClO_2 and Cl_2O for oxygen atoms.

Finally, the rates of production of ClO in reactions (3) and (8) are insufficient to account for the observed maximum ClO concentration at 10 to 20 μsec. For example, assuming instantaneous 50% photolysis of 0.25 torr of ClO_2, 75% of total concentration of ClO would be produced in ∿60 μsec by the reaction (8), if our value of 5×10^9 l $mole^{-1}$ sec^{-1} for k_8 is accepted.[31] Only 5 μsec are required through reaction (7) and the finite flash duration explains the observed maximum.

The total O_2^* produced by this mechanism is, therefore, less than 5% of the ClO_2 decomposed. A further restriction is imposed by the fact that at low flash energies and high Cl_2O to ClO_2 ratios, less O_2^* is produced in the presence of Cl_2O. In view of the correlation between this and the increase in the ClO production and the decrease in the ClO_2 decomposition, this can only be explained by the competition of oxygen atoms between Cl_2O and ClO_2 as said above. Therefore, even if O_2^* is produced by this mechanism it accounts only for a small fraction of the total O_2^*.

We conclude that O_2^* is produced in the reactions

$$O + ClO_2 \rightarrow ClO + O_2^* + 59 \text{ Kcals} \qquad (7)$$

$$O + ClO \rightarrow Cl + O_2^* + 55 \text{ Kcals} \qquad (6)$$

The first predominates at low flash energies, but is superseded by the second for a primary photolysis exceeding 67%. The evidence for the production of vibrationally excited species in

reactions of this type is strong[92-98] and in view of the similarity between them, it is reasonable to make the assumption that the O_2^* is produced with a similar energy distribution for $v'' \leq 12$. On that assumption, the linear dependence of O_2^* production on flash energy is a natural consequence of the reactions (7) and (6) as has already been shown in fig. (44).

Independent evidence for the production of O_2^* by reaction (6) has been obtained by the flash photolysis of Cl_2O and ClO radicals which will be discussed in the next sections.

Flash Photolysis of Cl_2O

The production of excited oxygen in the flash photolysis of Cl_2O can be explained in terms of reaction (6) but the other possibilities will also be considered. From the results of Cl_2O experiments, it is clear that oxygen atoms are necessary for the production of O_2^* and thus the possible reaction of oxygen atoms in the Cl_2O photolysis could be

$$O + Cl_2O \rightarrow Cl_2 + O_2^* + 83 \text{ Kcals} \qquad (36)$$

$$O + ClO \rightarrow Cl + O_2^* + 55 \text{ Kcals} \qquad (6)$$

$$O + Cl_2O \rightarrow 2\ ClO \qquad (35)$$

The immediate objection to reaction (36) is that the levels higher than $v'' = 14$ should be formed, but we could not observe them.

From steric considerations and the geometry of the activated complex it appears that reaction (36) should have a high activation energy and small rate constant. The rate constant of the reaction of oxygen atoms with Cl_2O was found to be 8.3×10^9 l mole^{-1} sec^{-1} by Phillips et al.[73] and 5.3×10^9 l mole^{-1} sec^{-1} by us. It was shown by them[73] that (35) is the probable reaction and a similar conclusion was also drawn by us from the measurement of the ClO concentration when Cl_2O and ClO_2 was flash photolysed with various ratios and different flash energies. If reaction (36) does occur to a reasonable extent, the total amount of ClO produced should be less when ClO_2 is flashed in the presence of Cl_2O than flashed without Cl_2O, unless the reaction (36) and (35) occur with equal ratio. Whereas if reaction (35) is predominant, the ratio of ClO produced when ClO_2 is flashed with and without the presence of Cl_2O should vary between 1:1.5 depending upon the ratio of Cl_2O/ClO_2, with the assumption that reaction (6) is neglected in both the cases. It was found from our results that the ratio of ClO with and without Cl_2O when ClO_2 is flashed at low flash energies, does lie between 1 to 1.5. At the same flash energies, the ratio goes more towards 1.5 if the ratio of Cl_2O to ClO_2 is increased. These ratios agree satisfactorily with the theoretical ones calculated by the known values of k_{35} and k_7 for different percentage photolysis of

ClO_2. As already mentioned in the case of ClO_2, this can only be explained if oxygen atoms react with Cl_2O via reaction (35) rather than (36).

If the oxygen atoms react with Cl_2O via reaction (36), the total amount of O_2^* formed in the presence of Cl_2O should be equal to that formed in the absence of Cl_2O when ClO_2 is flash photolysed using radiations above 3400 Å to prevent the photolysis of Cl_2O. But it has been found that the amount of excited oxygen formed decreases with the increase of Cl_2O to ClO_2 ratio. It can be seen from fig. (24) when the Cl_2O to ClO_2 ratio is 20, the O_2^* can hardly be seen.

The other possible reason for the production of O_2^* could have been due to the reaction

$$O + ClO_2 \rightarrow ClO + O_2^* + 59 \text{ Kcals} \quad (7)$$

This does seem to be reasonable as the delay in the appearance of ClO_2 has been observed when Cl_2O is flashed. But this can easily be ruled out since a similar delay has been observed when Cl_2O is flashed with radiation above 3100 Å where Cl_2O does not give any oxygen atoms in the primary process and also the oxygen atoms cannot stay long enough in the presence of Cl_2O and ClO whose rate constants for the reactions with oxygen atoms are very high.[31]

Finally, the results obtained in the case of Cl_2O together with those observed in the flash photolysis of ClO_2, i.e., the amount of O_2^* produced increases linearly with the

increase of primary photolysis, suggests that reaction (6) is responsible for the production of O_2^*. The reaction mechanism can be written as

$$Cl_2O + h\nu \rightarrow ClO + Cl$$
$$Cl_2O + h\nu \rightarrow 2\,Cl + O \qquad (22)$$

$$ClO + h\nu \rightarrow Cl + O$$

$$O + ClO \rightarrow Cl + O_2^* \qquad (6)$$

This mechanism agrees with the results that the amount of O_2^* produced with the pyrex reaction vessel is less than that when quartz reaction vessel was used. This is because the Cl_2O concentration is much greater than that of ClO and hence the oxygen atoms will be consumed by reaction (35) in preference to reaction (6), whereas in the case of quartz, the ratio of ClO to Cl_2O is increased. There are many reactions of atoms with stable molecules known which are similar to (35), e.g.

$$Cl + ClO_2 \rightarrow 2\,ClO$$

$$Br + ClO_2 \rightarrow ClO + BrO$$

$$Br + Cl_2O \rightarrow ClO + BrCl$$

and so on. Thus it is reasonable to assume that reaction (35) is more probable for reaction of oxygen atoms with Cl_2O.

Flash Photolysis of ClO

The production of O_2^* when ClO was flash photolysed can be explained by the simple mechanism

$$ClO + h\nu \rightarrow Cl + O$$

$$O + ClO \rightarrow Cl + O_2^* + 55 \text{ Kcals} \qquad (6)$$

because the highest vibrational level (v'' = 13, 14?) observed almost exactly agrees with the exothermicity of reaction (6). The only doubt can be the electronic state of the oxygen atoms involved since the primary phtolysis of ClO radicals can take place according to the following reactions:

$$ClO + h\nu \ (>2800 \text{ Å}) \rightarrow Cl + O\ (^3P) \qquad (6\text{-}1)$$

$$ClO + h\nu \ (<2800 \text{ Å}) \rightarrow Cl + O\ (^1D) \qquad (6\text{-}2)$$

Reaction (6-1) occurs when the light absorbed by ClO is in the region of diffuse bands and as suggested by Durie and Ramsay[16] that this transition leads to the formation of both atoms in the ground state. This can be achieved when ClO is flashed using pyrex reaction vessel only. The transition ($^2\pi \leftarrow {}^2\pi$), i.e., light absorbed in the continuum leads to the formation of ground state chlorine atoms and excited (^1D) oxygen atoms as in reaction (6-2). But it has been seen by many workers[100-103] that radiative life time of the transition

$$O\ (^1D) \rightarrow O\ (^3P) + h\nu$$

is very long as compared to the collisonal deactivation by other gases. Even 200 torr of argon or nitrogen was enough for the competition. Thus the primary reactions can be followed by

$$O\ (^1D) + ClO \rightarrow Cl(^2P) + O_2(X^3\Sigma^-_g) \qquad (6\text{-}3)$$

$$O\ (^1D) + M \rightarrow O\ (^3P) + M \qquad (6\text{-}4)$$

$$O\ (^3P) + ClO \rightarrow Cl\ (^2P) + O_2(X^3\Sigma^-_g) \qquad (6\text{-}5)$$

Reaction (6-3) can be neglected as the highest level of O_2^* corresponds to only 55 Kcals, whereas levels higher than 14 should be observed. Also the pressure of argon or nitrogen used was enough to quench the O (^1D) to the ground state. Therefore, it seems likely that the O_2^* is formed by reaction (6-5). This can also be seen from the results obtained in the case of a pyrex reaction vessel.

Thus the formation of O_2^* when ClO is flashed has confirmed the following points.

1) The linear increase in the amount of excited oxygen formed with the increase in the primary photolysis of ClO_2.

2) The formation of excited oxygen in the case of Cl_2O photolysis.

3) This is an addition of another reaction to the type of reactions postulated by Polanyi,[79]

$$A + BC \rightarrow AB^* + C$$

where AB^* is a vibrationally excited molecule.

B. Vibrational Energy Distribution in Excited Oxygen

The accurate measurement of the relative population of all the levels of O_2^* observed in the flash photolysis of ClO_2 is difficult because every band is, to some extent, overlapped by the spectrum of ClO_2 or of ClO. An additional problem for the lower levels, with the resolution used, is the overlap of the various O_2^* bands. However, the intensities of the (3,6), (5,7) and (0,12) bands were measured by plate photometry and the relative populations were obtained by using the transition probabilities given by Nicholls.[77] Since eye estimation of the other bands showed that the change in population between successive levels in the range v'' = 5 to v'' = 13 was small and constant, these measured values for the 6th, 7th, and 12th levels fairly represent the trend over this range. Between the 13th, 14th and 15th levels the intensity difference was much more marked and the highest level was barely detectable under most conditions.

To obtain the relative rates of production of O_2^* into the 6th, 7th, and 12th levels, the ratios of the measured concentrations were plotted against time and extrapolated to zero time delay, as can be seen in fig. (47-a). The results obtained by this method are compared, in Table XXIII, to those calculated from the linear extrapolation of the first order decay plots for each level to zero delays (fig. 48). The difference between the results obtained by these procedures arises from the more

Figure 47. A plot of the ratios of $N_{0,12}/N_{3,6}$ against time.

a) Curves are drawn with the assumption that O_2^* obeys Beer Lambert's law.

b) Curves are drawn by raising peak height to the power 1.75.

ClO_2=0.25 torr, Argon =200 torr.

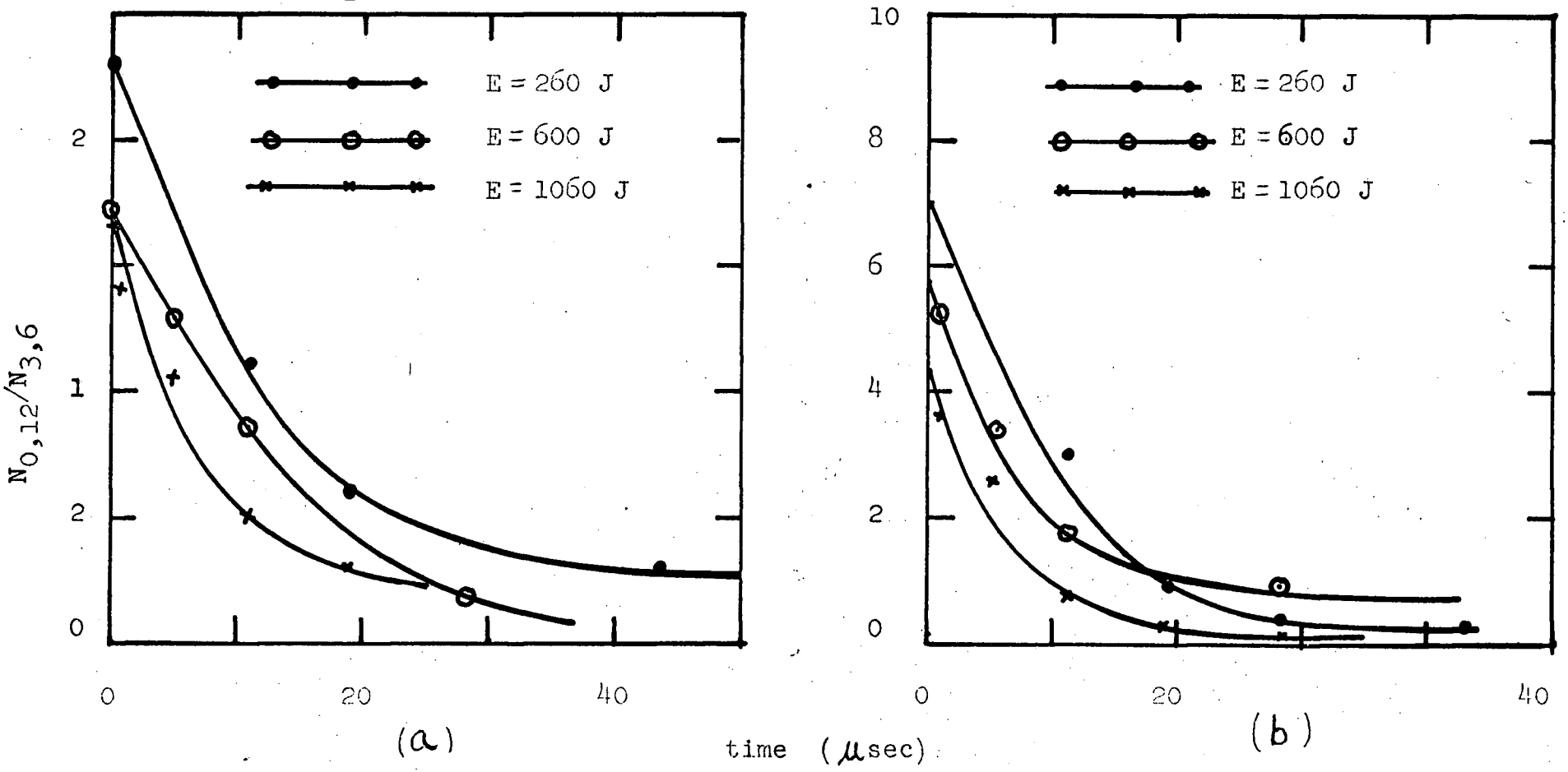
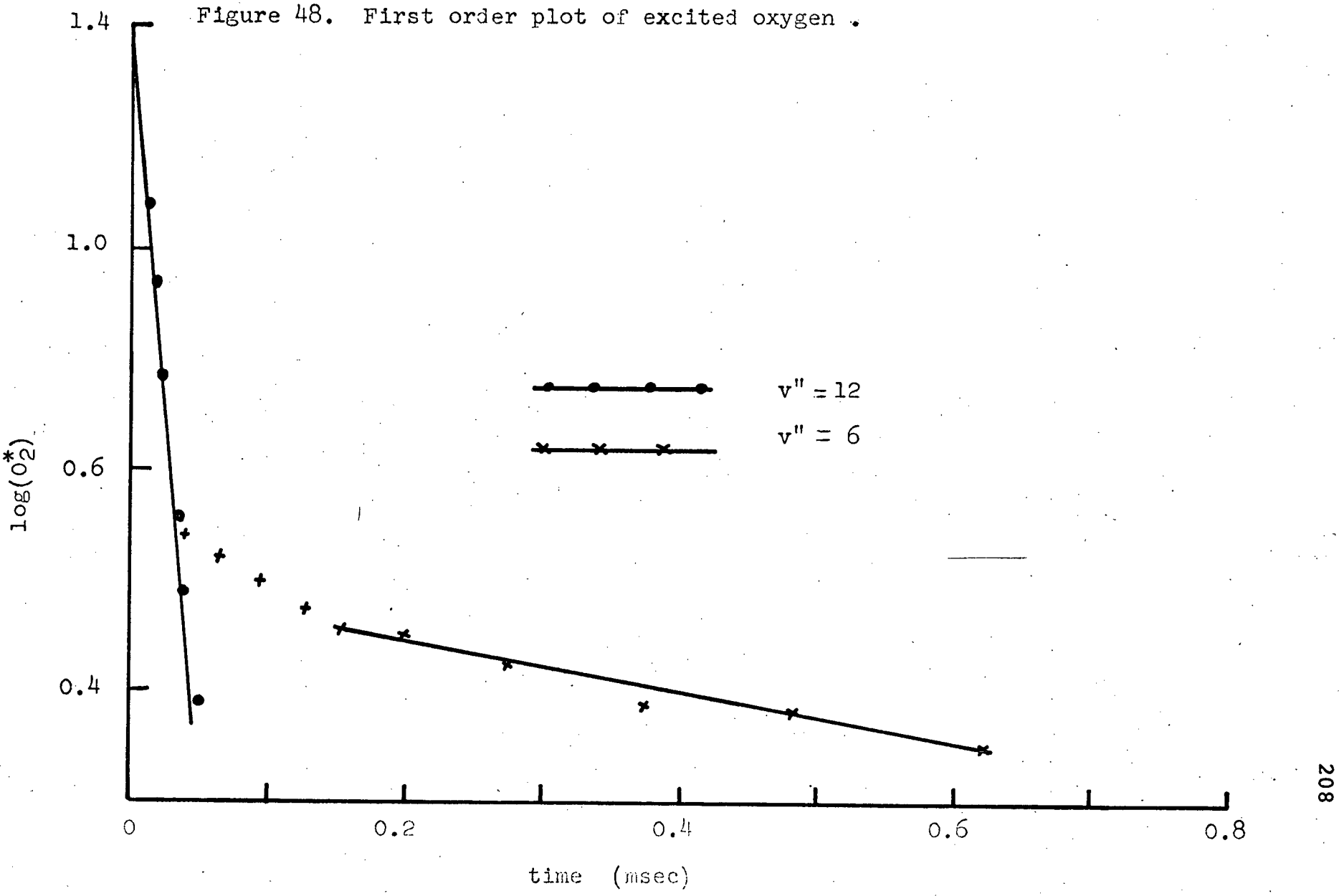


Figure 48. First order plot of excited oxygen .



rapid change in the distribution at very short delays (fig. 47-a). The first method takes this into account because measurements made at short delays (while the O_2^* concentration is still increasing) can also be used. The extrapolated population ratios, therefore, more accurately represent the initial distribution. This distribution is seen to be independent of ClO_2 pressure, total pressure and flash energy and is the same with quartz as well as with pyrex reaction vessels. The same results were obtained with light filters of 3100 Å, 3400 Å or 3700 Å cut off wavelength and the initial distribution was also unaffected by the presence of Cl_2 or of Cl_2O, though these gases had marked effects on the rate of relaxation on O_2^*.

To what extent this measured initial distribution represents the relative rates of production of O_2^* into various levels depends on three factors. The first concerns the experimental accuracy of the determination itself. Clearly the steepness of the curves at short delays and small uncertainty in the definition of zero time preclude high accuracy. Probably more important is nonlinearity in the dependence of O_2^* concentration on the plate density when the O_2^* bands were overlapped by other spectra. For example the two path method has shown that under our experimental conditions, the power 'n' to which the change in plate density should be raised in the relationship $[O_2] \alpha$ (change in plate density)^n, lies closer to 1.5 ± 0.25 than unity.

When this nonlinearity is taken into account, the average value for this initial ratio of populations of the levels 12th to 6th of O_2^* is found to be approximately five (fig. 47-b).

The second factor is the possibility of a very rapid change in the relaxation rate at short delays so that the extrapolation is not valid. The fact that the linear first order plot yields lower values for the initial population ratios than the plot of ratios indicates that species other than ClO_2 and ClO contribute to the relaxation. The oxygen atoms in the early stage are the only other species present in sufficient concentration and evidence that they are exceptionally efficient will be presented in the next section. However, the minimum half life for oxygen atoms in our system is approximately 4 μsec, so that the rate of relaxation would change by less than a factor of two. This change is already reflected in the extrapolation.

The third factor and the one which could drastically change the distribution within a microsecond, is the importance of optical pumping. A rather extreme example of this is known in the flash photolysis of cyangen and cyanogen halides.[78] In this case the CN radical is produced in the zeroth vibrational level and very rapidly reaches a high degree of vibrational excitation through absorption of radiation from the photolysis lamp.

$$CN\ (X^2\Sigma,\ v=0) + h\nu \longrightarrow CN(B^2\Sigma,\ v=0,\ 1,\ 2\ldots)$$

$$CN\ (B^2\Sigma,\ v=0,\ 1,2\ldots) \longrightarrow CN\ (X^2\Sigma,\ v=0,\ 1,\ 2\ldots)$$

These processes are repeated many times and the excited levels also absorb radiation. Convincing evidence that the distribution of O_2^* produced from ClO_2 has not been altered by a similar mechanism is provided by the fact that the same results are obtained with quartz and pyrex reaction vessels and with 3100 Å, 3400 Å and 3700 Å light filters. Supporting evidence has been obtained from similar light filter experiments using NO_2[64] as the source of O_2^*, the distribution again being unaffected.

We conclude that in the reaction of oxygen atoms with ClO_2, the rates of production of O_2^* into the levels v'' = 5 to v'' = 13 are approximately equal, but with a trend in favour of the higher levels. This trend appears to be uniform and the ratio of the rates for successive levels is probably 1.3 ± 0.2. From the linear increase in the O_2^* concentration in various levels with flash energy, we conclude that a similar distribution of O_2^* is produced in the reaction of oxygen atoms with ClO radical, although the direct measurement in this case is not possible due to the very small concentration produced. A similar conclusion can be drawn in the case of O_2^* produced when Cl_2O is flash photolysed, because it has been shown that it is the reaction of oxygen atoms with ClO which is responsible for the production of O_2^*.

For levels v'' = 15 and 14, no definite conclusion is possible but it seems that the apparent reversal of the trend is,

at least in part, due to the high rate of depopulation of these levels. If the levels v'' = 12 to v'' = 15 were initially equally populated, then with stepwise relaxation, the apparent half lives of these levels would be approximately in the ratio 7:5:3:1. The difference appears to be sufficient to account for the relatively low concentrations of the 14th and 15th levels observed.

In this connection, it is interesting to note that L.N.T.[21] also estimated the populations of the 5th, 6th and 7th levels to be equally populated, whereas that of the 8th level, highest observed by them, was appreciably less. This can be explained by the faster rate of depopulation of the 8th level in the absence of higher levels. Further evidence for the importance of the relaxation in determining the observed relative populations of the highest levels is provided by the effect of Cl_2O. When ClO_2 is flashed at high flash energies in the presence of Cl_2O, the rate of relaxation of all levels is decreased and the relative concentration of the 15th level of O_2^* is significantly increased, as is, to a lesser degree, that of the 14th level, although no 15th level of O_2^* was observed when Cl_2O was flash photolysed alone.

Table XXIII

Calculation of Relative Populations of Excited Oxygen

Plate no.	$[ClO_2]$ torr	Argon torr	Energy J	Filter Å	N_{12}/N_7^1 $[O_2^*]^1$	$[O_2^*]^{1.75}$	N_{12}/N_6^1 $[O_2^*]^1$	$[O_2^*]^{1.75}$	N_{12}/N_6^2 $[O_2^*]^1$	$[O_2^*]^{1.75}$
40	0.25	200	1060	--	1.6	4.7	1.3	3.3	0.66	1.1
34	0.25	75	1060	--	1.4	3.3	1.1	2.2	0.65	1.1
35	0.1	30	1060	--	1.5	4.7	--	--	--	--
30	0.25	500	1060	--	1.6	4.8	1.6	4.4	0.9	2.0
25	0.1	30	1060	3100	--	--	1.3	4.5	0.68	1.1
152	0.25	200	1060	3100	--	--	1.9	6.4	0.6	1.0
61	0.25	200	1060	3700	--	--	1.7	6.3	0.62	1.0
62*	0.25	200	1060	3700	--	--	1.6	6.3	0.58	0.8
36	0.25	75	600	--	1.5	4.0	1.1	3.2	0.7	1.2
27	0.25	200	600	--	1.7	4.6	1.7	5.8	1.3	3.5
37	0.1	30	600	--	1.6	3.7	2.0	5.5	0.7	1.4
26	0.1	150	600	--	1.9	4.8	--	--	--	--
29	0.1	500	600	--	1.3	3.8	1.6	5.1	0.8	1.7
25	0.1	30	600	3100	--	--	1.4	4.9	0.6	1.1
153	0.25	200	600	3100	--	--	2.0	7.5	1.0	2.5
154	0.1	200	600	3100	--	--	1.9	7.5	0.8	1.54
39	0.25	200	260	--	1.7	5.2	2.2	7.0	0.7	1.2
38	0.25	75	260	--	1.7	3.8	1.7	6.2	0.9	1.9
44	0.25	500	260	--	2.2	5.9	2.2	7.0	0.9	2.1
164	0.25	200	260	3100	--	--	1.6	6.2	0.7	1.1
118	0.25	200	260	3100	--	--	1.7	5.7	0.6	1.1
119	0.25	75	260	3100	--	--	1.7	6.0	0.6	1.0
					1.6 ± 0.2	4.4	1.7 ± 0.3	5.7 ± 1.4	0.73 ± 0.12	1.4

Note: N_{12}/N_7^1 and N_{12}/N_6^1 are values obtained from the plots of ratios of relative population vs. time. N_{12}/N_6^2 is obtained from the extrapolation of first order plot of $[O_2^*]$.

C. Relaxation of Excited Oxygen

The relaxation of the levels v'' = 6 and v'' = 12 was measured for several flash energies, using a pyrex reaction vessel and two mm of glass filter A. The results are listed in Table XXIV. The effect of the addition of Cl_2O and Cl_2 was also studied and is illustrated in Tables XXVIII and XIX respectively.

The decay of O_2^* was found to be first order over the entire period of measurement for the 12th level at all flash energies and for the 6th level at high flash energies. At lower energies, the first order plot for the 6th level became linear only after about 100 μsec, the initial rate of decay being appreciably faster. For all experiments, the results are conveniently expressed in terms of half-lives for each level measured from the linear first order plot given in Table XXIV. For the 6th level, the initial half-lives, i.e., those measured from the time of maximum O_2^* concentration, are given in parentheses.

1) Low Flash Energy

At low flash energies the results for the 6th level are similar to those reported by L.N.T.[21] These results may be properly compared since their measurements began 150 μsec after the beginning of the photoflash, by which time the decay was found to be first order in both studies. Again at low flash energies, the half-lives of both levels are independent of the

fraction of ClO_2 photolysed over the small range where the measurements were possible. This is consistent with the conclusion by L.N.T.[21] that ClO and ClO_2 have a similar efficiency in the relaxation of O_2^*. Since they found only a 10% decrease in the half-life of the 6th level when the ClO_2 decomposition was reduced from 90 - 100% to 50%, the rate constant for ClO and ClO_2 may be assumed to be equal. We find, as did L.N.T.[21] that the effect of the moderating gas is negligible so that the rate constant k_{50} for the decay of O_2^* may be calculated as follows.

$$-\frac{d \ln[O_2^*]}{dt} = k_{50}\{[ClO_2] + [ClO]\}$$

since the decomposition of ClO_2 is essentially complete before the beginning of the half-life period and the decay of ClO is strictly second order over this period.

$$-\frac{d \ln[O_2^*]}{dt} = k_{50}\left[C_1 + \frac{C_2}{1 + k_5 C_2 t}\right]$$

where C_1 and C_2 are the concentrations of ClO_2 and ClO respectively at the beginning of the half-life. Thus,

$$k_{50} = \ln 2 \left[C_1 t + \frac{\ln(1 + k_5 C_2 t)}{k_5} \right]^{-1}$$

and our results yield $k_{50}(12) = 1.8 \times 10^8$ l mole^{-1} sec^{-1} and $k_{50}(6) = 0.87 \times 10^8$ l mole^{-1} sec^{-1}, the latter results being in good agreement with the value of 1.0×10^8 l mole^{-1} sec^{-1} found by L.N.T.[21] for the relaxation of the 6th level by ClO.

These decay rate constants cannot, however, be directly identified with the rate constants for the process

Table XXIV

Half-Lives for the O_2^*(following the Flash Photolysis of ClO_2.

Plate no.	$[ClO_2]$ torr	Argon torr	Energy J	% Photo	Filter Å	$t_{1/2}$ (μsec) 0,12	3,6
	0.25	200	26	100	-	7	--
34	0.25	75	1060	100	-	10	26
40	0.25	200	1060	100	-	10	15
35	0.1	30	1060	100	-	13	--
30	0.25	500	1060	100	-	10	28
36	0.25	75	1060	100	-	20	29
27	0.25	200	600	100	-	15	30
26	0.1	150	600	100	-	20	41
37	0.1	30	600	100	-	24	--
29	0.1	500	600	100	-	20	29
152	0.25	200	1060	100	A	12	18
155	0.1	200	1060	100	A	20	50
153	0.25	200	600	100	A	18	35
154	0.1	200	600	100	A	20	40
120	0.1	200	600	100	A	35	60
25	0.1	200	600	100	A	36	69
63	0.25	200	1060	90	3400	15	--
61	0.25	200	1060	90	3700	130	380
118	0.25	200	260	80	A	100	650(140)
164	0.25	200	260	80	A	125	675(100)
119	0.25	200	260	80	A	115	600(110)
118	0.25	200	160	65	A	320	540
111	0.1	200	160	72	A	280	770
121	0.25	200	160	70	A	244	580
110	0.25	200	160	65	A	250	680

Note: A = glass filter.

$$O_2^*(v''=n) + ClO(ClO_2) \rightarrow O_2^*(v''=n-1) + ClO(ClO_2)$$

since, if the relaxation is stepwise, the presence of the levels higher than that followed must be taken into account. L.N.T.[21] noted that half-lives of levels lower than 6th were "slightly longer" and those for higher levels "slightly shorter" than that of the 6th level. On the basis of purely stepwise relaxation an appreciable difference would have been expected in the half-lives. If we assume that the populations of the 8th and higher levels were negligible at the start of the half-life there should have been a factor of approximately three between the half-lives of the 6th and 7th levels. On the same basis, we should have expected our value for the decay constant for the 6th level to have been lower than that of L.N.T.[21] by a factor of approximately five since we find an essentially equal population of all levels up to the 13th. Furthermore, the difference between $k_{50}(12)$ and $k_{50}(6)$ should be at least twice that observed if, as expected, the true relaxation rate for the 12th level is at least equal to that for the 6th level.

It appears either that relaxation occurs by a multi-quantum process or that it is slow enough for a near resonance exchange process

$$O_2^* (v = n) + O_2^*(v = m) \rightarrow O_2^*(v=n-1) + O_2^*(v = m+1)$$

to be competitive.

2) High Flash Energies

The rate of relaxation of O_2^* was found to be highly dependent on flash energy, the half-life of O_2^* decreasing by a factor of ∿35 where the energy was increased over the range 160 to 1060 J. This can be seen from fig.(50). This variation is illustrated for an initial pressure of 0.25 torr of ClO_2 in fig.(51) where the sharp decrease in the half-life is seen to occur over the range of energies corresponding to 40 to 60% primary photolysis. The other data are presented in Table XXIV. Also shown in fig.(51), are two theoretical curves, the calculation of which will be discussed below.

The rapid relaxation of O_2^* observed at higher energies is clearly due to species other than ClO and ClO_2 or O_2 and we propose that the species responsible for the rapid relaxation are chlorine and oxygen atoms. The complete mechanism following photolysis is thus

$$O + ClO_2 \rightarrow ClO + O_2^* \quad (7)$$

$$O + ClO \rightarrow Cl + O_2^* \quad (6)$$

$$Cl + ClO_2 \rightarrow 2\ ClO \quad (8)$$

$$ClO(ClO_2) + O_2^*(v''=n) \rightarrow ClO(ClO_2) + O_2^*(v''< n) \quad (50)$$

$$Cl + O_2^*(v''=n) \rightarrow Cl + O_2^*(v''< n) \quad (52)$$

$$O + O_2^*(v''=n) \quad O + O_2^*(v''< n) \quad (53)$$

Figure 49. Rise and Decay of O_2^*. a) Lower levels b) v" = 12

ClO_2 = 0.25 torr, Argon = 75 torr, E = 600 J

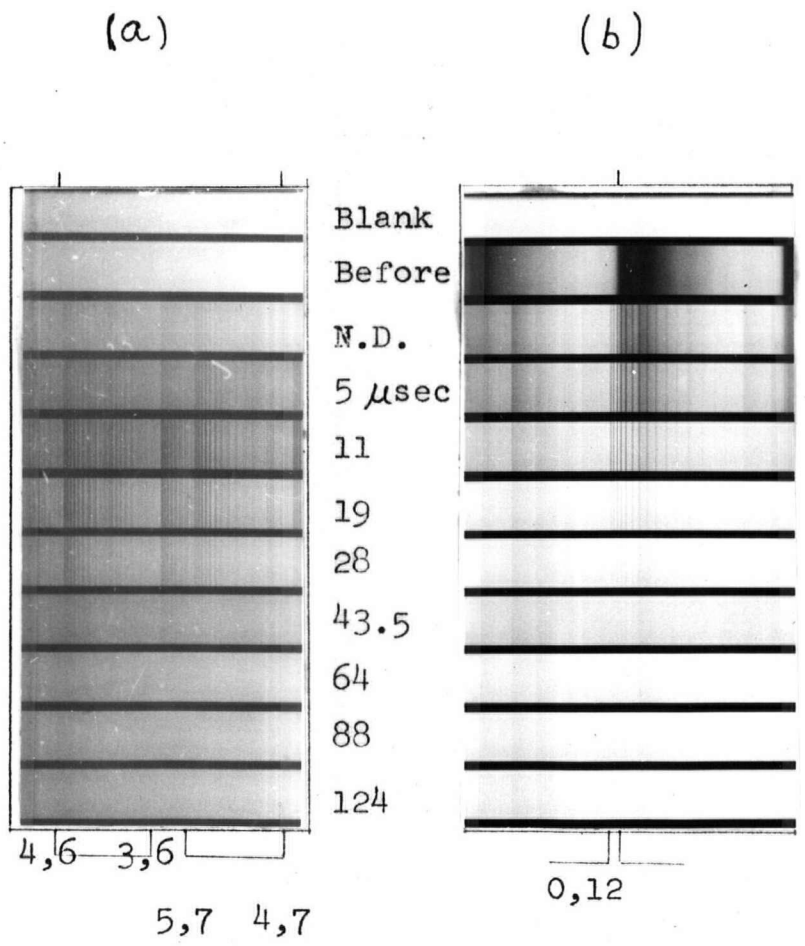


Figure 50. Decay of O_2^* (v"=12) when ClO_2 is flashed at high and low flash energies.

a) ClO_2 = 0.25 torr, Argon = 200 torr, E = 1060 J.

b) ClO_2 = o.25 torr, Argon = 200 torr, E = 260 J.

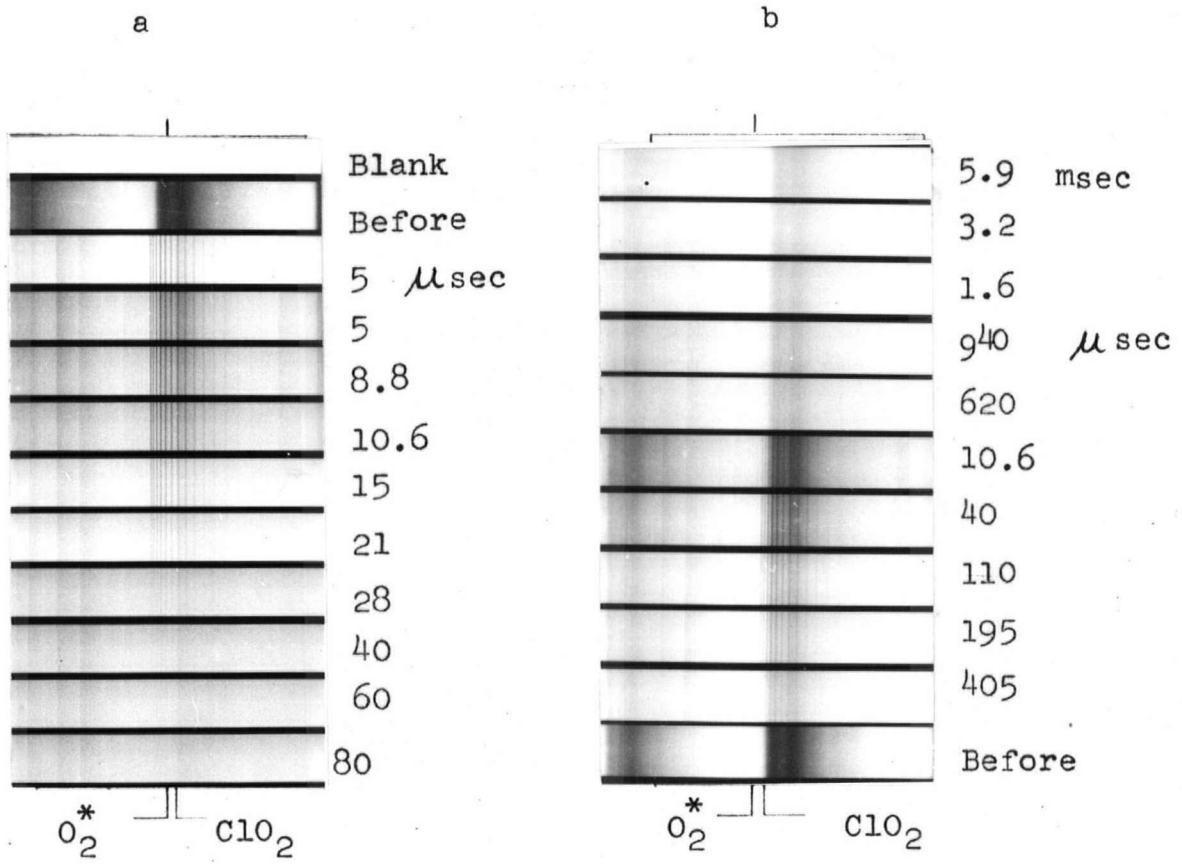
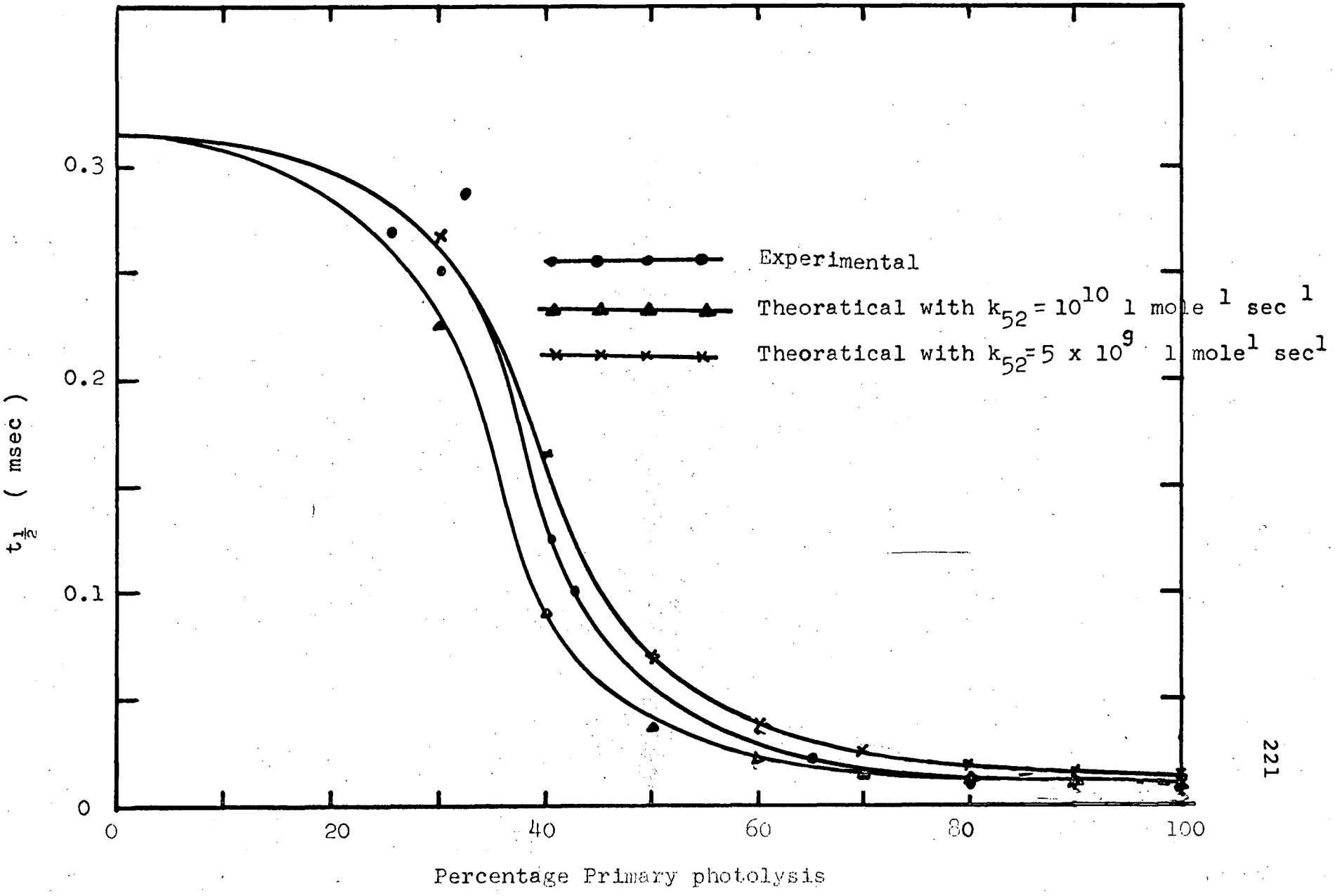


Figure 51. A plot of $t_{\frac{1}{2}}$ of O_2^* (v"= 12) against percentage primary photolysis of ClO_2.



Qualitatively this mechanism predicts the following sequence of events. At low energies when $[ClO_2] > [ClO]$ and reaction (6) is unimportant, those chlorine atoms which are produced react very rapidly with the remaining ClO_2 while the oxygen atoms react even more rapidly, so that neither contributes to the relaxation of O_2^* over the period used for measurements. As the energy increases both the total concentration of chlorine atoms produced and their life-times increase. Their presence begins to have an appreciable effect on the relaxation of O_2^*. This can be seen in fig.(48) in that the early measurements depart from the first order plot of O_2^*. Above 50% primary photolysis, the concentration of chlorine atoms produced in reaction (6) exceeds that of the ClO_2 remaining and stays essentially constant during the relaxation. This concentration thereafter increases almost linearly with energy.

At still higher energies, the oxygen atoms must be taken into account. At low and moderate energies, it is reasonable to consider the production of oxygen atoms by photolysis and their removal by reaction with ClO and ClO_2 to occur at comparable rates ($t_{1/2}(o) < 3$ μsec for 0.25 torr of ClO_2) and the concentration of oxygen atoms is very low. At very high energies, a better approximation would be to consider the photolysis to occur virtually instantaneously followed by chemical reactions. The total concentration of oxygen atoms present during the formation of O_2^* is thus increased, both by virtue of the

total photolysis and the increase of $t_{½}$ of oxygen atoms. Under these conditions, the half-life of O_2^* is comparable with that of oxygen atoms so that [O] > [Cl] during the decay of O_2^* and reaction (53) is rate determining.

The evidence in favour of this explanation is convincing. The rate constant for reaction (6) is known to be very high and the independent evidence for the importance of this reaction in the flash photolysis of ClO_2 is discussed in connection with the variation of the apparent extinction coefficient of ClO and of the initial rate of decay of ClO with flash energy. Our absolute values for k_7 and k_6 calculated on this basis are consistent with the lower limit values of Clyne and Coxon[23] and, more important for the present purpose, our value for $k_7/k_6 = 4.4$ is in excellent agreement with the value of 4 found by Clyne and Coxon.[23] The fact that the initial rapid decay of ClO at the highest energies occurs essentially after photolysis is completed, also supports the assumption that, at these energies, the oxygen atoms are major cause of rapid relaxation of O_2^*.

Further evidence can also be seen in that atoms have been proposed as very fast quenchers. It has been found that nitrogen atoms have a very high efficiency for the relaxation of $N_2(A^3\Sigma^+_u)$ in low levels (v = 0,1), the rate constants found to be 3×10^{10} l mole^{-1} sec^{-1},[104-106] and 3×10^9 l mole^{-1} sec^{-1},[107] where for higher levels an upper limit of 3×10^8 l mole^{-1} sec^{-1} has been found.[108] Oxygen atoms have

also been found to be very efficient for the vibrational relaxation of oxygen[109] and nitrogen[110] although both these systems have been studied with shock tubes at very high temperatures. The rapid relaxation of O_2^* by atoms produced from Cl_2O and ClO and the effect of Cl_2 and Cl_2O on the relaxation of O_2^* provide further evidence for the high efficiency of chlorine and oxygen atoms. These results obtained from these systems will be discussed in this chapter.

Thus the relaxation of O_2^* by atoms may be represented in terms of a strong interaction. The oxygen atoms may be forming an $O\text{-}O_2$ complex and thus resembling the ozone molecule, which is quite stable. With chlorine atoms, the Cl-O-O radical which has been proposed in the photolysis of Cl_2/O_2, has been observed in U.V. spectrum.[18] Since both the chlorine and oxygen are paramagnetic, their attraction for O_2^* is quite likely.

The mechanism was also tested quantitatively in the following manner.

a) Relaxation of O_2^* by chlorine atoms

The total concentration of chlorine atoms produced for each percentage primary photolysis was calculated at intervals of 10%. For these calculations, the ratio of k_7/k_6 was taken to be 4.4 and for each, the calculation included the effect of changing ClO_2 and ClO concentration as the photolysis and the oxygen atom reaction proceeded. The final ClO_2 and ClO concentration were thus calculated. For the 0 to 60% photolysis, the

rate of production of oxygen atoms by photolysis was assumed to be sufficiently slow for the oxygen atom to be removed by reaction with ClO_2 and ClO as fast as they are produced. The calculation was repeated for another extreme assumption, i.e., all oxygen atoms are produced instantaneously and then react. It can be seen from the Table XXV that there is only a difference of three to four percent between the two. For 70 to 100% photolysis, the latter assumption had to be used to obtain 70% photolysis and in fact 85% photolysis was achieved experimentally, which is further evidence for the importance of oxygen atoms at the highest energies. The results of these calculations are shown in Table XXV, the concentration of all species being given as a percentage of the initial ClO_2 concentration.

Table XXV

Concentrations of ClO_2, ClO and Cl Atoms Present After the Primary Photolysis and Chemical Reactions

% Photolysis	$[ClO_2]$ %	[ClO] %	[Cl] %	$[ClO_2]$ %	[ClO] %	[Cl] %
10	80.2	19.5	0.3	80.2	19.5	0.3
20	61.3	37.3	0.4	61.1	37.8	1.1
30	43.7	52.6	3.7	42.8	54.4	2.8
40	27.8	64.4	7.8	25.8	68.4	5.8
50	14.7	70.7	14.6	11.0	78.0	11.0
60	5.4	69.2	25.4	0.5	79.0	20.5
70	1.0	58.1	40.9			
80	--	40.0	60.0			
90	--	20.0	80.0			
100	--	--	100.0			

The half-life of O_2^* for the 12th level was calculated as follows.

For less than 40% photolysis, the removal of chlorine atoms by ClO_2 in the reaction (8) was taken to be psuedo first order, using average value of ClO_2 concentration and our value of $k_8 = 5.0 \times 10^9$ l mole^{-1} sec^{-1}. For 50% photolysis, the second order equation was used. For 60% photolysis, the chlorine atom concentration is given by equation (s). The appropriate equations are then

$$[Cl] = [O]_o - \frac{a}{b\, e^{k_6\, a t_{-1}}} + [Cl]_o \qquad (s)$$

where $a = [ClO]_{1o} - [O]'_o$

$$b = \frac{[ClO]_{1o}}{[O]'_o}$$

For less than 40% photolysis

$$\ln 2 = \frac{k'_{52}}{k'_8} \left(1 - e^{-k'_8\, t_{1/2}} \right) + k'_{50} t_{1/2} \qquad (t)$$

When the primary photolysis = 50%,

$$\ln 2 = \frac{k_{52}}{k_8} \ln (1 + k''_8\, t_{1/2}) + k'_{50}\, t_{1/2} \qquad (u)$$

and if the primary photolysis $\geq$ 60%,

$$\ln 2 = k_{52} t_{1/2} ([O]_o + a + [Cl]_o) - \frac{k_{52}}{k_6} \ln \left(\frac{b\, e^{k_6 a\, t_{1/2}} - 1}{b - 1} \right) \qquad (v)$$

where $k'_{52} = k_{52}[Cl]_o$

$k'_8 = k_8[ClO_2]$

$k''_8 = k_8[ClO_2]_o$

$k'_{50} = k_{50}([ClO_2]_o + [ClO]_o)$

The details of the above equations have been discussed in Appendix 2.

The results for the trial values of $k_{52} = 5 \times 10^9$ and 10×10^9 l mole^{-1} sec^{-1} were calculated and listed in Table XXVI. The $t_{1/2}$ was plotted in fig.(51). The value of 320 μsec was assumed to correspond to the lowest possible energy. A value of $k_{52} = 7 \times 10^9$ l mole^{-1} sec^{-1} is thus obtained from the fit at moderate energies where the effect of oxygen atoms is unlikely to be important. The value of k_{52} was calculated at the highest energy corresponding to 82% primary photolysis assuming that oxygen atoms do not play any part in the relaxation. A value of 2×10^{10} l mole^{-1} sec^{-1} was obtained for k_{52} but this value does not satisfy the experimental plot and was thus rejected.

b) Relaxation by oxygen atoms

At the highest energy, when the primary photolysis is around 85%, the oxygen atoms are in much greater concentration than chlorine atoms. An equation for the relaxation of O_2^* by oxygen atoms was derived by assuming that all the ClO_2 has been

Table XXVI

Calculated Half-life of O_2^* at Various % Primary Photolysis of ClO_2 Using Equations (t), (u), (v)

Prim. Photo. %	$t_{1/2}(12,0)$ μsec A	B
0	320	320
30	240	200
40	165	90
50	50	30
60	38	24
70	30	18
80	20	13
90	13	10
100	11	8

Note: A = half-lives are calculated with $k_{52} = 5.0 \times 10^9$ $1\ mole^{-1}\ sec^{-1}$;

B = half-lives are calculated with $k_{52} = 10.0 \times 10^9$ $1\ mole^{-1}\ sec^{-1}$.

decomposed by the time (10 μsec) measurements were started. It has been actually observed that at this time the ClO_2 concentration was always <5%. The oxygen atom's concentration was calculated in the same manner as described in Chapter IV, section A, i.e. $[ClO]_o - [ClO]'_o$. The equation obtained (details as described in Appendix 2) is:

$$-\frac{d[O_2^*]}{dt} = k_{53}[O] + k_{52}([Cl]_o + [Cl]_t)$$

$$[O] = \frac{a}{b\, e^{k_6 a\, t} - 1}$$

$$[Cl] = [O]_o - \frac{a}{b\, e^{k_6 a\, t} - 1}$$

$$\ln 2 = a\left(\frac{k_{53} - k_{52}}{k_6}\right)\left[\frac{\ln b\, e^{k_6 a\, t_{1/2}} - 1}{k_6\, a\, (b-1)} - t_{1/2}\right]$$

$$+ k_{52}[O]_o t_{1/2} + k_{52}[Cl]_o t_{1/2}$$

where $a = [ClO]_{1o} - [O]'_o$

$$b = \frac{[ClO]_{1o}}{[O]'_o}$$

Substituting the experimental values of $t_{1/2}$, k_7, k_6, k_{50} and k_{52}, the values of k_{53} obtained are listed in Table XXVII. The average of three experiments is $1.8 \pm 0.8 \times 10^{10}$ l mole^{-1} sec^{-1}. Though there is a variation of a factor of two among the results themselves, considering the measurements of the half-life of O_2^* the agreement is not bad. It was found that an error of 10% in $t_{1/2}$ of O_2^* would make an error of 25% in the final value of k_{53}.

Table XXVII

Rate Constants for Quenching of O_2^* (0,12) by ClO, ClO_2, Cl and O atoms

Plate no.	$[ClO_2]$ torr	Argon torr	Energy J	Prim. Photo. %	$k_{50}\times10^{-8}$ (l mole^{-1} sec^{-1})	$k_{52}\times10^{-9}$ (l mole^{-1} sec^{-1})	$k_{53}\times10^{-9}$ (l mole^{-1} sec^{-1})
107	.08	75	1060	85	--	--	18
152	.25	200	1060	80	--	--	10
154	.09	200	600	62	--	--	25
						7.0	--
118	0.25	200	160	30	1.6	--	--
121	0.1	200	160	30	1.8	--	--
110	0.1	200	160	30	2.0	--	--
			Average		1.8±.2	7.0	1 8±7

3) Effect of Cl_2O on the Relaxation of O_2^*

ClO_2 was flashed in the presence of Cl_2O with the ratios varied from 1:4 to 1:20. The total pressure of argon was kept constant at 200 torr. The flash energies used were enough to cause primary photolysis of ClO_2 from 22 to 85%. A Corning 0-52 filter was used to prevent the photolysis of Cl_2O. The

half-life of the 12th level was measured and is listed in Table XXVIII. The $t_{1/2}$ in comparable experiments without Cl_2O are also listed for comparison. The lower levels could not be measured due to the Cl_2O continuum. The difference in the behaviour of O_2^* with and without Cl_2O is illustrated in fig. (52).

It can be seen from Table XXVIII that $t_{1/2}$ of 12th level has been increased dramatically by Cl_2O, the extent depending upon its pressure. No quantitative measurements were made but the results can be explained qualitatively with the help of results described in the case of ClO_2 alone. It is clear that Cl_2O acts as a scavenger for both oxygen and chlorine atoms and thus helps in decreasing the relaxation rate. This can be seen from the following example. For an initial pressure of 0.1 torr of ClO_2 and 85% primary photolysis, approximately 70% of oxygen atoms will react with ClO to give chlorine atoms. The half-life of oxygen atoms is nearly equal to that of O_2^*. But in the presence of 0.4 torr of Cl_2O, the half-life of oxygen atoms is reduced from 8 to$\sim$4 μsec and at the same time only 14% instead of 70% of the oxygen atoms will react with ClO to give chlorine atoms. In the presence of Cl_2O, the half-life of chlorine atoms is also reduced to 30 to 60 μsec, depending upon the pressure of Cl_2O.

At low flash energies, the Cl_2O, as expected from this argument, is found to have much less effect.

Figure 52. Rise and Decay of $O_2^*(v''=12)$ when ClO_2 is flashed with and without Cl_2O.

a) ClO_2 = 0.25 torr, Argon=200 torr, E = 1060 J.

b) ClO_2 0.25 torr, Cl_2O = 1.0 torr, Argon = 200 torr, E = 1060 J.

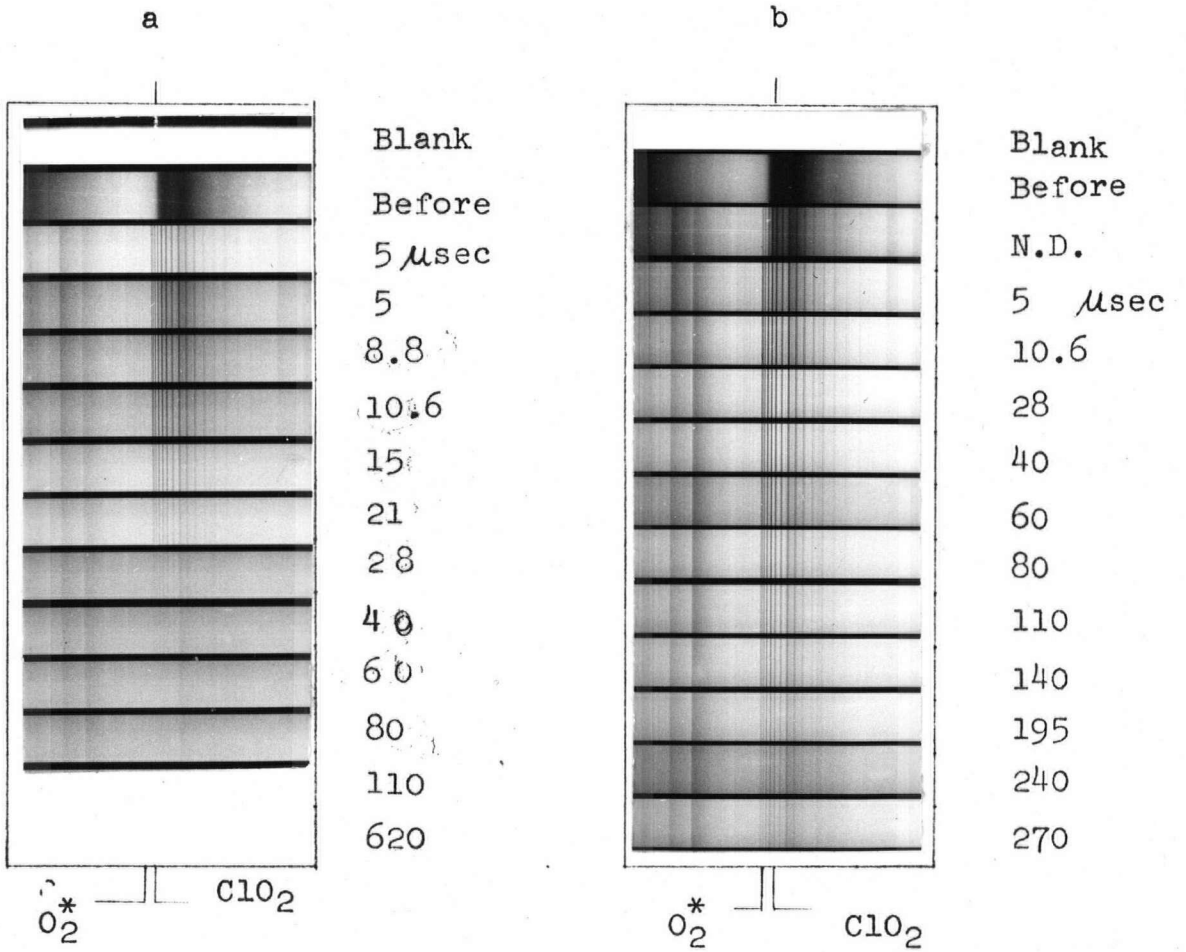


Table XXVIII

Comparison of $t_{1/2}$ of O_2^* (0,12) level With and Without Cl_2O Using 3400 Å Filter

Plate no.	$[ClO_2]$ (10^{-6}M)	$[Cl_2O]$ (10^{-6}M)	Energy J	Prim.Photo. %	$t_{1/2}$ (μsec)
63	13.7	--	1060	85	15
64	13.7	55.0	1060		120
155	5.5	--	1060	85.0	19
65	5.5	22.0	1060		230
66	1.4	27.5	1060		250
177	4.0	--	600	40.0	103
177	4.0	44.0	600		236
180	4.7	--	600	40.0	130
180	4.7	36.2	600		200
179	4.8	--	260	30	206
179	4.8	36.2	260		315
176	4.1	--	260	22	200
176	4.1	57.0	260		270

4) Effect of Chlorine on the Relaxation of O_2^*

Mixtures of ClO_2 and Cl_2 (in the ratios of 1:5 to 1:10) were flashed using flash energies of 1060, 260 and 160 J. Two filters, 3700 and 3100 Å, were used. The half-life of the 12th

level was measured and is listed in Table XXIX. For comparison $t_{1/2}$ without Cl_2, is also listed in Table XXIX. The difference in the behaviour of O_2^* with and without Cl_2 is illustrated in fig. (53).

It can be seen from Table XXIX that at each flash energy the half-life is decreased in the presence of Cl_2. It also decreases with increase of Cl_2 pressure at the same energy. The above results can easily be explained with the help of the previous results, i.e., chlorine atoms are efficient in removing the O_2^*. It is, however, also possible that the effect is due to the chlorine molecule rather than atoms, since it was not possible to vary the chlorine atom concentration at the same Cl_2 pressure without simultaneously changing the degree of photolysis of ClO_2 which itself changes the rate of relaxation of O_2^*. An attempt was made to differentiate between the effect due to chlorine atoms and chlorine molecules by varying the flash energy over a 4-fold range using 3700 Å filter. Since the absorption of Cl_2 and ClO_2 are in the same region, the results of these experiments were equivocal, being equally well explained by relaxation by chlorine molecules with a rate constant 6.5×10^7 l mole^{-1} sec^{-1} or by chlorine atoms with a rate constant of 2.8×10^9 l mole^{-1} sec^{-1}. The latter possibility is reasonably consistent with our previous estimate though no firm conclusion can be drawn until the relaxation of O_2^* by chlorine has been independently measured, no data on this has yet been seen in the literature.

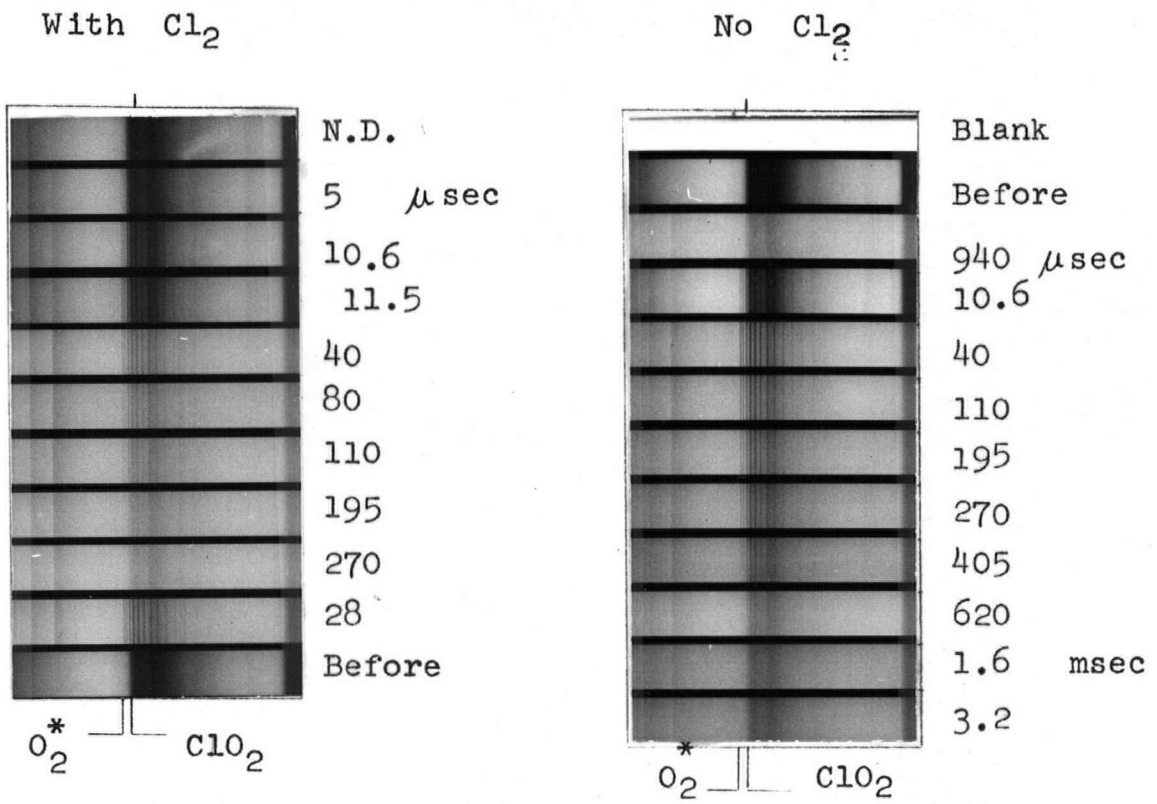


Figure 53. Comparison of Decay of O_2^* (0,12) level following the flash photolysis of ClO_2 in the presence and absence of Cl_2.

ClO_2 = 0.25 torr, Cl_2 = 2.5 torr, Argon = 200 torr, E = 260 J, Filter = Glass filter A.

Table XXIX

Comparison of $t_{1/2}$ of $O_2^*(0, 12)$ Level With and Without Cl_2

Plate no.	$[ClO_2]$ torr	$[Cl_2]$ torr	Filter	Prim. Photo. %	Energy J	$t_{1/2}$(μsec)
40	0.25	--	--	85	1060	10
46	0.25	2.5	--	85	1060	7
61	0.25	--	3700	45	1060	130
62	0.25	2.5	3700	45	1060	55
164	0.25	--	R	40	260	125
164	0.25	2.5	P	40	260	45
118	0.25	--	P	30	160	320
59	0.25	1.25	P	30	160	95
59	0.25	2.5	P	30	160	60

5) Decay of Excited Oxygen in Case of Cl_2O and ClO Photolysis

The relaxation of the half-life of 12th level was measured for four flash energies, using both pyrex and quartz reaction vessels. Measurements of lower levels were not possible because the continuum of Cl_2O was always present. The results are listed in Table XXX.

No attempt was made to calculate the rate constant of quenching of O_2^* by various species. Because of the two primary processes it is difficult to calculate the amount of oxygen and chlorine atoms formed. The results confirm the theory developed

from the ClO_2, ClO_2/Cl_2O systems (i.e., chlorine and oxygen atoms play the important role in the relaxation of O_2^*). For the same flash energy and pressure, the half-life of O_2^* produced from Cl_2O is greater than that produced from ClO_2. This can be explained as follows.

Firstly, the extinction coefficient of Cl_2O is much less than the ClO_2 and therefore there is a lower percentage of primary photolysis and lower concentration of chlorine and oxygen atoms. Secondly, the concentration of Cl_2O present after the primary photolysis is always higher than ClO_2 and the larger proportion of atoms will react with Cl_2O rather than quenching O_2^*.

It has also been observed that at the same initial pressure of Cl_2O, the half life decreases with increase in the flash energy as can be seen from fig. (54). The increase of flash energy will increase the production of atoms and decrease the Cl_2O concentration and hence increase the rate of relaxation of O_2^*.

In the flash photolysis of ClO radical, only a low concentration of O_2^* is formed and the decay was rapid. The spectrum was too weak to do any quantitative measurements. Qualitatively, however, the results support the conclusion drawn previously. The rapid relaxation can be explained by the presence of chlorine atoms produced in the primary process as

Figure 54. A first order plot of O_2^*.

Cl_2O = 1.0 torr, Argon = 200 torr, E = 1060 J.

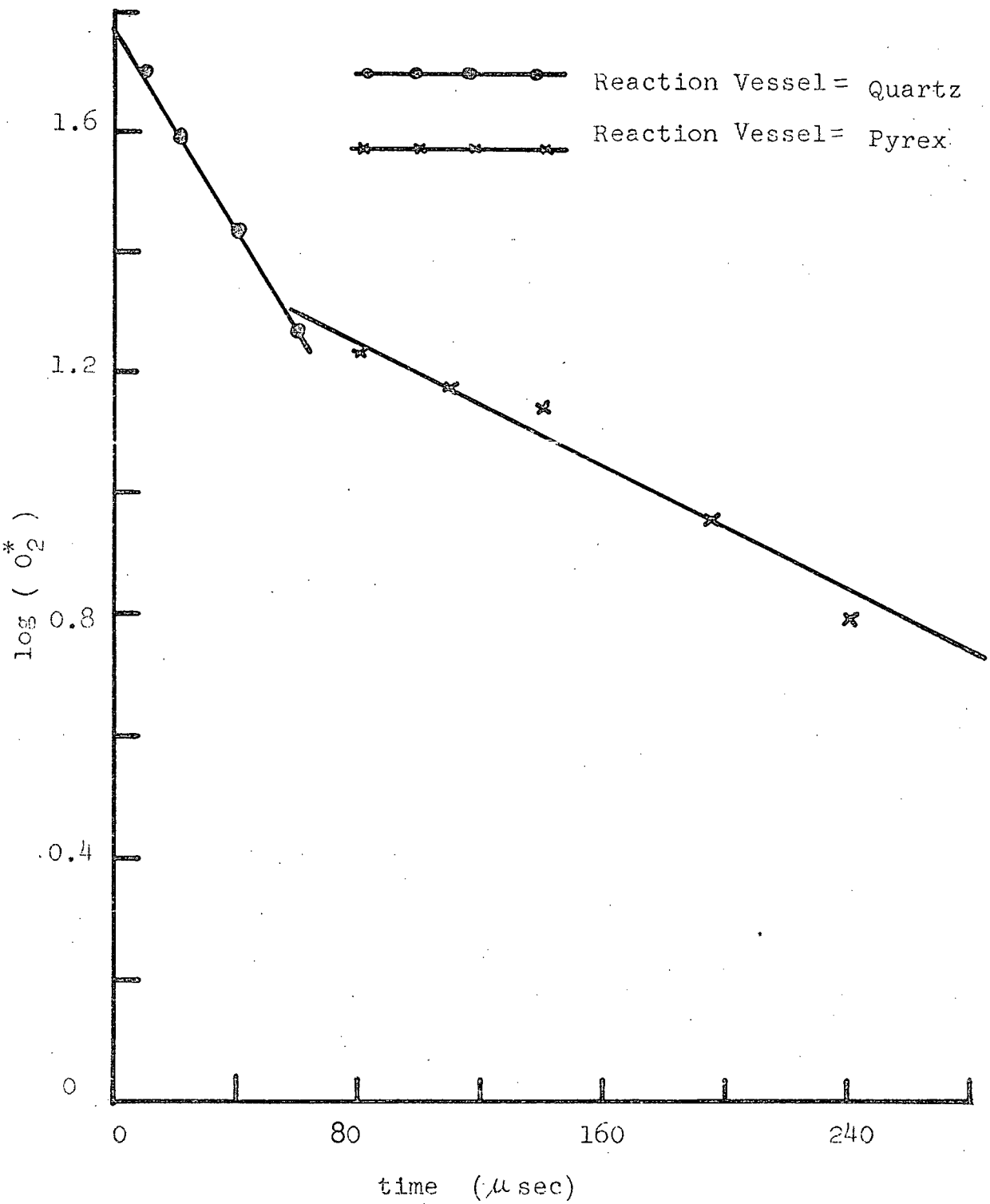


Table XXX

Half-Lives for the $O_2^*(0,12)$ following the flash photolysis of Cl_2O.

Plate no.	R.V.	$[Cl_2O]$ torr	Argon torr	Energy J	$t_{1/2}(0,12)$ (μsec)
5	P	1.0	100	800	125
70	P	1.0	200	1060	120
71	P	0.5	200	1060	150
3	Q	1.0	200	800	17
6	Q	1.0	100	800	15
7	Q	0.5	75	800	27
77	Q	0.5	200	600	35
79	Q	1.0	200	260	35
80	Q	0.5	200	260	60
81	Q	0.25	200	260	85
102	Q	1.0	200	600	38

well as by the chlorine atoms remaining from the first flash and formed by reaction (6). The chlorine atom concentration was calculated directly from reactions (6-1) and (6-2) and that remaining from the first flash taking into account the recombination of chlorine atoms found by Linnett and Booth[79] and Bader and Ogryzlo.[29,30] Taking 1.8×10^{10} l mole^{-1} sec^{-1}

and 7×10^9 l mole^{-1} sec^{-1} for k_{53} and k_{52}, respectively, and the concentrations of atoms found above, the half-life for the 12th level was found to be between 5 to 20 μsec, depending upon the initial ClO_2 pressure and ClO concentration before the auxiliary flash. The experimental value for the total life time was found to vary from 20 to 60 msec and thus the agreement is quite good.

CHAPTER VII

CONCLUSION

The flash photolysis of ClO_2 at room temperature and with radiation of 2800 to 3700 Å has been investigated. The following reactions have been shown to occur and to account completely for all observations.

$ClO_2 + h\nu \rightarrow ClO + O$

$O + ClO_2 \rightarrow ClO + O_2^*(v'' \leq 15)$ $\quad k_7 = 3.1 \times 10^{10}$ l mole^{-1}sec^{-1}

$O + ClO \rightarrow Cl + O_2^*(v'' \leq 14)$ $\quad k_6 = 7 \times 10^9$ l mole^{-1}sec^{-1}

$2\ ClO \rightarrow Cl_2 + O_2$ $\quad k_5 = 2.7 \times 10^7$ l mole^{-1} sec^{-1}

$ClO(ClO_2) + O_2^*(v''=12) \rightarrow ClO(ClO_2) + O_2^*(v''<12)$

$\quad k_{50} = 2 \times 10^8$ l mole^{-1} sec^{-1}

$ClO(ClO_2) + O_2^*(v''=6) \rightarrow ClO(ClO_2) + O_2^*(v''<6)$

$\quad k_{50} = 0.8 \times 10^8$ l mole^{-1}sec^{-1}

$Cl + O_2^*(v''=12) \rightarrow Cl + O_2^*(v''<12)$ $\quad k_{52} = 7 \times 10^9$ l mole^{-1}sec^{-1}

$Cl + O_2^*(v''=6) \rightarrow Cl + O_2^*(v''<6)$ $\quad k_{52} = 2 \times 10^9$ l mole^{-1} sec^{-1}

$O + O_2^*(v''=12) \rightarrow O + O_2^*(v''<12)$ $\quad k_{53} = 2 \times 10^{10}$ l mole^{-1} sec^{-1}

$O + O_2^*(v''=6) \rightarrow O + O_2^*(v''<6)$ $\quad k_{53} = 9 \times 10^9$ l mole^{-1} sec^{-1}

The mechanism differs from the mechanism originally proposed by the addition of reactions 6, 52 and 53 and by the omission of reactions involving ClO_3 and Cl_2O_3 and it extends earlier work by the measurements of the rate constants k_7, k_6, k_{52}, k_{53} and $k_{50}(v''=12)$. A further important difference between the present study and previous work is the demonstration

that the energy of highest vibrational level of O_2^* produced in reactions 7 and 6 is that corresponding to the exothermicity of the reactions (59, 55 Kcals) rather than to v'' = 8 (34 Kcals).

Measurements of the relative values for k_7 for the levels v'' = 5 to v'' = 13 have shown that these are approximately equal. Unless there is a discontinuity in the values for k_7 for the levels v'' = 0 to v'' = 5, it follows that the major part of the energy of the reaction appears initially in the form of vibrational excitation of O_2.

The exceptionally high values of k_{52} and k_{53} are explained by the strong interaction between Cl and O atoms and O_2^* which may lead to the transient formation of the intermediates Cl-O-O and O-O-O.

The flash photolysis of Cl_2O and the chlorine and bromine photosensitised decomposition of Cl_2O have been studied. The rate constants for all the reactions involved have been measured.

$Cl_2O + h\nu \rightarrow ClO + Cl$

$Cl_2 + h\nu \rightarrow 2\ Cl$

$Br_2 + h\nu \rightarrow 2\ Br$

$Cl + Cl_2O \rightarrow ClO + Cl_2$	$k_{19} = 4.1 \times 10^8$ l mole^{-1} sec^{-1}
$Br + Cl_2O \rightarrow BrCl + ClO$	$k_{25} = 6.1 \times 10^8$ l mole^{-1} sec^{-1}
$ClO + Cl_2O \rightarrow ClO_2 + Cl_2$	$k_{20} = 2.6 \times 10^5$ l mole^{-1} sec^{-1}
$ClO + Cl_2O \rightarrow Cl + Cl_2 + O_2$	$k_{21} = 6.5 \times 10^5$ l mole^{-1} sec^{-1}
$ClO + ClO \rightarrow Cl_2 + O_2$	$k_5 = 2.9 \times 10^7$ l mole^{-1} sec^{-1}

The values obtained for rate constants k_{20} and k_{21} are higher by factor 3 and 10 than those previously reported, while the value for k_{19} agrees with the value previously given as a lower limit. Reaction 25 is of interest in that the alternative reaction

$$Br + Cl_2O \rightarrow BrO + Cl_2$$

does not occur.

The quantum yield for the photolysis and chlorine photosensitised decomposition of Cl_2O has been measured and found to agree with that predicted from the values of the rate constants found.

The flash photolysis of mixtures of Cl_2O and ClO_2 has been used to measure the value of the rate constant

$$O + Cl_2O \rightarrow 2\ ClO \qquad k_{35} = 5.3 \times 10^9\ 1\ mole^{-1} sec^{-1}$$

and it has been shown that the alternative reaction

$$O + Cl_2O \rightarrow O_2 + Cl_2$$

does not occur to a measurable extent. A significant new result of the study of Cl_2O is the observation that O_2^* is produced by reaction 6 following the secondary photolysis of ClO.

The rate constants for the reactions

$$Cl + ClO_2 \rightarrow 2\ ClO \qquad k_8 = 5.0 \times 10^9\ 1\ mole^{-1}\ sec^{-1}$$

$$Br + ClO_2 \rightarrow BrO + ClO \qquad k_{16} = 7.2 \times 10^9\ 1\ mole^{-1}\ sec^{-1}$$

have been measured by flash photolysing mixtures of Cl_2 and Br_2 with ClO_2. It has been established that neither of the reactions

$$Cl + ClO_2 \rightarrow Cl_2 + O_2 \qquad (12)$$

$$Br + ClO_2 \rightarrow BrCl + O_2 \qquad (14)$$

are significant. This contradicts previous results (obtained by a flow technique) in which the absence of BrO as an observable product of reaction 16 and the presence of electronically excited BrCl lead to the proposal that reaction 14 predominated. The extinction coefficient of BrO radical has been measured and using this value and the measured rate of decay of BrO produced by flashing Br_2/O_2 and Br_2/ClO_2 mixtures, absolute rate constants for the reactions of BrO with BrO and ClO have been measured:

$$BrO + ClO \rightarrow BrCl + O_2 \qquad k_{40} = 1.5\times10^9 \text{ l mole}^{-1} \text{ sec}^{-1}$$

$$BrO + BrO \rightarrow Br_2 + O_2 \qquad k_{39} = 1.3\times10^9 \text{ l mole}^{-1} \text{ sec}^{-1}$$

Reaction 40 could explain the production of $BrCl^*$ ($^3\pi^o_+$ $v \leq 8$). Another interesting feature of these reactions is that their rate constants are so much higher than k_5.

k_5 itself is interesting in that there appears to be two mechanisms for the reaction. The values previously obtained by flash photolysis of ClO_2, Cl_2O and of Cl_2/O_2 mixtures lie in the range 1.9 to 8.3×10^7 l mole^{-1} sec^{-1}. These values have been measured and the reaction also studied using Cl_2O/ClO_2

and Cl_2/Cl_2O as sources of ClO. The same value has been obtained from all systems and is independent of total pressure in the range 75 to 200 torr. The value of 1.4×10^7 l mole^{-1} sec^{-1} obtained at low (1 to 4 torr) pressure by a fast flow technique appears to be reliable and the mechanism at these pressures involves the formation of peroxy radical

$$2\ ClO \rightarrow ClOO + Cl$$

$$Cl + ClOO \rightarrow Cl_2 + O_2$$

The possible involvement of a common intermediate $(ClO)_2$ is discussed.

The overall mechanism for the bromine photosensitised decomposition of ClO_2 appears to be complex with evidence that a very rapid recombination of Br atoms occurs in the presence of ClO_2, possibly due to the formation of $ClO_2 \cdot Br$ complex.

A new technique has been developed whereby the products of flash photolysis can themselves be flash photolysed. This technique has been applied to the ClO radical and has contributed significantly to the conclusions reached on reactions 6, 52 and 53.

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APPENDICES

APPENDIX I

Quantum Yield of Cl_2O Decomposition by ClO

After the photolytic flash and the reaction of chlorine atoms with Cl_2O, the reactions taking place in this system are

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (5)$$

$$ClO + Cl_2O \rightarrow ClO_2 + Cl_2 \quad (20)$$

$$ClO + Cl_2O \rightarrow Cl + Cl_2 + O_2 \quad (21)$$

$$Cl + Cl_2O \rightarrow ClO + Cl_2 \quad (19)$$

and the decay of ClO and Cl_2O can be written as

$$-\frac{d[ClO]}{dt} = k_5[ClO]^2 + k_{20}[ClO][Cl_2O]$$

$$-\frac{d[Cl_2O]}{dt} = k_{20}[ClO][Cl_2O] + 2k_{21}[ClO][Cl_2O]$$

$$= (k_{20} + 2\,k_{21})[ClO][Cl_2O]$$

Dividing the two equations

$$\frac{d[ClO]}{d[Cl_2O]} = \frac{k_5[ClO]^2 + k_{20}[ClO][Cl_2O]}{(k_{20} + 2\,k_{21})[ClO][Cl_2O]} = \frac{k_{20}}{k_{20}+2k_{21}} + \frac{k_5}{k_{20}+2k_{21}}\frac{[ClO]}{[Cl_2O]}$$

Let $x = [ClO]$

$y = [Cl_2O]$

$$\frac{k_{20}}{k_{20} + 2k_{21}} = a \qquad \text{and} \qquad \frac{k_5}{k_{20} + 2k_{21}} = b$$

So the above equation becomes

$$\frac{dx}{dy} = a + b\frac{x}{y}$$

or

$$\frac{dx}{dy} - b\frac{x}{y} = a$$

which is a standard form of the equation of type

$$\frac{dx}{dy} - P(y)x = Q(y)$$

where $P(y) = \frac{b}{y}$ and $Q(y) = a$

The solution of the above equation is

$$x = c\,y^b + \frac{y\,a}{1-b}$$

where c = constant of integration

when $[ClO] = 0$, $[Cl_2O] = [Cl_2O]_\infty$

i.e. $x = 0$, $y = y_\infty$

and $c = -\frac{y_\infty a}{(1-b)\,y_\infty^{\,b}} = \frac{a}{(b-1)y_\infty^{\,b-1}}$

therefore $x = \frac{a\,y^b}{(b-1)y_\infty^{\,b-1}} - \frac{y\,a}{(b-1)} = \frac{y\,a}{b-1}\left[\left(\frac{y}{y_\infty}\right)^{b-1} - 1\right]$

or $\frac{x}{y} = \frac{a}{b-1}\left[\left(\frac{y}{y_\infty}\right)^{b-1} - 1\right]$

If $x = x_o$, $y = y_o$ $\qquad [ClO] = [ClO]_o$

$[Cl_2O] = [Cl_2O]_o$

$$\frac{x_o}{y_o} = \frac{a}{b-1}\left[\left(\frac{y_o}{y_\infty}\right)^{b-1} - 1\right]$$

or $$\left(\frac{y_o}{y_\infty}\right)^c = \frac{c}{a}\frac{x_o}{y_o} + 1 \qquad [b-1 = c]$$

or $$\frac{y_o}{y_\infty} = \left(1 + \frac{c}{a}\frac{x_o}{y_o}\right)^{1/c}$$

$$\frac{y_\infty}{y_o} = \left(1 + \frac{c}{a}\frac{x_o}{y_o}\right)^{-1/c}$$

$$\frac{y_o - (y_o - y_\infty)}{y_o} = \left(1 + \frac{c}{a}\frac{x_o}{y_o}\right)^{-1/c}$$

$$1 - \frac{\Delta y_\infty}{y_o} = \left(1 + \frac{c}{a}\frac{x_o}{y_o}\right)^{-1/c}$$

$$\Delta y_\infty = \Delta[Cl_2O]_\infty = y_o\left[1 - \left(1 + \frac{c}{a}\frac{x_o}{y_o}\right)^{-1/c}\right]$$

$$\phi = \frac{\Delta[Cl_2O]_\infty}{[ClO]_o} = \frac{[Cl_2O]_o}{[ClO]_o}\left[1 - \left(1 + \frac{c}{a}\frac{[ClO]_o}{[Cl_2O]_o}\right)^{-1/c}\right]$$

APPENDIX II

Chlorine Atom Concentration

a) For less than 40% photolysis, the removal of chlorine atoms by ClO_2, reaction (8), was taken as psuedo first order

$$[Cl] + ClO_2 \rightarrow 2\ ClO \qquad (8)$$

Thus the chlorine atoms concentration can be given as

$$-\frac{d[Cl]}{dt} = k_8[ClO_2][Cl] = k_8'[Cl]$$

where $k_8' = k_8[ClO_2]$

$$[Cl] = [Cl]_o\, e^{-k_8' t}$$

b) For 50% primary photolysis, the second order equation was used because the amount of chlorine atoms produced will be nearly same as $[ClO_2]$ left. So the chlorine atom

$$-\frac{d[Cl]}{dt} = k_8[Cl][ClO_2] = k_8[Cl]^2 \qquad [Cl] = [ClO_2]$$

concentration can be represented in terms of ClO_2

$$[Cl] = \frac{[Cl]_o}{1 + k_8[Cl]_o t} = \frac{[ClO_2]_o}{1 + k_8[ClO_2]_o t}$$

c) For $\geq$ 60% photolysis, the chlorine atom produced by reaction (6)

$$O + ClO \rightarrow O_2^* + Cl \qquad (6)$$

is given by

$$\frac{d[Cl]}{dt} = -\frac{d[O]}{dt} = k_6[O][ClO]$$

since the decay of chlorine atoms in the absence of ClO_2 is negligible over the period concerned. The other assumption involved is that by the time the measurements were started, ClO_2 has been decomposed and the oxygen atom concentration can be calculated as described in Chapter IV-A, i.e.,

$$[O]_o = [ClO]_o - [ClO]_o'$$

Also, at the time of measurements (10 μsec), some of the oxygen atoms must have been reacted with ClO to give chlorine atoms. This can be calculated from fig.(12) as follows:

$$[Cl]_o = [O]_o - [O]_o'$$

where $[O]_o^1$ = concentration of oxygen atoms at 10 μsec and this can be determined as

$$[O]_o' = [ClO]_{10} - [ClO]_{10}'$$

Now $[ClO] = [ClO]_{10} - ([O]_o' - [O]) = [ClO]_{10} - [O]_o' + [O]$

therefore $-\frac{d[O]}{dt} = k_6[O]([ClO]_{10} - [O]_o' + [O])$

$$[O] = \frac{a}{b\, e^{k_6 a t} - 1}$$

where $b = \frac{[ClO]_{10}}{[O]_o'}$ and $a = [ClO]_{10} - [O]_o'$

and $[Cl] = [O]_o^1 - \frac{a}{b\, e^{k_6 at} - 1}$

Thus the total concentration of chlorine atoms is

$$[Cl] = [Cl]_o + [O]'_o - \frac{a}{b\, e^{k_6 at} - 1}$$

Relaxation of O_2^*

Neglecting the effect of oxygen atoms, the relaxation of O_2^* can be represented as

$$- \frac{d[\ln O_2^*]}{dt} = k_{52}[Cl] + k_{50}([ClO] + [ClO_2])$$

a) For $\leq$ 40% photolysis,

$$- \frac{d[\ln O_2^*]}{dt} = k_{52}[Cl]_o\, e^{-k_8' t} + k_{50}([ClO] + [ClO_2])$$

$$= k_{52}'\, e^{-k_8' t} + k_{50}'$$

where $k_{52}' = k_{52}[Cl]_o$ and $k_{50}' = k_{50}([ClO] + [ClO_2])$

$$\text{or} \quad - \ln[O_2^*] = - \frac{k_{52}'}{k_8'}\, e^{-k_8' t} + k_{50}'\, t + c$$

when $t = 0$, $[O_2^*] = [O_2^*]_o$

$$\text{or} \quad - \ln[O_2^*]_o = - \frac{k_{52}'}{k_8'} + C$$

$$\text{or} \quad c = -\ln[O_2^*]_o + \frac{k_{52}'}{k_8'}$$

$$\text{therefore} \quad \ln \frac{[O_2^*]_o}{[O_2^*]} = \frac{k_{52}'}{k_8'} (1 - e^{-k_8' t}) + k_{50}'\, t$$

when $t = t_{1/2}$, $[O_2^*] = \frac{1}{2}[O_2^*]$

$$\ln 2 = \frac{k'_{52}}{k'_8}\left(1 - e^{-k'_8 t_{1/2}}\right) + k'_{50}\, t_{1/2}$$

b) For 50% photolysis,

$$-\frac{d[\ln O_2^*]}{dt} = k_{52}\frac{[ClO_2]_o}{1 + [ClO_2]_o k_8 t} + k'_{50}$$

when $t = 0$, $[O_2^*] = [O_2^*]_o$

and also $t = t_{1/2}$, $[O_2^*] = \frac{1}{2}[O_2^*]$

therefore $$\ln 2 = \frac{k_{52}}{k_8}\ln(1 + [ClO_2]_o\, k_8 t_{1/2}) + k'_{50}\, t_{1/2}$$

c) For $\geq$ 60% photolysis,

$$-\frac{d[\ln O_2^*]}{dt} = k_{52}\left([Cl]_o + [O]'_o - \frac{a}{b\, e^{k_6 a t} - 1}\right) + k'_{50}$$

$$-\ln[O_2^*] = k_{52}([Cl]_o + [O]'_o)t - k_{52}a\left[\frac{\ln(b\, e^{k_6 a t} - 1)}{k_6 a} - t\right] + k'_{50}\, t + c$$

when $t = 0$, $[O_2^*] = [O_2^*]_o$

or $$c = -\ln[O_2^*]_o + \frac{\ln(b-1)}{k_6} k_{52}$$

and also when $t = t_{1/2}$, $[O_2^*] = \frac{1}{2}[O_2^*]_o$

$$\ln 2 = k_{52}([Cl]_o + [O]'_o)t_{1/2} - \frac{k_{52}}{k_6}\ln\left(\frac{b\, e^{k_6 a t_{1/2}} - 1}{b - 1}\right) + t_{1/2}\, a\, k_{52} + k'_{50}\, t_{1/2}$$

$$= k_{52}[\,[Cl]_o + [O]'_o + a\,]t_{1/2} - \frac{k_{52}}{k_6} \ln\left(\frac{b\,e^{k_6 a\, t_{1/2}} - 1}{b - 1}\right)$$

$$+ k'_{50}\, t_{1/2}$$

Relaxation of O_2^* by oxygen atoms

The equation for relaxation of O_2^* by oxygen atoms was derived in the similar manner as that derived for chlorine atoms when photolysis $\geq$ 60%. The rate of relaxation of O_2^* is given by

$$-\frac{d[\ln O_2^*]}{dt} = k_{53}[O] + k_{52}[Cl]$$

The term k'_{50} can be neglected, being very small.

Substituting the values of oxygen and chlorine atoms

$$-\frac{d[\ln O_2^*]}{dt} = k_{53} \cdot \frac{a}{b\,e^{k_6 at} - 1} + k_{52}\left[\,[Cl]_o + [O]'_o - \frac{a}{b\,e^{k_6 at} - 1}\right]$$

$$= (k_{53} - k_{52})\frac{a}{b\,e^{k_6 at} - 1} + k_{52}([Cl]_o + [O]'_o)$$

$$\text{or} \quad \ln 2 = (k_{53} - k_{52})\,\frac{1}{k_6}\left[\ln \frac{b\,e^{k_6 a\, t_{1/2}} - 1}{b - 1} - k_6 a\, t_{1/2}\right]$$

$$+ k_{52}([Cl]_o + [O]'_o)\, t_{1/2}$$