A STUDY OF MANGANESE(III) OXIDATION OF HINDERED PHENOLS

by

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B.Sc., University of British Columbia, 1969

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the Department

of

Chemistry

We accept this thesis as conforming to the

required standard

THE UNIVERSITY OF BRITISH COLUMBIA

March, 1972

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## ABSTRACT

The complex of manganese(III) with trans-1,2-diaminocyclohexane-
tetraacetic acid was prepared and its formula shown to be $KMn^{III}CyDTA(H_2O)$,
where CyDTA is an abbreviation for trans-1,2-diaminocyclohexanetetraacetic
acid anion. A mechanistic study of the oxidation of 2,4,6-tri-t-butylphenol
with this complex was carried out in methanol under three conditions:
(1) in the presence of acid; (2) in the presence of base; (3) in the
absence of acid and base.

Under acidic conditions, the oxidant is $HMn^{III}CyDTA(H_2O)$ and the
rate-determining step of the reaction involves a hydrogen atom abstraction
from the O-H group of 2,4,6-tri-t-butylphenol by the oxidant. A kinetic
isotope effect of 4.8 was obtained at $25^{\circ}$. The activation parameters are
$\Delta H^* = 15.7$ Kcal.mole$^{-1}$ and $\Delta S^* = -10.4$ e.u. The small effect observed for
substitution in the para position is consistent with the radical character
of the reaction. A $\rho$ value of 0.39 was obtained from a Hammett plot of
$\log k_3/k_{3H}$ versus $\sigma_p^-$.

Under basic conditions, the oxidant is $Mn^{III}CyDTA(OH)^{2-}$ and there
are two competitive reactions: one that involves electron-transfer from
2,4,6-tri-t-butylphenoxy anion to $Mn^{III}CyDTA(OH)^{2-}$ and another that
involves hydrogen atom abstraction from 2,4,6-tri-t-butylphenol by
$Mn^{III}CyDTA(OH)^{2-}$. The activation parameters are $\Delta H^* = 10.2$ Kcal.mole$^{-1}$,
$\Delta S^* = -23$ e.u. for the former reaction; $\Delta H^* = 10.2$ Kcal.mole$^{-1}$,

$\Delta S^*$ = -29 e.u. for the latter reaction. A kinetic isotope effect of 1.9 was obtained for the latter reaction at $25^\circ$. The rate of electron-transfer from 2,4,6-tri-t-butylphenoxy anion to $Mn^{III}CyDTA(OH)^{2-}$ is 104 times faster than the rate of hydrogen atom abstraction from 2,4,6-tri-t-butylphenol by $Mn^{III}CyDTA(OH)^{2-}$. The effect on reaction rate for substitution in the para position is large, a $\rho$ value of 2.3 being obtained from a Hammett plot of log $k_9/k_{9H}$ versus $\sigma_p^-$ ($k_9$ is the rate constant for the reaction between 2,4,6-tri-t-butylphenol and $Mn^{III}CyDTA(OH)^{2-}$).

Under neutral conditions, the oxidant is $Mn^{III}CyDTA(H_2O)^-$ and the rate-determining step of the reaction involves hydrogen atom abstraction from the O-H group of 2,4,6-tri-t-butylphenol by the oxidant. A kinetic isotope effect of 5.9 was obtained at $25^\circ$. The activation parameters are $\Delta H^*$ = 10.9 Kcal.mole$^{-1}$ and $\Delta S^*$ = -39 e.u. The small effect observed for substitution in the para position is consistent with the radical character of the reaction, a $\rho$ value of -0.07 being obtained from a Hammett plot of log $k_{3a}/k_{3aH}$ versus $\sigma_p^-$. The compound 3,5-di-t-butyl-4-hydroxybenzaldehyde, however, has an anomalously high rate. This anomaly is also observed under acidic conditions.

The oxidising power of $Mn^{III}CyDTA(OH)^{2-}$ is 360 times greater than that of $Mn^{III}CyDTA(H_2O)^-$ with respect to hydrogen atom abstraction from 2,4,6-tri-t-butylphenol. This difference in oxidising strength suggests that an 'inner-sphere'-type mechanism is involved in the reactions. The

difference in oxidising strength between $Mn^{III}CyDTA(OH)^{2-}$ and $Mn^{III}CyDTA(H_2O)^-$ is even greater in 95 % dimethyl sulfoxide solvent - $5.4 \times 10^7$.

Oxidation of 2,4,6-tri-t-butylphenol with potassium ferricyanide in methanol in the presence of hydrochloric acid is shown to be a reversible reaction. The lack of data on the ionization constants of $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ prevented a detailed study of the equilibria involved.

My help cometh from the Lord.

Psalm 121:2


".... it is the gift of God: not of works,

lest any man should boast."

Ephesians 2: 8,9

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# ACKNOWLEDGMENT

I wish to take this opportunity to express my sincere thanks to Professor R. Stewart for his excellent guidance throughout this research. His innumerable valuable comments and advice are most gratefully acknowledged.

The various discussions with Dr. B. R. James have proved very helpful. His suggestions are very much appreciated.

I am also indebted to: Mr. S. Rettig and Dr. J. Trotter for their information on the crystal structure of the manganese(III) complex; Mr. P. Borda for doing the microanalysis of compounds; and Miss P. Watson for recording the nmr spectra of compounds.

This study was completed under a Colombo Plan scholarship granted by the Canadian International Development Agency. I am therefore thankful to them for the part this financial support played throughout this study.

My personal thanks should go to my wife Sien for her patience and understanding. Many of her thoughtful suggestions have directly or indirectly contributed to the completion of this work. It is to her that this thesis is affectionately dedicated.

## I. INTRODUCTION

The chemistry of hindered phenols (phenols that have bulky ortho substituents) has been studied rather extensively after Cook[1,2] and Müller[3] and co-workers made their independent discovery of the stable 2,4,6-tri-t-butylphenoxy radical (I) in 1953. There are three main reasons for this interest. Firstly, many hindered phenols form relatively stable phenoxy radicals which provide valuable information on the structure of the unpaired electron, its behaviour and properties. Secondly, they are convenient models for investigating reactivity and its relation to structure[4]. Thirdly, both the phenols and their phenoxy radicals have been found to be important in the inhibition of autoxidation of organic substances. An excellent review article[5] on the role of phenols and phenoxy radicals in autoxidation inhibition has been written by Ingold. Two good summaries of the chemistry of stable phenoxy radicals are given by Attwicker[6] and Mihailovic[7].
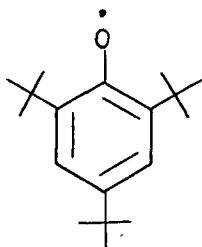
I

## (A) <u>Generation of phenoxy radicals</u>

The most commonly used reagents to generate phenoxy radicals from phenols in high yields are inorganic oxidising agents which can undergo one-electron reduction. Some of these oxidising reagents are potassium ferricyanide, lead dioxide, silver oxide, mercuric oxide and manganese dioxide. These reactions are usually carried out in a heterogeneous system (e.g. solution of the phenol in benzene, and the oxidising agent either in suspension or in an aqueous phase).

### (i) <u>Alkaline potassium ferricyanide</u>

Potassium ferricyanide in base was first used to generate 2,4,6-tri-t-butylphenoxyl from its phenol[1-3]. Although this reagent generally gives high yields of phenoxy radicals a large excess of reagent is needed to achieve a high yield. Mechanistic details of the oxidation process involved are still not well understood. The reactions of this reagent with phenols have been reviewed by Thyagarajan[8].

### (ii) <u>Lead dioxide</u>

Lead dioxide oxidises phenols to phenoxy radicals in quantitative yields only when this reagent is high in active oxygen and when the solutions are dilute in phenol (less than 0.04 molar)[9]. It is commonly used to generate phenoxy radicals <u>in situ</u> because the procedure involved is simple and oxidation occurs immediately (e.g. it has been found in this

work that 2,4,6-tri-t-butylphenoxyl can be generated immediately by syringing benzene which has been flushed with nitrogen into a mixture of the solid phenol and solid lead dioxide in an oxygen-free container which is stoppered with a rubber cap).

(iii) <u>Silver oxide and mercuric oxide</u>

Silver oxide and mercuric oxide are inferior reagents to alkaline potassium ferricyanide and lead dioxide for the purpose of generating phenoxy radicals from phenols. Freshly prepared samples of silver oxide must be used to obtain high yields of phenoxy radicals[10].

(iv) <u>Manganese dioxide</u>

Highly active manganese dioxide has been used to produce apparently high yields of phenoxy radicals[11]. It is not as commonly used as potassium ferricyanide and lead dioxide.

(v) <u>Metals</u>

Another method which gives quantitative yields of phenoxy radicals involves the reactions of 4-halo-2,5-cyclohexadienones (II) with metals as shown in equation (1).

$$II \qquad R = Cl, \ Br \qquad M = Hg, \ Ag, \ Cu, \ Zn, \ Na-K \qquad (1)$$
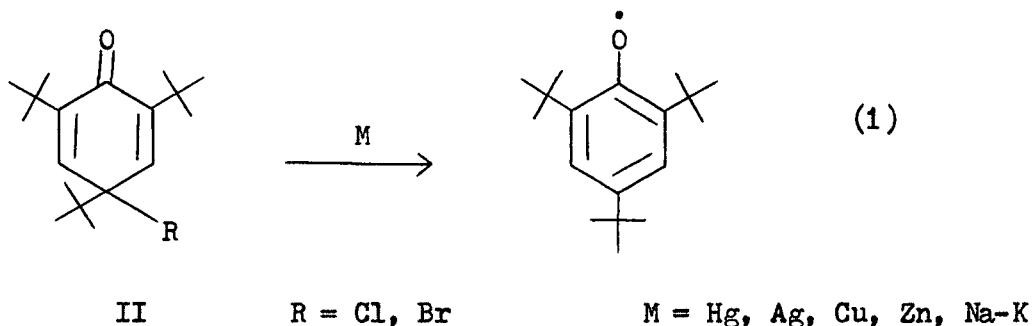
This method is convenient because the metal halide by-product can be removed by filtration[12].

(vi) Other methods

There are many other methods of generating phenoxy radicals, e.g. flash photolysis[13], electrochemical methods[14], thermal dissociation of phenoxy dimers etc. These methods cannot be adapted to preparative scale. However, a method like flash photolysis when used in conjunction with electron spin resonance (esr) spectroscopy enables very short-lived phenoxy radicals like 2,6-di-t-butylphenoxyl (III a) to be detected[13].

(B) Physical properties of phenoxy radicals

Phenoxy radicals (III) can be isolated in solid form only when R, R' and R" are bulky groups (e.g. I is a dark blue crystalline solid with a melting point of 96-98°). They are highly coloured both as solids and in solutions. Those phenoxy radicals which exist as dimers in the solid state are generally colourless. Some examples of phenoxy radicals which

can be isolated as solid monomers are I and III b while III c, III d
and III e are some of the phenoxy radicals which exist as solid dimers[6].
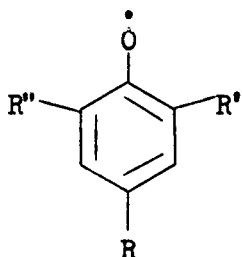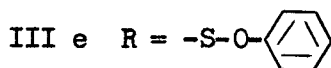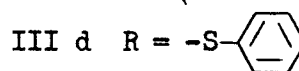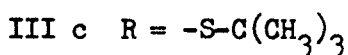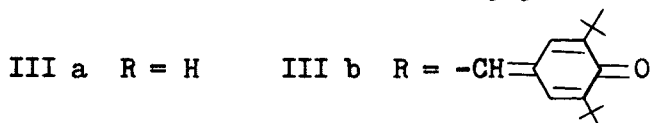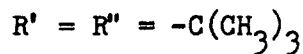


Phenoxy radicals, because of their unpaired electron, are
paramagnetic. The Gouy method of measuring magnetic susceptibility can be
used to detect them if they are stable. This method was first used to
prove that I was essentially monomeric[15]. It is still quite useful for
the quantitative determination of radical content. But it suffers from
three disadvantages namely (i) the sample of radical used must be stable;
(ii) the sample of radical must be pure and (iii) it is difficult to
account for the diamagnetic part of susceptibility in the calculation of
the magnetic moment of radicals[16].

Even very short-lived phenoxy radicals can now be detected by the
powerful technique known as electron spin resonance (esr) spectrometry.
This technique which requires very low concentrations of radicals (as low
as $10^{-9}$ molar), has been used to elucidate detailed structures of

phenoxy and other radicals.

(i) ESR spectra of phenoxy radicals

The hyperfine structure of esr spectra of phenoxy radicals provides
information on the interaction of the magnetic moment of the unpaired
electron with the magnetic moments of the nuclei covered by the molecular
orbital of the unpaired electron. From the magnitude of the hyperfine
splitting constants the spin density of the unpaired electron in the
various parts of the molecule can be calculated. For example, the presence
of a triplet of 1 : 2 : 1 in intensity ratio in the esr spectrum of I
indicates resonance structures I and I a are both important.



    I          I a          I b          I c          I d
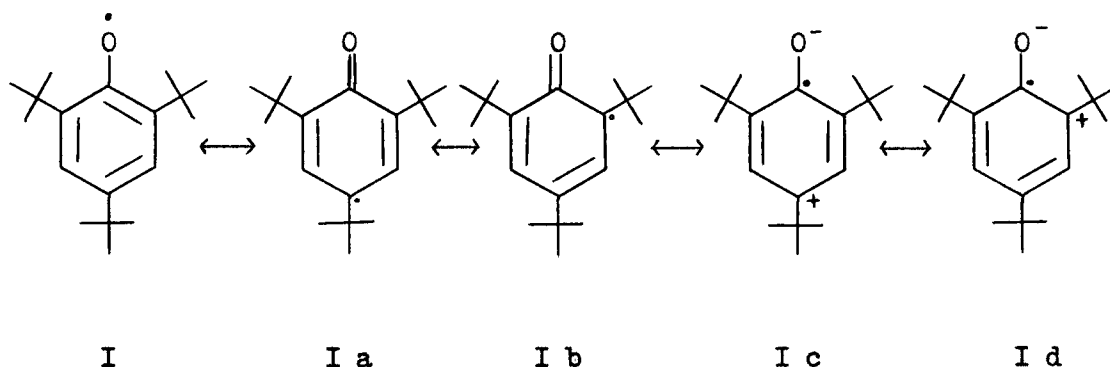
The triplet is due to the interaction of the unpaired electron with the
two equivalent meta-hydrogen atoms. This explanation is supported by the
observations of a doublet esr spectrum of 1 : 1 intensity ratio when one
of the meta-hydrogen atoms is replaced by deuterium, and a singlet esr

spectrum when both the meta-hydrogen atoms are replaced by deuterium[17].
The distribution of spin density of the unpaired electron on the various
atoms of I has been calculated[18-20] and found to be as follows:
$O$ 36 %; $C_1$ 4.5 %; $C_2 = C_6$ 12.5 %; $C_3 = C_5$ 5 %; $C_4$ 25 %. These results
indicate that the unpaired electron density is greater at the para- than
at the meta- position.

Attempts to correlate the magnitude of splitting constants with
different substituents in phenoxy radicals have been made[4], but the
relation is not yet clear. Little attention has been paid to the
determination of an accurate value of the gyromagnetic ratio (or g-factor)
of the unpaired electron in phenoxy radicals because, apparently, little
structural information can be obtained from this parameter.

Further information on the use of esr technique in the investigation
of phenoxy radicals is found in review articles[4,20]. The theoretical
aspect of this technique is well described in several books[21,22].

(ii) <u>Infrared spectra of phenoxy radicals</u>

Perhaps the most characteristic feature of the infrared spectra of
phenoxy radicals is the absence of the O-H band in the 3700 $cm^{-1}$ region[9].
The presence of the 1600 $cm^{-1}$ band indicates the presence of a carbonyl
function which is contributed by resonance structures I a and I b.

### (iii) Visible spectra of phenoxy radicals

Unlike most phenols, phenoxy radicals show strong absorption bands in the visible region. The band in the 400 nm region is usually much stronger than that in the 600 nm region[4]. The brilliant colour of most phenoxy radicals is attributed to the contribution of the conjugated keto forms and charge separation forms (see resonance structures I a to I d).

### (C) Chemical properties of phenoxy radicals

### (i) Dimerisation

Dimerisation reactions of phenoxy radicals can be divided into two main groups - (ia) carbon-oxygen dimerisation and (ib) carbon-carbon dimerisation.

### (ia) Carbon-oxygen dimerisation

Certain phenoxy radicals undergo carbon-oxygen dimerisation to form quinol ethers. For example, alkyl or aryl 2,6-di-t-butyl-p-hydroxybenzoates (IV) when oxidised give the quinol ethers (V) as shown in equation (2)[23,24].



$$\text{(2)}$$

R = Me, t-Bu, Ph

IV          V          VI
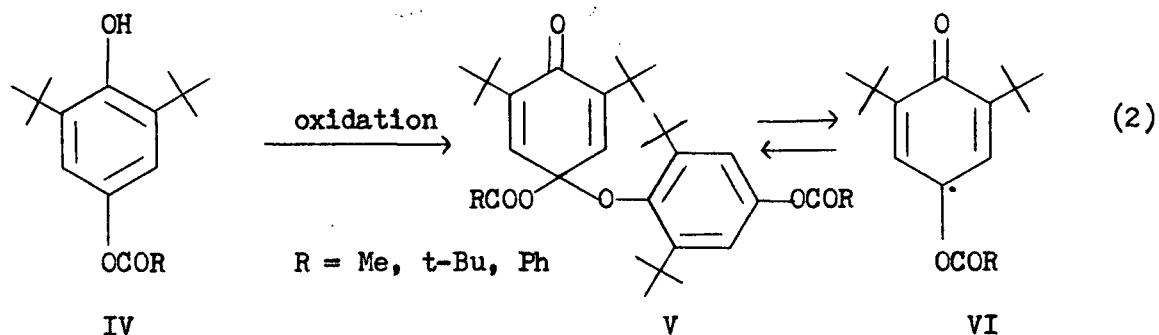
Carbon-oxygen dimerisations, e.g. to form V, are reversible.

Some 2,6-di-substituted phenols when oxidised undergo carbon-oxygen dimerisations to form polyphenyl ethers[25,26].

(1b) Carbon-carbon dimerisation

Many phenoxy radicals[10,27-29] undergo carbon-carbon dimerisations in the following manner:

$$2 \quad \text{VII} \longrightarrow \text{VIII} \qquad (3)$$

and / or

IX
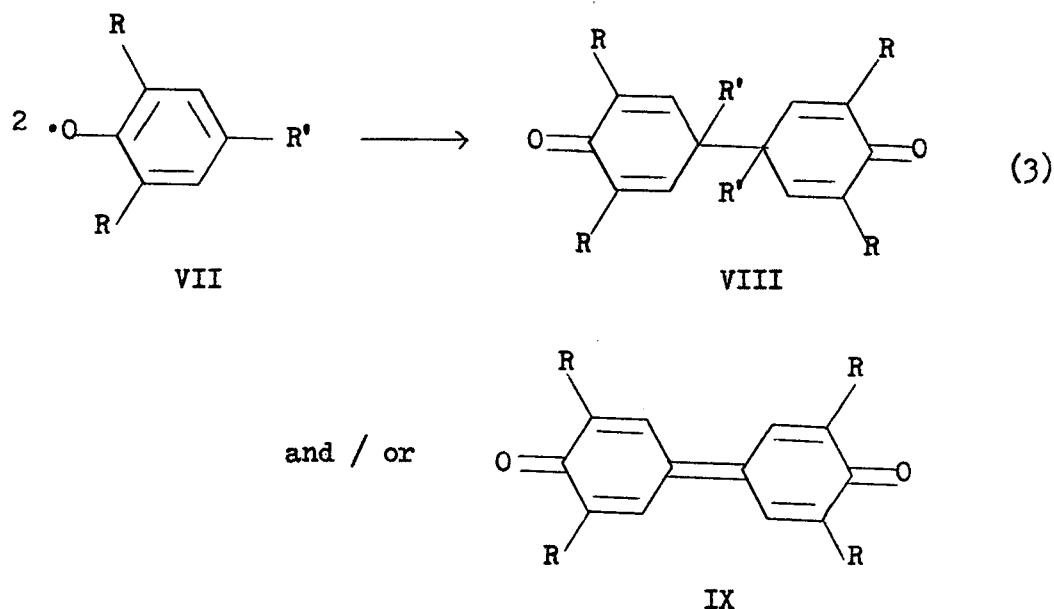
Oxidation[30] of 2,6-di-t-butylphenol with base and oxygen gives IX (R = t-Bu) whereas oxidation of the same compound with silver oxide gives both VIII and IX (R = t-Bu, R' = H).

The formation of galvinoxyl (XI) from 2,6-di-t-butyl-4-formylphenoxyl

(X) has been reported[31] although the mechanism of the reaction has not
been investigated. Apparently the radical X has undergone carbon-carbon
dimerisation with loss of a carbon unit.



$$X \longrightarrow XI \qquad (4)$$

X                    XI
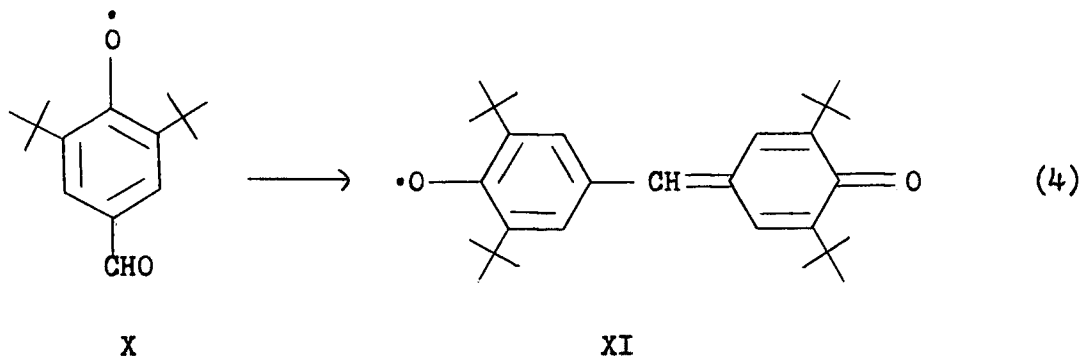
Because of steric hindrance highly hindered phenoxy radicals such
as 2,4,6-tri-t-butylphenoxyl (I) do not undergo carbon-carbon dimerisation.

(ii) Addition of other radicals

Even phenoxy radicals which are stable with respect to dimerisation
add small radicals to themselves quite readily. For example, I forms a
peroxide with oxygen (XII) and it adds nitrogen dioxide to form XIII[2,10].



$$2 \; I + O_2 \longrightarrow XII \qquad (5)$$

I                    XII

(6)
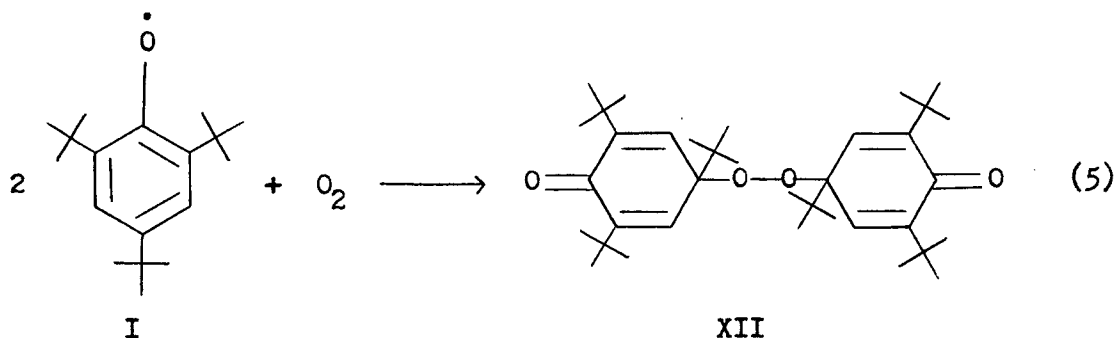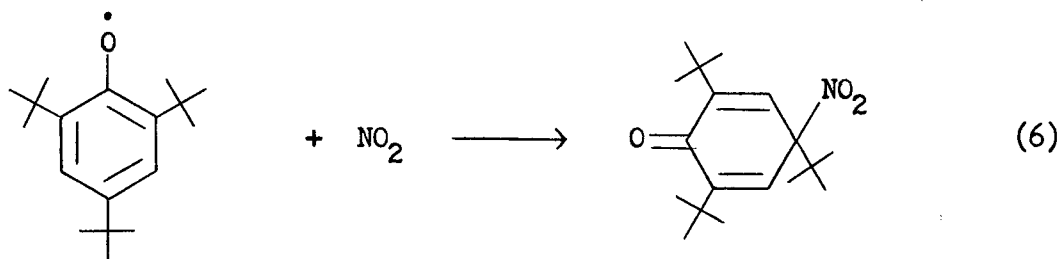
XIII

In the case of 2,6-di-t-butylphenoxyl carbon-carbon dimerisation must be very much faster than peroxide formation with oxygen because XIV has not been detected.
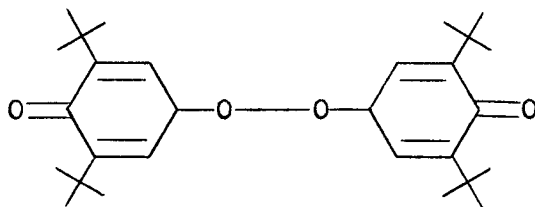


XIV

(iii) Disproportionation

Hindered phenoxy radicals which possess an $\alpha$-hydrogen on the 4-substituent (XV) disproportionate to starting phenols and quinone methides (XVI) as shown in equation (7).

$$2 \quad \text{XV} \longrightarrow \quad + \quad \text{XVI} \qquad (7)$$
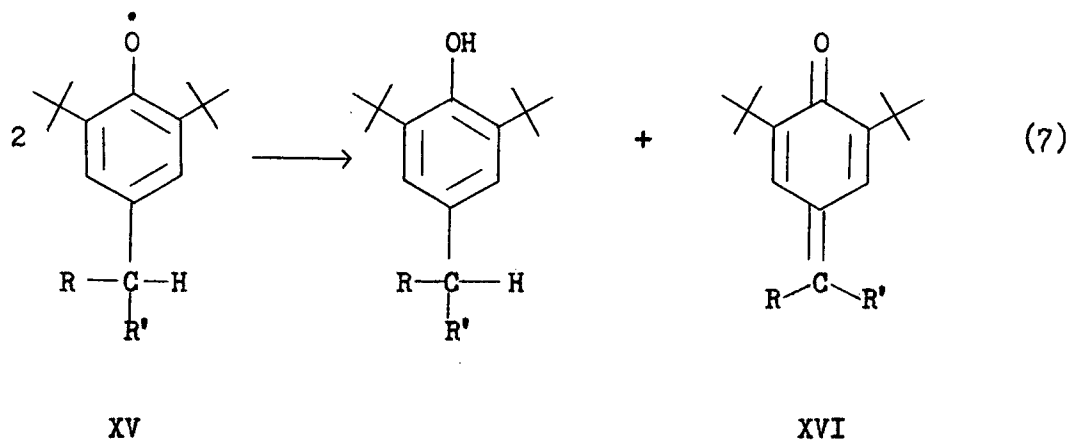
Some examples of 2,6-di-t-butylquinone methides are listed in Table I.

TABLE I

## 2,6-di-t-butylquinone methides (XVI)

| XVI | | References |
|-----|-----|------------|
| R | R' | |
| H | H | 32 |
| H | Me | 33 |
| H | Ph | 34 |
| Me | Ph | 34 |
| H | OMe | 34 |

The rate of disproportionation of some examples of XV has been studied[33,35-37]. The kinetic results obtained cannot always be explained in terms of equation (7), e.g. the rate of disproportionation of XV when R = H, R' = Me was found to be first-order with respect to radical concentration[36] and to depend on the solvent used. However, when R = R' = Me, or R = Me, R' = Et, disproportionation was reported to give good second-order kinetics[33], consistent with equation (7). Moreover, the rates of these second-order reactions were found to be insensitive to the solvent used. Recently[37], the disproportionation of XV, R = R' = H, was reported to be second-order with respect to the radical concentration, with a specific rate constant $k_d$ = 3.33 x $10^2$ $M^{-1}sec^{-1}$ in tetrahydrofuran and $k_d$ = 4.59 x $10^2$ $M^{-1}sec^{-1}$ in benzene at $24^o$. Further investigation of the mechanism of disproportionation of phenoxy radicals is needed.

(iv) <u>With acids</u>

Phenoxy radicals react with acids as illustrated in equations (8) and (9). Mechanistic details of such reactions are lacking.

$$+ \ HNO_3 \longrightarrow \qquad\qquad (9)$$
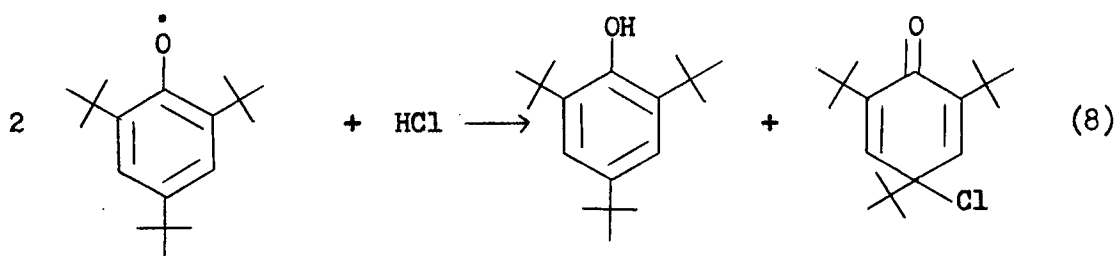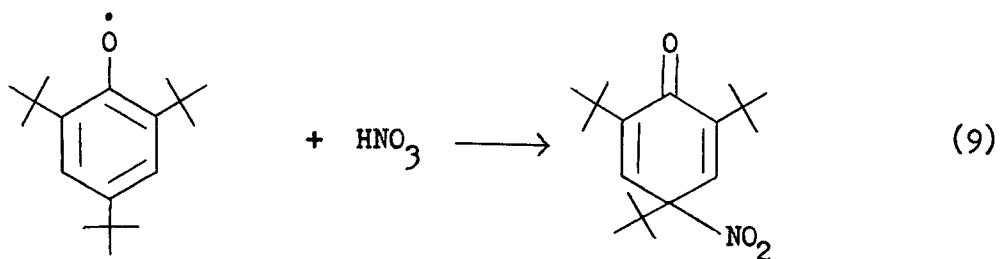
## (v) With base

Very little is known about the reaction of phenoxy radicals with base. Since they can be obtained quantitatively by oxidation of phenols with alkaline potassium ferricyanide, they must be generally unreactive towards base. (For example, I was obtained in nearly 100 % yield[2,9] by the oxidation of the phenol with alkaline potassium ferricyanide in water-benzene mixture for two hours). It is quite surprising that galvinoxyl (XI), which is stable to air, reacts with base[38] in methanol quickly to form XVII.

$$+ \ OH^- \ \xrightarrow{\text{MeOH}} \qquad\qquad (10)$$

XI          XVII
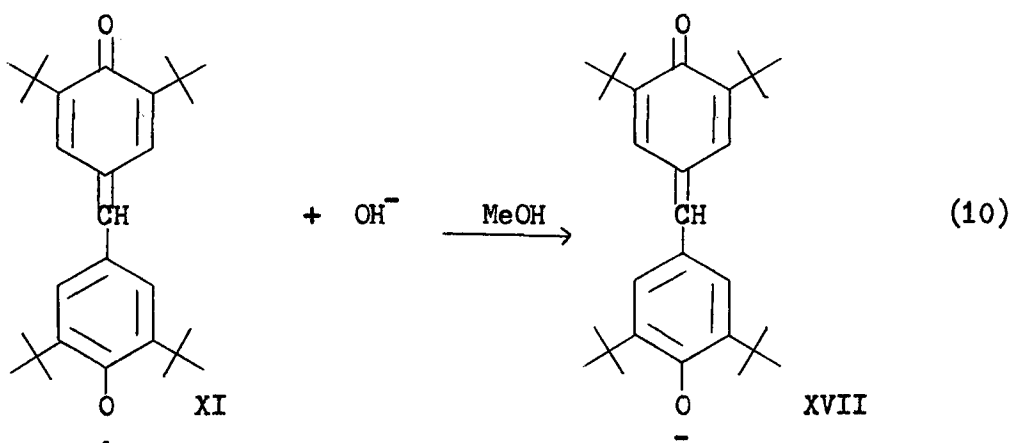
(vi) <u>With phenols</u>

Phenoxy radicals react with phenols to give a variety of products depending on the structural features of the radicals and the phenols and on the conditions used. Some reactions give mixed quinol ethers[6] as shown in equation (11). Some produce other phenoxy radicals as shown in equation (12). The equilibrium constants[39] for equation (12) have been determined for R = t-Bu and R = Me. They are 51.7 and 210 respectively at $25^{\circ}$.

The rate constant for the intermolecular hydrogen transfer between I and its phenol has been determined by nuclear magnetic resonance line-broadening technique[40]. It was found to be 300 $M^{-1}sec^{-1}$; the activation energy is $1 \pm 0.5$ Kcal.mole$^{-1}$.



$$\tag{11}$$

(12)
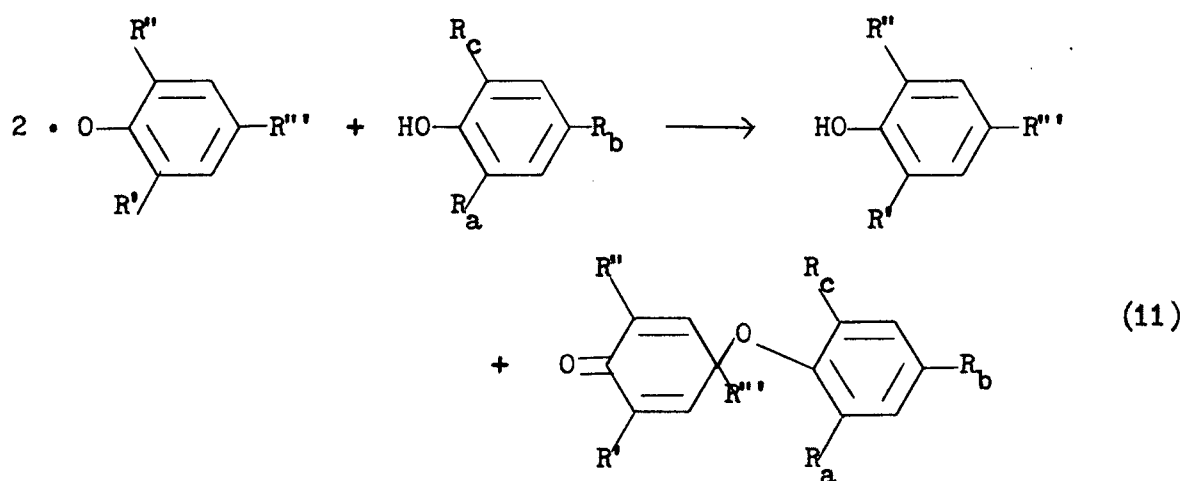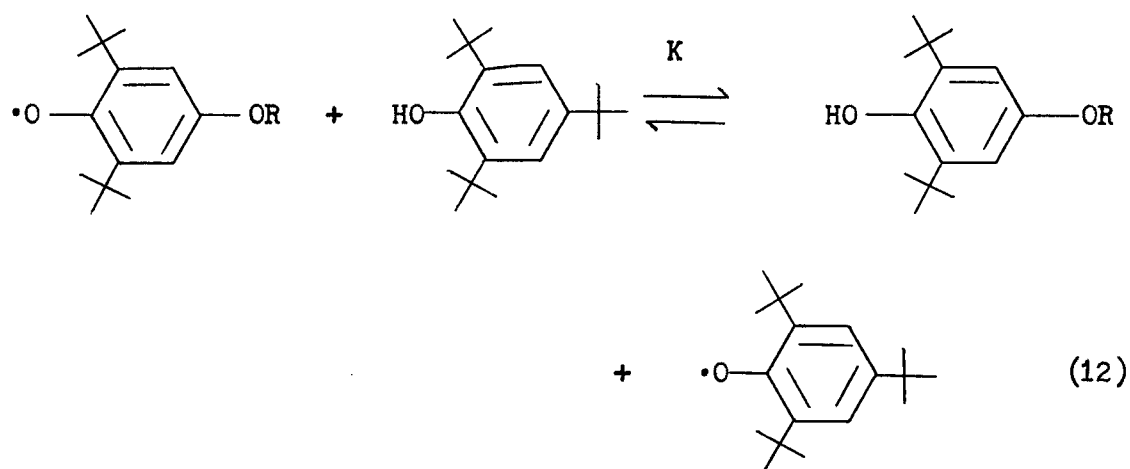
## II. AIM OF THE PRESENT RESEARCH

Although oxidation of hindered phenols using oxidising agents which are capable of undergoing one-electron reduction has often been carried out no mechanistic studies have hitherto been made. This deficiency is mainly due to the fact that all such reactions have been done in heterogeneous media, thus making kinetic investigation using simple technique difficult.

The main aim of this research was to study the mechanistic details of oxidation of 2,4,6-tri-t-butylphenol with potassium trans-1,2-diamino-cyclohexanetetraacetatomanganate(III). The latter compound will be referred to as Mn$^{III}$ complex throughout this thesis; its structure is shown in Figure 1. This oxidant which has only recently been prepared[41] was chosen for four reasons: (1) it is a stable solid and can be stored in the dark for months without showing any sign of decomposition; (2) it is a one-electron oxidant; (3) no Mn$^{III}$ compound has hitherto been used to oxidise hindered phenols (presumably because most Mn$^{III}$ compounds are unstable, especially in basic condition); (4) it is soluble in non-aqueous solvents like methanol and dimethyl sulfoxide. The compound 2,4,6-tri-t-butylphenol was used as reductant because it is known to give a very stable phenoxy radical, I. Oxidation of some other 4-substituted-2,6-di-t-butylphenols with the same oxidant was carried out to gain some information about the structure of the transition states of these processes.
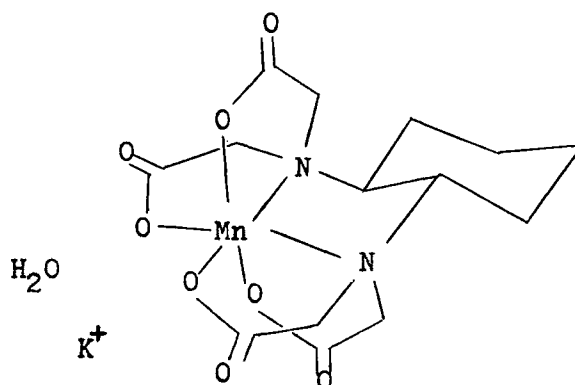
Figure 1. Structure of potassium trans-1,2-di-aminocyclohexanetetra-
acetatomanganate(III).

Oxidation of 2,4,6-tri-t-butylphenol was also carried out with potassium ferricyanide so that the relative oxidising power of the $Mn^{III}$ complex and potassium ferricyanide could be compared.

III. EXPERIMENTAL

(i) Instruments used

All rates were measured on a Bausch and Lomb Spectronic 505 spectrophotometer fitted with a constant temperature block. A Cary 16 spectrophotometer equipped with a constant temperature block was used to measure extinction coefficients. An E-3 EPR spectrometer was used to record electron spin resonance spectra. Melting points of compounds were measured with a 'Buchi' melting-point apparatus. A Beckman aquameter model KF-2 was used to determine water content of the $Mn^{III}$ complex by the Karl Fischer method. All syringes used were equipped with Chaney adapters calibrated at desired volumes. All straight line graphs were calculated by the method of least squares and plotted using a Hewlett-Packard plotter and calculator model 9125A.

(ii) Chemicals and purifications[*]

3,3',5,5'-tetra-t-butyl-p-diphenoquinone (XVIII) was prepared by oxidation of XXXIV with alkaline potassium ferricyanide in a water-benzene mixture. The crude product was recrystallised from hot methanol. M.p. 246-247° (Lit. 246°)[29].

* The identity of each phenol was checked by its nmr spectrum.

Bis-(1,3,5-tri-t-butyl-2,5-cyclohexadiene-4-one) peroxide (XII) was

prepared by oxidation of XXIII with potassium ferricyanide in a water-

benzene mixture in the presence of oxygen[2]. The crude product was

recrystallised from hot methanol. M.p. 148-149° (Lit. 148-149°)[2].


3,5-di-t-butyl-4-hydroxybenzaldehyde (XXI) was synthesised by oxidation

of XX with bromine in aqueous acetic acid[42]. The crude product obtained

was recrystallised twice from hot acetone. M.p. 189-190° (Lit. 189-190°)[43,44].

Since this compound is shown to have an anomalously high rate (see

Sections VII and IX), its elemental analysis data and nmr spectrum (see

Figure 2) are given to show its authenticity.

Analysis - Found: C 76.86 %; H 9.48 %.

         Cal'd: C 76.82 %; H 9.39 %.


2,6-di-t-butyl-4-bromophenol (XXII) was synthesised by bromination of

XXXIV in glacial acetic acid. Glacial acetic acid (30 ml.) was added to

5.1 g (25 mmoles) of XXXIV in a 50 ml. round-bottomed flask. The contents

were stirred with a magnetic stirer and 1.4 ml. (25 mmoles) of bromine

was added dropwise to the mixture, which was stirred for half an hour.

The contents of the vessel were then poured into a beaker containing

70 ml. of water, whereupon a pale yellow solid precipitated immediately.

The crude product was recrystallised from hot methanol. Yield 90 %;

m.p. 83-83.5° (Lit. 83-83.5°)[45].

Figure 2. N.M.R. spectrum of 3,5-di-t-butyl-4-hydroxybenzaldehyde in $CCl_4$.

(offset 100 Hz).
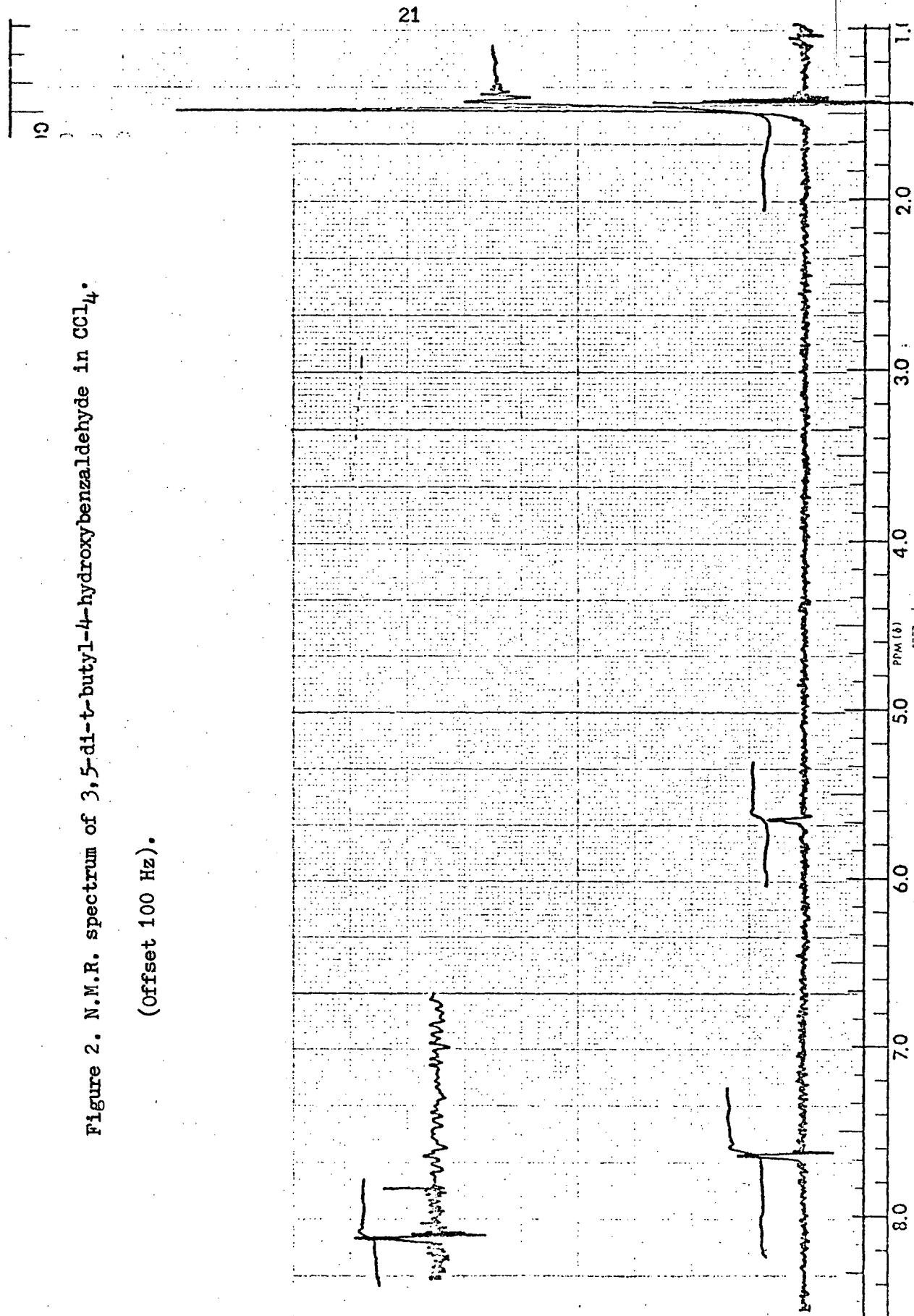
2,6-di-t-butyl-4-chlorophenol (XXIV) was prepared[45] by chlorination of XXXIV in carbon tetrachloride at $0^{\circ}$. The crude product was recrystallised from hot methanol and then vacuum sublimed. M.p. $74-76^{\circ}$ (Lit. $75-76^{\circ}$; $72-74^{\circ}$)[9,45].

2,6-di-t-butyl-4-iodophenol (XXV) was prepared[45] by reacting iodine bromide with XXXIV in dioxane. The crude product was recrystallised from hot methanol and then vacuum sublimed. M.p. $77-79^{\circ}$ (Lit. $76.5-78.5^{\circ}$)[45].

2,6-di-t-butyl-4-acetylphenol (XXVI) was prepared[46] by reacting acetyl chloride with XXXIV in the presence of aluminium chloride at $0^{\circ}$. The crude product was recrystallised twice from hot ethanol. M.p. $150-151^{\circ}$ (Lit. $147-148^{\circ}$; $150-151^{\circ}$)[46,47].

2,6-di-t-butyl-4-benzoylphenol (XXXII) was prepared[46] by reacting benzoyl chloride with XXXIV in the presence of aluminium chloride at $0^{\circ}$. The crude product was recrystallised thrice from hot methanol. M.p. $124-124.5^{\circ}$ (Lit. $124-125^{\circ}$)[46].

2,6-di-t-butyl-4-hydroxyphenol (XXIX) was prepared[3] by reduction of XIX with lithium aluminium hydride. The crude product was recrystallised from hot methanol and then vacuum sublimed. M.p. $103-104^{\circ}$ (Lit. $110-111^{\circ}$)[3].

2,6-di-t-butyl-4-cyanophenol (XXXIII) was prepared according to the method described by Cohen[42]. The crude product was recrystallised from hot methanol. M.p. $145-146^{\circ}$ (Lit. $147^{\circ}$)[42].

The following phenols were purchased from commercial sources.

2,4,6-tri-t-butylphenol (XXIII) was purchased from Aldrich Chemical
Company. It was recrystallised from hot ethanol. M.p. 131-132° (Lit. 130-
131°; 131-132°)[48,10].

2,6-di-t-butylphenol (XXXIV) was purchased from Aldrich Chemical Company.
It was purified by recrystallisation from hot methanol, followed by
vacuum sublimation. M.p. 37.5° (Lit. 36-37°)[10].

2,6-di-t-butyl-4-methylphenol (XX) was obtained from Eastman Organic
Chemicals. It was recrystallised from hot ethanol. M.p. 70-70.5°.

3,5-di-t-butyl-4-hydroxybenzoic acid (XXX) was purchased from Aldrich
Chemical Company. It was recrystallised from hot methanol. M.p. 221-222°
(Lit. 217-218°)[49].

2,6-di-t-butyl-4-hydroxymethylphenol (XXVIII) was obtained from K & K
Laboratories. It was recrystallised from hot methanol. M.p. 142-143°.

2,6-di-t-butyl-4-dimethylaminomethylphenol (XXXI) was obtained from
K & K Laboratories. It was recrystallised from hot methanol. M.p. 92-94°.

3,5-di-t-butyl-4-hydroxybenzyl ether (XXVII) was obtained from K & K
Laboratories. It was recrystallised from hot methanol. M.p. 137-137.5°.

Tetramethylammonium hydroxide was obtained as 10 % and 25 % solutions in water from Eastman Organic Chemicals. It was used without further purification.

Tetrapropylammonium hydroxide was obtained as 10 % solution in water from Eastman Organic Chemicals. It was used without further purification.

Tetrabutylammonium hydroxide was obtained as 10 % solution in methanol from Eastman Organic Chemicals. It was used without further purification.

Potassium hydroxide and sodium hydroxide were obtained as standard solutions from British Drug Houses. They were used without further purification.

Lithium hydroxide solution was prepared by dissolving a weighed sample of the compound (reagent grade) in a known volume of distilled water. Its exact concentration was found by titration against standard acid.

Acids (sulphuric, perchloric and hydrochloric) used were of reagent grade. They were standardised by titration against standard base.

The following deuterated compounds were obtained from Merck, Sharp and Dohme of Canada Ltd. They were used without further purification.

Deuterium oxide (99.7 atom % purity).

Methanol-O-d (99 atom % purity).

Methanol-$d_4$ (99.5 atom % purity).

Deuterium chloride (38 % w/w in Deuterium oxide).

Sodium deuteroxide (40 % w/w in Deuterium oxide).

t-Butylamine was obtained from Eastman Organic Chemicals. It was used without further purification.

Methanol used was 'Baker Instra-Analyzed' grade obtained from J. T. Baker Chemical Company. It was used without further purification.

Chromotropic acid, di-sodium salt (4,5-di-hydroxynapthalene-2,7-di-sulfonic acid, di-sodium salt) was purchased from British Drug Houses and was used without further purification.

Nitrogen gas was high purity nitrogen (L grade, from Liquid Air Company).

Water was boiled distilled water which was cooled by flushing high purity nitrogen into it.

Potassium ferricyanide was obtained from Baker & Adamson Chemical Company. It was recrystallised from a saturated solution of it in water.

Potassium trans-1,2-diaminocyclohexanetetraacetatomanganate(III) was prepared according to the method used by Hamm and Suwyn[41]. It was purified by recrystallisation from methanol-water. M.p. 201-203°. Elemental analysis indicates that this compound has one molecule of water per molecule of compound instead of 2.5 molecules as reported by Hamm and

Suwyn[41]. (See the crystal structure of this compound in Figure 7 of

Section IV-vi(c)).

Analysis - Found: C 36.98 %; N 6.0 %; H 4.46 %.

　　　　　Cal'd: C 37.00 %; N 6.17 %; H 4.40 %.[*]

　　　　　Cal'd: C 34.92 %; N 5.82 %; H 4.78 %.[**]

[*] Calculated from $KMn^{III}C_{14}H_{18}N_2O_8(H_2O)$, M. W. = 454.0

[**] Calculated from $KMn^{III}C_{14}H_{18}N_2O_8(2.5H_2O)$, M. W. = 481.0

(iii) Method used in kinetic study

　　　Spectrophotometry offers an attractive method for studying the

mechanistic details of oxidation of 2,4,6-tri-t-butylphenol with

$KMn^{III}CyDTA(H_2O)$ (CyDTA is used as an abbreviation for the ligand,

trans-1,2-diaminocyclohexanetetraacetic acid anion) because the former

does not absorb in the visible region whereas the latter has a broad peak

in the 500 nm region. Therefore, the disappearance of the oxidant can be

followed by monitoring the decrease in absorbance near 500 nm. Moreover,

the production of 2,4,6-tri-t-butylphenoxyl can be followed because it

has a strong, sharp, peak at 400 nm which is distinct from the broad

peak of the oxidant.

(iv) Preparation of stock solutions

　　　A solution of 2,4,6-tri-t-butylphenol was prepared as follows:

a sample of this compound (0.1700 g) was dissolved in 25 ml. of methanol in a 25 ml. volumetric flask to give a concentration of 2.59 x $10^{-2}$ molar phenol solution. This phenol solution was transferred to a 25 ml. Erlenmeyer flask which was then sealed with a rubber cap. The solution was flushed with nitrogen for about twenty five minutes and then thermostated in a constant temperature water-bath at the desired temperature for half an hour before it was used for a kinetic run.

A 6.92 x $10^{-2}$ molar $KMn^{III}CyDTA(H_2O)$ stock solution was prepared by dissolving 15.7 mg of the compound in 0.5 ml. of distilled water in a small vial which was sealed with a rubber cap. The solution was flushed with nitrogen for about ten minutes. The vial was then wrapped with aluminium foil (to prevent slow decomposition of the compound by light) and thermostated at the desired temperature.

Tetramethylammonium hydroxide solutions (10 % and 25 %) were available in 100 ml. bottles. Several 3 ml. aliquots of the base were transferred into vials under a nitrogen atmosphere in a glove bag. These vials of tetramethylammonium hydroxide solutions were capped with rubber stoppers, and stored in a desiccator. When needed for an experiment, one vial of the base was thermostated at the desired temperature and transferred to the reaction mixture by means of a syringe. By this means, stock solutions of the base were not exposed to the atmosphere.

(v) <u>Kinetic runs</u>

A 1 cm. cell containing 3 ml. of methanol was placed in the reference cell holder of a Bausch and Lomb Spectronic 505 spectrophotometer. Another matching 1 cm. cell capped with a silicone disc(a silicon disc can be pierced by a syringe several times without any leakage occurring) was placed in the sample cell holder. The cell holders were thermostated at the desired temperature. Two syringe needles were pierced into the silicone disc, one for the nitrogen inlet and the other for the outlet. Air in the sample cell was flushed out by nitrogen for about a minute. Nitrogen was kept running through the sample cell while 3 ml. of 2,4,6-tri-t-butylphenol stock solution was transferred into it by means of a 5 ml. syringe equipped with a Chaney adapter calibrated at 3 ml. volume. Nitrogen was bubbled through the sample cell for another minute. A 50 $\mu$l. aliquot of 10 % tetramethylammonium hydroxide solution was syringed into the sample cell by means of a 50 $\mu$l. syringe equipped with a Chaney adapter calibrated at 50 $\mu$l. volume. A baseline from 350 nm to 650 nm was recorded on the chart paper of the spectrophotometer. The reaction was initiated by introducing 25 $\mu$l. of the stock $Mn^{III}$ complex solution into the sample cell by means of another 50 $\mu$l. syringe equipped with a Chaney adapter calibrated at 25 $\mu$l. volume. The sample cell was shaken briefly to mix the reactants well. Spectra from 350 nm to 650 nm were recorded at various time intervals.

A similar procedure was followed for reactions carried out under acidic conditions except that hydrochloric acid was used instead of base. Each kinetic run was done in duplicate.

(vi) Methods used in product analysis

Products which give absorption spectra were identified by spectrophotometry, their absorption spectra being compared with those of authentic samples.

Free radicals were analysed by esr spectrometry. A typical esr spectrum was recorded as follows: at the completion of the reaction, 0.05 ml. of the reaction mixture was syringed into an oxygen-free esr aqueous solution sample cell model E-248-1 (from Varian Associates) and an esr spectrum was quickly recorded.

Carbon dioxide was analysed qualitatively by the phenolphthalein-sodium carbonate indicator method[50]. Two test-tubes (10 cm. in height and 1.5 cm. in diameter), one as a sample tube and the other as a 'control' tube were used. A drop of phenolphthalein-sodium carbonate indicator was placed at the flattened end of a 4 cm. glass rod whose other end was attached to a rubber cap which fitted the mouth of the test-tube. This glass rod was inserted into the 'control' test-tube (see Figure 3). Methanol (3 ml.) was syringed into the sample tube and 0.050 ml. of hydrochloric acid was then added. The reaction was initiated by introducing

0.025 ml. of $3 \times 10^{-2}$ M of the $Mn^{III}$ complex into the sample tube. A similar glass rod with a drop of phenolphthalein-sodium carbonate indicator at the flattened end of it was inserted into the sample tube carefully so that the drop of indicator would not fall into the reaction mixture. Carbon dioxide evolved would turn the pink indicator colourless. The 'control' tube was used to ensure that the colour change of the indicator was not due to carbon dioxide from the atmosphere. This method is not applicable to reactions done in the presence of base because any carbon dioxide evolved would react quickly with the base.



glass rod

rubber cap

indicator

test-tube

reaction mixture

sample tube                    'control'
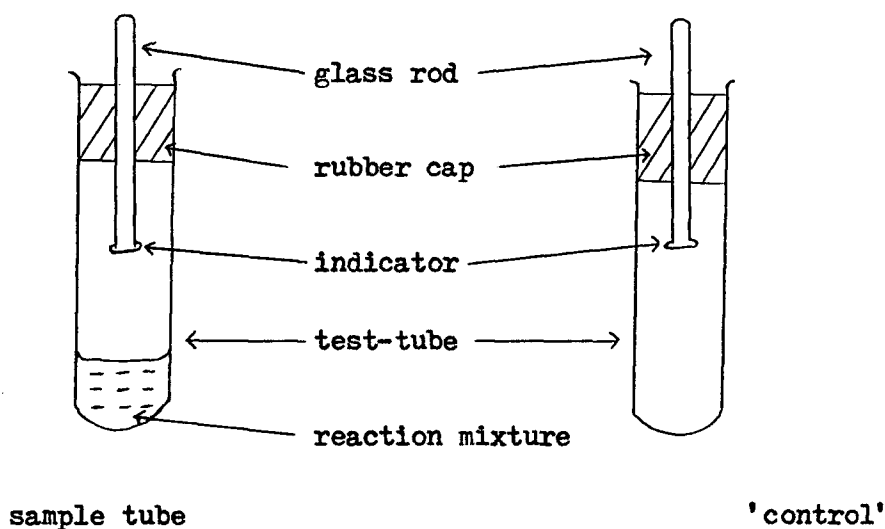
Figure 3

Formaldehyde was analysed by a modified 'chromotropic acid' method[51-54]. At the completion of a reaction, the 3 ml. of reaction

mixture in a 1 cm. cell was transferred into a 10 ml. volumetric falsk.

A 1 ml. aliquot of 2 % chromotropic acid was added, followed by 6 ml. of

concentrated sulphuric acid. A pink colour develops when formaldehyde is

present. (No explanation has yet been given for the appearance of this

pink colour). A 3 ml. aliquot of this solution was transferred into a

1 cm. cell and its absorbance at 580 nm taken. A known concentration of

formaldehyde in 3 ml. of methanol was placed in another 10 ml. volumetric

flask. To this solution was added 1 ml. of 2 % chromotropic acid, followed

by 6 ml. of concentrated sulphuric acid. A pink colour developed

immediately and its absorbance at 580 nm was recorded. Thus, the unknown

concentration of formaldehyde in the reaction mixture could be calculated.

Three 'controls' were used to check whether (i) the $Mn^{III}$ complex, (ii)

tetramethylammonium hydroxide, and (iii) 2,4,6-tri-t-butylphenol,

interfere with this method of analysing for formaldehyde. The first

'control' was done as follows: a 3 ml. sample of the $Mn^{III}$ complex in

methanol (about $6 \times 10^{-4}$ M) was placed in a 10 ml. volumetric flask. A

1 ml. aliquot of 2 % chromotropic acid followed by 6 ml. of concentrated

sulphuric acid were added to it. No pink colour was seen. In the second

'control', 0.05 ml. of 10 % tetramethylammonium hydroxide was added to

a 3 ml. standard solution of formaldehyde in methanol. This solution

was left to stand for 25 minutes and then 1 ml. of 2 % chromotropic acid

followed by 6 ml. of concentrated sulphuric acid were added. A pink

colour developed. In the third 'control', 3 ml. of methanol containing

known concentrations of 2,4,6-tri-t-butylphenol and formaldehyde was

placed in a 10 ml. volumetric flask. This solution was left to stand for 20 minutes and then 2 ml. of distilled water was added to precipitate the phenol. To 3 ml. of the solution was added 1 ml. of 2 % chromotropic acid followed by 6 ml. of concentrated sulphuric acid. No pink colour was seen. The results of the three 'controls' show that the Mn$^{III}$ complex and tetramethylammonium hydroxide do not interfere with the 'chromotropic acid' method whereas 2,4,6-tri-t-butylphenol does interfere with this test.

IV. SOME RELATED WORK

(i) Determination of extinction coefficient of 3,3',5,5'-tetra-t-butyl-p-diphenoquinone in methanol

A 2.5 mg sample of 3,3',5,5'-tetra-t-butyl-p-diphenoquinone (XVIII) was dissolved in 10 ml. of spectroscopic grade acetone. (It was found that this amount of XVIII dissolved in 25 ml. of methanol with difficulty. Therefore, acetone was used as solvent for practical convenience). A 0.025 ml. aliquot of this stock solution was syringed into 3 ml. of methanol in a 1 cm. cell, and the absorbance at 419 nm was recorded. Absorbance readings at various other concentrations of the compound were recorded similarly. A plot of absorbance at 419 nm versus concentration of the compound yields a straight line passing through the origin, indicating Beer's law is obeyed (see Figure 4). The slope of the plot gives a value of 79,000 for the extinction coefficient of XVIII at 419 nm in methanol.



XVIII

Figure 4. Beer's law plot for 3,3',5,5'-tetra-t-butyl-p-diphenoquinone.
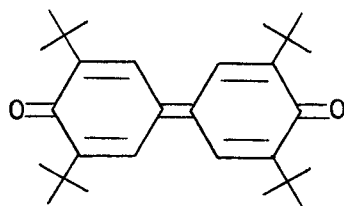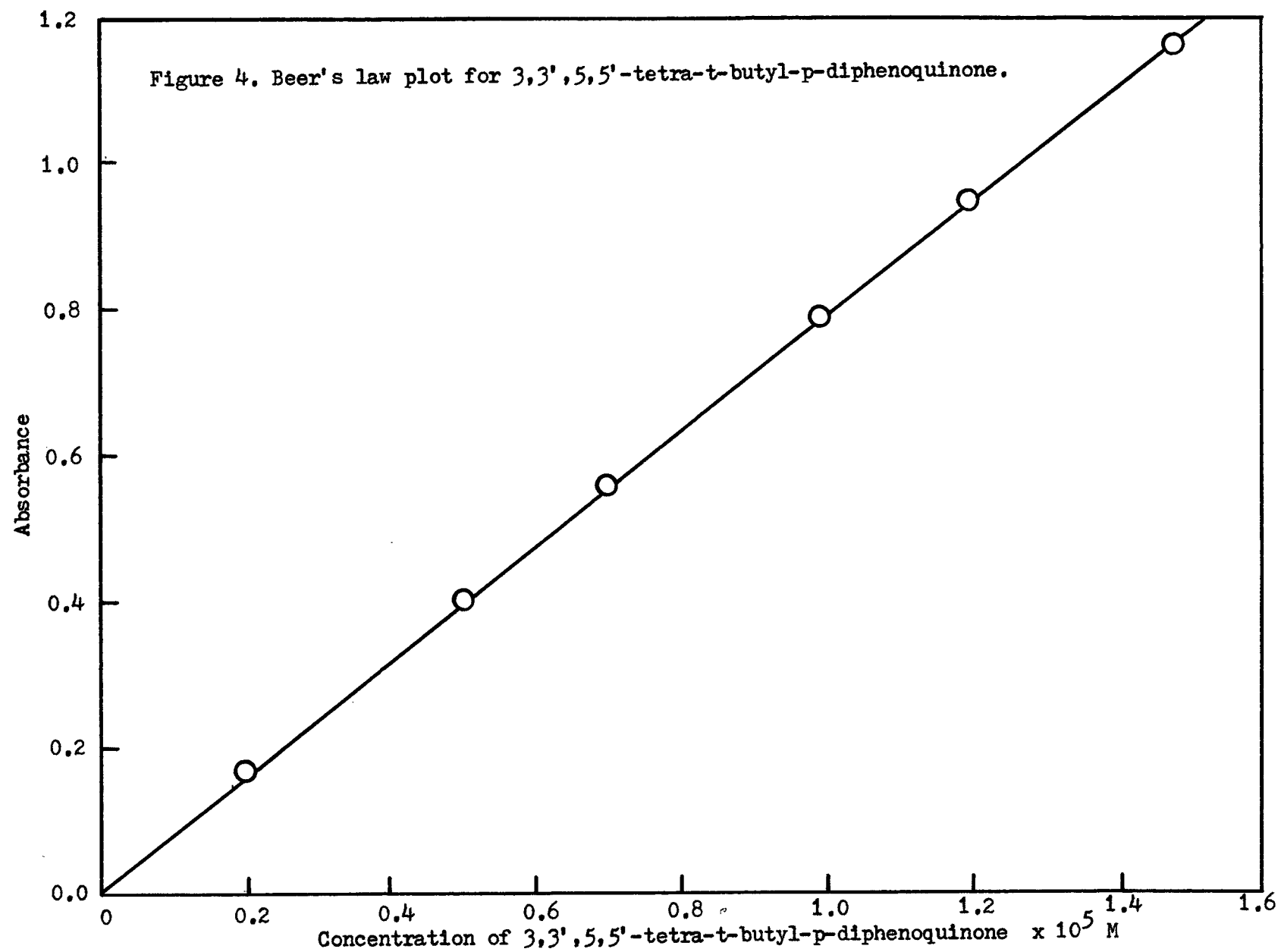
(ii) <u>Determination of extinction coefficient of bis-(1,3,5-tri-t-butyl-</u>
<u>2,5-cyclohexadiene-4-one) peroxide in methanol</u>

A 6.4 mg sample of bis-(1,3,5-tri-t-butyl-2,5-cyclohexadiene-4-one)

peroxide (XII) was dissolved in 5 ml. of methanol in a 5 ml. volumetric

flask. A 0.025 ml. aliquot of this stock solution was syringed into 3 ml.

of methanol in a 1 cm. cell, and the absorbance at 240 nm was recorded.

Absorbance readings at various other concentrations of the compound were

similarly recorded. A plot of absorbance at 240 nm versus concentration of

the compound gives a straight line passing through the origin, indicating

Beer's law is obeyed (see Figure 5). From the slope, a value of 22,010

was obtained for the extinction coefficient of XII at 240 nm in methanol.

(Compare with the value of 25,800 at 240 nm in benzene)[2].
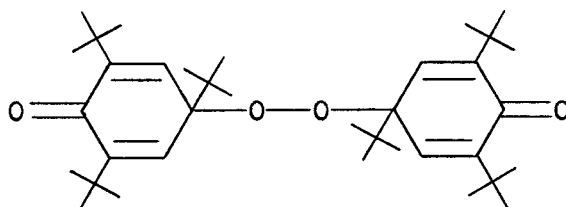


XII
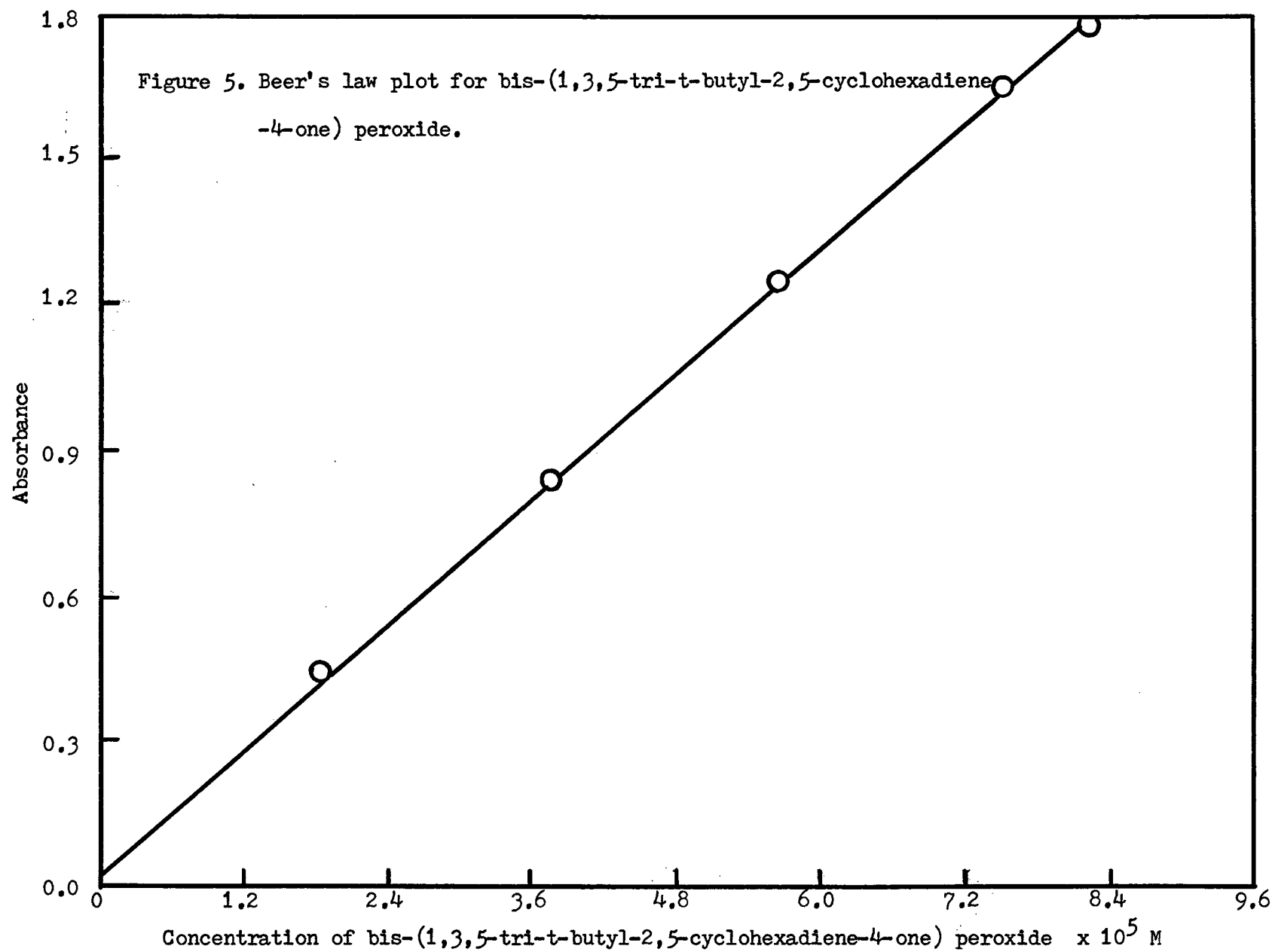
Figure 5. Beer's law plot for bis-(1,3,5-tri-t-butyl-2,5-cyclohexadiene -4-one) peroxide.

(iii) <u>Determination of extinction coefficient of 2,4,6-tri-t-butylphenoxyl</u>
<u>in methanol</u>

It is difficult to prepare a pure sample of 2,4,6-tri-t-butylphenoxyl
(I) because of its reactivity towards oxygen. The method used here to
determine its extinction coefficient avoids the difficult step of
isolating a pure solid sample. It involves the generation of I from its
phenol using lead dioxide as the oxidant, and determining the concentration
of I from the amount of XII that is formed. The procedure is as follows:
a 9.8 mg sample of XXIII was mixed with 0.1 g of lead dioxide in a 2 ml.
centrifuge tube. The tube was sealed with a rubber cap and the contents
flushed with nitrogen. A 1.5 ml. aliquot of methanol (which had been
flushed with nitrogen) was syringed into the tube through the rubber cap
and the contents of the tube were shaken for one minute. Then, the tube
was placed in a centrifuge for two minutes to bring the solid lead dioxide
to the bottom of the tube. A clear blue solution of I appeared above the
lead dioxide layer. A 0.025 ml. aliquot of this clear blue solution was
syringed into each of: (a) two 1 cm. cells each containing 3 ml. of
oxygen-free methanol and capped with a silicone rubber disc, and (b) two
test-tubes each containing 3 ml. of methanol saturated with oxygen.
Absorbance readings at 400 nm for I in the two oxygen-free cells were
recorded. The solutions in the two test-tubes containing oxygen were left
to stand for a few hours to ensure that all of I was converted to XII and
then the absorbance at 240 nm was recorded for each sample. (The absorbance

of 2,4,6-tri-t-butylphenol is at its minimum in this region. Therefore,

any unreacted 2,4,6-tri-t-butylphenol would make a negligible contribution

to the absorbance at 240 nm). Knowing the extinction coefficient of XII

(see Section IV-ii), its concentration could be calculated, and

doubling this concentration gives the concentration of I (see equation

(13)). Thus, the extinction coefficient of I could be determined,

assuming that the same quantity of I was formed in the two sets of

experiments. It was found that all duplicate samples gave results in good

agreement with one another. This procedure was followed for three other

quantities of 2,4,6-tri-t-butylphenol (up to 23.8 mg) with the weight of

lead dioxide used being kept at 0.1 g. The results are summarised in

Table II. An average value of $1955 \pm 66$ was obtained for the extinction

coefficient of I at 400 nm in methanol. (Compare with the value of 2050

at 400 nm reported in benzene)[55].

$$2 \quad \text{I} \quad + \quad O_2 \quad \longrightarrow \quad \text{XII} \qquad (13)$$

I                                    XII
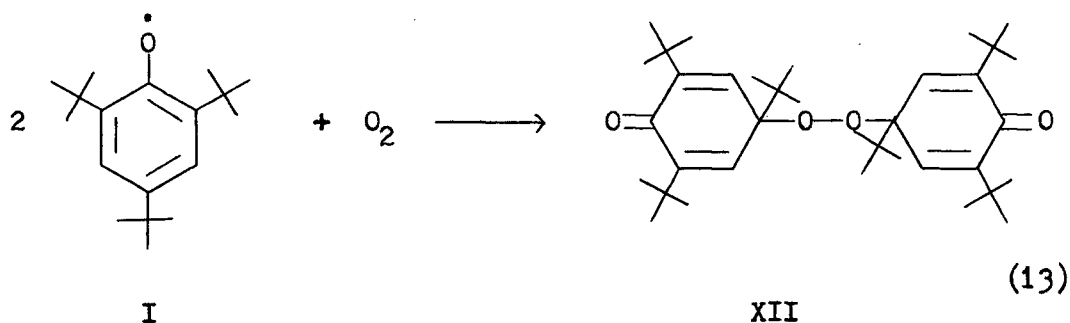
TABLE II

Absorbance and yield of 2,4,6-tri-t-butylphenoxyl for various

concentrations of 2,4,6-tri-t-butylphenol used

| (PhOH)[a](M) | Absorbance(400nm) | (PhO·)[b,c](M) | $\epsilon_{400nm}^d$ | % yield[e] of PhO· |
|---|---|---|---|---|
| $2.07 \times 10^{-4}$ | 0.220 | $1.13 \times 10^{-4}$ | 1943 | 55 |
| $3.09 \times 10^{-4}$ | 0.327 | $1.60 \times 10^{-4}$ | 2049 | 52 |
| $4.03 \times 10^{-4}$ | 0.386 | $2.04 \times 10^{-4}$ | 1896 | 51 |
| $5.00 \times 10^{-4}$ | 0.471 | $2.44 \times 10^{-4}$ | 1933 | 49 |

a PhOH = 2,4,6-tri-t-butylphenol

b PhO· = 2,4,6-tri-t-butylphenoxyl

c concentration of 2,4,6-tri-t-butylphenoxyl was calculated from that of XII

d $\epsilon_{400nm}$ was calculated by dividing absorbance by concentration of I

e yield calculated by dividing the values in column 3 by those in column 1

(iv) <u>Determination of the equilibrium constant between 2,4,6-tri-t-</u>
<u>butylphenol and its anion in methanol</u>

The equilibrium constant K (defined in equation (15)) for the
equilibrium shown in equation (14) was determined spectrophotometrically
as described below.

$$PhOH + OH^- \; \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \; PhO^- + H_2O \qquad (14)$$
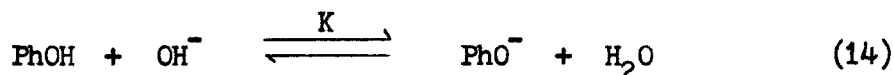
$$K = (PhO^-)/(PhOH)(OH^-) \qquad (15)$$

<u>Abbreviations used:</u>

PhOH = 2,4,6-tri-t-butylphenol
PhO$^-$ = 2,4,6-tri-t-butylphenoxy anion

To a 3 ml. solution of 2,4,6-tri-t-butylphenol of known concentration
in methanol in a 1 cm. cell was added 0.050 ml. of a standard base
followed by 0.025 ml. of distilled water (water content in the cell was
maintained at 2.5 % by volume). The concentration of 2,4,6-tri-t-butylphenoxy
anion formed was determined from its absorbance at 302 nm using an
extinction coefficient value[56] of 4400. (At this wavelength 2,4,6-tri-t-
butylphenol does not have any absorbance). Knowing the concentration of
2,4,6-tri-t-butylphenoxy anion, the final concentrations of base and
2,4,6-tri-t-butylphenol could be calculated as could K using equation (15).

This procedure was repeated for other concentrations of base and an average value of K was calculated. The value of K was also determined in methanol-O-d containing deuteroxide ion. The results obtained are shown in Table III.

TABLE III

Equilibrium constant for ionization of 2,4,6-tri-t-butylphenol in methanol at $25^\circ$

| Base | Solvent | Conc. of base(M) | $(PhO^-)(M)$ | $(PhOH)(M)$ | $K(M^{-1})$ |
|------|---------|------------------|--------------|-------------|-------------|
| TMA[a] | $CH_3OH$ | $0.89 \times 10^{-2}$ | $0.54 \times 10^{-4}$ | $2.51 \times 10^{-2}$ | 0.241 |
| | | $1.77 \times 10^{-2}$ | $1.09 \times 10^{-4}$ | $2.50 \times 10^{-2}$ | 0.246 |
| | | $2.66 \times 10^{-2}$ | $1.68 \times 10^{-4}$ | $2.50 \times 10^{-2}$ | 0.253 |
| | | | | Average K | 0.247 |
| NaOH | $CH_3OH$ | $0.81 \times 10^{-2}$ | $0.78 \times 10^{-4}$ | $4.05 \times 10^{-2}$ | 0.238 |
| | | $3.21 \times 10^{-2}$ | $3.10 \times 10^{-4}$ | $4.02 \times 10^{-2}$ | 0.240 |
| | | | | Average K | 0.239 |
| NaOD | $CH_3OD$ | $1.01 \times 10^{-2}$ | $1.18 \times 10^{-4}$ | $2.55 \times 10^{-2}$ | 0.458 |
| | | $2.03 \times 10^{-2}$ | $2.27 \times 10^{-4}$ | $2.54 \times 10^{-2}$ | 0.440 |
| | | | | Average K | 0.449 |

a TMA = Tetramethylammonium hydroxide

The equilibrium isotope effect, $K_H/K_D$, is 0.53. This value is within the usual range[57] of equilibrium isotope effects for reactions similar to that shown in equation (14). For example, the value of $K_H/K_D$ for the equilibrium shown in equation (16) was found to be 0.70 by Swain and co-workers[58] using a spectroscopic technique and 0.74 by Ballinger and Long[59] using a conductivity method.

$$CH_2ClCH_2OH + OH^- \underset{\longleftarrow}{\overset{K_b}{\longrightarrow}} CH_2ClCH_2O^- + H_2O \qquad (16)$$
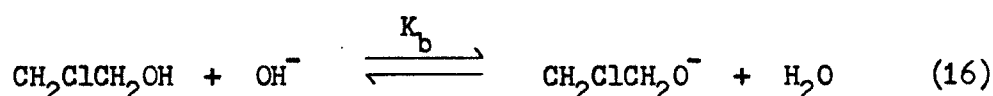
This equilibrium isotope effect has two major causes: (i) $OD^-$ is a stronger base than $OH^-$; (ii) $D_2O$ is a weaker acid than $H_2O$. These two factors shift the equilibrium shown in equation (14) more towards the right when the deuterated solvent is used. The fact that $OD^-$ is a stronger base than $OH^-$ has been shown by many workers[57-61]; e.g. the equilibrium constant for equation (17) was found to be $3.9$[59] and $3.2$[58]. The acid strength of $D_2O$ has also been shown to be weaker than that of $H_2O$[62-64]. An equilibrium isotope effect[63], $K_H/K_D$, on the autoprotolysis of water (see equation (18)) was found to be 9.08 at $25°$.

$$2\ OD^- + H_2O \underset{\longleftarrow}{\overset{K_c}{\longrightarrow}} 2\ OH^- + D_2O \qquad (17)$$

$$2\ H_2O \underset{\longleftarrow}{\overset{K_d}{\longrightarrow}} H_3O^+ + OH^- \qquad (18)$$
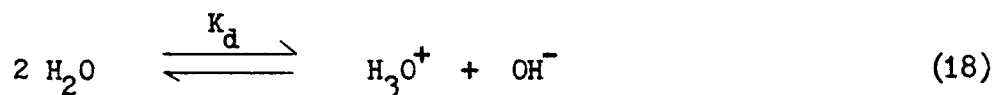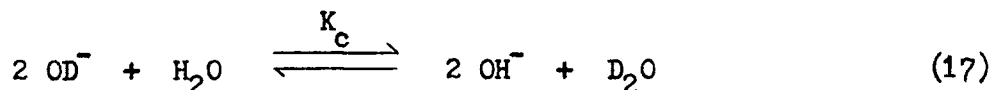
(v) <u>Spectra of the Mn$^{III}$ complex in methanol</u>

KMn$^{III}$CyDTA(H$_2$O) has been reported[41] to exist in two different

forms in water. In acidic and neutral conditions, the pink species with

a formula believed to be Mn$^{III}$CyDTA(H$_2$O)$^-$ predominates, whereas in basic

condition the yellow species with a formula believed to be Mn$^{III}$CyDTA(OH)$^{2-}$

predominates. The pK$_a$ value for the equilibrium between these two species

(equation (19)) was reported to be 8.1[41].

$$Mn^{III}CyDTA(H_2O)^- \xrightleftharpoons{K_a} Mn^{III}CyDTA(OH)^{2-} + H^+ \qquad (19)$$
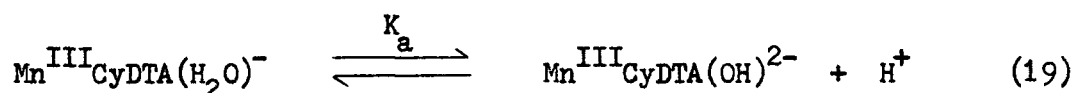
In methanol a similar equilibrium exists. In the absence of base,

the pink species Mn$^{III}$CyDTA(H$_2$O)$^-$ predominates (absorption maximum at

510 nm). When base is added the pink colour immediately changes to

yellow owing to the formation of Mn$^{III}$CyDTA(OH)$^{2-}$ (absorption maximum at

466 nm). When acid is added to the yellow solution the colour reverts

back to pink immediately. The interconvertibility between these two

species is also observed in aqueous medium. In this work, it was found

that another form of the complex exists in methanol in the presence of an

excess of acid (see curve B of Figure 6). This third species is also

pink in colour but its visible spectrum shows it to be different from

the other two species. Its absorption maximum in the visible is at 520

nm. Addition of an excess base immediately changes this species to the

yellow species, and when acid is added to the resulting yellow solution,

Figure 6. Visible spectra of $KMn^{III}CyDTA(H_2O)$ in methanol*.

A. $6 \times 10^{-4}$ M of the $Mn^{III}$ complex in methanol

B. $6 \times 10^{-4}$ M of the $Mn^{III}$ complex + 6.1 $\times 10^{-2}$ M HCl in methanol

C. $6 \times 10^{-4}$ M of the $Mn^{III}$ complex + 1.8 $\times 10^{-2}$ M base in methanol

* 1 cm cell used

  2.5 % water (v/v)
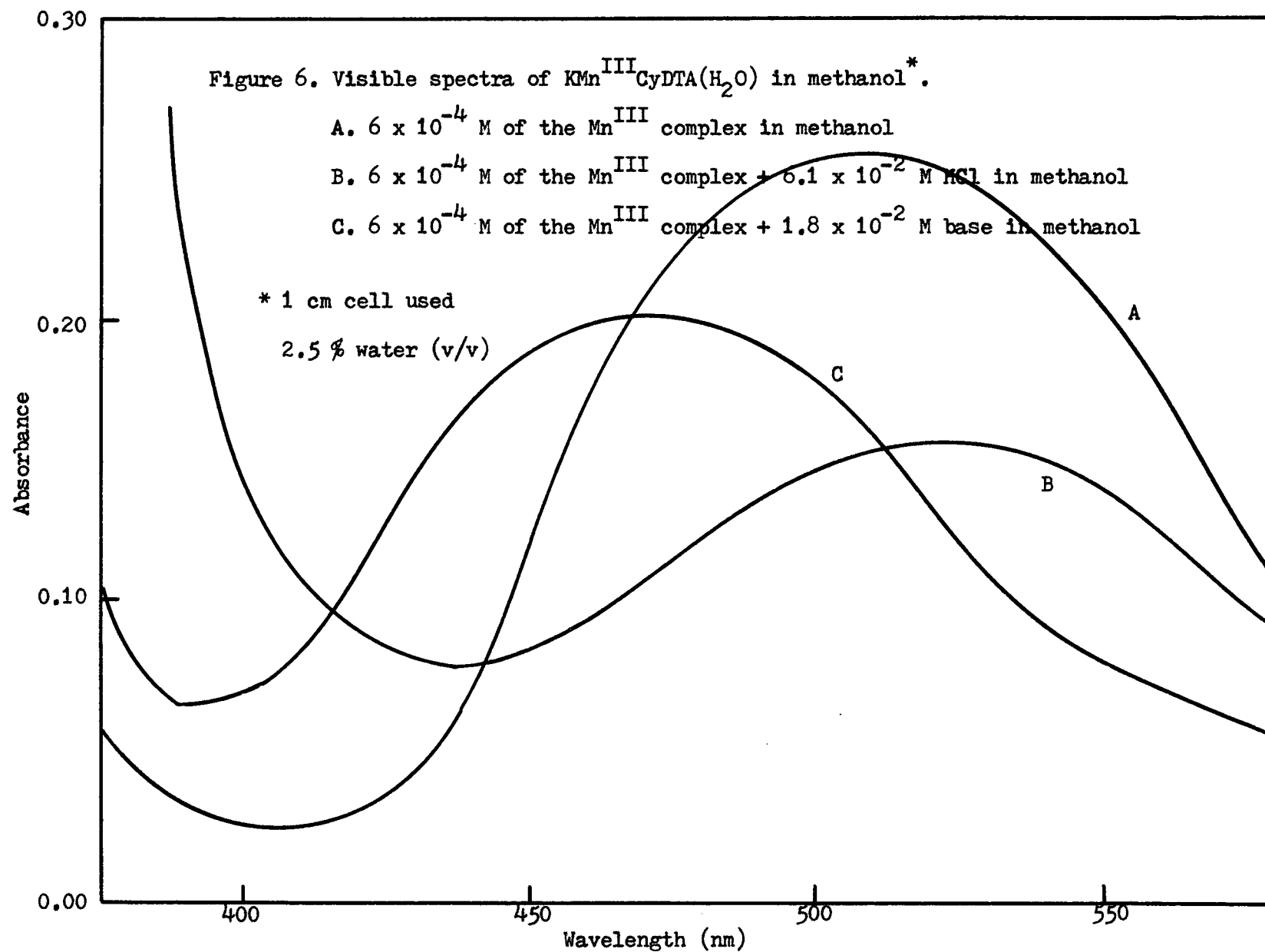
the pink colour appears immediately. This third species is probably a protonated form of the $Mn^{III}$ complex with formula $HMn^{III}CyDTA(H_2O)$. (Kinetic evidence presented in Sections VI and VII of this thesis indicates the presence of such a protonated form). Protonation probably occurs at a carboxylate arm of the ligand which becomes free from coordination with the $Mn^{III}$ ion. (The following compounds all have a free, protonated, carboxylate arm: $Cr^{III}YH(H_2O)$[65,66]; $Fe^{III}YH(H_2O)$[65-67]; $Ga^{III}YH(H_2O)$[65-67]; $Ni^{III}YH(H_2O)$[68]; where Y is ethylenediaminetetraacetic acid anion. In the unprotonated form, all these complexes have all the four carboxylate arms coordinated to the central metal ion).

An attempt to measure the ionization constant of the protonated form of the $Mn^{III}$ complex by spectrophotometric method failed because of its rapid reaction with methanol (see Section VI).

No spectral change was observed when acid was added to an aqueous solution of the $Mn^{III}$ complex.

(vi) <u>Molecular formula and crystal structure of the Mn$^{III}$ complex</u>

(a) <u>Brief remarks</u>

Few manganese(III) compounds have been prepared and characterised owing to their tendency to disproportionate to form manganese(II) ion and manganese(IV) oxide (see equation (20)).

$$2 \text{ Mn}^{III} + 2 \text{ H}_2\text{O} \rightleftharpoons \text{Mn}^{II} + \text{MnO}_2 + 4 \text{ H}^+ \qquad (20)$$
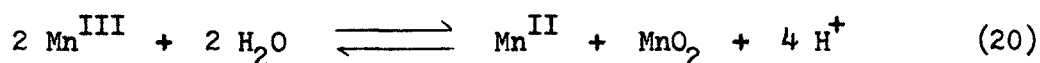
Hamm and Suwyn[41], using a method similar to that described by Yoshino and co-workers[69], prepared a solid trans-1,2-diaminocyclohexanetetraacetic acid complex of manganese(III) in 1966. This complex was assigned a formula of KMn$^{III}$CyDTA·2.5H$_2$O on the basis of elemental analytical data (CyDTA is used as an abbreviation for the trans-1,2-diaminocyclohexanetetraacetic acid anion ligand). They found that this complex was stable at room temperature when it was stored in the dark, and that it existed in two forms in solution. In acidic solution, a pink species with a formula believed to be Mn$^{III}$CyDTA(H$_2$O)$^-$ predominated, and under basic conditions, the predominant species was yellow in colour with a formula believed to be Mn$^{III}$CyDTA(OH)$^{2-}$. The pK$_a$ value for the pink species, Mn$^{III}$CyDTA(H$_2$O)$^-$, was found to be 8.1. The standard potential for equation (21) was found to be 0.814 v[41].

$$\text{Mn}^{III}\text{CyDTA}(\text{H}_2\text{O})^- + \text{e}^- \rightleftharpoons \text{Mn}^{II}\text{CyDTA}(\text{H}_2\text{O})^{2-} \qquad (21)$$
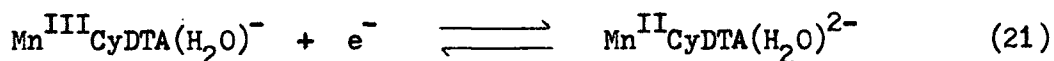
In this work, the $Mn^{III}$ complex was prepared using the procedure described by Hamm and Suwyn. The crude product was then recrystallised from hot methanol-water solvent. It was noted that elemental analytical results indicated a formula of $KMn^{III}CyDTA(H_2O)$ and the melting point (decomposition point) of a recrystallised sample of the complex was higher than that of the crude product (201-203° and about 180°, respectively). The lack of information on the melting point and purification procedure in reference 41 prompted an investigation on the exact molecular formula and structure of this complex. A Karl Fischer titration to determine the water content of the complex and an X-ray single crystal diffraction study to determine the structure of the complex were carried out. The results (described below) support a formula of $KMn^{III}CyDTA(H_2O)$.

## (b) Karl Fischer titration

A Beckman Aquameter Model KF-2 automatic titrator was used in the determination of water. The Karl Fischer reagent (from Fisher Scientific Company) used was first standardised with reagent grade sodium tartrate dihydrate $(Na_2C_4H_4O_6 \cdot 2H_2O)$ in anhydrous methanol. A typical titration was carried out as follows: to a beaker was added some methanol which contained some water and titration with Karl Fischer reagent was carried out automatically until the methanol in the beaker was anhydrous. Then, a known weight of sodium tartrate dihydrate was added to this anhydrous methanol and an automatic titration was started again until the end-point

was reached. The volume of Karl Fischer reagent used was recorded. The number of millilitres of Karl Fischer reagent needed to titrate one milligram of water was calculated (the water content in a sample of sodium tartrate dihydrate could be calculated from its molecular formula). This procedure was repeated for two more weighed samples of sodium tartrate dihydrate and an average value of the results was taken. For the $Mn^{III}$ complex, a weighed sample of this complex (100 mg) was first dissolved in 2 ml. of anhydrous dimethyl sulfoxide (DMSO); then this solution was added to the anhydrous methanol in the beaker and an automatic titration was carried out. A 2 ml. aliquot of the same sample of DMSO was also titrated to correct for any water present in it. (The $Mn^{III}$ complex does not dissolve in methanol easily, therefore DMSO was used as solvent. The percentages of DMSO and methanol in the titration vessel were about 5 % and 95 % respectively). The titration of the $Mn^{III}$ complex was carried out in duplicate at two different times. A similar titration on a crude sample of the $Mn^{III}$ complex was also carried out. This crude sample had a lower and indistinct decomposition point (about $170^{o}$).

The crude sample of the $Mn^{III}$ complex was found to contain 6.6 % water, corresponding to 1.7 moles of water of crystallisation. This is close to the value expected for $KMn^{III}CyDTA \cdot 2.5H_2O$ assuming that one molecule of water is rather firmly coordinated to the $Mn^{III}$ ion.

Only 0.6 % of water was detected in a recrystallised sample of the

Mn$^{III}$ complex, indicating that there is little, if any, water of crystallisation in the sample. Elemental analysis and crystal structure show that one water molecule is present in each molecule of the complex. This water molecule is probably coordinated quite firmly to the complex since it is not released to the methanol solvent immediately. It was found that this water molecule was released to the methanol solvent in about thirty minutes. After a sample of the recrystallised complex was kept in anhydrous methanol in the titration vessel for thirty minutes water was released corresponding to 4.0 % of the weight of the complex, that is 1.0 mole of water per mole of complex. It is not certain whether a methanol molecule replaces the water molecule in the Mn$^{III}$ complex or whether the water is released as a result of the slow decomposition of the Mn$^{III}$ complex in the Karl Fischer reagent mixture.

The fact that the mono-aquo complex is obtained pure by recrystallisation from 60 % methanol and 40 % water mixed solvent suggests that water is the preferred ligand. Attempts to determine the equilibrium concentration of water and methanol in the complex in the presence of 97 % methanol-3 % water (the mixture used in the kinetic studies) failed. Flash evaporation of such solutions produced a solid residue which was partly decomposed and gave variable amounts of water.

Throughout this thesis it will be assumed that water is the ligand present in the complex during the oxidation steps.

## (c) Crystal structure of $KMn^{III}CyDTA(H_2O)$

An X-ray single crystal structure study on $KMn^{III}CyDTA(H_2O)$ was carried out in this department by Mr. S. Rettig and Dr. J. Trotter. The crystal was shown to be triclinic and contain two molecules of the complex per unit cell. The structure of the complex is shown in Figure 7 and the various bond lengths and bond angles are listed in Tables IV and V respectively.

The structure indicates a slightly distorted octahedron of $Mn^{III}$ ion with the four carboxylate groups bonded to the $Mn^{III}$ ion in two ways ($O_2-C_8 = O_8-C_{14} = 1.258 \pm 0.008$ A$^\circ$; $O_4-C_{10} = O_6-C_{12} = 1.232 \pm 0.008$ A$^\circ$). The cyclohexane ring is in a chair conformation and the angles in the ring are close to $109.5^\circ$. The two nitrogen atoms attached to the cyclohexane ring are in trans-di-equatorial conformation.

The position of the water molecule seems to vary in the molecule. The major position is at a distance of $3.68 \pm 0.02$ A$^\circ$ from the $Mn^{III}$ ion and the other position is $4.55 \pm 0.02$ A$^\circ$ from the $Mn^{III}$ ion. These two values are much longer than a normal metal-water bond (about 2.1 A$^\circ$), suggesting that the $Mn^{III}$ ion is six-coordinated. (Compare with $Fe^{III}EDTA(H_2O)^-$ and $Mn^{II}EDTA(H_2O)^{2-}$ which contain seven-coordinated metal ions)[70,71]. However, Karl Fischer titrations (Section IV-vi(b)) indicated that this water molecule is bound in the complex. Thus, this water molecule is probably coordinated to the $Mn^{III}$ ion in solution.

Figure 7. Model in perspective of the sexadentate six-coordinate $Mn^{III}CyDTA(H_2O)^-$. The atoms, $O_1$, $O_3$, $O_5$, $O_7$, $N_1$ and $N_2$, form the vertices of a distorted octahedron.

$O_{9'}$ (0.38)[*]

$O_9$ (0.62)[**]
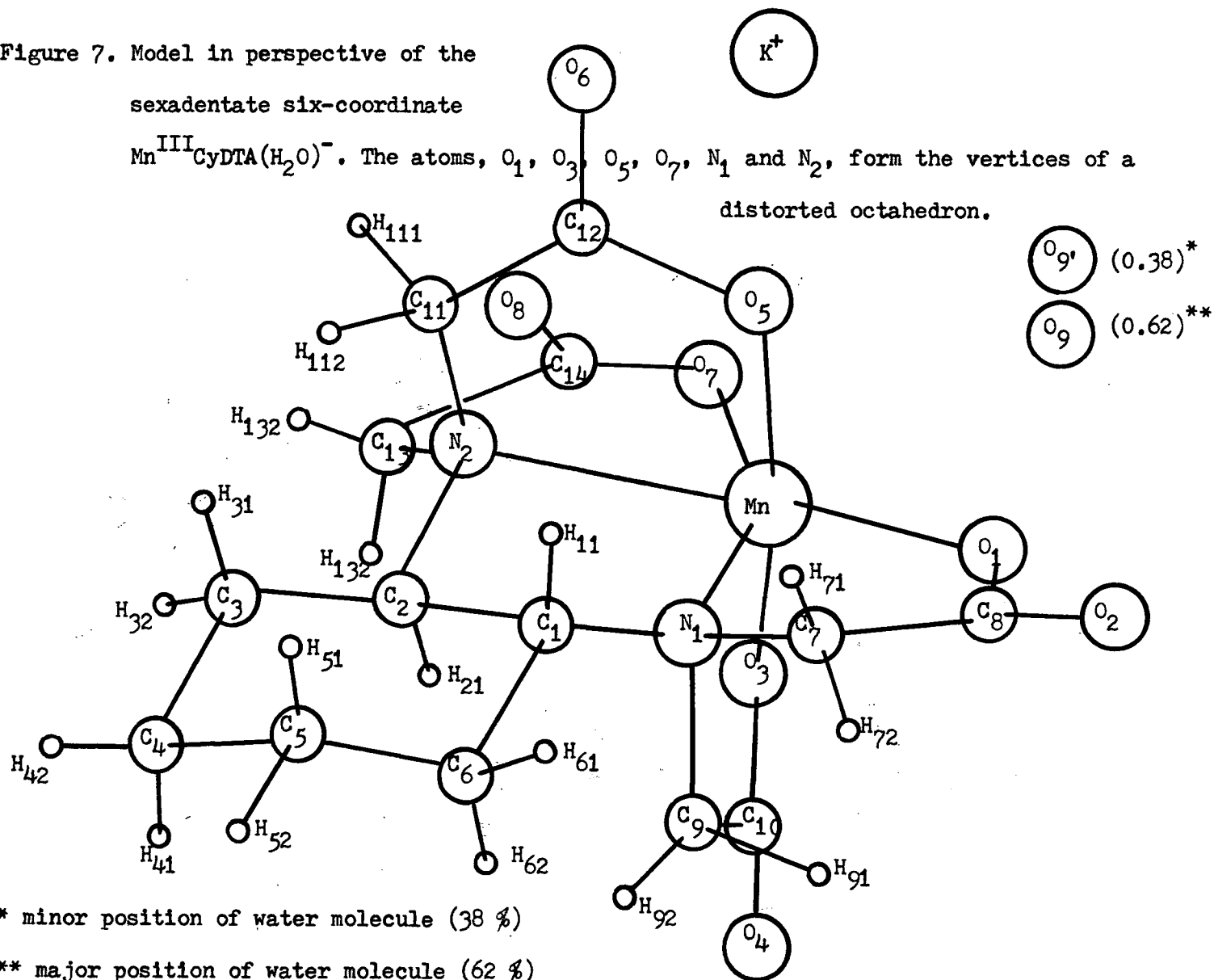
* minor position of water molecule (38 %)

** major position of water molecule (62 %)

TABLE IV

## Individual bond lengths in $KMn^{III}CyDTA(H_2O)$

| Bond | Length ($A^o$) ($\pm 0.008$) | Bond | Length ($A^o$) ($\pm 0.008$) | Bond | length ($A^o$) ($\pm 0.080$) |
|---|---|---|---|---|---|
| $Mn-O_1$ | 2.064 | $N_1-C_1$ | 1.495 | $C_1-H_{11}$ | 1.012 |
| $Mn-O_3$ | 1.880 | $N_1-C_7$ | 1.510 | $C_2-H_{21}$ | 1.010 |
| $Mn-O_5$ | 1.893 | $N_1-C_9$ | 1.487 | $C_3-H_{31}$ | 0.986 |
| $Mn-O_7$ | 2.002 | $N_2-C_2$ | 1.503 | $C_3-H_{32}$ | 0.869 |
| $Mn-N_1$ | 2.249 | $N_2-C_{11}$ | 1.482 | $C_4-H_{41}$ | 0.951 |
| $Mn-N_2$ | 2.278 | $N_2-C_{13}$ | 1.470 | $C_4-H_{42}$ | 0.969 |
| $O_1-C_8$ | 1.284 | $C_1-C_2$ | 1.566 | $C_5-H_{51}$ | 1.150 |
| $O_2-C_8$ | 1.258 | $C_1-C_6$ | 1.543 | $C_5-H_{52}$ | 1.084 |
| $O_3-C_{10}$ | 1.323 | $C_2-C_3$ | 1.538 | $C_6-H_{61}$ | 0.992 |
| $O_4-C_{10}$ | 1.234 | $C_3-C_4$ | 1.530 | $C_6-H_{62}$ | 0.922 |
| $O_5-C_{12}$ | 1.308 | $C_4-C_5$ | 1.556 | $C_7-H_{71}$ | 0.953 |
| $O_6-C_{12}$ | 1.230 | $C_5-C_6$ | 1.539 | $C_7-H_{72}$ | 1.085 |
| $O_7-C_{14}$ | 1.303 | $C_7-C_8$ | 1.521 | $C_9-H_{91}$ | 1.041 |
| $O_8-C_{14}$ | 1.257 | $C_9-C_{10}$ | 1.508 | $C_9-H_{92}$ | 1.010 |
| | | $C_{11}-C_{12}$ | 1.540 | $C_{11}-H_{111}$ | 0.893 |
| | | $C_{13}-C_{14}$ | 1.530 | $C_{11}-H_{112}$ | 1.007 |
| | | | | $C_{13}-H_{131}$ | 1.181 |
| | | | | $C_{13}-H_{132}$ | 0.907 |

TABLE V

Bond angles in KMn$^{III}$CyDTA(H$_2$O)

| Bond angle | degree ($\pm$ 0.2) | Bond angle | degree ($\pm$ 0.5) | Bond angle | degree ($\pm$ 0.5) |
|---|---|---|---|---|---|
| O$_1$MnO$_3$ | 96.1 | MnN$_1$C$_1$ | 108.4 | C$_4$C$_5$C$_6$ | 110.6 |
| O$_1$MnO$_5$ | 87.4 | MnN$_1$C$_7$ | 103.8 | C$_1$C$_6$C$_5$ | 110.7 |
| O$_1$MnO$_7$ | 129.3 | MnN$_1$C$_9$ | 103.4 | N$_1$C$_7$C$_8$ | 111.2 |
| O$_1$MnN$_1$ | 76.5 | C$_1$N$_1$C$_7$ | 113.5 | O$_1$C$_8$O$_2$ | 124.6 |
| O$_1$MnN$_2$ | 152.3 | C$_1$N$_1$C$_9$ | 114.8 | O$_1$C$_8$C$_7$ | 116.7 |
| O$_3$MnO$_5$ | 175.5 | C$_7$N$_1$C$_9$ | 111.7 | O$_2$C$_8$C$_7$ | 118.7 |
| O$_3$MnO$_7$ | 87.9 | MnN$_2$C$_2$ | 108.4 | N$_1$C$_9$C$_{10}$ | 114.7 |
| O$_3$MnN$_1$ | 82.3 | MnN$_2$C$_{11}$ | 103.8 | O$_3$C$_{10}$O$_4$ | 123.2 |
| O$_3$MnN$_2$ | 93.4 | MnN$_2$C$_{13}$ | 104.4 | O$_3$C$_{10}$C$_9$ | 116.6 |
| O$_5$MnO$_7$ | 92.0 | C$_2$N$_2$C$_{11}$ | 115.3 | O$_4$C$_{10}$C$_9$ | 120.2 |
| O$_5$MnN$_1$ | 95.9 | C$_2$N$_2$C$_{13}$ | 112.8 | N$_2$C$_{11}$C$_{12}$ | 114.7 |
| O$_5$MnN$_2$ | 82.3 | C$_{11}$N$_2$C$_{13}$ | 111.0 | O$_5$C$_{12}$O$_6$ | 122.7 |
| O$_7$MnN$_1$ | 153.5 | N$_1$C$_1$C$_2$ | 110.3 | O$_5$C$_{12}$C$_{11}$ | 117.0 |
| O$_7$MnN$_2$ | 76.9 | N$_1$C$_1$C$_6$ | 113.4 | O$_6$C$_{12}$C$_{11}$ | 120.3 |
| N$_1$MnN$_2$ | 79.1 | N$_2$C$_2$C$_1$ | 107.1 | N$_2$C$_{13}$C$_{14}$ | 110.0 |
| MnO$_1$C$_8$ | 117.3 | N$_2$C$_2$C$_3$ | 113.6 | O$_7$C$_{14}$O$_8$ | 124.3 |
| MnO$_3$C$_{10}$ | 120.5 | C$_1$C$_2$C$_3$ | 113.9 | O$_7$C$_{14}$C$_{13}$ | 117.2 |
| MnO$_5$C$_{12}$ | 120.7 | C$_2$C$_3$C$_4$ | 110.5 | O$_8$C$_{14}$C$_{13}$ | 118.5 |
| MnO$_7$C$_{14}$ | 118.6 | C$_3$C$_4$C$_5$ | 108.7 | | |

## V. DECOMPOSITION OF THE $Mn^{III}$ COMPLEX IN METHANOL[*] IN THE PRESENCE OF BASE

### (i) Products

A trace of formaldehyde (see Section III-vi for analytical method) and manganese dioxide (see discussion at the end of this section) were produced from the decomposition of the $Mn^{III}$ complex in methanol in the presence of base.

### (ii) Analysis of kinetic results

Decomposition of the $Mn^{III}$ complex in methanol was carried out in the presence of excess tetramethylammonium hydroxide. Plots of logarithm of absorbance of the $Mn^{III}$ complex versus time are linear up to about 50 % of reaction. The decomposition of the $Mn^{III}$ complex was not followed beyond 50 % of reaction because of the appearance of a broad absorption band extending from the 300 nm region into the 400 nm region that is due to manganese dioxide formed in the reaction. The decomposition of the $Mn^{III}$ complex can be expressed by equation (22). Figure 8 is a typical plot made using equation (23).

$$- d(Mn^{III})/dt = k_d(Mn^{III}) \qquad (22)$$

[*] 2.5 % water (v/v)

Figure 8. Plot of log $A_{Mn}$ versus time for the decomposition of the $Mn^{III}$ complex in methanol in the presence of base.

$(Mn^{III}) = 5.4 \times 10^{-4}$ M

$(OH^{-}) = 1.78 \times 10^{-2}$ M

Temperature = $25^{o}$
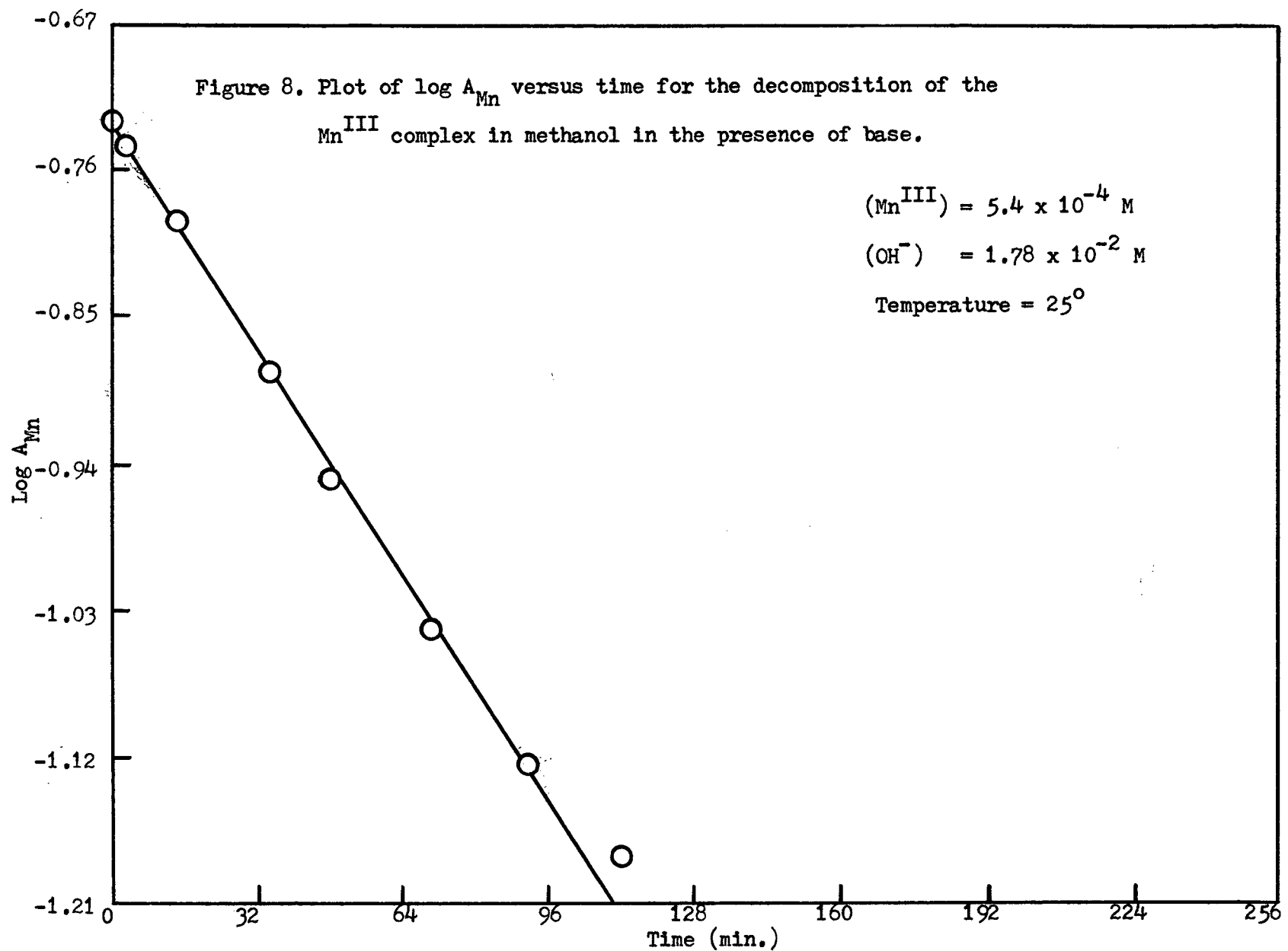
Integrating equation (22) gives equation (23).

$$\text{Log } A_{Mn} - \log A_o = -k_d t / 2.303 \tag{23}$$

$(Mn^{III})$ = concentration of the $Mn^{III}$ complex

$k_d$ = pseudo-first order rate constant

$A_{Mn}$ = absorbance of the $Mn^{III}$ complex at 466 nm at time t

$A_o$ = absorbance of the $Mn^{III}$ complex at 466 nm at time zero

When the concentration of the $Mn^{III}$ complex was kept constant, $k_d$ was found to vary linearly with the concentration of tetramethylammonium hydroxide (see Table VI and Figure 9). Thus, $k_d$ is a base-dependent term.

TABLE VI

Variation of $k_d$ with base concentration at $25^o$

| $(TMA)^*(M)$ | $k_d (sec^{-1})$ |
|---|---|
| $0.71 \times 10^{-2}$ | $0.96 \times 10^{-4}$ |
| $0.90 \times 10^{-2}$ | $1.04 \times 10^{-4}$ |
| $1.43 \times 10^{-2}$ | $1.49 \times 10^{-4}$ |
| $1.78 \times 10^{-2}$ | $1.80 \times 10^{-4}$ |
| $2.65 \times 10^{-2}$ | $2.77 \times 10^{-4}$ |

\* TMA = Tetramethylammonium hydroxide     $(Mn^{III}) = 5.4 \times 10^{-4}$ M

Figure 9. Plot of $k_d$ versus base concentration.

$(Mn^{III}) = 5.4 \times 10^{-4}$ M

Temperature = $25^o$

Concentration of tetramethylammonium hydroxide  $x\ 10^2$ M

$k_d \times 10^4\ sec^{-1}$
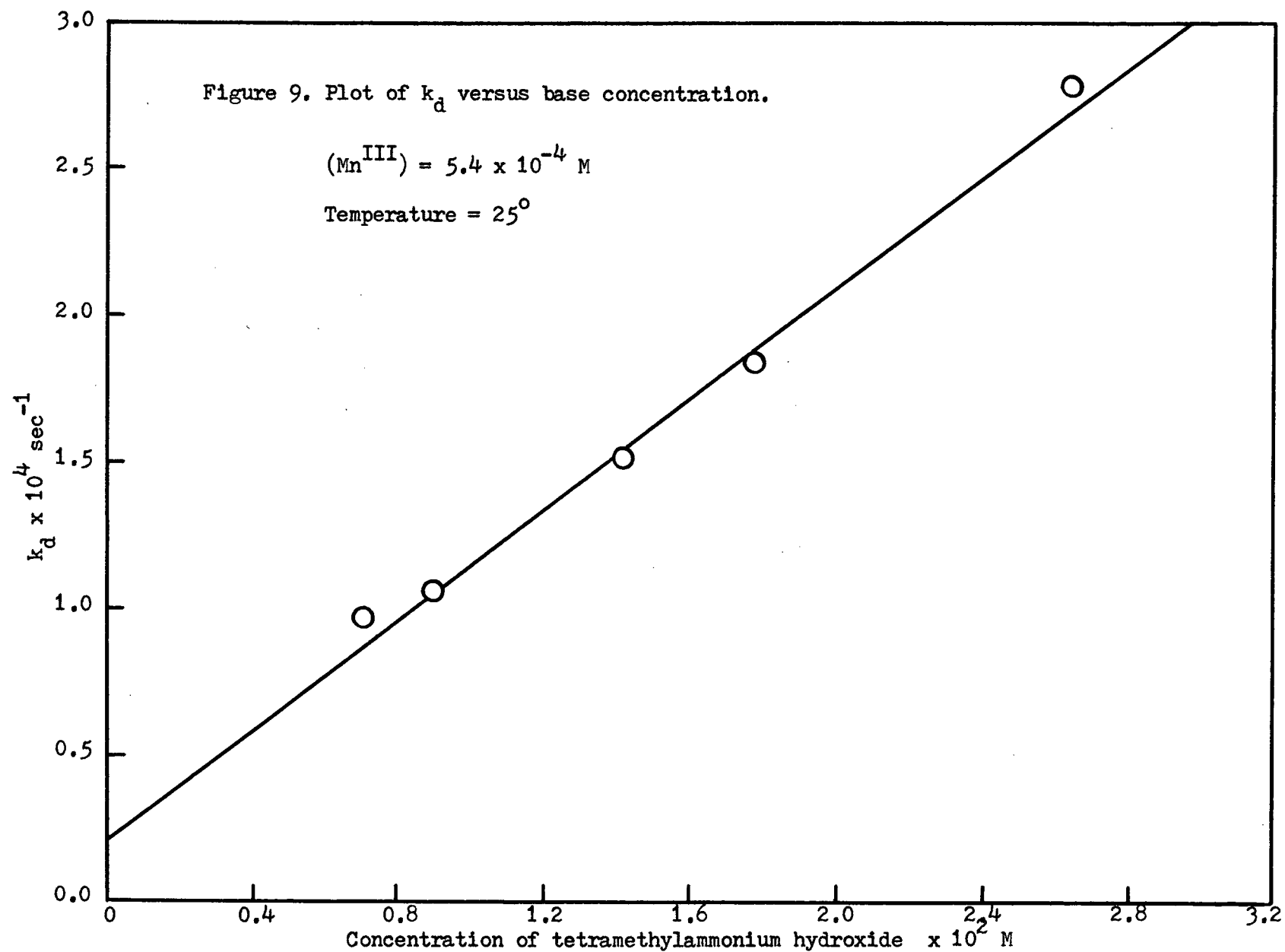
The following stoichiometric reaction is postulated:

$$2 \, Mn^{III} + 4 \, OH^- \xrightarrow{k_7} Mn^{II} + MnO_2 + 2 \, H_2O \qquad (24)$$
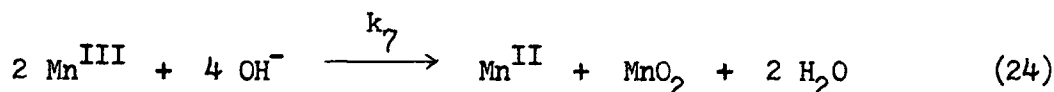
The rate of disappearance of the $Mn^{III}$ complex is given by equation (25).

$$- d(Mn^{III})/dt = 2k_7(OH^-)(Mn^{III}) \qquad (25)$$

Since $(OH^-) \gg (Mn^{III})$, $2k_7(OH^-)$ is a constant. Equation (25) is identical to equation (22) with

$$2k_7(OH^-) = k_d \qquad (26)$$

Integrating equation (25) gives equation (27).

$$\log A_{Mn} - \log A_o = - k_d t/2.303 \qquad (27)$$

(iii) Determination of rate constant

For each concentration of tetramethylammonium hydroxide, $k_d$ was evaluated from the slope of a plot of $\log A_{Mn}$ versus time (see equation (27) and Figure 8). Then a plot of $k_d$ versus base concentration (see equation (26) and Figure 9) yielded the value of $2k_7$ from its slope. The value of $k_7$ was found to be $4.7 \times 10^{-3} \, M^{-1} sec^{-1}$.

(iv) Activation parameters

The decomposition of the $Mn^{III}$ complex in methanol in the presence of base was studied at other temperatures in order to determine the values of the activation enthalpy ($\Delta H^*$) and activation entropy ($\Delta S^*$). According to transition-state theory, these two parameters are related to the reaction rate constant by equation (28).

$$k = KT\exp(-\Delta H^*/RT)\exp(-\Delta S^*/R)/h \qquad (28)$$

where k = reaction rate constant

K = Boltzman constant = $3.30 \times 10^{-24}$ cal.deg.$^{-1}$

T = absolute temperature

h = Planck constant = $1.584 \times 10^{-34}$ cal.sec.

R = gas constant = 1.987 cal.deg.$^{-1}$mole$^{-1}$

Taking the logarithm of both sides of equation (28) and substituting the appropriate values of K, h and R, equation (28) is transformed into equation (29).

$$\log k/T = 10.32 + \Delta S^*/4.574 - \Delta H^*/4.574T \qquad (29)$$

A plot of log k/T versus 1/T yields a slope of $\Delta H^*/4.574$ and an intercept of $10.32 + \Delta S^*/4.574$.

Using the data in Table VII, log $k_7/T$ was plotted against $1/T$ (see Figure 10). The values found for $\triangle H^*$ and $\triangle S^*$ are 16.1 Kcal.mole$^{-1}$ and -15.0 e.u. respectively.

TABLE VII

Variation of $k_7$ with temperature

| Temperature($^\circ$C) | $k_7(M^{-1}sec^{-1})$ |
|---|---|
| 25 | $(4.9 \pm 0.2) \times 10^{-3}$ |
| 30 | $(8.2 \pm 0.3) \times 10^{-3}$ |
| 35 | $(12.7 \pm 0.5) \times 10^{-3}$ |
| 40 | $(19.4 \pm 0.6) \times 10^{-3}$ |

(v) Discussion

The disappearance of the Mn$^{III}$ complex in methanol in the presence of base is due to its decomposition and not to oxidation of methanol by the complex. There are two pieces of evidence supporting this view. Firstly, only a trace of formaldehyde was detected. If the Mn$^{III}$ complex oxidised methanol under basic condition, then one mole of formaldehyde would be produced from every two moles of the complex (see Section VI). Secondly, in aqueous and dimethyl sulfoxide media, similar broad bands extending from the 300 nm region into the 400 nm region were observed when

Figure 10. Plot of log $k_7/T$ versus $1/T$ for decomposition of the $Mn^{III}$ complex in methanol in the presence of base.

$\Delta H^* = 16.1$ Kcal.mole$^{-1}$

$\Delta S^* = -15.0$ e.u.

Correlation coefficient = -0.9998

Y-axis: Log $k_7/T$

X-axis: $1/T$ ($^oK$)$^{-1}$ x $10^3$
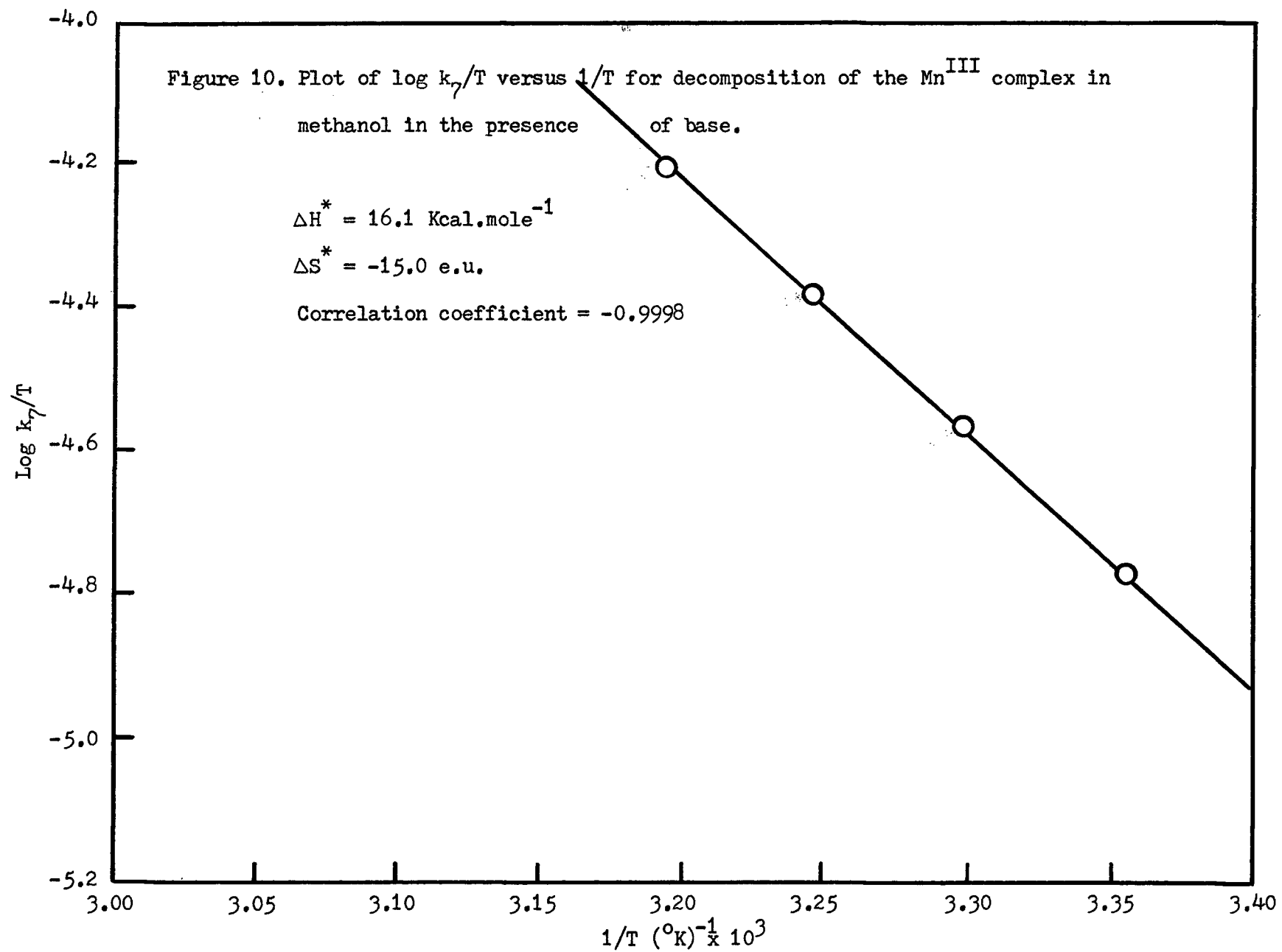
tetramethylammonium hydroxide was added to the $Mn^{III}$ complex in these two media. In dimethyl sulfoxide solvent, brownish precipitates of manganese dioxide appeared immediately and the solution was golden yellow. The golden yellow colour observed in all three media is probably due to dissolved manganese dioxide. (Hamm and Suwyn[41] have reported that the $Mn^{III}$ complex decomposes into manganese dioxide in water of pH above 11). When the reaction mixture at the completion of a reaction was oxidised by lead dioxide no spectrum due to the $Mn^{III}$ complex could be obtained, thus indicating the $Mn^{II}$ formed in the reaction mixture was not complexed to CyDTA ligands.

The decomposition of the $Mn^{III}$ complex was not followed beyond 50 % of reaction because of the appearance of a broad absorption band extending from the 300 nm region into the 400 nm region that is due to manganese dioxide formed in the reaction. The value of $k_7$ obtained is probably smaller than the true value of $k_7$ because the decrease of the $Mn^{III}$ complex peak at 466 nm with time is not corrected for absorbance contribution from the manganese dioxide formed in the reaction. The value of $k_7$ is sensitive to the extent of reaction followed: e.g. the value of $k_7$ for 50 % reaction is slightly smaller than that for 40 % reaction. In order to have a consistent way of computing all the values of $k_7$, only least squares plots (Figure 8) with a correlation coefficient of at least 0.999 are used.

## VI. REACTION OF THE Mn$^{III}$ COMPLEX WITH METHANOL*(SOLVENT) IN THE PRESENCE OF ACID

### (i) Products

Three products - Mn$^{II}$ complex, formaldehyde and carbon dioxide were identified. One mole of formaldehyde was produced for every two moles of the Mn$^{III}$ complex used. (See Section III-vi for methods used in product analysis).

### (ii) Analysis of kinetic results

Reaction of the Mn$^{III}$ complex with methanol (solvent) was carried out with excess hydrochloric acid present. Plots of logarithm of $A_{Mn}$ versus time are linear up to greater than 80 % of the reaction, indicating that the rate of disappearance of the Mn$^{III}$ complex can be expressed by equation (30). Figure 11 is a typical plot of equation (31).

$$- d(Mn^{III})_{tot}/dt = k_b(Mn^{III})_{tot} \qquad (30)$$

where $(Mn^{III})_{tot}$ = total concentration of the Mn$^{III}$ complex,

$k_b$ = pseudo-first order rate constant.

Integrating equation (30) gives equation (31).

* 2.5 % water (v/v)

Figure 11. Plot of log $A_{Mn}$ versus time for reaction between the $Mn^{III}$ complex and methanol in the presence of acid.

$(HCl) = 1.63 \times 10^{-2}$ M

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

Temperature $= 25^{\circ}$
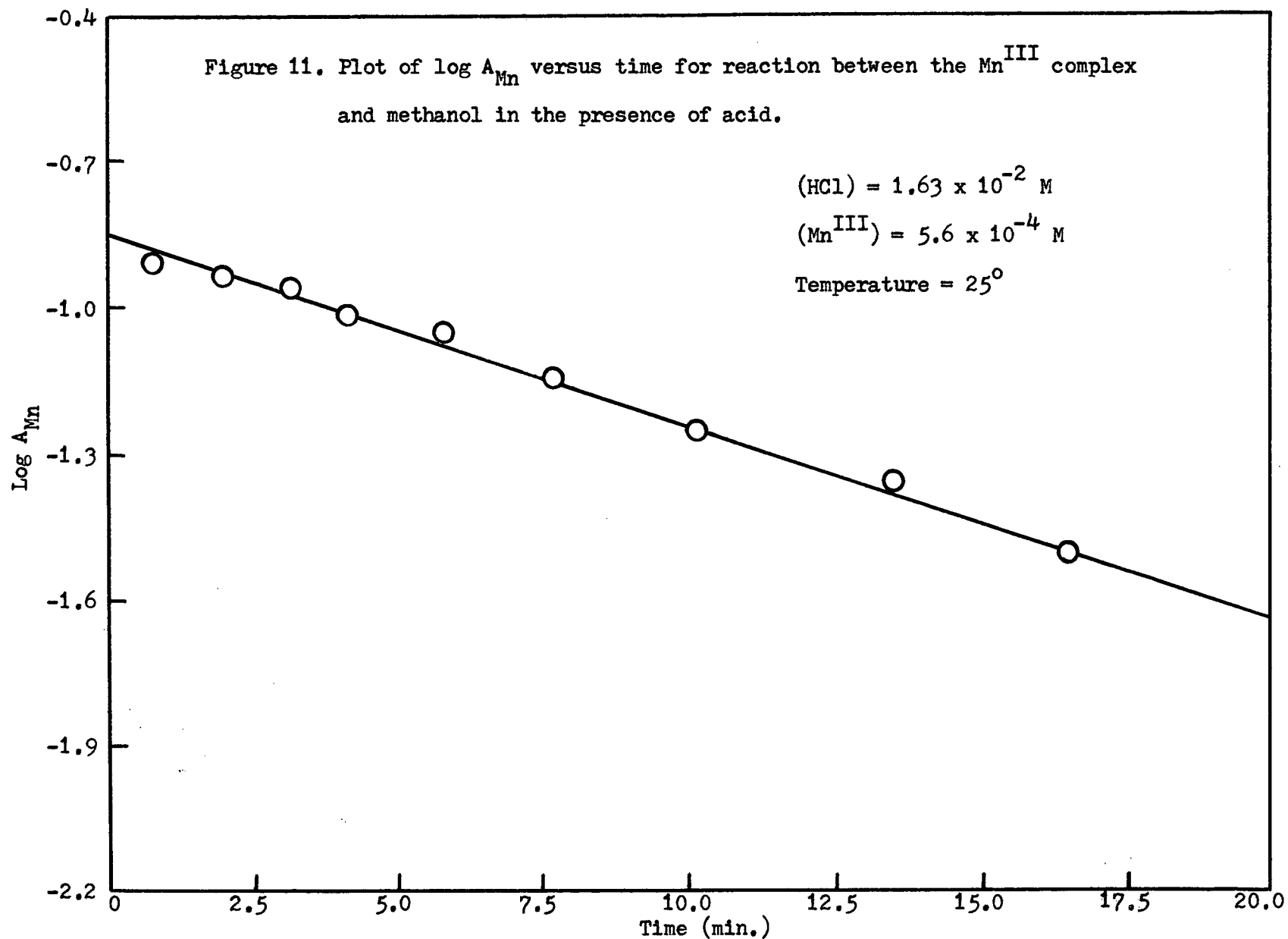
$$\log A_{Mn} - \log A_o = -k_b t/2.303 \qquad (31)$$

where $A_{Mn}$ = absorbance of the $Mn^{III}$ complex at 520 nm at time t,

$A_o$ = absorbance of the $Mn^{III}$ complex at 520 nm at time zero.

When the concentration of the $Mn^{III}$ complex was kept constant, $k_b$ was found to increase with increase in the acid concentration (see Table VIII and Figure 12). The curved plot in Figure 12 suggests that the oxidant involved in the rate-determining step of the reaction is a protonated species.

TABLE VIII

Variation of $k_b$ with hydrochloric acid concentration at $25^o$

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

| (HCl)(M) | $k_b$(sec$^{-1}$) |
|---|---|
| $0.81 \times 10^{-2}$ | $0.88 \times 10^{-3}$ |
| $1.63 \times 10^{-2}$ | $1.54 \times 10^{-3}$ |
| $4.07 \times 10^{-2}$ | $2.46 \times 10^{-3}$ |
| $6.09 \times 10^{-2}$ | $2.93 \times 10^{-3}$ |
| $10.15 \times 10^{-2}$ | $4.50 \times 10^{-3}$ |
| $14.44 \times 10^{-2}$ | $5.40 \times 10^{-3}$ |
| $38.40 \times 10^{-2}$ | $8.40 \times 10^{-3}$ |

Figure 12. Observed rate constant, $k_b$, versus acid concentration.

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

Temperature = $25^o$
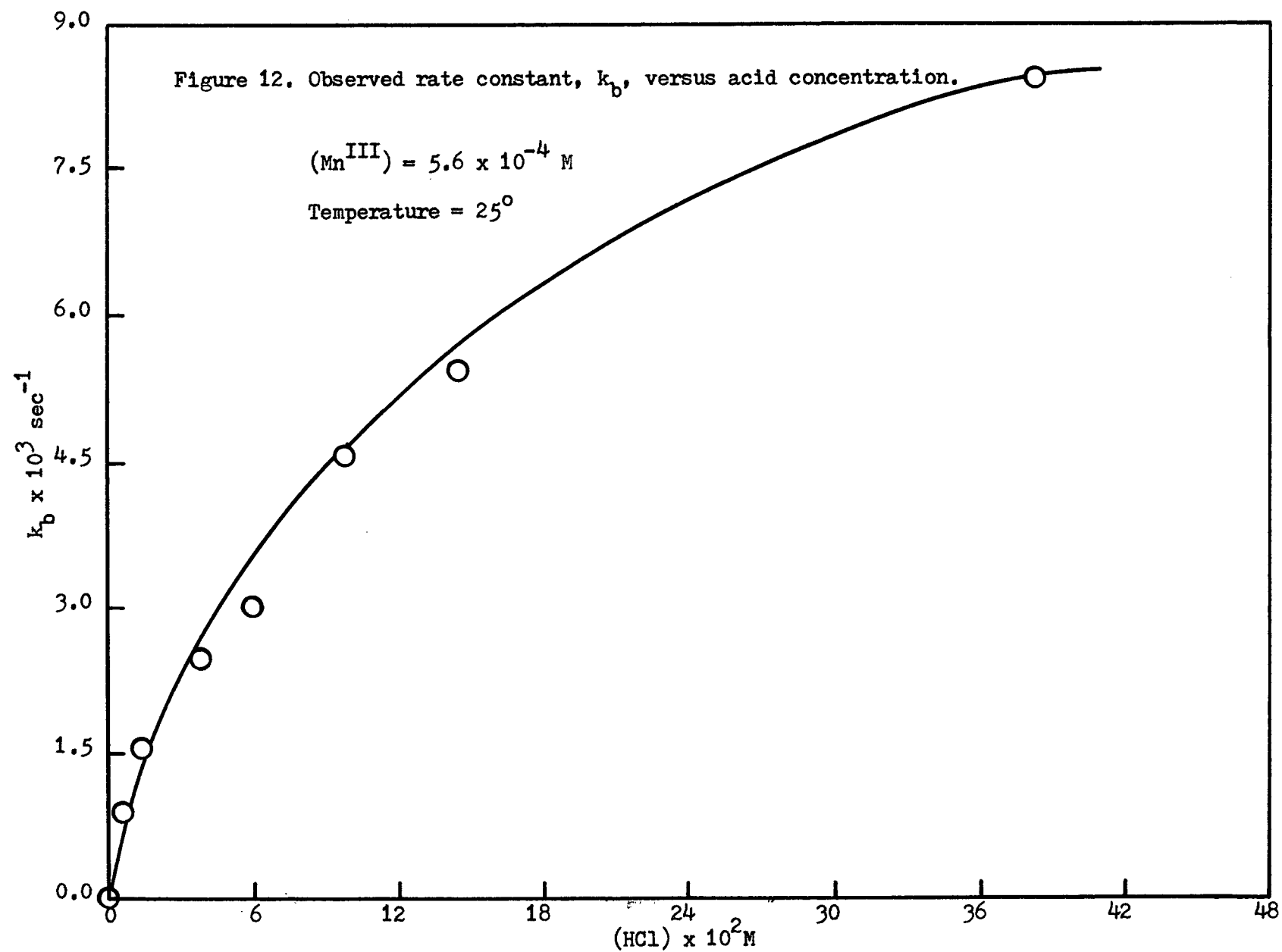
(iii) <u>Mechanism</u>

The following reactions are postulated to explain the kinetic results obtained.

$$Mn_p^{III-} + H^+ \underset{\longleftarrow}{\overset{K'}{\longrightarrow}} HMn_p^{III}o \quad , \text{ fast} \tag{32}$$

$$HMn_p^{III}o + CH_3OH \overset{k_1}{\longrightarrow} \cdot CH_2OH + Mn^{II} + H^+ \tag{33}$$

$$HMn_p^{III}o + \cdot CH_2OH \overset{k_2}{\longrightarrow} HCHO + Mn^{II} + H^+ , \text{ fast} \tag{34}$$

$$Mn_p^{III-} + \cdot CH_2OH \overset{k_4}{\longrightarrow} HCHO + Mn^{II} + H^+ , \text{ fast} \tag{35}$$

<u>Abbreviations used:</u>

$$Mn_p^{III-} = Mn^{III}CyDTA(H_2O)^-$$

$$HMn_p^{III}o = HMn^{III}CyDTA(H_2O)$$
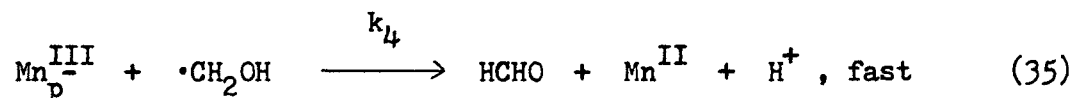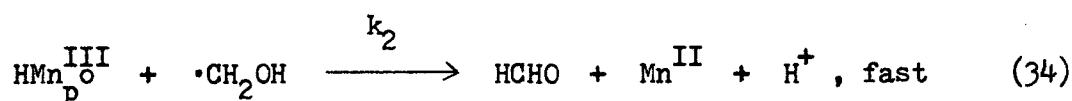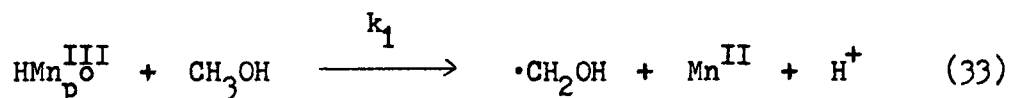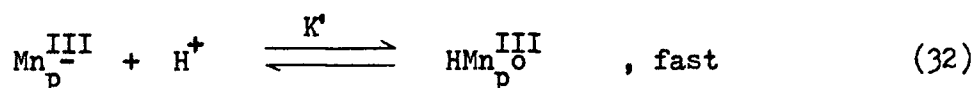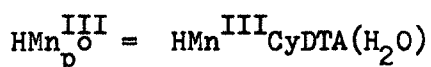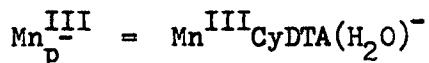
Equation (33) shows the rate-determining step. The rate of disappearance of the $Mn^{III}$ complex is given by equation (36).

$$- d(Mn^{III})_{tot}/dt = 2k_1 (HMn_p^{III}o)(CH_3OH) \tag{36}$$

where $(Mn^{III})_{tot}$ = total concentration of the $Mn^{III}$ complex

$$= (HMn_p^{III}\overset{0}{}) + (Mn_p^{III-})$$

The concentration of $HMn^{III}CyDTA(H_2O)$ can be expressed in terms of the total concentration of the $Mn^{III}$ complex by using the relationship in equation (37).

$$(HMn_p^{III}\overset{0}{})/(Mn_p^{III-}) = K^{\bullet}(H^+) \qquad (37)$$

Substituting $(Mn_p^{III-}) = (Mn^{III})_{tot} - (HMn_p^{III}\overset{0}{})$ in equation (37) and rearranging, equation (38) is obtained.

$$(HMn_p^{III}\overset{0}{}) = K^{\bullet}(H^+)(Mn^{III})_{tot}/(1 + K^{\bullet}(H^+)) \qquad (38)$$

Therefore, equation (36) can be expressed as follows:

$$- d(Mn^{III})_{tot}/dt = 2k_1^{\bullet}K^{\bullet}(H^+)(Mn^{III})_{tot}/(1 + K^{\bullet}(H^+)) \qquad (39)$$

where $k_1^{\bullet} = k_1(CH_3OH)$.

Integrating equation (39) yields equation (40).

$$\log A_{Mn} - \log A_o = - 2k_1^{\bullet}K^{\bullet}(H^+)t/2.303(1 + K^{\bullet}(H^+)) \qquad (40)$$

Equation (40) is identical to equation (31) with

$$k_b = 2k_1' K' (H^+)/(1 + K' (H^+)) \qquad (41)$$

(iv) Determination of rate constant

The value of $k_b$ was obtained from the slope of a plot of log $A_{Mn}$ versus time (see equation (40) and equation (41)). This was done for each concentration of acid. In order to determine $k_1$ the value of $K'$ must be known. Equation (37) could not be used to solve for $K'$ because $(Mn_p^{III}-)$ and $(HMn_p^{III}o)$ could not be determined. An indirect method was used to estimate the magnitude of $K'$. From a plot of $k_b$ versus concentration of acid (see Figure 12), the maximum value of $k_b$ was estimated to be in the region of $8.4 \times 10^{-3}$ sec$^{-1}$. At the maximum value of $k_b$ all the Mn$^{III}$ complex exists in the protonated form and equation (36) becomes equation (42).

$$- d(HMn_p^{III}o)/dt = 2k_1 (HMn_p^{III}o)(CH_3OH) \qquad (42)$$

Therefore,

$$2k_1 (CH_3OH) = k_{bmax} \qquad (43)$$

where $k_{bmax}$ = maximum value of $k_b$.

The solvent used was 97.5 % in methanol (v/v) giving a value of 24.1 M for the concentration of methanol. Knowing $k_{bmax}$ ($8.4 \times 10^{-3}$ sec$^{-1}$) and ($CH_3OH$) (24.1 M), $k_1$ was calculated and found to be $1.74 \times 10^{-4}$ M$^{-1}$sec$^{-1}$.

The value of K' was calculated for each value of (HCl) using equation (41). The results are shown in Table IX. An average value of K' = 12 $\pm$ 2 was obtained.

## TABLE IX

### K' calculated from equation (41)

| (HCl)(M) | K' (M$^{-1}$) |
|---|---|
| $0.81 \times 10^{-2}$ | 14 |
| $1.63 \times 10^{-2}$ | 14 |
| $4.07 \times 10^{-2}$ | 10 |
| $6.09 \times 10^{-2}$ | 9 |
| $10.15 \times 10^{-2}$ | 11 |
| $14.44 \times 10^{-2}$ | 12 |

(v) Reactions with deuterated methanols

Reactions of the Mn$^{III}$ complex with methanol-$d_4$, methanol-$d_3$ and methanol-O-d in the presence of deuterium chloride (hydrogen chloride was used for reaction with methanol-$d_3$) were carried out to obtain some

information about the mechanism of the reaction between the $Mn^{III}$ complex and methanol. In the cases of methanol-$d_4$ and methanol-$d_3$ the reactions were carried out at a single acid concentration. In the case of methanol-O-d the reaction was carried out at various deuterium chloride concentrations in order to obtain the value of the equilibrium constant $K'$ (see equation (32)).

Table X summarises the results obtained for the reaction between the $Mn^{III}$ complex and methanol-O-d in the presence of deuterium chloride. Figure 13 is a plot of $k_b$ versus deuterium chloride concentration. From the maximum value of $k_b$, a value of $k_1 = 1.39 \times 10^{-4}$ $M^{-1}sec^{-1}$ was calculated (see equation (43)). The equilibrium constant $K'$ was found to be $25 \overset{+}{_{-}} 2$.

TABLE X

<u>Variation of $k_b$ with deuterium chloride concentration at $25^{o}$</u>

$(Mn^{III}) = 5.7 \times 10^{-4}$ M               Solvent = $CH_3OD$

| (DCl)(M) | $k_b(sec^{-1})$ | $K'(M^{-1})^{*}$ |
|---|---|---|
| $2.05 \times 10^{-2}$ | $2.20 \times 10^{-3}$ | 24 |
| $4.89 \times 10^{-2}$ | $3.80 \times 10^{-3}$ | 27 |
| $9.78 \times 10^{-2}$ | $6.16 \times 10^{-3}$ | — |
| $13.04 \times 10^{-2}$ | $6.64 \times 10^{-3}$ | — |
| $19.60 \times 10^{-2}$ | $6.75 \times 10^{-3}$ | — |

* calculated from equation (41) using $k_1 = 1.39 \times 10^{-4}$ $M^{-1}sec^{-1}$.

Figure 13. Observed rate constant, $k_b$, versus concentration of deuterium chloride.

$(Mn^{III}) = 5.7 \times 10^{-4}$ M

Solvent = $CH_3OD$

Temperature = $25^\circ$

$k_b \times 10^3$ sec$^{-1}$

$(DCl) \times 10^2$ M

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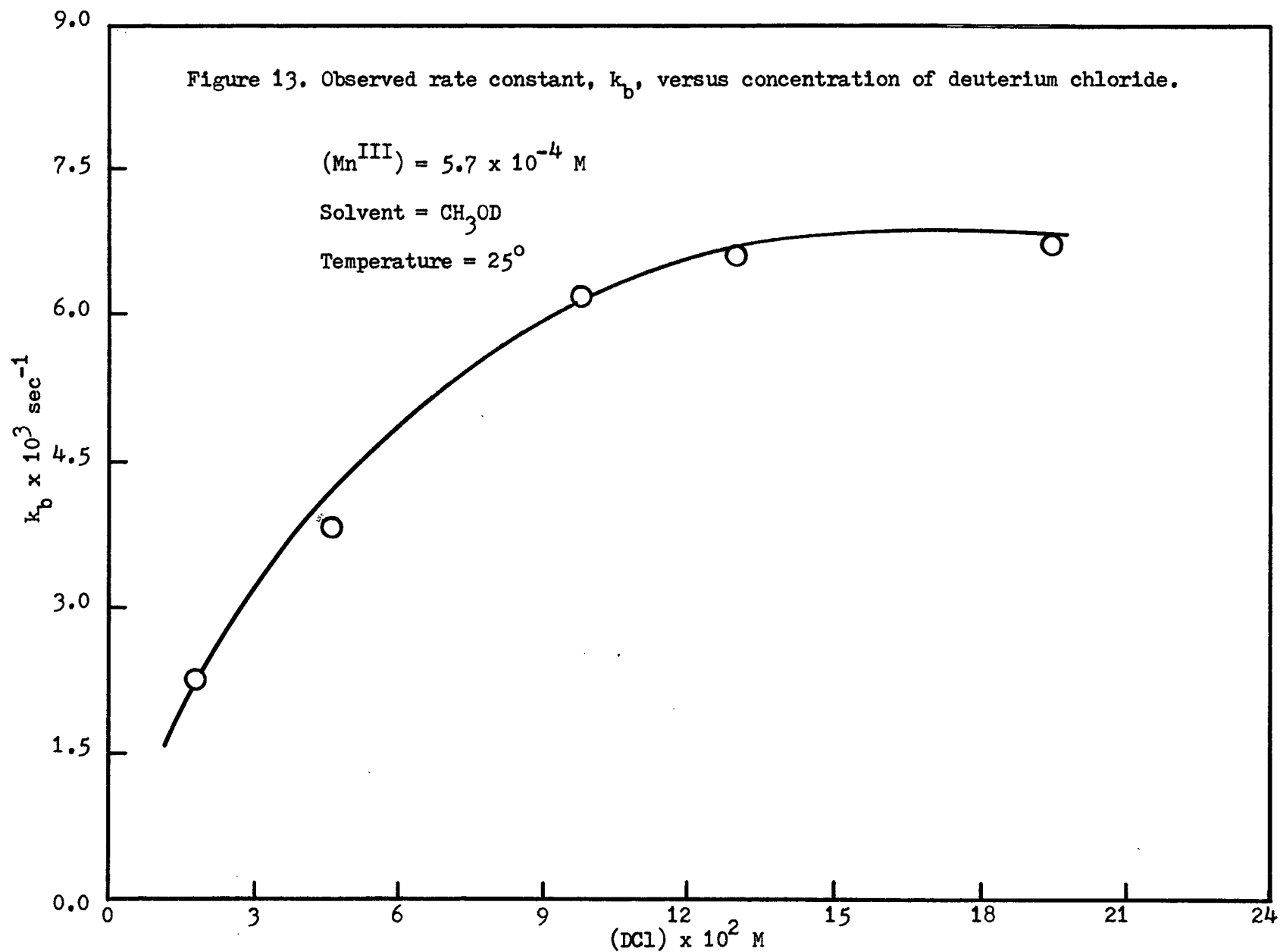
The values of the rate constant, $k_1$, for the four methanols are given in Table XI and compared in Table XII. It can be seen that the kinetic isotope effects are small.

TABLE XI

Rates for oxidation of isotopic methanols at 25°

$(Mn^{III}) = 5.6 \times 10^{-4}$ M          $(HCl) = (DCl) = 2.05 \times 10^{-2}$ M

| Experiment | Acid | Solvent | $k_b(sec^{-1})$ | $k_1(M^{-1}sec^{-1})^a$ |
|------------|------|---------|-----------------|--------------------------|
| A | HCl | $CH_3OH$ | $2.10 \times 10^{-3}$ | $1.64 \times 10^{-4}$ <br> $(1.74 \times 10^{-4})^b$ |
| B | DCl | $CH_3OD$ | $2.20 \times 10^{-3}$ | $1.14 \times 10^{-4}$ <br> $(1.39 \times 10^{-4})^b$ |
| C | DCl | $CD_3OD$ | $2.03 \times 10^{-3}$ | $1.04 \times 10^{-4}$ |
| D | HCl | $CD_3OH$ | $1.68 \times 10^{-3}$ | $1.38 \times 10^{-4}$ |

a calculated from equation (41) using $K' = 12$ for $CH_3OH$ and $CD_3OH$, and $K' = 25$ for $CD_3OD$ and $CH_3OD$.

b calculated from $k_{bmax}$ (see equation (43)).

TABLE XII

Isotope effects in oxidation of methanol at $25^\circ$

| Experiments compared | Compounds compared | $k_{1H}/k_{1D}$ |
|---|---|---|
| A, B | $CH_3OH$, $CH_3OD$ | $1.3 \pm 0.1^a$ |
| C, D | $CD_3OD$, $CD_3OH$ | $1.3$ |
| A, D | $CH_3OH$, $CD_3OH$ | $1.2 \pm 0.1^a$ |
| B, C | $CH_3OD$, $CD_3OD$ | $1.2 \pm 0.1^a$ |

a an average value of the bracketed and unbracketed values of $k_1$

(see Table XI) was used in the calculations.

(vi) Activation parameters

Reaction of the $Mn^{III}$ complex with methanol in the presence of acid was carried out at several temperatures in order to evaluate the values of the activation enthalpy ($\Delta H^*$) and activation entropy ($\Delta S^*$). The data used in the plot in Figure 14 were taken from Table XIII. The values found for $\Delta H^*$ and $\Delta S^*$ are 15.9 Kcal.mole$^{-1}$ and -22.5 e.u. respectively.

Figure 14. Plot of log $k_1/T$ versus $1/T$ for reaction between the $Mn^{III}$ complex and methanol in the presence of acid.

$\triangle H^* = 15.9$ Kcal.mole$^{-1}$

$\triangle S^* = -22.5$ e.u.

correlation coefficient

$= -0.9981$
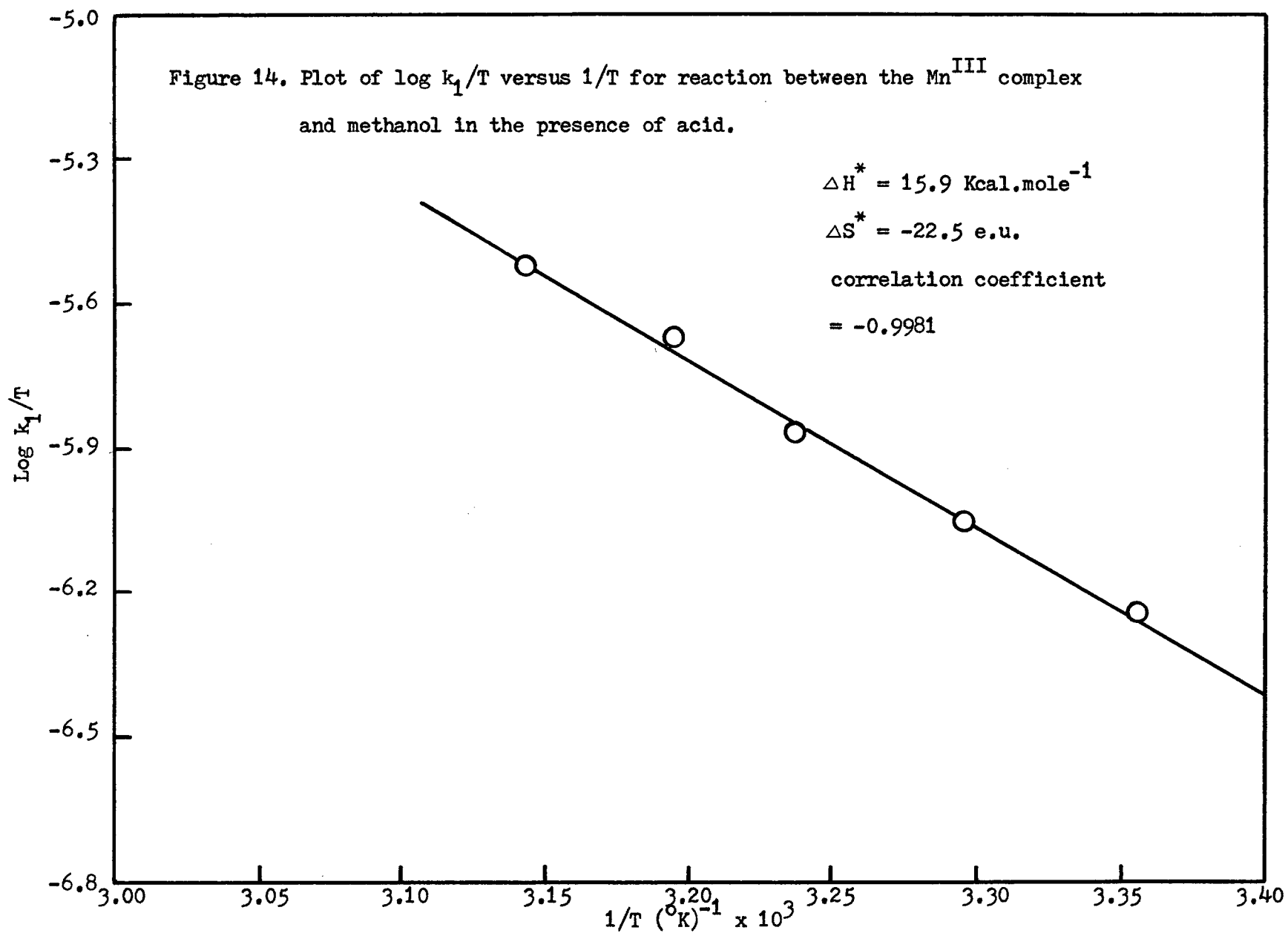
TABLE XIII

Variation of $k_1$ with temperature

| Temperature($^{\circ}$C) | $k_1$ ($M^{-1}sec^{-1}$) |
|---|---|
| 25.0 | $(1.7 \pm 0.0) \times 10^{-4}$ |
| 30.4 | $(2.7 \pm 0.1) \times 10^{-4}$ |
| 35.8 | $(4.2 \pm 0.1) \times 10^{-4}$ |
| 40.0 | $(6.7 \pm 0.1) \times 10^{-4}$ |
| 45.0 | $(9.6 \pm 0.5) \times 10^{-4}$ |

(vii) Discussion

The mechanism postulated for the reaction of the $Mn^{III}$ complex with methanol in the presence of acid involves the formation of hydroxymethyl radical as the rate-determining step. The hydroxymethyl radical immediately reacts with another molecule of the $Mn^{III}$ complex by transferring a hydrogen atom to it to form formaldehyde. Thus, two moles of the $Mn^{III}$ complex should yield one mole of formaldehyde, and analysis for formaldehyde showed that one mole of formaldehyde was indeed produced for every two moles of the $Mn^{III}$ complex consumed. The reaction postulated is further substantiated by the kinetic results obtained for the oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol in the presence of acid (see Section VII). (Recently, Wells and Barnes[72] reported

the results of a study of the oxidation of methanol by $Mn^{III}$ ion in aqueous perchloric acid. They found that one mole of formaldehyde was produced for every two moles of $Mn^{III}$ consumed).

Carbon dioxide was also observed as one of the reaction products. It is probably formed from some decomposition of the CyDTA ligands. This is a minor reaction compared with the oxidation of methanol by the $Mn^{III}$ complex since the resulting $Mn^{II}$ in the reaction mixture could be oxidised back to more than half the original concentration of the $Mn^{III}$ complex with lead dioxide (as evidenced by similar visible spectrum). Since the $Mn^{III}$ complex disappears rather rapidly under the conditions used (methanol solvent with acid present) the actual concentration of the $Mn^{III}$ complex obtained by oxidising the $Mn^{II}$ in the reaction mixture with lead dioxide was probably higher than that observed.

The kinetic isotope effects observed for $CH_3OD$, $CD_3OD$ and $CD_3OH$ (see Table XII) are too small to account for a transition state which involves either the cleavage of the O–H bond or of the C–H bond as the rate-determining step in the reaction. Thus, it is likely that electron transfer rather than hydrogen atom transfer from methanol to the $Mn^{III}$ complex is involved in the oxidation process. Equation (33) can be divided into equations (33a) and (33b). The small kinetic isotope effect observed for $CH_3OD$ is likely due to the replacement of the $H_2O$ ligand by $D_2O$ ligand in the $Mn^{III}$ complex. The replacement of $CH_3$ by $CD_3$ gives a

secondary isotope effect.

$$HMn_p^{III}\overset{}{o^I} + CH_3OH \xrightarrow{\;\;k_1\;\;} Mn^{II} + CH_3\overset{+}{O}H \qquad (33a)$$

$$CH_3\overset{+}{O}H \longrightarrow \cdot CH_2OH + H^+ \text{, fast} \qquad (33b)$$
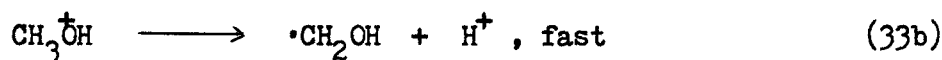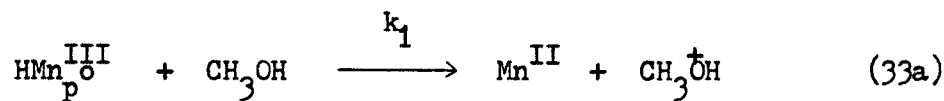
Equation (32) is postulated as the pre-equilibrium which is set up before oxidation occurs. Experimental work[73-75] has shown that the value of $K'$ is larger for deuterio acids because the zero-point energy of a deuterio acid is lower than that of the corresponding protio acid. Table XIV gives a list of acids of different strengths and their respective ratios of $K_H/K_D$. (K is equivalent to $1/K'$ in equation (32). See the definition of K in equation (44)). The ratio of $K_H/K_D$ was found to increase approximately linearly with increase in the $pK_H$ values[73]. The K value of $HMn^{III}CyDTA(H_2O)$ (= $1/K'$) is 0.08 and its '$pK_H$' value is 1.1. The ratio of $K_H/K_D$ for $HMn^{III}CyDTA(H_2O)$ is 2.1, which is of the expected magnitude according to the values shown in Table XIV. This observed isotope effect on the equilibrium constant $K'$ supports the presence of the pre-equilibrium shown in equation (32) before the occurrence of the rate-determining reaction.

The protonated form of the $Mn^{III}$ complex, $HMn^{III}CyDTA(H_2O)$, is a more powerful oxidant than $Mn^{III}CyDTA(H_2O)^-$ since in the absence of acid the reaction of the complex with methanol was found to be very much

## TABLE XIV

**Dissociation constants of deuterioacids in deuterium oxide**[73]

| Acid | $pK_H$ | $K_H/K_D$ |
|------|--------|-----------|
| Oxonium ion | -1.74 | 1.00 |
| Chloroacetic acid | 2.76 | 2.74 |
| 2,6-di-nitrophenol | 3.58 | 2.84 |
| 2,4-di-nitrophenol | 4.02 | 3.28 |
| Benzoic acid | 4.21 | 3.13 |
| Acetic acid | 4.74 | 3.33 |
| 2,5-di-nitrophenol | 5.17 | 3.32 |
| p-nitrophenol | 7.24 | 3.61 |
| o-nitrophenol | 7.25 | 3.71 |
| Bicarbonate ion | 10.25 | 3.95 |
| 2-chloroethanol | 14.31 | 5.00 |

$$HA + H_2O \overset{K}{\underset{}{\rightleftharpoons}} H_3O^+ + A^- \qquad (44)$$
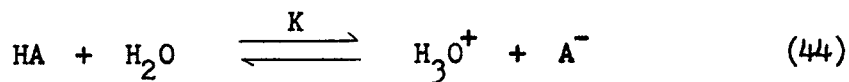
$$K = (H_3O^+)(A^-)/(HA)$$

slower. A pseudo-first order rate constant of $2.24 \times 10^{-6} sec^{-1}$ at $25^{\circ}$ was obtained. It is not certain whether this rate is for the oxidation of methanol or for the decomposition of the $Mn^{III}$ complex because in the aqueous system[41] the rate of decomposition of $Mn^{III}CyDTA(H_2O)^{-}$ was reported to be $6.8 \times 10^{-6} sec^{-1}$ at $25^{\circ}$.

Hydroxymethyl radical was written as the reaction intermediate instead of methoxy radical because the C-H bond is weaker than the O-H bond in methanol (C-H bond strength = 92 Kcal.mole$^{-1}$; O-H bond strength = 102 Kcal.mole$^{-1}$)[76,77]. However, this does not rule out the possibility of formation of some methoxy radicals. Several studies[78-81] on hydrogen atom abstraction from methanol by methyl and trifluoromethyl radicals have shown that these radicals do attack the O-H bond whereas the esr spectrum of the radical[82,83] generated by the reaction between methanol and t-butoxy radical indicates that only hydroxymethyl radical is produced.

VII. <u>OXIDATION OF 2,4,6-TRI-t-BUTYLPHENOL WITH THE Mn$^{III}$ COMPLEX IN</u>

<u>METHANOL$^*$ IN THE PRESENCE OF ACID</u>

(i) <u>Product</u>

2,4,6-Tri-t-butylphenoxyl was identified (see the absorption peak

at 400 nm in Figure 15 and esr spectrum in Figure 16).

(ii) <u>Analysis of kinetic results</u>

Oxidation was carried out with excess 2,4,6-tri-t-butylphenol and

hydrochloric acid present. Plots of logarithm of absorbance at 520 nm

versus time are linear up to greater than 80 % of the reaction, indicating

that the rate of disappearance of the Mn$^{III}$ complex can be expressed by

equation (45). Figure 17 is a typical plot of equation (46).

$$- d(Mn^{III})_{tot}/dt = k_a (Mn^{III})_{tot} \qquad (45)$$

where $(Mn^{III})_{tot}$ = total concentration of the Mn$^{III}$ complex

$k_a$ = pseudo-first order rate constant.

Integrating equation (45) gives equation (46).

$^*$ 2.5 % water (v/v)

Figure 15. Visible spectrum showing the absorption bands of 2,4,6-tri-t-butylphenoxyl (A) and the Mn$^{III}$ complex (B) in methanol in the presence of acid.

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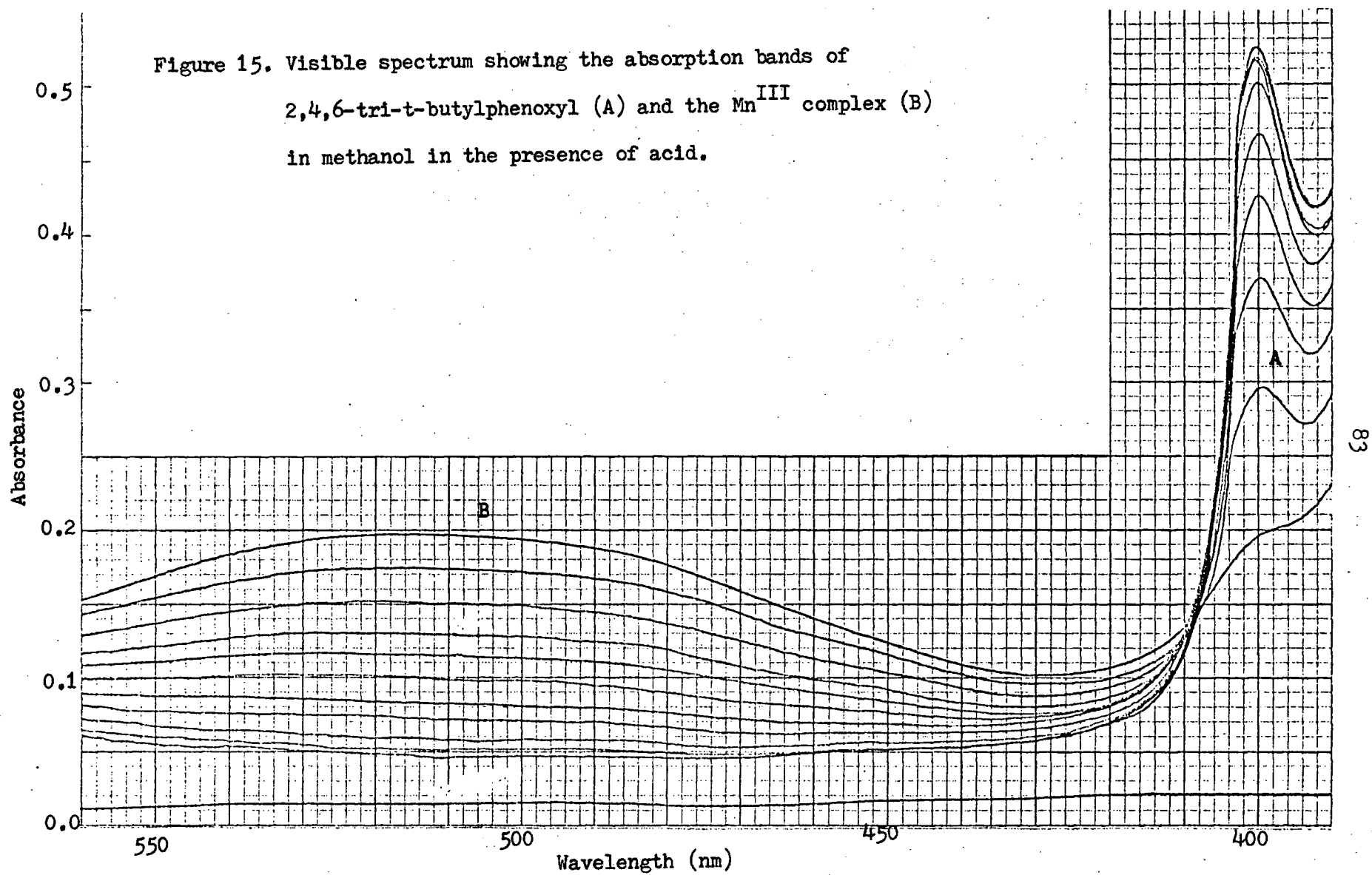
Figure 16. ESR spectrum of 2,4,6-tri-t-butylphenoxyl in methanol.

Figure 17. Plot of log $A_{Mn}$ versus time for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol in the presence of acid.

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(HCl) \ \ = 1.63 \times 10^{-2}$ M

$(PhOH) \ = 5.10 \times 10^{-2}$ M

Temperature = $25^{o}$

Log $A_{Mn}$

Time (min.)
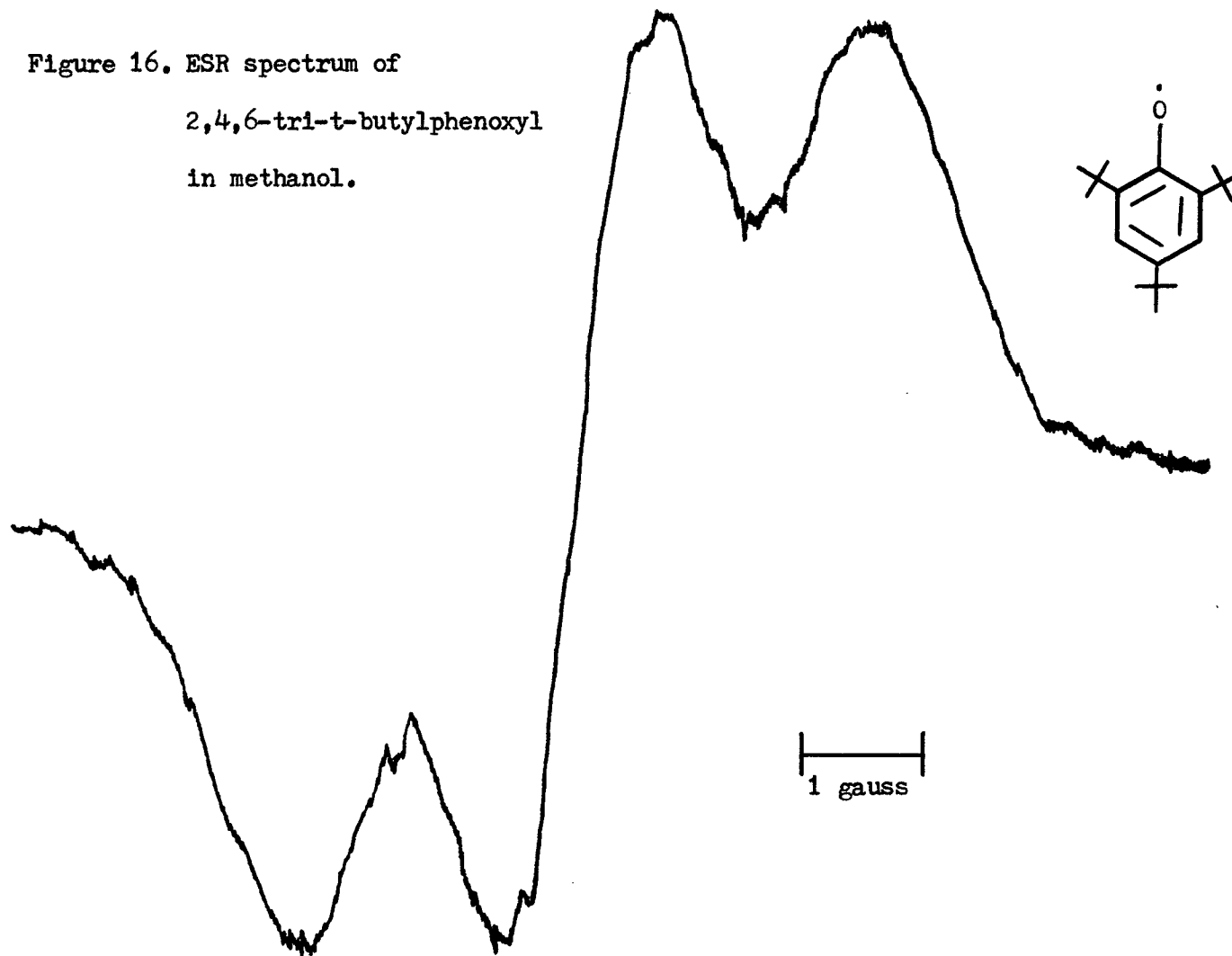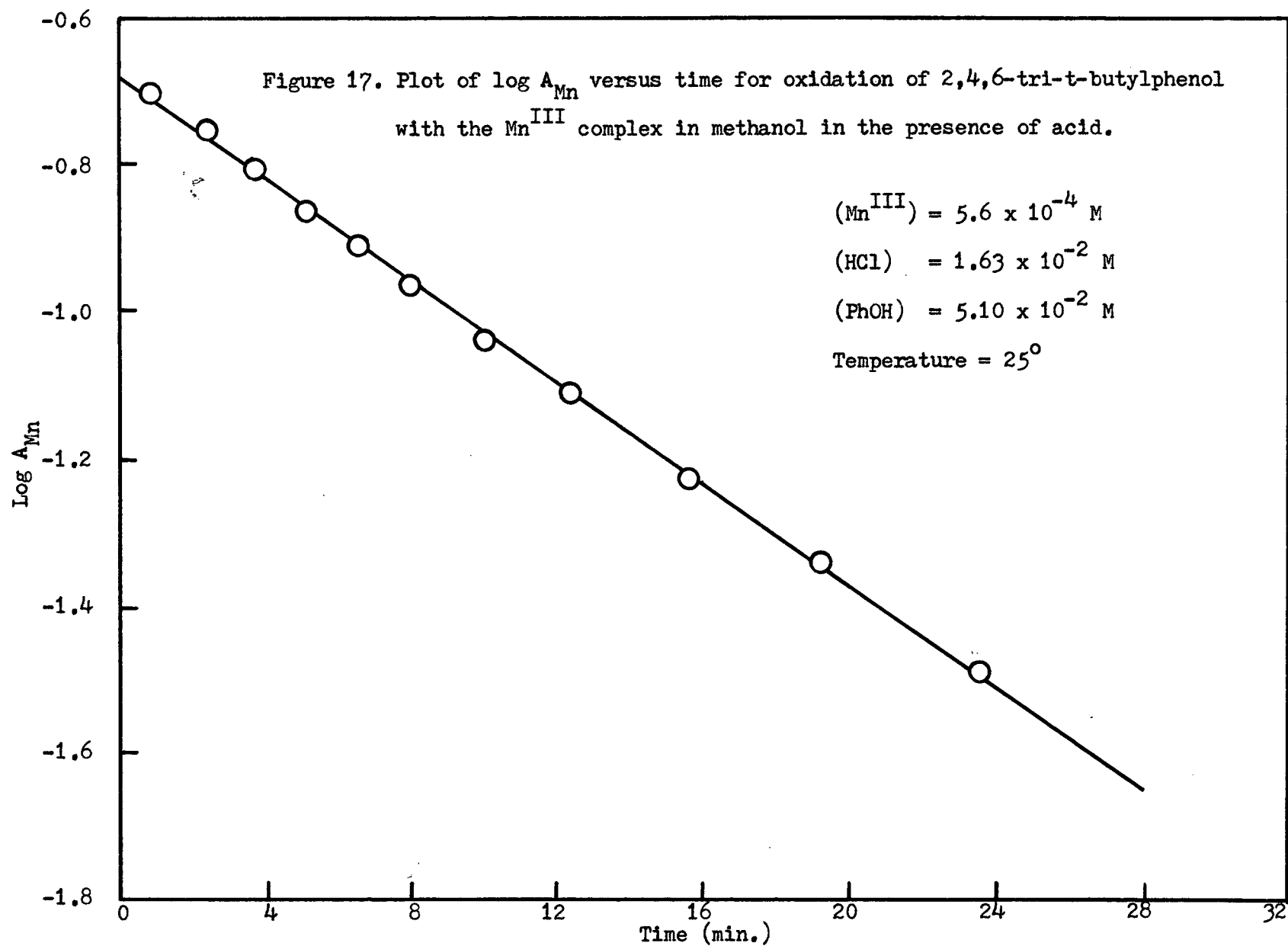
$$\log A_{Mn} - \log A_o = - k_a t/2.303 \qquad (46)$$

where $A_{Mn}$ = absorbance of the $Mn^{III}$ complex at 520 nm at time t

$A_o$ = absorbance of the $Mn^{III}$ complex at 520 nm at time zero.

When the concentrations of 2,4,6-tri-t-butylphenol and the $Mn^{III}$ complex were kept constant and the concentration of hydrochloric acid was varied, the values of $k_a$ obtained were found to increase with increase in the acid concentration (see Table XV and Figure 18). The curved plot in Figure 18 suggests that the oxidant involved in the rate-determining step of the reaction is a protonated species (compare with Figure 12).

TABLE XV

Variation of $k_a$ with acid concentration at 25°

$(Mn^{III}) = 5.6 \times 10^{-4}$ M $\qquad (PhOH^*) = 5.10 \times 10^{-2}$ M

| (HCl)(M) | $k_a(sec^{-1})$ |
|---|---|
| $1.63 \times 10^{-4}$ | $3.18 \times 10^{-5}$ |
| $0.81 \times 10^{-2}$ | $1.04 \times 10^{-3}$ |
| $1.63 \times 10^{-2}$ | $1.74 \times 10^{-3}$ |
| $4.07 \times 10^{-2}$ | $2.30 \times 10^{-3}$ |
| $6.09 \times 10^{-2}$ | $2.79 \times 10^{-3}$ |
| $10.15 \times 10^{-2}$ | $4.45 \times 10^{-3}$ |
| $14.44 \times 10^{-2}$ | $5.16 \times 10^{-3}$ |

* PhOH is used as an abbreviation for 2,4,6-tri-t-butylphenol.

Figure 18. Observed rate constant, $k_a$, versus acid concentration.

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(PhOH) = 5.10 \times 10^{-2}$ M

Temperature = $25^{\circ}$

$k_a \times 10^3$ sec$^{-1}$

$(HCl) \times 10^2$ M
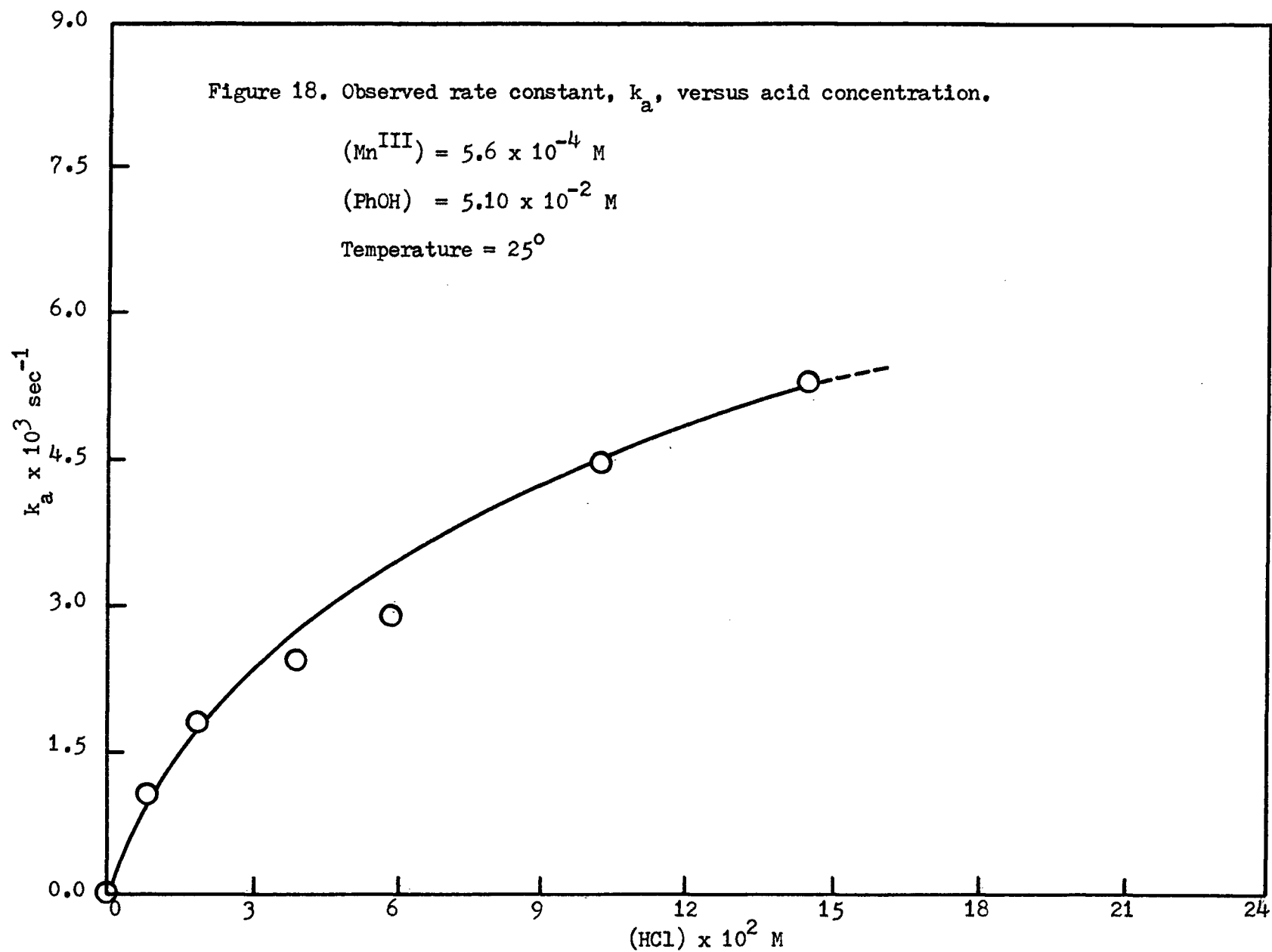
The values of $k_a$ were found to increase with increase in the concentration of 2,4,6-tri-t-butylphenol when the concentrations of the acid and the $Mn^{III}$ complex were kept constant (see Table XVI and Figure 19). From the data in Table XVI, it can be seen that doubling the concentration of 2,4,6-tri-t-butylphenol increases the value of $k_a$ by less than 50 %. Therefore, $k_a$ is likely to be a composite rate constant; at least one term in $k_a$ is independent of the concentration of 2,4,6-tri-t-butylphenol.

TABLE XVI

Variation of $k_a$ with concentration of 2,4,6-tri-t-butylphenol at 25°

$(Mn^{III}) = 5.6 \times 10^{-4}$ M          $(HCl) = 1.63 \times 10^{-2}$ M

| $(PhOH)^*$ (M) | $k_a$ (sec$^{-1}$) |
|---|---|
| $1.57 \times 10^{-2}$ | $1.17 \times 10^{-3}$ |
| $3.00 \times 10^{-2}$ | $1.50 \times 10^{-3}$ |
| $5.10 \times 10^{-2}$ | $1.74 \times 10^{-3}$ |
| $6.64 \times 10^{-2}$ | $2.12 \times 10^{-3}$ |
| $7.74 \times 10^{-2}$ | $2.30 \times 10^{-3}$ |
| $9.22 \times 10^{-2}$ | $2.69 \times 10^{-3}$ |

* PhOH is used as an abbreviation for 2,4,6-tri-t-butylphenol.

Figure 19. Observed rate constant, $k_a$, versus concentration of 2,4,6-tri-t-butylphenol. Part (i).

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(HCl) = 1.63 \times 10^{-2}$ M

Temperature = $25°$
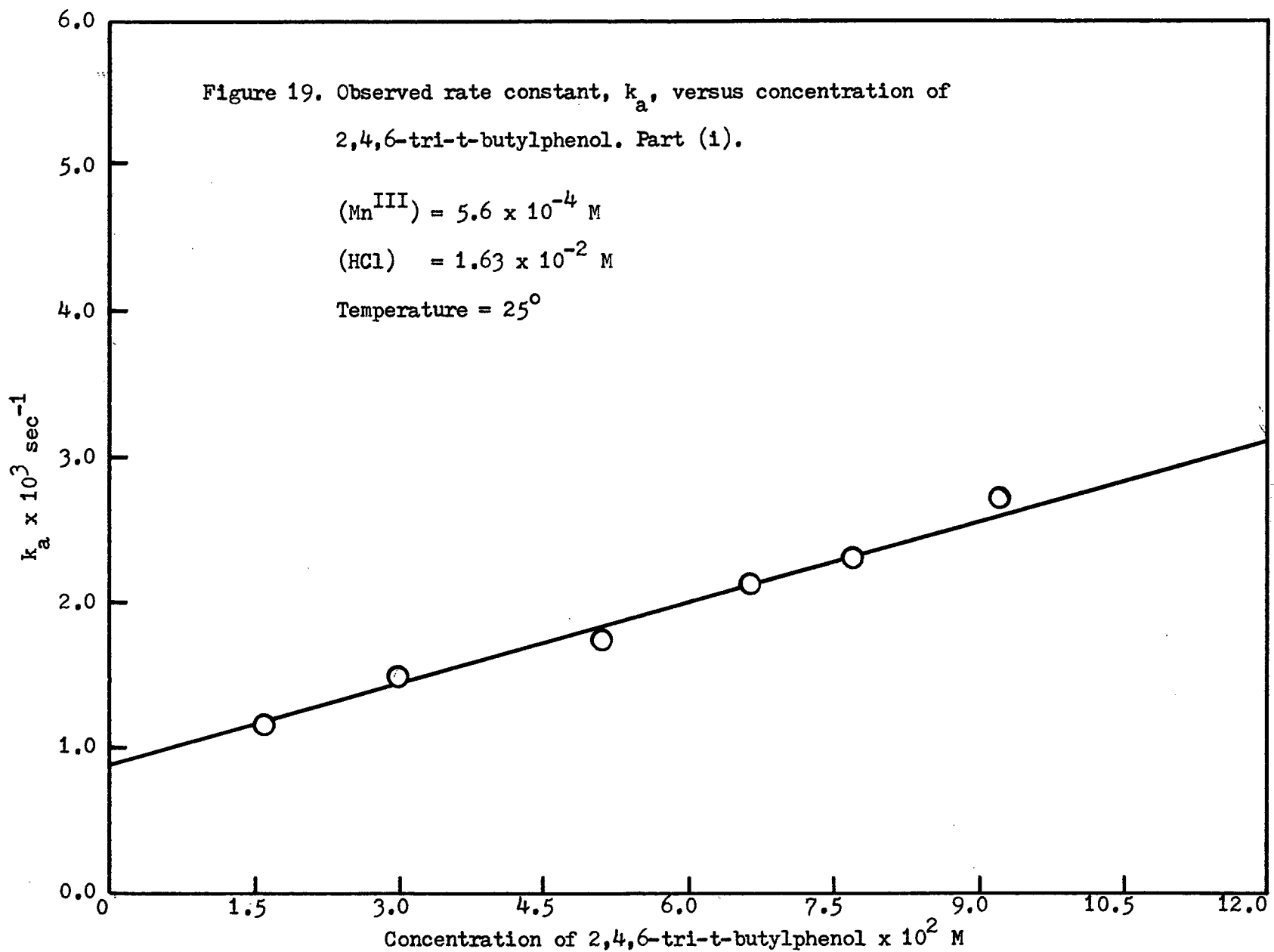
With constant concentrations of 2,4,6-tri-t-butylphenol and hydrochloric acid, but different concentrations of the $Mn^{III}$ complex, the values of $k_a$ were found to be approximately constant (see Table XVII), indicating that the rate of disappearance of the $Mn^{III}$ complex is first order with respect to its concentration, thus supporting equation (45).

TABLE XVII

Variation of $k_a$ with the $Mn^{III}$ complex concentration at $25^o$

$(PhOH)^* = 5.10 \times 10^{-2}$ M $\qquad\qquad$ (HCl) $= 1.63 \times 10^{-2}$ M

| $(Mn^{III})(M)$ | $k_a(sec^{-1})$ |
|---|---|
| $5.6 \times 10^{-4}$ | $1.74 \times 10^{-3}$ |
| $6.9 \times 10^{-4}$ | $2.05 \times 10^{-3}$ |
| $7.7 \times 10^{-4}$ | $2.19 \times 10^{-3}$ |
| $9.0 \times 10^{-4}$ | $2.10 \times 10^{-3}$ |
| $17.2 \times 10^{-4}$ | $2.30 \times 10^{-3}$ |

* PhOH is used as an abbreviation for 2,4,6-tri-t-butylphenol.

(iii) Mechanism

The following reactions are postulated.

$$Mn_p^{III-} + H^+ \xrightleftharpoons{K'} HMn_p^{III}_o \quad , \text{ fast} \qquad (32)$$

$$HMn_p^{III}o + CH_3OH \xrightarrow{k_1} \cdot CH_2OH + Mn^{II} + H^+ \qquad (33)$$

$$HMn_p^{III}o + \cdot CH_2OH \xrightarrow{k_2} HCHO + Mn^{II} + H^+ \text{ , fast} \qquad (34)$$

$$Mn_p^{III-}o + \cdot CH_2OH \xrightarrow{k_4} HCHO + Mn^{II} + H^+ \text{ , fast} \qquad (35)$$

$$HMn_p^{III}o + PhOH \xrightarrow{k_3} Mn^{II} + H^+ \; PhO\cdot \qquad (47)$$

$$\cdot CH_2OH + PhOH \xrightarrow{k_5} CH_3OH + PhO\cdot \text{ , fast} \qquad (48)$$
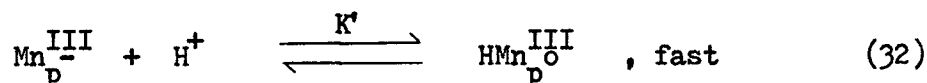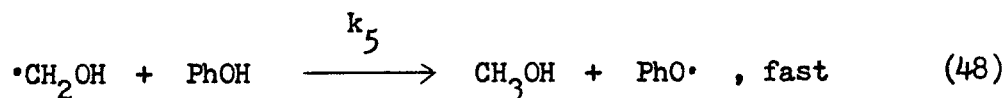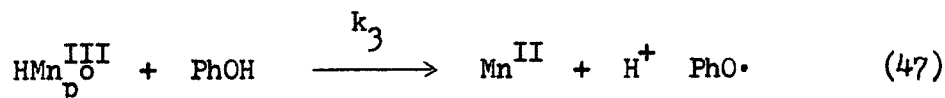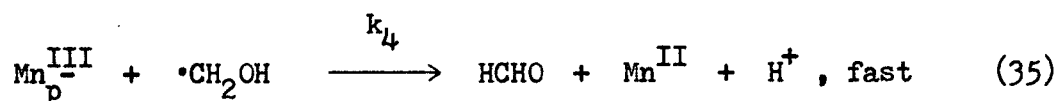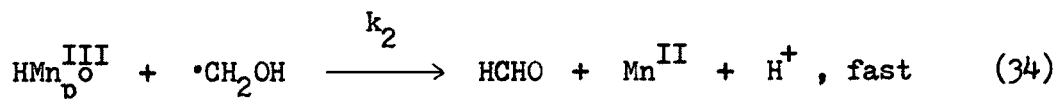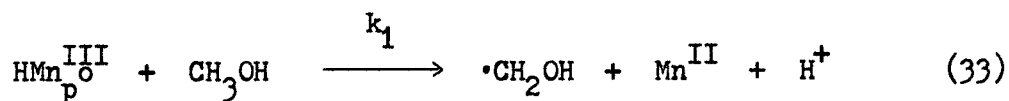
Abbreviations used:

PhOH = 2,4,6-tri-t-butylphenol

PhO· = 2,4,6-tri-t-butylphenoxyl

$Mn_p^{III-} = Mn^{III}CyDTA(H_2O)^-$

$HMn_p^{III}o = HMn^{III}CyDTA(H_2O)$

Equations (33) and (47) are the rate-determining steps in the disappearance of the $Mn^{III}$ complex. The rate of disappearance of the $Mn^{III}$ complex is given by equation (49).

$$- d(Mn^{III})_{tot}/dt = 2rk_1(HMn_p^{III}o)(CH_3OH) + k_3(HMn_p^{III}o)(PhOH) \qquad (49)$$

The parameter r is to account for the competitive reactions in equations (34), (35) and (48). The maximum value of r is 1 and the minimum value of r is 0.5. When r = 1 all the hydroxymethyl radicals react with the $Mn^{III}$ complex. When r = 0.5 all the hydroxymethyl radicals react with 2,4,6-tri-t-butylphenol. Expressing $(HMn_p^{III}o)$ in terms of $(Mn^{III})_{tot}$, equation (49) is transformed into equation (50). (See Section VI-iii).

$$- d(Mn^{III})_{tot}/dt = rk_b(Mn^{III})_{tot} + k_3 K'(H^+)(PhOH)(Mn^{III})_{tot}/(1+K'(H^+))$$

$$(50)$$

$$k_b = 2k_1(CH_3OH)K'(H^+)/(1 + K'(H^+)) \qquad (41)$$

Since $(PhOH)$, $(H^+) \gg (Mn^{III})_{tot}$, $k_c = k_3 K'(H^+)(PhOH)/(1 + K'(H^+))$ is a constant. Thus, equation (50) becomes:

$$- d(Mn^{III})_{tot}/dt = (rk_b + k_c)(Mn^{III})_{tot} \qquad (51)$$

Equation (51) is identical to equation (45) with

$$k_a = rk_b + k_c \qquad (52)$$

Integrating equation (51) gives equation (53).

$$\log A_{Mn} - \log A_o = (rk_b + k_c)t/2.303 \qquad (53)$$

(iv) Determination of rate constants

The values of $k_1$ and $K'$ have already been determined in Section VI. A value of $k_a$ was determined for each concentration of 2,4,6-tri-t-butyl-phenol from the slope of a plot of $\log A_{Mn}$ versus time (equation (53)). Figure 17 is such a plot. A plot of $k_a$ versus concentration of 2,4,6-tri-t-butylphenol (see equation (52)) gave a slope of $k_3 K' (H^+)/(1 + K' (H^+))$ = 1.80 x $10^{-2}$ $M^{-1} sec^{-1}$ and an intercept of $rk_b$ = 9.0 x $10^{-4}$ $sec^{-1}$ (see Figure 19). Knowing $K'$ and $(H^+)$ the value of $k_3$ was calculated and found to be $(1.1 \pm 0.1)$ x $10^{-1}$ $M^{-1} sec^{-1}$ at $25°$. At this concentration of acid (1.63 x $10^{-2}$ M), $k_b$ = 1.54 x $10^{-3}$ $sec^{-1}$ (from Table VIII) and this gives a value of r = 0.58. This value of r close to 0.5 indicates that in the range of 2,4,6-tri-t-butylphenol concentration used (1.57 x $10^{-2}$ M to 9.22 x $10^{-2}$ M) the hydroxymethyl radicals react almost solely with 2,4,6-tri-t-butylphenol. This is understandable because the concentration of 2,4,6-tri-t-butylphenol is very much more than that of the $Mn^{III}$ complex (5.6 x $10^{-4}$ M).

(v) Kinetic isotope effect

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol-O-d and deuterium chloride was carried out at $25°$ to determine whether the O-H bond of the phenol is cleaved in the rate-determining step of the reaction. A value of 2.50 x $10^{-2}$ $M^{-1} sec^{-1}$ was obtained for $k_3$, giving a kinetic isotope effect of 4.8. This value indicates that the

O-H bond of 2,4,6-tri-t-butylphenol is cleaved in the rate-determining step of the reaction.

(vi) <u>Activation parameters</u>

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in the presence of hydrochloric acid in methanol was carried out at several temperatures in order to evaluate the values of the activation enthalpy $(\Delta H^{*})$ and activation entropy $(\Delta S^{*})$. The data used in the plot in Figure 20 were taken from Table XVIII. The values found for $\Delta H^{*}$ and $\Delta S^{*}$ are 15.7 Kcal.mole$^{-1}$ and -10.4 e.u. respectively.

TABLE XVIII

<u>Variation of $k_3$ with temperature</u>

| <u>Temperature($^{o}$C)</u> | <u>$k_3$($M^{-1}sec^{-1}$)</u> |
|---|---|
| 25.0 | $(1.1 \pm 0.0) \times 10^{-1}$ |
| 30.4 | $(1.7 \pm 0.1) \times 10^{-1}$ |
| 35.8 | $(2.5 \pm 0.0) \times 10^{-1}$ |
| 40.0 | $(3.8 \pm 0.0) \times 10^{-1}$ |
| 45.0 | $(6.4 \pm 0.3) \times 10^{-1}$ |

Figure 20. Plot of log $k_3/T$ versus $1/T$ for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol in the presence of acid.

$\Delta H^* = 15.7$ Kcal.mole$^{-1}$

$\Delta S^* = -10.4$ e.u.

Correlation coefficient $= -0.9948$
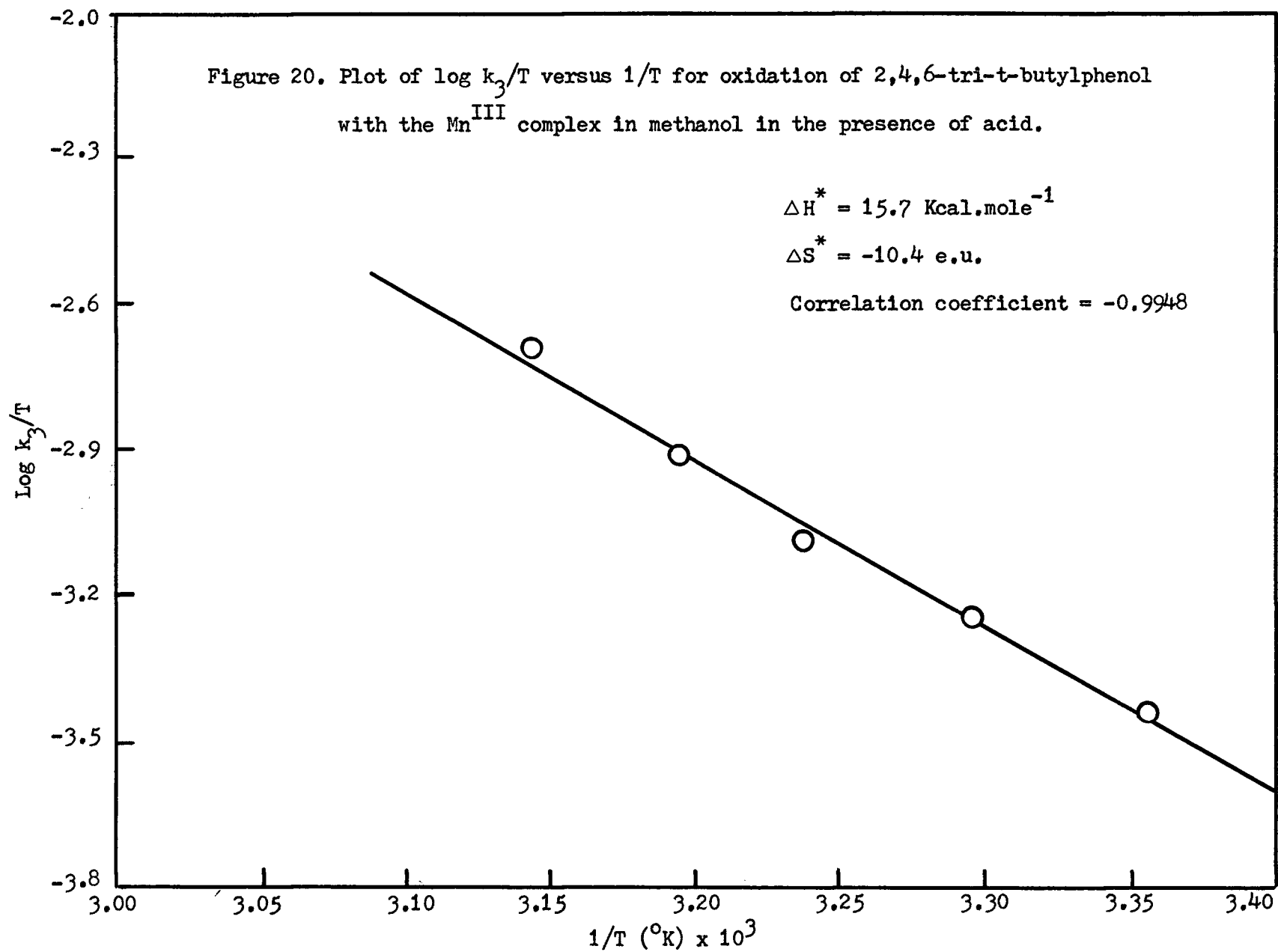
(vii) <u>Oxidations of phenol, benzaldehyde and benzoic acid</u>

Oxidations of phenol, benzaldehyde and benzoic acid with the Mn$^{III}$ complex in methanol in the presence of hydrochloric acid were carried out at $25^{\circ}$ to determine the rates of oxidation of the unhindered OH, CHO and COOH functional groups. Each oxidation was carried out with excess acid and substrate. The values of $k_3$ were obtained in a manner similar to that in Section VII-viii (below). The results obtained are shown in Table XIX.

TABLE XIX

<u>Oxidation rates of phenol, benzaldehyde and benzoic acid at $25^{\circ}$</u>

$(Mn^{III}) = 6.0 \times 10^{-4}$ M $\qquad\qquad$ $(HCl) = 1.63 \times 10^{-2}$M
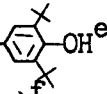
| <u>Substrate</u> | $\underline{k_3(M^{-1}sec^{-1})}$ |
|---|---|
| Phenol | 42 |
| Benzaldehyde | $1.1 \times 10^{-2}$ |
| Benzoic acid | no reaction |

(viii) <u>Substituent effect</u>

Oxidation of a number of 4-substituted-2,6-di-t-butylphenols with the Mn$^{III}$ complex in methanol in the presence of hydrochloric acid was carried out at $25^{\circ}$. Oxidation was carried out with excess acid and phenol. The value of $k_3$ for each phenol was determined from equation (52) with r = 0.5. The values of $k_3$ are tabulated with the $\sigma_p$ and $\sigma_p^-$ values in Table XX and the oxidation products are listed in Table XXI.

TABLE XX

Rates, $\sigma_p$, and $\sigma_p^-$ values of some 4-substituted-2,6-di-t-butylphenols

(under acidic conditions at $25^\circ$)

| Compound | Substituent | $k_3(M^{-1}sec^{-1})$ | $\sigma_p^{\;a}$ | $\sigma_p^{-\;a}$ | $\log k_3/k_{3H}^{\;b}$ |
|---|---|---|---|---|---|
| XXIX | OH | > 84 | -0.357 | -0.357 | > 2.9 |
| XXIII | t-Bu[c] | $1.38 \times 10^{-1}$ | -0.197 | -0.197 | 0.111 |
| XX | CH$_3$ | $2.90 \times 10^{-1}$ | -0.170 | -0.170 | 0.433 |
| XXVIII | CH$_2$OH[d] | $2.17 \times 10^{-1}$ | | | 0.332 |
| XXVII | CH$_2$OCH$_2$—⟨⟩—OH[e] | $0.80 \times 10^{-1}$ | | | -0.126 |
| XXXI | CH$_2$N(CH$_3$)$_2$[f] | $1.66 \times 10^{-1}$ | | | 0.191 |
| XXXIV | H | $1.07 \times 10^{-1}$ | 0 | 0 | 0 |
| XXIV | Cl | $1.41 \times 10^{-1}$ | +0.226 | +0.226 | 0.120 |
| XXII | Br | $1.45 \times 10^{-1}$ | +0.232 | +0.232 | 0.132 |
| XXV | I | $1.69 \times 10^{-1}$ | +0.276 | +0.276 | 0.199 |
| XXXII | COC$_6$H$_5$ | $3.53 \times 10^{-1}$ | +0.459 | +0.459 | 0.515 |
| XXX | COOH | $1.26 \times 10^{-1}$ | +0.265 | +0.728 | 0.071 |
| XXVI | COCH$_3$ | $5.19 \times 10^{-1}$ | +0.516 | +0.874 | 0.686 |
| XXXIII | CN | $2.50 \times 10^{-1}$ | +0.628 | +1.00 | 0.365 |
| XXI | CHO | 20.7 | +0.216 | +1.126 | 2.286 |

a values taken from reference 84; b $k_{3H}$ is the rate constant for

2,6-di-t-butylphenol; c calculated for run with (HCl) = $1.63 \times 10^{-2}$ M;

d, e $\sigma_p$ and $\sigma_p^-$ values are likely to be close to those of CH$_3$ group

(the value of $k_3$ was corrected for a statistical factor of 2 for XXVII -

two equivalent OH groups); f the amino group is protonated, (HCl) = 2(XXVII).

For all runs: (HCl) = $1.63 \times 10^{-2}$M; (Mn$^{III}$) = $5.6 \times 10^{-4}$M;

(PhOH) = $2 \times 10^{-2}$M ($4.13 \times 10^{-3}$M used for XXI)

TABLE XXI

Oxidation products[*] from oxidation of some 4-substituted-2,6-di-t-
butylphenols with the $Mn^{III}$ complex under acidic conditions in methanol

| Compound | Product |
| --- | --- |
| XXIX | XIX |
| XXIII | XXXVIII  R = t-Bu |
| XX | XXXV |
| XXVIII | XXXVI, XVIII |
| XXVII | XVIII, XXXV |
| XXXI | XXXVI, XVIII |
| XXXIV | XXXVI, XVIII |
| XXIV | XXXVII  R = Cl, XVIII |
| XXII | XXXVII  R = Br, XVIII |
| XXV | XVIII |
| XXXII | XXXVIII  R = $COC_6H_5$ |
| XXX | XXXVI, XVIII |
| XXVI | XXXVIII  R = $COCH_3$ |
| XXXIII | XXXIII, XVIII |
| XXI | XXXVI, XVIII |

* XXXVIII detected by esr spectrometry

XIX detected by spectrophotometry (strong absorption band at 320 nm)

XVIII detected by spectrophotometry (strong absorption band at 419 nm)

* XXXVI and XXXVII detected indirectly - by oxidising them to XVIII

XXXV isolated as a colourless solid, m.p. 97-98° (Lit. 98-99°)[85];

<u>nmr spectrum in CCl$_4$</u>

| | | | | | | |
|---|---|---|---|---|---|---|
| chemical shift ($\delta$, ppm) | This work | 1.43 | 3.25 | 4.18 | 4.97 | 6.97 |
| | Reference 85 | 1.40 | 3.24 | 4.21 | 5.00 | 7.00 |
| number of H's | This work | 18 | 3 | 2 | 1 | 2 |
| | Reference 85 | 18 | 3 | 2 | 1 | 2 |
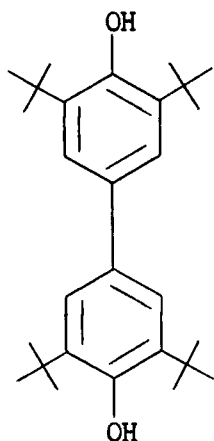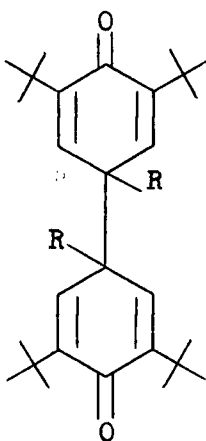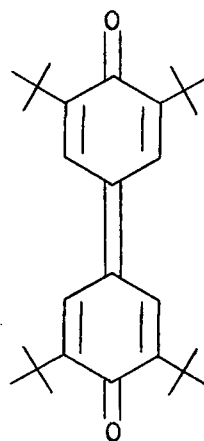


XXXVI    XXXVII    XVIII
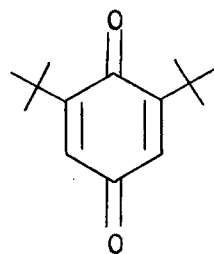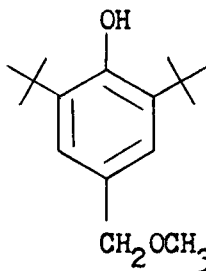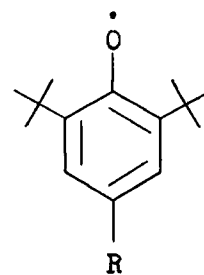


XIX    XXXV    XXXVIII

(ix) <u>Discussion</u>

In the proposed mechanism, 2,4,6-tri-t-butylphenol and the $Mn^{III}$

complex compete for the hydroxymethyl radicals. If this is true, a plot

of $k_a$ versus the concentration of 2,4,6-tri-t-butylphenol is expected to

show a minimum value of $k_a$ at a certain concentration of the phenol

because the two terms, $rk_b$ and $k_c$, oppose each other (see equation (52)).

As the concentration of 2,4,6-tri-t-butylphenol is increased $k_c$ will

also increase because this term is proportional to the concentration of

2,4,6-tri-t-butylphenol. But $rk_b$ will decrease since the hydroxymethyl

radicals will more likely react with 2,4,6-tri-t-butylphenol. When the

concentration of 2,4,6-tri-t-butylphenol is decreased, $rk_b$ will increase

and $k_c$ decrease. Thus, a minimum value of $k_a$ is expected at a certain

concentration of 2,4,6-tri-t-butylphenol. Figure 21 is such a plot and

it indeed shows the expected shape. Data used in Figure 21 were taken

from Table XXII.

At equal concentration of the $Mn^{III}$ complex and 2,4,6-tri-t-butylphenol

r was calculated and found to be 0.7. This value implies that hydroxymethyl

radical reacts faster with 2,4,6-tri-t-butylphenol (by abstracting a

hydrogen atom from 2,4,6-tri-t-butylphenol) than with the $Mn^{III}$ complex

(by transferring a hydrogen atom to the $Mn^{III}$ complex). Using this value

of r, $k_5/(k_2 + k_4)$ was found to be 1.5.

TABLE XXII

<u>Variation of $k_a$ with concentration of 2,4,6-tri-t-butylphenol at 25°</u>

<u>(includes data from Table XVI)</u>

$(Mn^{III}) = 5.6 \times 10^{-4}$ M                    $(HCl) = 1.63 \times 10^{-2}$ M

| $(PhOH)^*$ (M) | $k_a$ (sec$^{-1}$) |
|---|---|
| $3.47 \times 10^{-6}$ | $1.51 \times 10^{-3}$ |
| $3.47 \times 10^{-5}$ | $1.38 \times 10^{-3}$ |
| $5.53 \times 10^{-4}$ | $1.12 \times 10^{-3}$ |
| $5.29 \times 10^{-3}$ | $1.04 \times 10^{-3}$ |
| $7.70 \times 10^{-3}$ | $1.13 \times 10^{-3}$ |
| $9.70 \times 10^{-3}$ | $1.14 \times 10^{-3}$ |
| $1.57 \times 10^{-2}$ | $1.17 \times 10^{-3}$ |
| $3.00 \times 10^{-2}$ | $1.50 \times 10^{-3}$ |
| $5.10 \times 10^{-2}$ | $1.74 \times 10^{-3}$ |
| $6.64 \times 10^{-2}$ | $2.12 \times 10^{-3}$ |
| $7.74 \times 10^{-2}$ | $2.30 \times 10^{-3}$ |
| $9.22 \times 10^{-2}$ | $2.69 \times 10^{-3}$ |

* PhOH is used as an abbreviation for 2,4,6-tri-t-butylphenol.

Figure 21. Observed rate constant, $k_a$, versus concentration of 2,4,6-tri-t-butylphenol. Part (ii).

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(HCl) = 1.63 \times 10^{-2}$ M

Temperature = $25^o$

y-axis: $k_a \times 10^3$ sec$^{-1}$

x-axis: Concentration of 2,4,6-tri-t-butylphenol x $10^2$ M
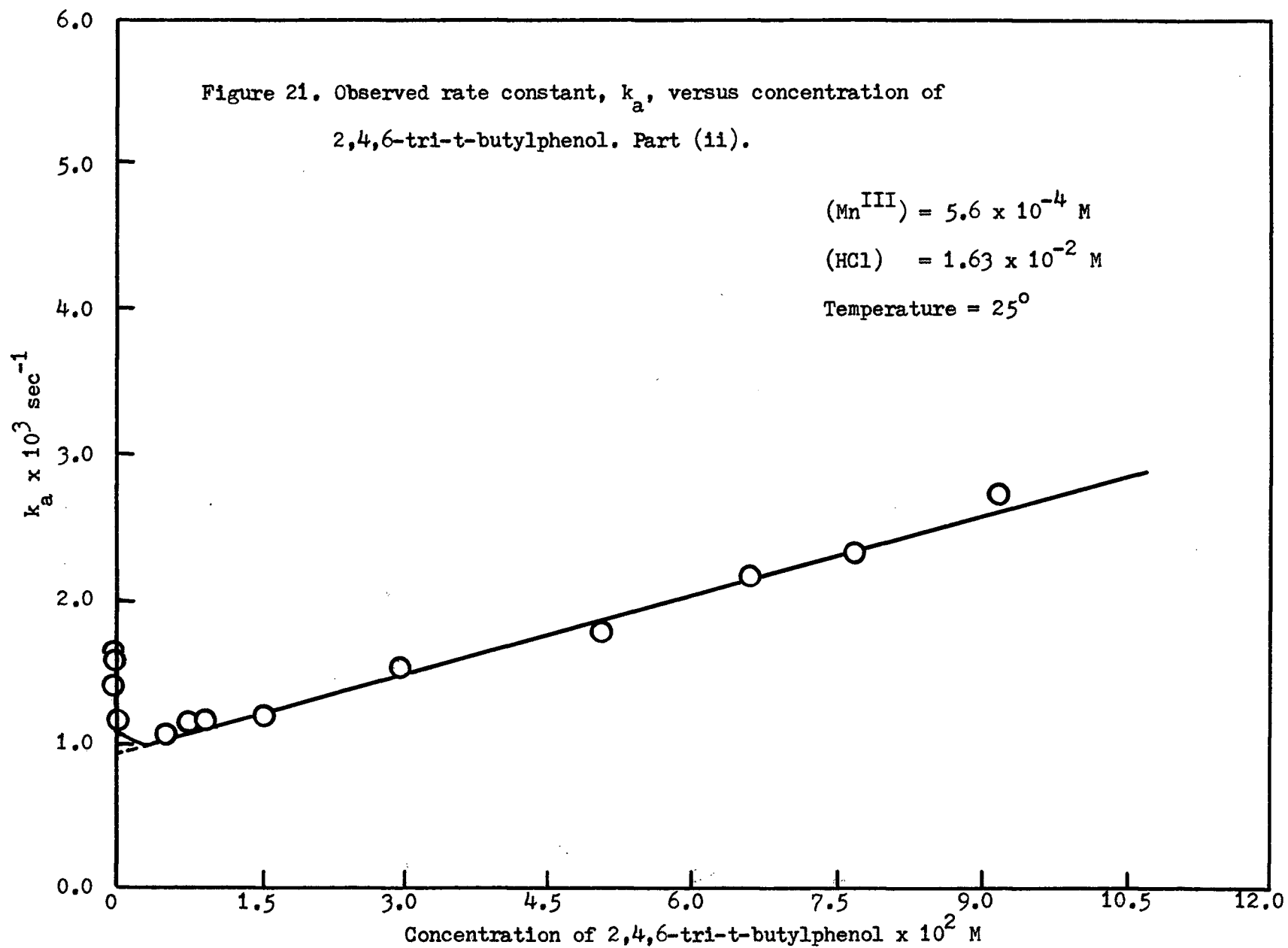
That the oxidant is not $Mn^{III}CyDTA(H_2O)^-$, but a different form of

the $Mn^{III}$ complex, is indicated by the very slow oxidation of 2,4,6-tri-

t-butylphenol with the $Mn^{III}$ complex in methanol when no acid is present

(see Section IX). This more powerful $Mn^{III}$ complex present in acidic

medium is probably a protonated species as indicated by the reversible

change of its visible spectrum in methanol (see Section IV-v), by the

curved plots of observed rate constant versus acid concentration (see

Figures 12 and 18), and by the equilibrium isotope effect (see Section

VI-vii).

The effect on the oxidation rate of varying the 4-substituent (see

Table XX) rules out electron-transfer from hindered phenol to $Mn^{III}$

complex. If electron-transfer were involved in the oxidation reaction

the transition state would look like XXXIX and electron-withdrawing

groups should retard the reaction.
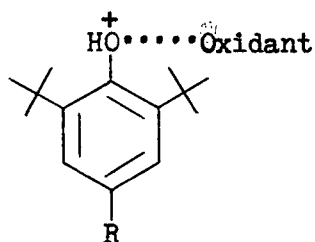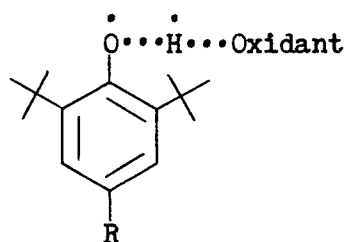


XXXIX                          XXXX

The similar oxidation rates of most 4-substituted-2,6-di-t-butylphenols

suggest that a radical intermediate (XXXX) is formed in the transition state. Both electron-withdrawing and electron-donating substituents will stabilise this transition state and their effects on the rate are usually small.

A Hammett plot of log $k_3/k_{3H}$ versus $\sigma_p^-$ correlates the substituent effects as well as that of log $k_3/k_{3H}$ versus $\sigma_p$ ($k_3$ is the rate constant for a 4-substituted-2,6-di-t-butylphenol and $k_{3H}$ is the rate constant for 2,6-di-t-butylphenol). Figures 22 and 23 are such plots. It can be seen from Figures 22 and 23 that the slopes are practically zero (0.23 and 0.38 respectively), indicating the effects of substituents are very small.

Two 4-substituted compounds, the 4-hydroxy and 4-formyl compounds, deviate considerably from the straight line plots in Figures 22 and 23. For the 4-hydroxy compound it is the unhindered OH group that is oxidised by the $Mn^{III}$ complex. (It reacts 420 times faster than the hindered OH group - compare the rates of 2,6-di-t-butylphenol and phenol in Tables XIX and XX). The point for the 4-hydroxy substituent has thus been omitted from the plots. The rate of the 4-hydroxy substituent is too fast to be measurable, but $k_3$ was estimated to be greater than 84 $M^{-1}sec^{-1}$. It is not clear why the 4-formyl compound has an anomalously high rate. The unhindered CHO group is about ten times less reactive than the hindered OH group (compare the rates of benzaldehyde and 2,6-di-t-butyl-phenol in Tables XIX and XX). It is therefore not likely that the CHO

Figure 22. Plot of log $k_3/k_{3H}$ versus $\sigma_p^-$.

slope = $\ell$ = 0.23

Figure 23. Plot of log $k_3/k_{3H}$ versus $\sigma_p$.

slope = $\rho$ = 0.38
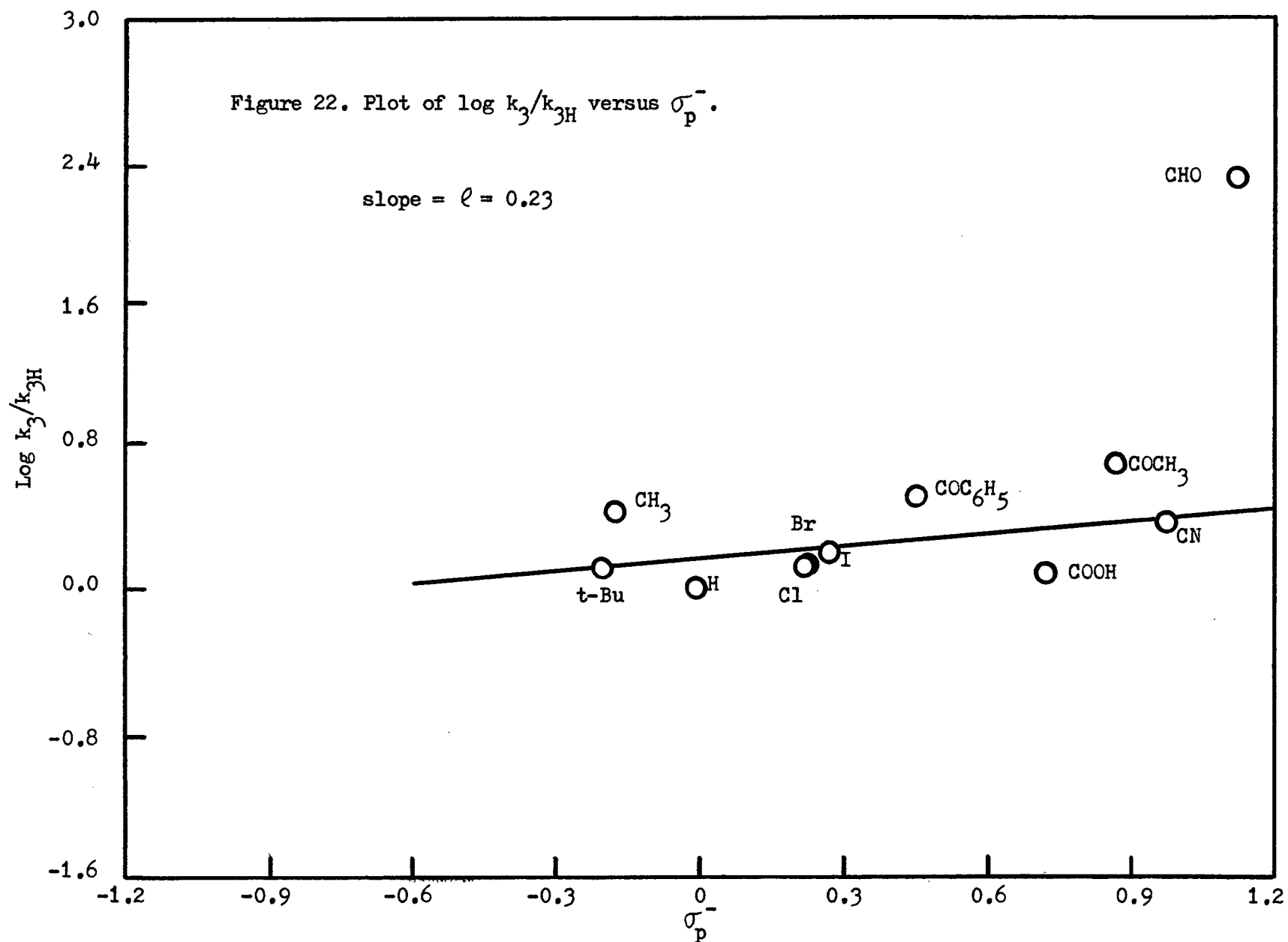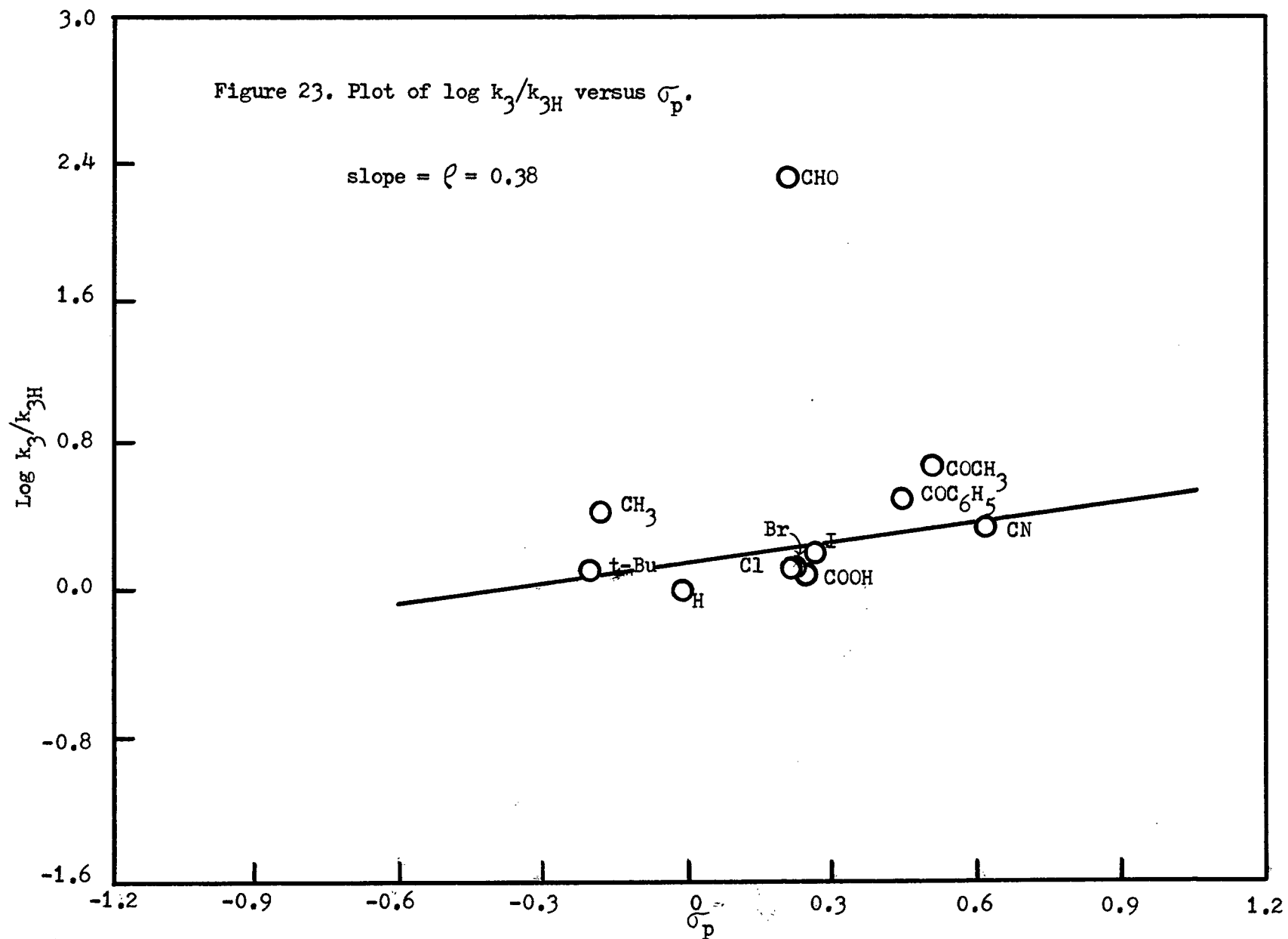
group is oxidised instead of the OH group unless the $\rho$ value of the

reaction is more negative than -3.8. A similar oxidation of the 4-formyl

compound with the $Mn^{III}$ complex in methanol-O-d in the presence of

deuterium chloride showed a kinetic isotope effect of 4.9 (the value of

$k_3$ in methanol-O-d was found to be 4.2 $M^{-1}sec^{-1}$), thus indicating that

it is the OH group that is oxidised by the $Mn^{III}$ complex. (Compare this

kinetic isotope effect with that of 2,4,6-tri-t-butylphenol below).

The observed kinetic isotope effect $(k_{3H}/k_{3D})$ of 4.8 for the

oxidation of 2,4,6-tri-t-butylphenol indicates that O-H bond is cleaved

in the rate-determining step of the reaction. Since the rate is first

order with respect to the concentration of $HMn^{III}CyDTA(H_2O)$ and first

order with respect to the concentration of 2,4,6-tri-t-butylphenol, these

two molecules form an activated complex which involves the bridging of

the OH group of the hindered phenol and probably a ligand of the $Mn^{III}$

complex. The OH group of 2,4,6-tri-t-butylphenol can be bridged via the

hydrogen atom to either the coordinated water molecule or a carbonyl

group of $HMn^{III}CyDTA(H_2O)$. Water and carboxylate carbonyl ligands are

well known in their function as bridging ligands in 'inner-sphere'

electron-transfer reactions. (An 'inner-sphere' electron-transfer

reaction is one in which the two reactants involved are bridged through

a common atom or ligand during the electron-transfer process and bond

breaking occurs in the reaction). Available data[86-88] indicate that a

coordinated water molecule is better than a non-conjugated carboxylate

carbonyl group as a bridging group in the 'inner-sphere' electron-transfer reactions (see Table XXIII). The three carbonyl groups of the three carboxylate ligands which are coordinated to the $Mn^{III}$ ion and the carbonyl group of the free carboxylic arm are not likely to differ from the carboxylic ligands shown in Table XXIII in their abilities to bridge with a reactant in an electron-transfer reaction. Therefore, the coordinated water ligand of $HMn^{III}CyDTA(H_2O)$ is likely to be the ligand involved in the hydrogen atom transfer reaction. The reaction mechanism involved may be pictured as: (i) the formation of an activated complex between $HMn^{III}CyDTA(H_2O)$ and 2,4,6-tri-t-butylphenol as represented by XXXXI. The hydrogen atom is then transferred from 2,4,6-tri-t-butylphenol to the coordinated water ligand to form intermediate XXXXII and 2,4,6-tri-t-butylphenoxyl in a rate-determining step. (ii) Intermediate XXXXII quickly loses a proton to give $HMn^{II}CyDTA(H_2O)^-$.



$$\left[ HMn^{III}CyDTA(H_2O)\cdots H \cdots O \!-\!\!\bigcirc\!\!- \right] \xrightarrow{\;k_3\;} \cdot O\!-\!\!\bigcirc\!\!- $$

XXXXI

$$ + \left[ HMn^{II}CyDTA(H_3O^+) \right] $$

XXXXII

$$HMn^{II}CyDTA(H_2O)^- + H^+ \longleftarrow$$
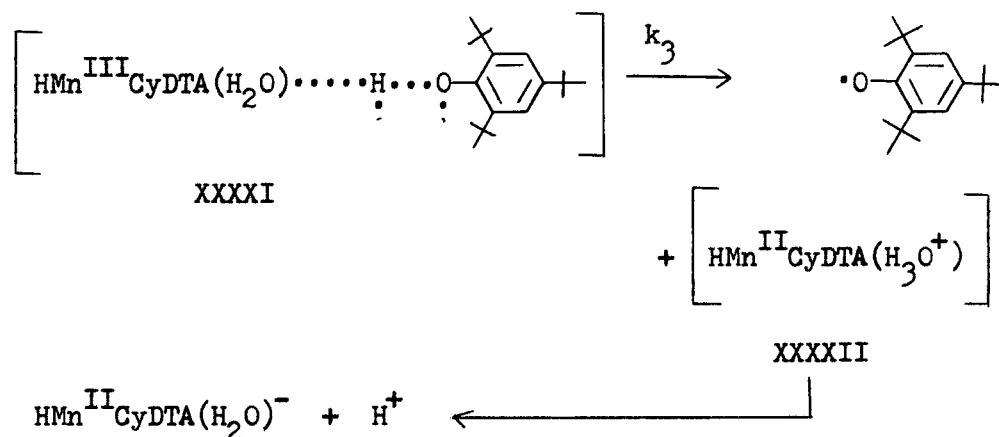
In the activated complex, XXXXI, the oxygen atom of the phenol has radical character and such a structure is consistent with the small effect on the reaction rate exerted by 4-substituents.

It was reported in Section VI that a kinetic isotope effect of 1.3 results from replacing the coordinated water ligand by deuterium oxide ligand. Taking this isotope effect contribution into account the kinetic isotope effect due to the O-H bond cleavage is 3.7.

TABLE XXIII

Comparison of rates of reduction by $Cr^{2+}$ of $Co^{III}(NH_3)_5L$ complexes by 'inner-sphere' mechanism at $25^{\circ}$ and ionic strength of 1.0

| L | $k(M^{-1}sec^{-1})$ | Reference |
|---|---|---|
| $H_2O$ | 0.56 | 89 |
| $CH_3COO^-$ | 0.35, 0.18 | 88, 90 |
| $CH_3(CH_2)_2COO^-$ | 0.08 | 91 |
| $CH_3CH=CHCOO^-$ | 0.18 | 91 |
| $(CH_3)_3CCOO^-$ | 0.009 | 92 |
| $C_6H_5COO^-$ | 0.15 | 88 |
| $HO_2CCH_2CH_2COO^-$ | 0.19 | 90 |

The oxidation of compound XXXI (2,6-di-t-butyl-4-dimethylamino-methylphenol) has an interesting feature. When the concentrations of acid and XXXI are equal the reaction with the $Mn^{III}$ complex is very slow. When acid is in excess the reaction occurs at a normal rate, that is, similar to those of the other 4-substituted-2,6-di-t-butylphenols. In the absence of acid the reaction is very rapid (very much faster than the reaction between 2,4,6-tri-t-butylphenol and the $Mn^{III}$ complex in the absence of acid). These observations can be explained as follows.

When the concentrations of XXXI and acid are equal all the acid is taken up by the amino group of the 4-substituent of XXXI. The reaction is then between $Mn^{III}CyDTA(H_2O)$ and the protonated form of XXXI (see equations (54) and (55)). Since $Mn^{III}CyDTA(H_2O)^-$ is a poor oxidant compared to $HMn^{III}CyDTA(H_2O)$ the reaction observed is slow (see Section IX).



$$\text{XXXI} \qquad\qquad \text{XXXXIII} \qquad\qquad (54)$$

$$\text{XXXXIII} + Mn^{III}CyDTA(H_2O)^- \xrightarrow{k_{3a}} \text{products} \qquad (55)$$
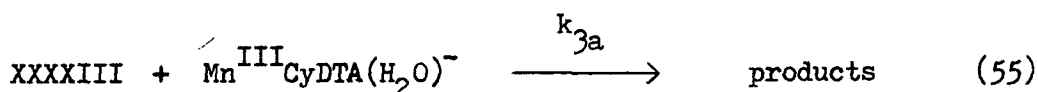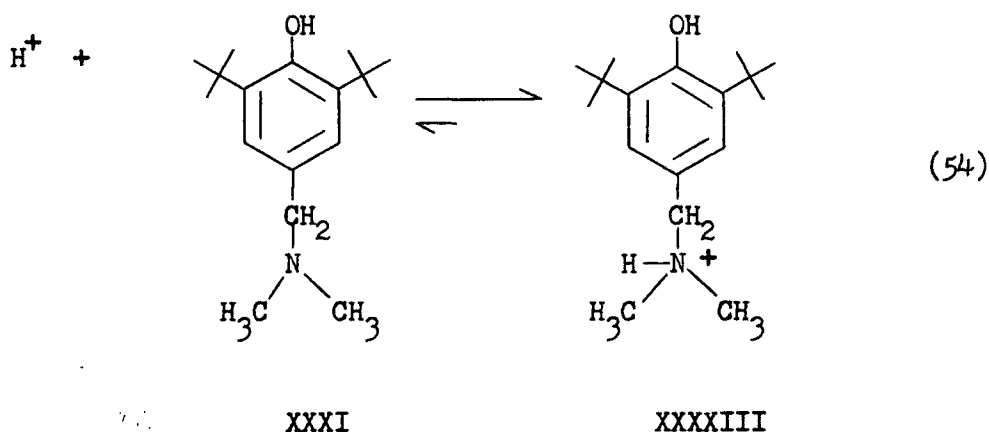
When the concentration of acid is more than that of XXXI the

reaction is between XXXI and $HMn^{III}CyDTA(H_2O)$ and the rate is of the

right magnitude expected for $k_3$ (see Table XX).

In the absence of acid XXXI removes a proton from $Mn^{III}CyDTA(H_2O)^-$

to form XXXXIII and $Mn^{III}CyDTA(OH)^{2-}$, the latter is a more powerful

oxidant than $Mn^{III}CyDTA(H_2O)^-$ and thus the reaction is rapid (see equations

(56) and (57)). (Also see Sections VIII and IX for evidence showing

$Mn^{III}CyDTA(OH)^{2-}$ to be a stronger oxidant than $Mn^{III}CyDTA(H_2O)^-$).

$$Mn^{III}CyDTA(H_2O)^- \ + \ XXXI \ \rightleftharpoons \ Mn^{III}CyDTA(OH)^{2-} \ + \ XXXXIII$$

$$(56)$$

$$Mn^{III}CyDTA(OH)^{2-} \ + \ XXXI \ and/or \ XXXXIII \ \xrightarrow{k_9} \ products$$

$$(57)$$
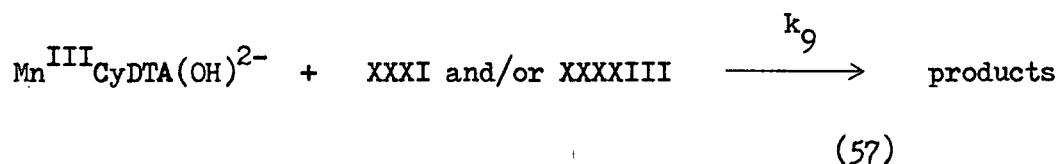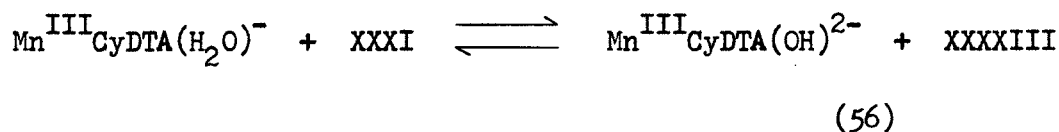
Oxidation of 4-substituted-2,6-di-t-butylphenols with the $Mn^{III}$

complex in methanol in the presence of hydrochloric acid gave the

corresponding 4-substituted-2,6-di-t-butylphenoxyls. The esr spectra of

the following 4-substituted-2,6-di-t-butylphenoxyls were recorded:

4-t-Bu, 4-COCH$_3$ and 4-COC$_6$H$_5$. The esr spectra of 4-CH$_3$ and 4-CN radicals

were recorded under basic and neutral conditions but not under acidic

condition because they reacted rapidly under the latter condition. The

Figure 24. ESR spectrum of 2,6-di-t-butyl-4-benzoylphenoxyl in methanol.

2.5 gauss
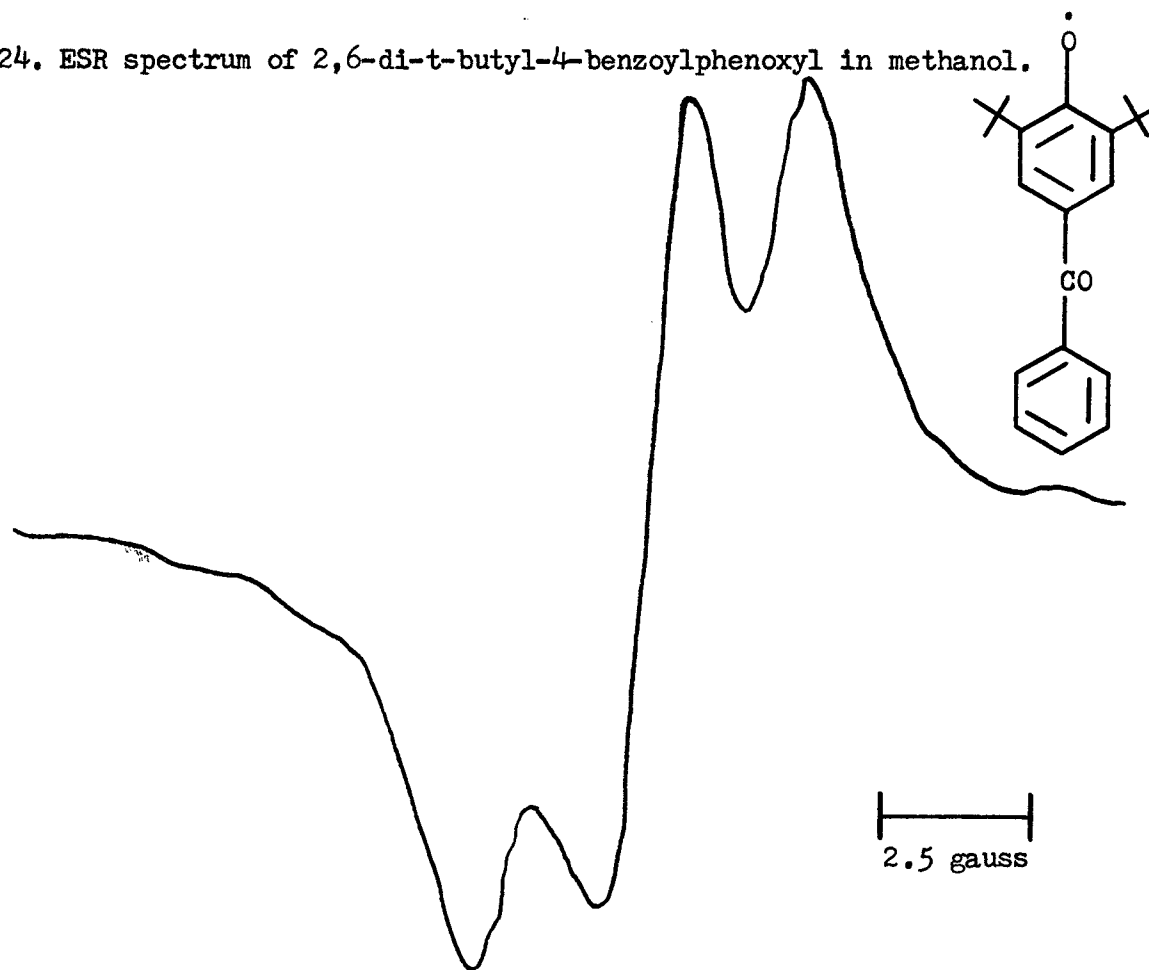
Figure 25. ESR spectrum of 2,6-di-t-butyl-4-acetylphenoxyl in methanol.

1 gauss
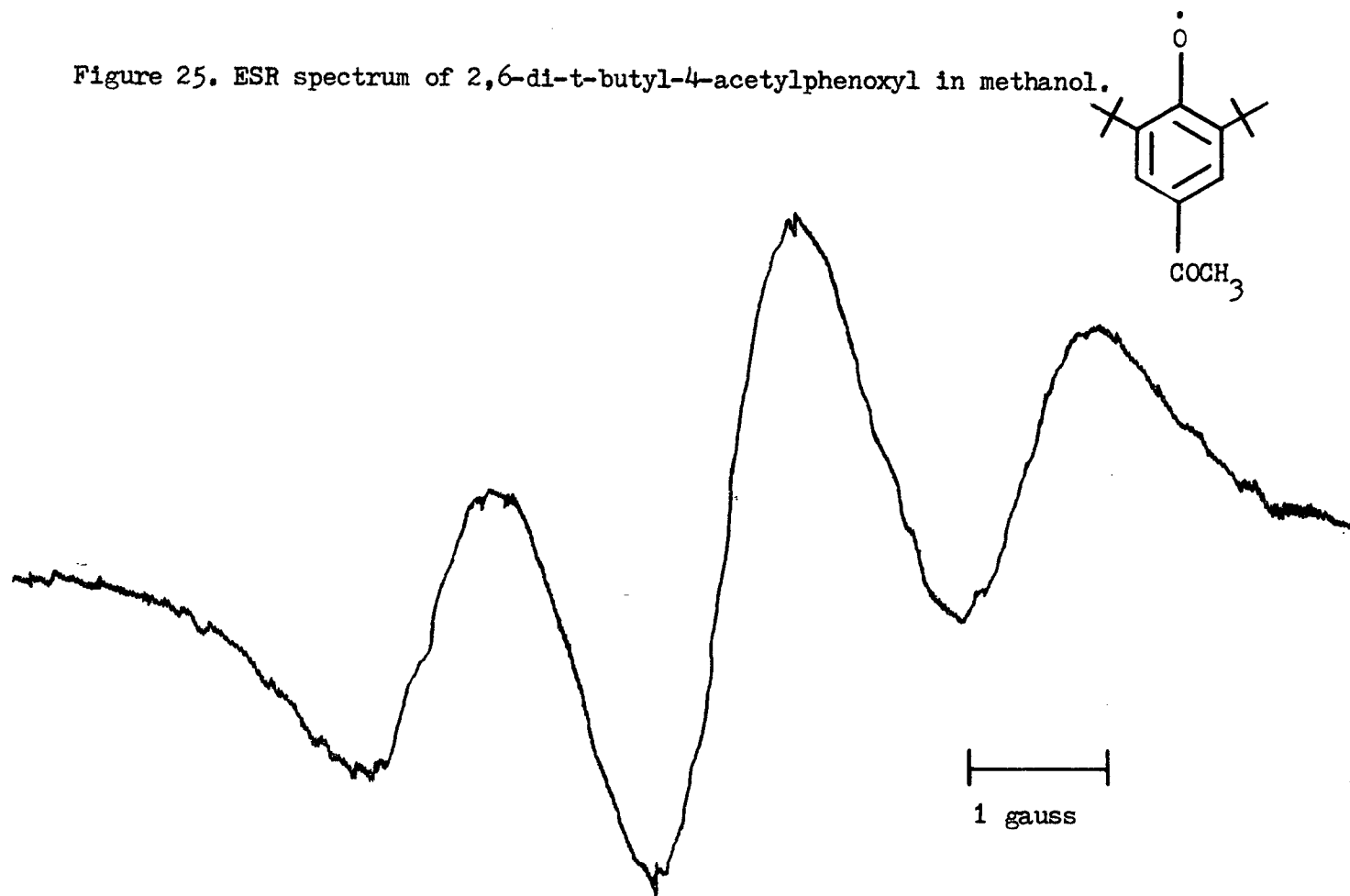
Figure 26. ESR spectrum of 2,6-di-t-butyl-4-methylphenoxyl in methanol.

5 gauss
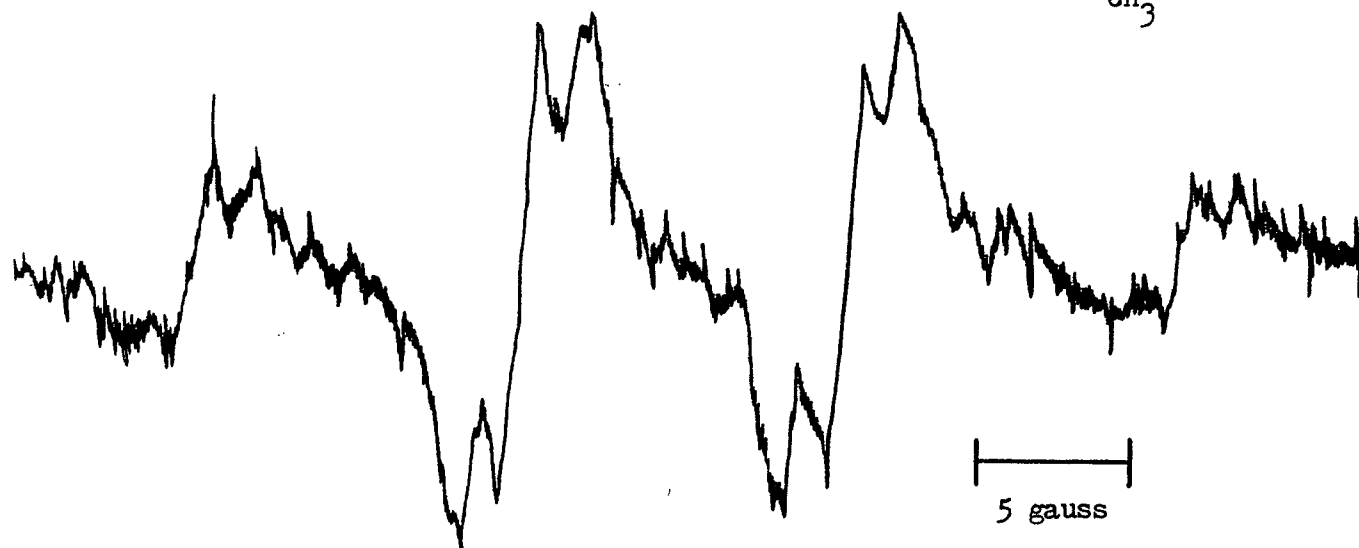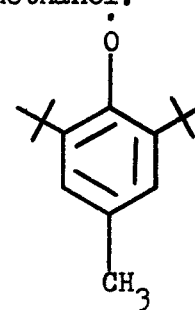
Figure 27. ESR spectrum of 2,6-di-t-butyl-4-cyanophenoxyl in methanol.
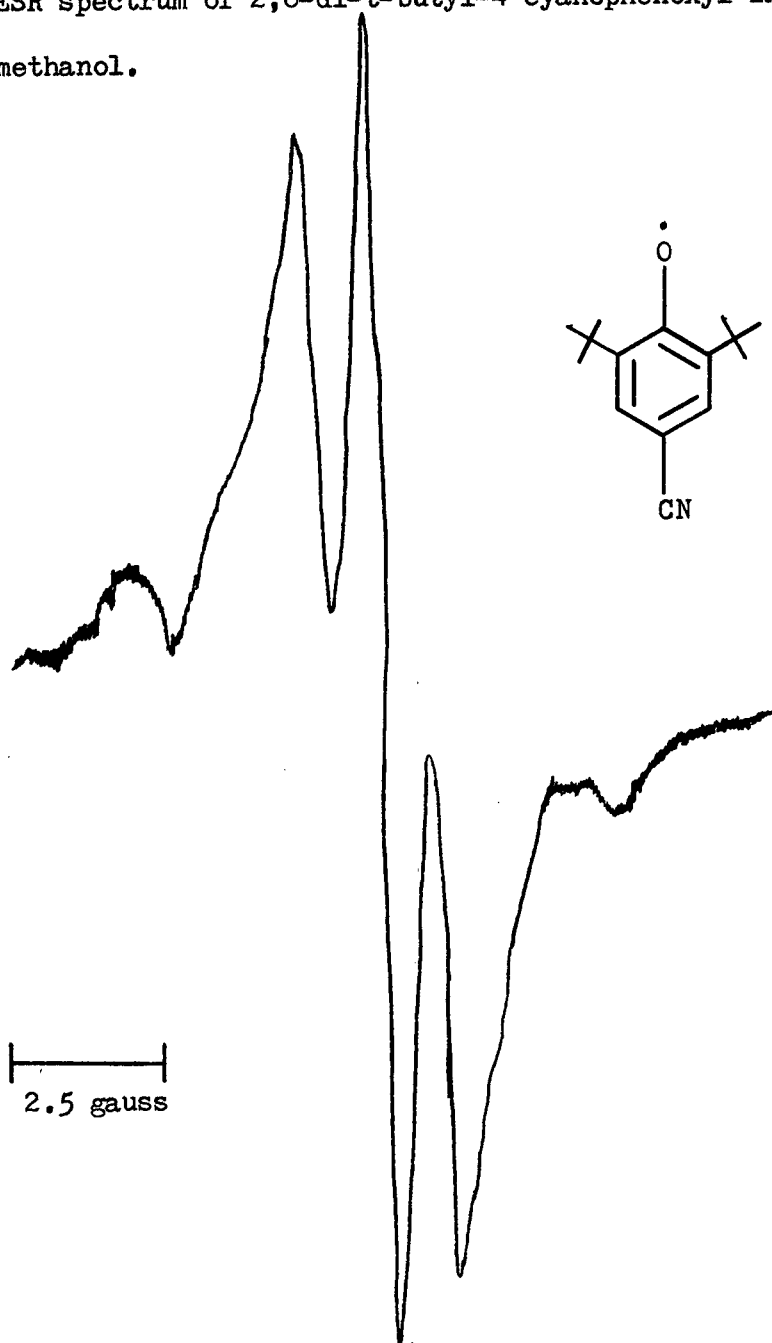
other 4-substituted-2,6-di-t-butylphenoxyls reacted rapidly and they
could not be detected by esr spectrometry. The probable reaction steps
involved for the different 4-substituted-2,6-di-t-butylphenols in the
oxidation reactions are shown below.

## All substituents



XXXVIII
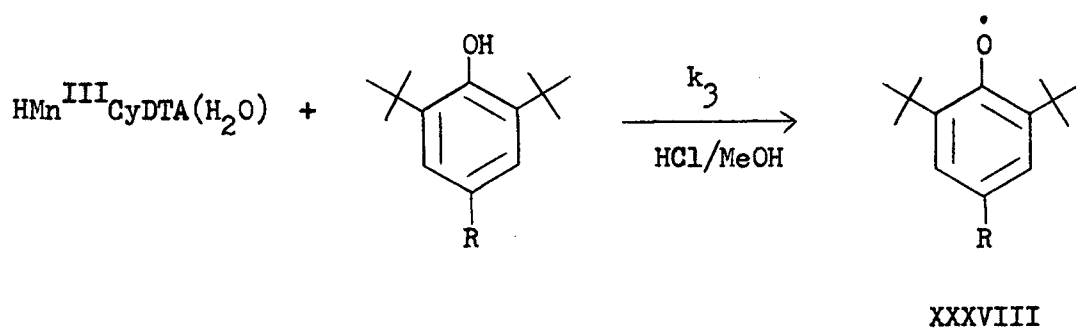
## R = H, Cl, Br, I (see reference 45)



2 XXXVIII ⟶    XXXVII          XVIII

R = OH



XIX

R = CN
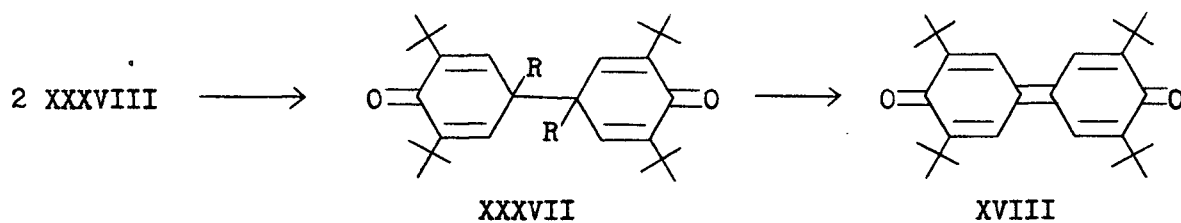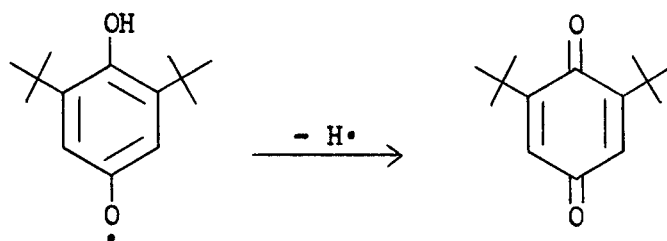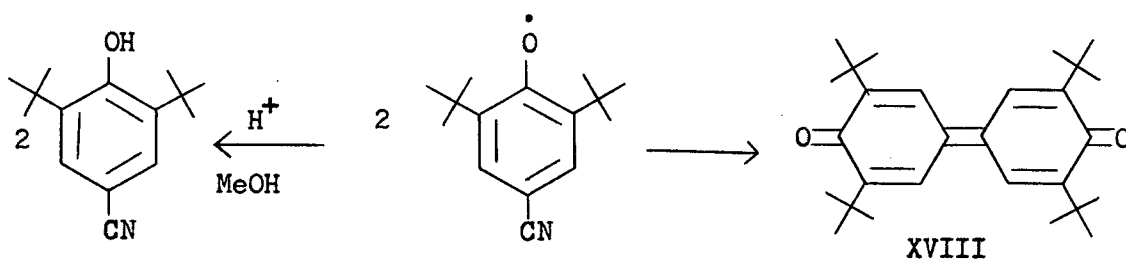


XXXIII                                          XVIII

R = CH₃ (see reference 85)



XXXV

$\underline{R = CH_2OCH_2}$—⟨benzene⟩—$\underline{OH}$



H$^+$/MeOH

$-$ HCHO

XXXV

XXXVI
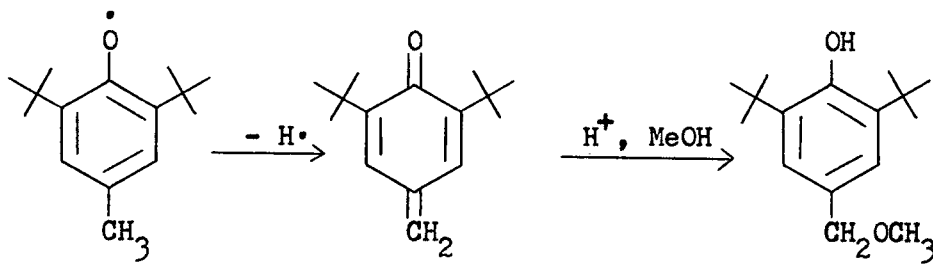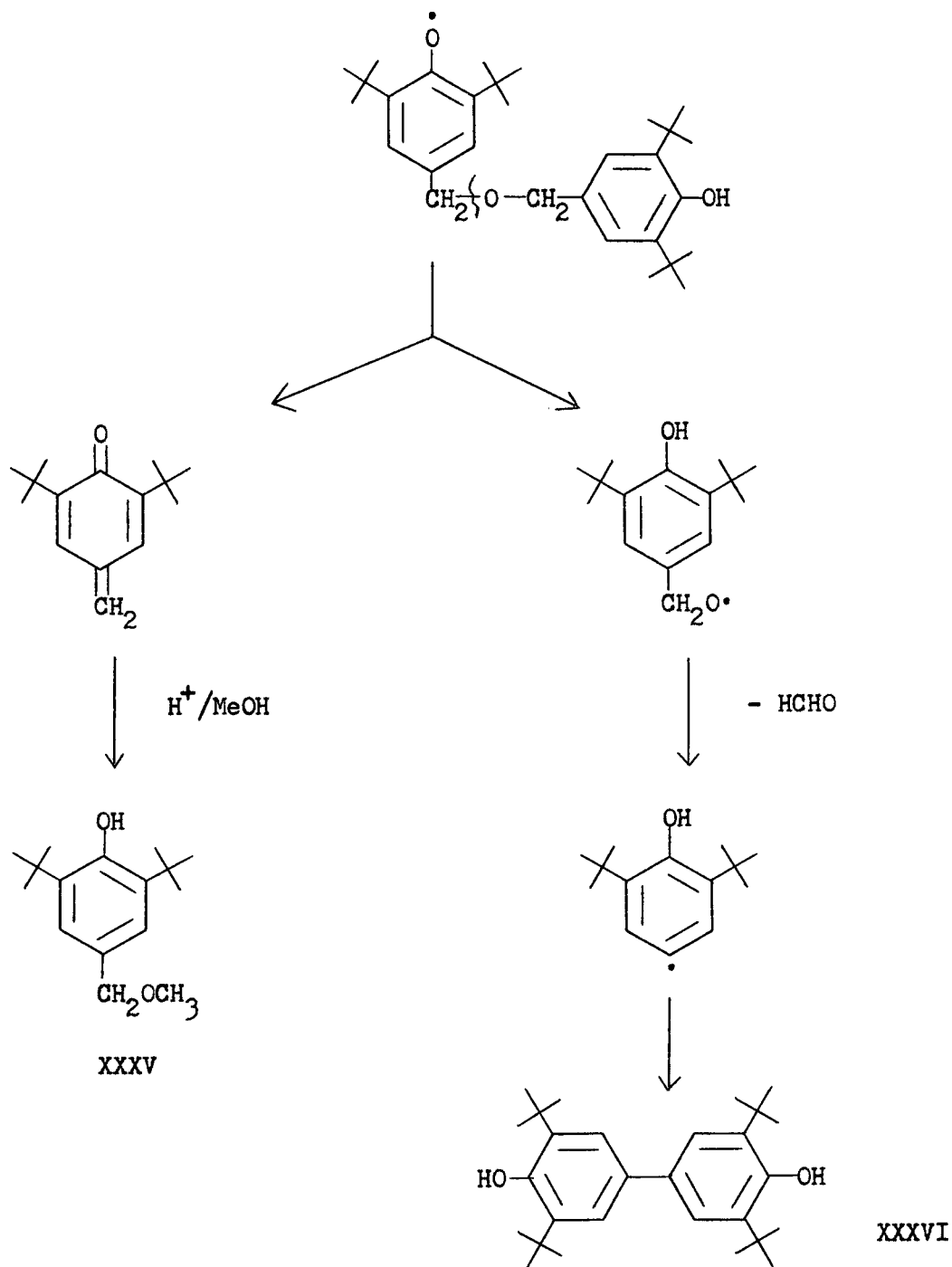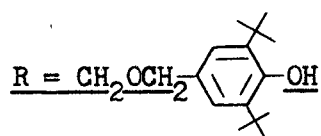
R = CH₂OH, COOH, CHO (see reference 34)
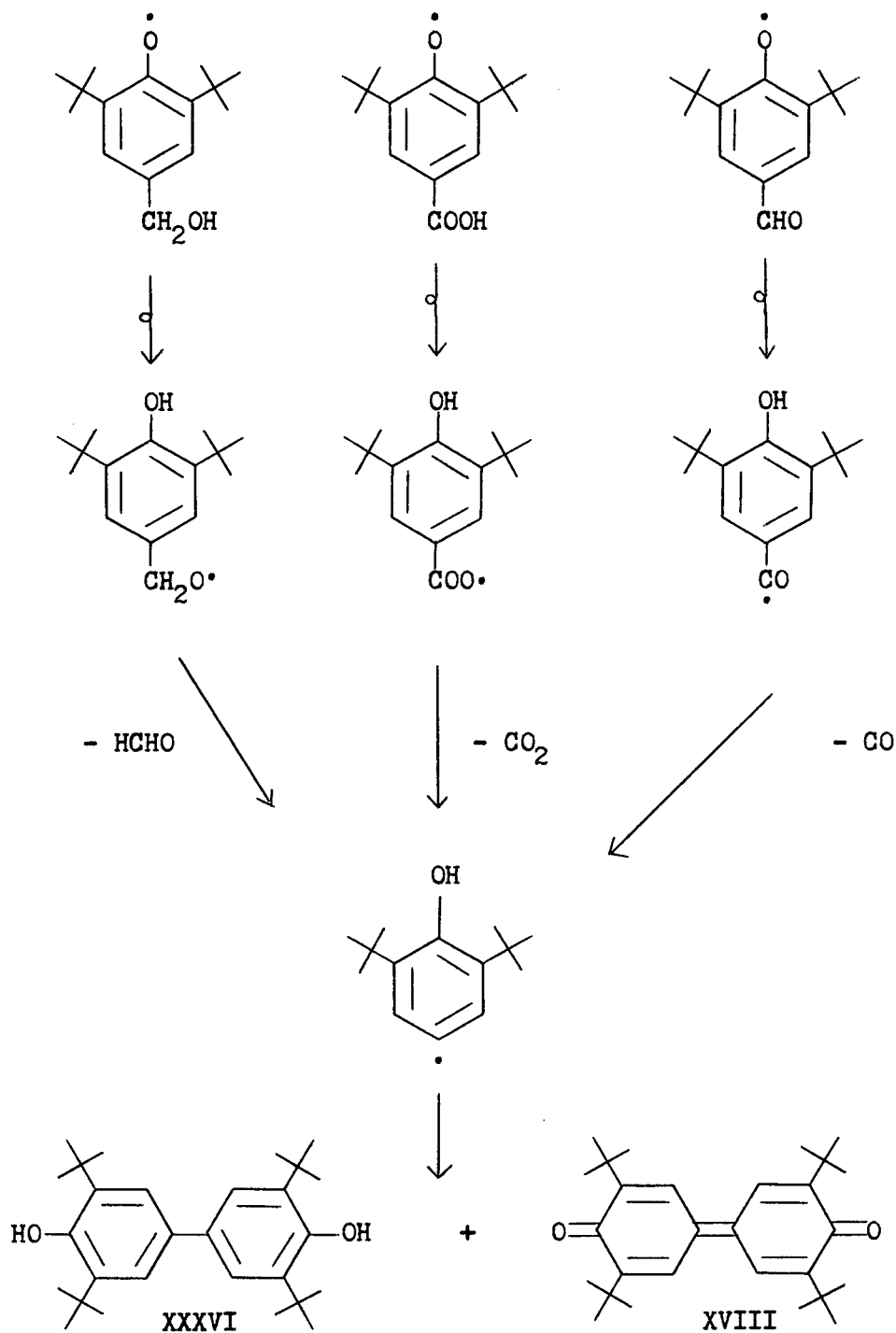
## VIII. OXIDATION OF 2,4,6-TRI-t-BUTYLPHENOL WITH THE Mn$^{III}$ COMPLEX IN METHANOL* IN THE PRESENCE OF BASE

### (i) Product

2,4,6-Tri-t-butylphenoxyl was formed quantitatively as seen from its absorbance at 400 nm (Figure 28).

### (ii) Analysis of kinetic results

Oxidation of 2,4,6-tri-t-butylphenol with the Mn$^{III}$ complex was carried out with excess 2,4,6-tri-t-butylphenol and tetramethylammonium hydroxide present. Plots of logarithm of $A_{Mn}$ versus time are linear up to more than 80 % of reaction, indicating that the rate of disappearance of the Mn$^{III}$ complex can be expressed by equation (58). Figure 29 is a typical plot of equation (59).

$$- d(Mn^{III})_{tot}/dt = k_e(Mn^{III})_{tot} \qquad (58)$$

Integrating equation (58) gives equation (59).

$$\log A_{Mn} - \log A_o = - k_e t/2.303 \qquad (59)$$

where  $(Mn^{III})_{tot}$ = total Mn$^{III}$ complex concentration

$k_e$ = pseudo-first order rate constant

$A_{Mn}$ = absorbance of the Mn$^{III}$ complex at 486 nm at time t

$A_o$ = absorbance of the Mn$^{III}$ complex at 486 nm at time zero.

* 2.5 % water (v/v)

Figure 28. Visible spectrum showing absorption bands of 2,4,6-tri-t-butylphenoxyl (A) and the $Mn^{III}$ complex (B) in methanol in the presence of base.

Figure 29. Plot of log $A_{Mn}$ versus time for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol in the presence of base.

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(PhOH) = 2.52 \times 10^{-2}$ M

$(TMA) = 1.78 \times 10^{-2}$ M

Temperature $= 25^{\circ}$
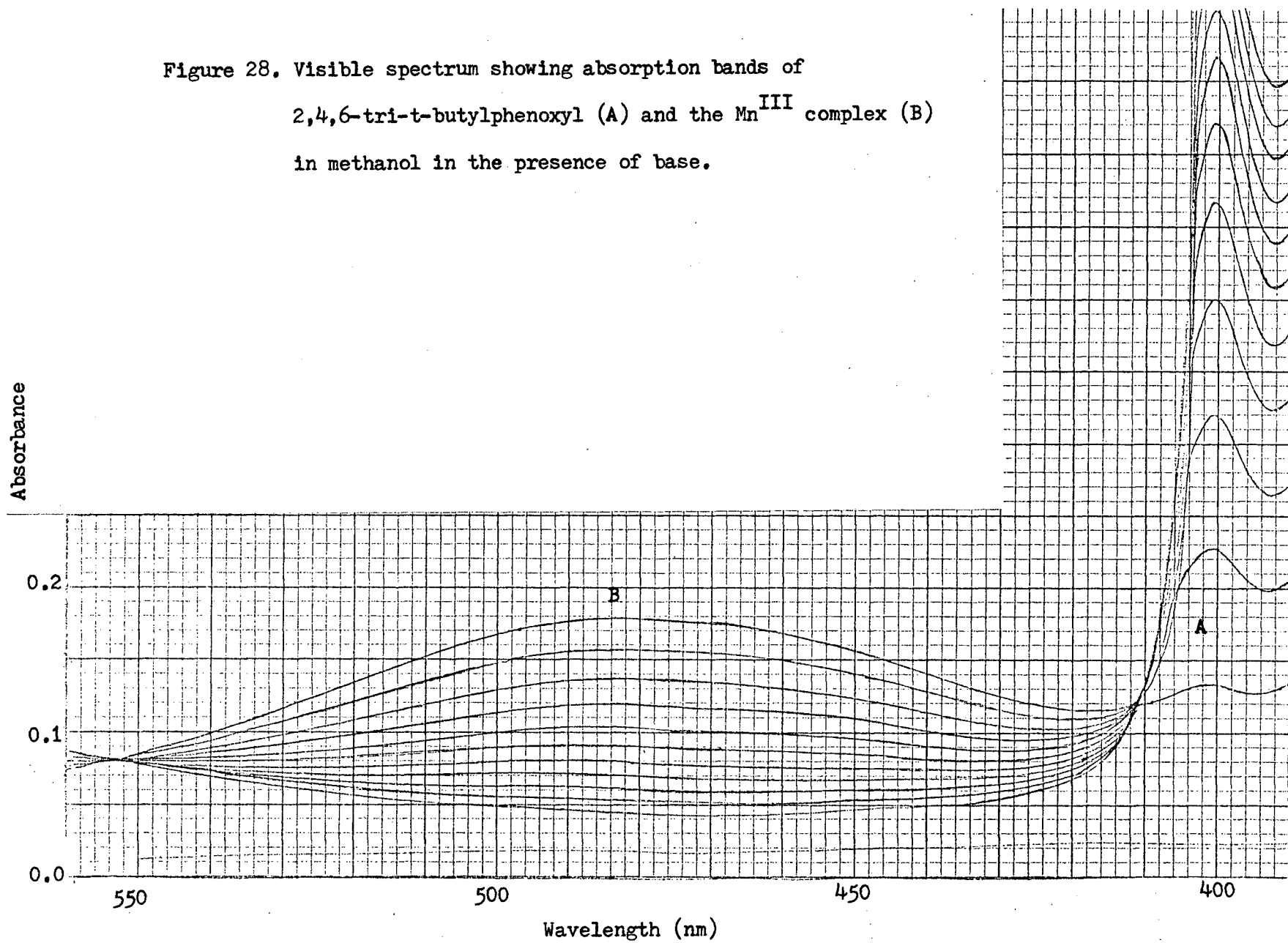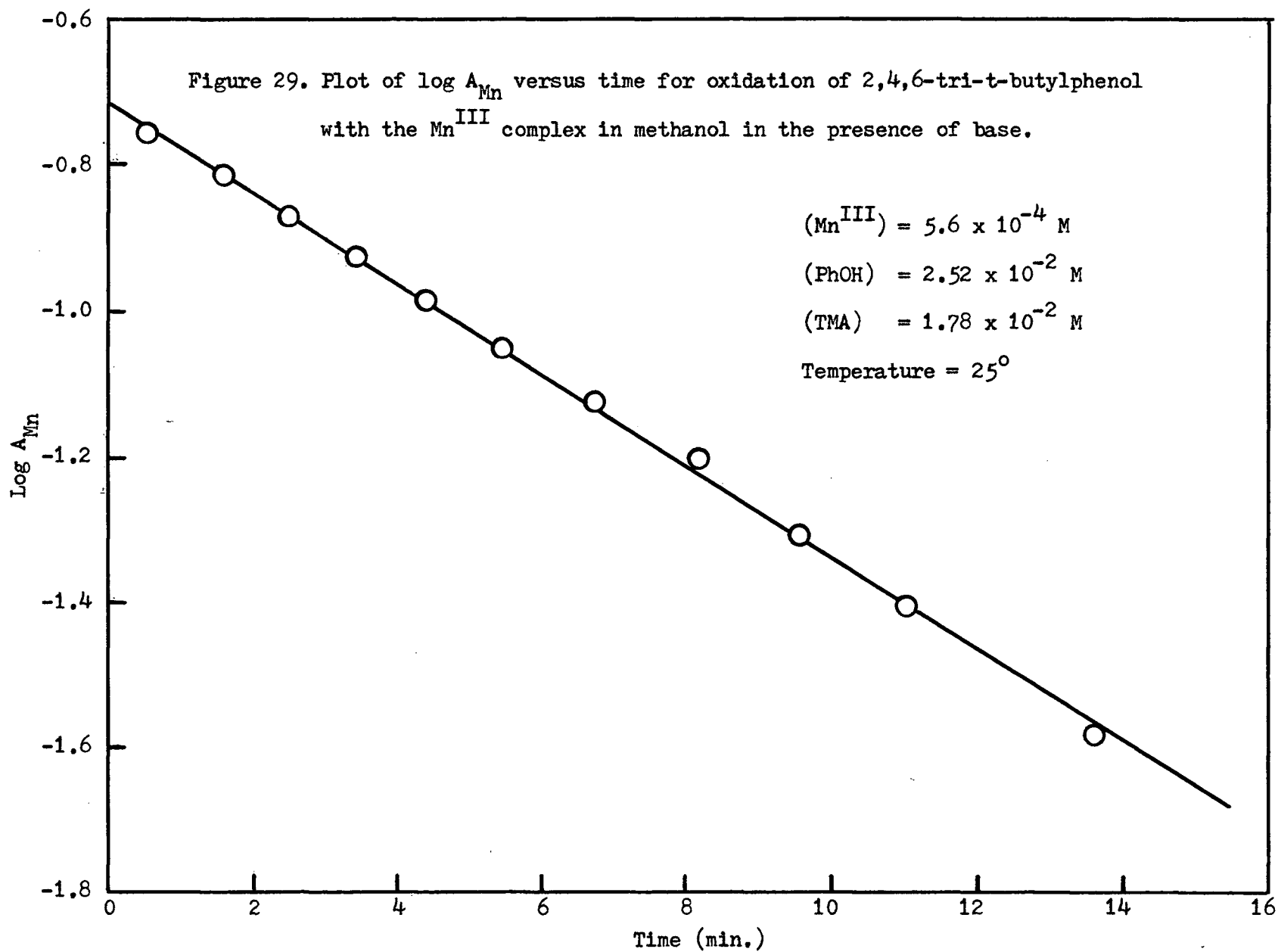
The value of $k_e$ was found to increase slightly with an increase in the concentration of tetramethylammonium hydroxide while the concentrations of the $Mn^{III}$ complex and 2,4,6-tri-t-butylphenol were kept constant (see Table XXIV).

TABLE XXIV

Variation of $k_e$ with base concentration at $25^\circ$

$(Mn^{III}) = 5.6 \times 10^{-4}$ M        $(PhOH)^* = 2.52 \times 10^{-2}$ M

| $(TMA)^{**}(M)$ | $k_e (sec^{-1})$ |
|---|---|
| $0.54 \times 10^{-2}$ | $1.95 \times 10^{-3}$ |
| $0.90 \times 10^{-2}$ | $2.15 \times 10^{-3}$ |
| $1.78 \times 10^{-2}$ | $2.34 \times 10^{-3}$ |
| $2.65 \times 10^{-2}$ | $2.60 \times 10^{-3}$ |
| $4.46 \times 10^{-2}$ | $2.75 \times 10^{-3}$ |

* PhOH = 2,4,6-tri-t-butylphenol

** TMA = tetramethylammonium hydroxide

When the concentrations of the $Mn^{III}$ complex and tetramethylammonium hydroxide were kept constant, $k_e$ was found to increase linearly with the concentration of 2,4,6-tri-t-butylphenol (Table XXV and Figure 31).

Figure 30. Observed rate constant, $k_e$, versus base concentration.

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(PhOH) = 2.5 \times 10^{-2}$ M

Temperature = $25^o$

The y-axis is labeled $k_e \times 10^3$ sec$^{-1}$.

The x-axis is labeled Concentration of tetramethylammonium hydroxide $\times 10^2$ M.

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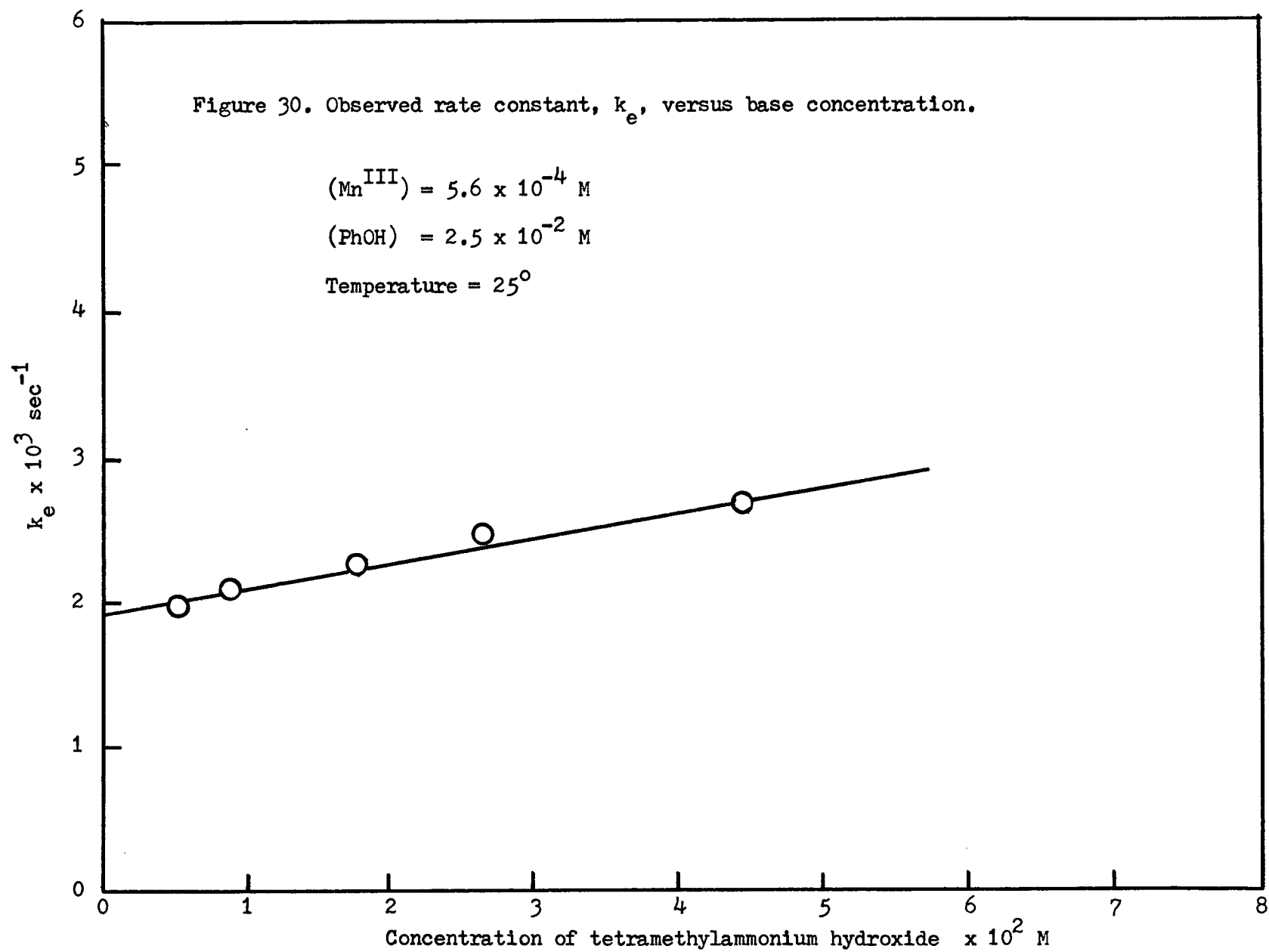
TABLE XXV

Variation of $k_e$ with concentration of 2,4,6-tri-t-butylphenol at 25°

$(Mn^{III}) = 5.6 \times 10^{-4}$ M          $(TMA)^* = 1.78 \times 10^{-2}$ M

| $(PhOH)^{**}$ (M) | $k_e$ (sec$^{-1}$) |
|---|---|
| $0.43 \times 10^{-2}$ | $0.68 \times 10^{-3}$ |
| $0.87 \times 10^{-2}$ | $0.94 \times 10^{-3}$ |
| $1.26 \times 10^{-2}$ | $1.16 \times 10^{-3}$ |
| $1.94 \times 10^{-2}$ | $1.96 \times 10^{-3}$ |
| $2.52 \times 10^{-2}$ | $2.34 \times 10^{-3}$ |
| $2.92 \times 10^{-2}$ | $2.65 \times 10^{-3}$ |

 * TMA = tetramethylammonium hydroxide

** PhOH = 2,4,6-tri-t-butylphenol

When the concentrations of 2,4,6-tri-t-butylphenol and base were kept constant, and the concentration of the $Mn^{III}$ complex was varied, $k_e$ was found to remain almost constant (see Table XXVI), indicating that the rate of disappearance of the $Mn^{III}$ complex is indeed first order with respect to its own concentration.

Figure 31. Observed rate constant, $k_e$, versus concentration of 2,4,6-tri-t-butylphenol.

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(TMA) = 1.78 \times 10^{-2}$ M

Temperature $= 25^{\circ}$

$k_e \times 10^3$ $sec^{-1}$

Concentration of 2,4,6-tri-t-butylphenol $\times 10^2$ M

127
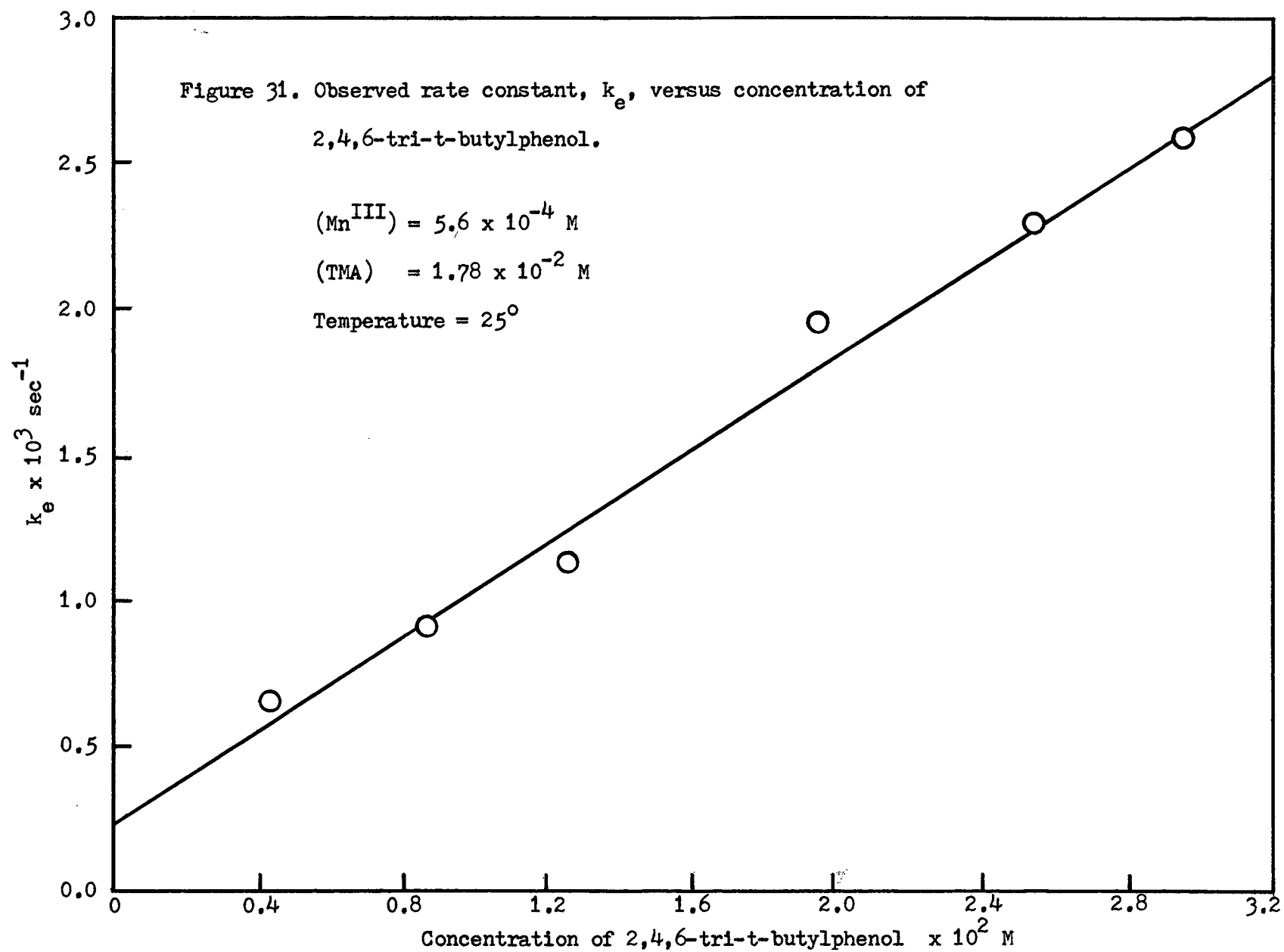
## TABLE XXVI

**Variation of $k_e$ with concentration of the $Mn^{III}$ complex at $25^o$**

$(TMA)^* = 1.78 \times 10^{-2}$ M

$(PhOH)^{**} = 2.52 \times 10^{-2}$ M

| $(Mn^{III})(M)$ | $k_e(sec^{-1})$ |
|---|---|
| $4.5 \times 10^{-4}$ | $2.30 \times 10^{-3}$ |
| $5.6 \times 10^{-4}$ | $2.34 \times 10^{-3}$ |
| $7.5 \times 10^{-4}$ | $2.20 \times 10^{-3}$ |
| $11.0 \times 10^{-4}$ | $2.48 \times 10^{-3}$ |

\* TMA = tetramethylammonium hydroxide

\*\* PhOH = 2,4,6-tri-t-butylphenol

### (iii) Mechanism

The following reactions are considered.

$$Mn^{III}_p + OH^- \underset{}{\overset{K_2}{\rightleftharpoons}} Mn^{III}_y + H_2O \qquad (60)$$

$$PhOH + OH^- \underset{}{\overset{K}{\rightleftharpoons}} PhO^- + H_2O \qquad (14)$$

$$2\ Mn^{III}_y + 4\ OH^- \xrightarrow{k_7} Mn^{II} + MnO_2 + 4\ H_2O \qquad (24)$$

$$\text{Mn}_y^{III--} + \text{PhO}^- \xrightarrow{k_8} \text{Mn}^{II} + \text{PhO}\cdot \qquad (61)$$

$$\text{Mn}_y^{III--} + \text{PhOH} \xrightarrow{k_9} \text{Mn}^{II} + \text{PhO}\cdot + \text{H}^+ \qquad (62)$$

$$\text{Mn}_p^{III-} + \text{PhOH} \xrightarrow{k_{3a}} \text{Mn}^{II} + \text{PhO}\cdot + \text{H}^+ \qquad (63)$$

$$\text{Mn}_p^{III-} + \text{PhO}^- \xrightarrow{k_{10}} \text{Mn}^{II} + \text{PhO}\cdot \qquad (64)$$

<u>Abbreviations used:</u>

$\text{Mn}_y^{III--} = \text{Mn}^{III}\text{CyDTA(OH)}^{2-}$

$\text{Mn}_p^{III-} = \text{Mn}^{III}\text{CyDTA(H}_2\text{O)}^-$

PhOH = 2,4,6-tri-t-butylphenol

PhO$^-$ = 2,4,6-tri-t-butylphenoxy anion
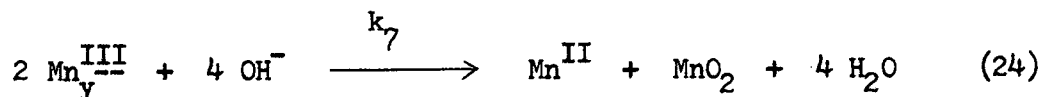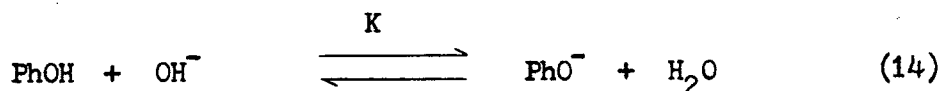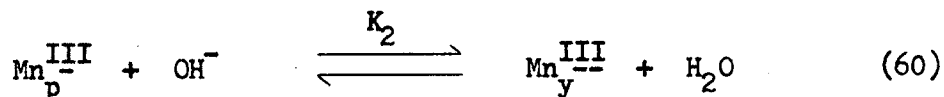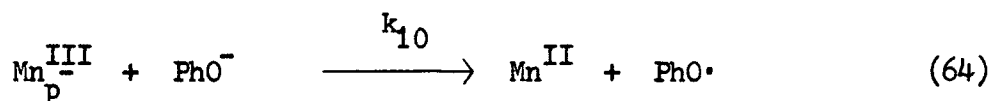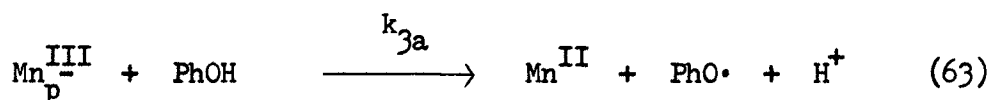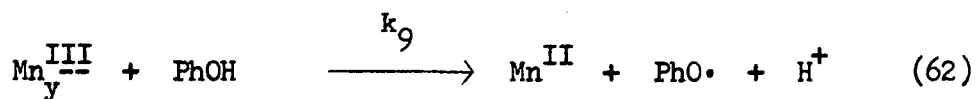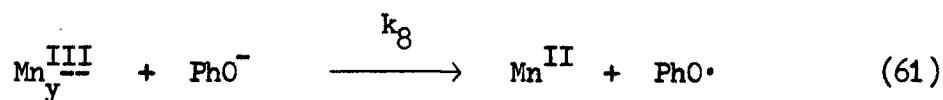
PhO· = 2,4,6-tri-t-butylphenoxyl
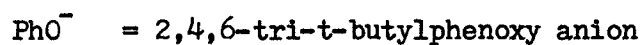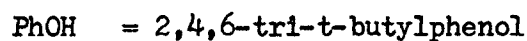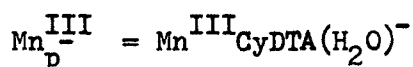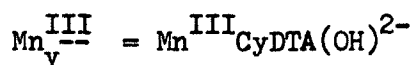
Equation (63) can be ignored because the reaction between 2,4,6-tri-t-butylphenol and $\text{Mn}^{III}\text{CyDTA(H}_2\text{O)}^-$ is very slow (see Section IX). Equation (64) can also be ignored because in the presence of excess base the concentration of $\text{Mn}^{III}\text{CyDTA(H}_2\text{O)}^-$ is negligible. Therefore, the rate of disappearance of the $\text{Mn}^{III}$ complex is given by equation (65).

$$- d(Mn^{III})_{tot}/dt = 2k_7(OH^-)(Mn_y^{III--}) + k_8(PhO^-)(Mn_y^{III--}) + k_9(PhOH)(Mn_y^{III--})$$

$$(65)$$

In excess base, the total $Mn^{III}$ complex concentration, $(Mn^{III})_{tot}$, is equal to $(Mn_y^{III--})$, and using the relationship in equation (15), equation (65) can be written in the form of equation (66).

$$- d(Mn_y^{III--})/dt = ( 2k_7(OH^-) + k_8K(PhOH)(OH^-) + k_9(PhOH) )(Mn_y^{III--})$$

$$(66)$$

Equation (66) is identical to equation (58) with

$$k_e = 2k_7(OH^-) + k_8K(PhOH)(OH^-) + k_9(PhOH) \qquad (67)$$

Integrating equation (66) gives equation (68).

$$\log A_{Mn} - \log A_o = - k_e t/2.303 \qquad (68)$$

The rate of formation of 2,4,6-tri-t-butylphenoxyl was followed at 400 nm. It is given by equation (69).

$$d(PhO\cdot)/dt = ( k_8K(PhOH)(OH^-) + k_9(PhOH) )(Mn_y^{III--}) \qquad (69)$$

Let $\qquad k_r = k_8 K(PhOH)(OH^-) + k_9(PhOH)$ $\qquad$ (70)

and from equation (68) $(Mn_y^{III--})$ can be expressed as follows:

$$(Mn_y^{III--}) = (Mn_y^{III--})_o \exp(-k_e t) \qquad (71)$$

where $(Mn_y^{III--})_o$ is the initial concentration of the $Mn^{III}$ complex.

Substituting equations (70) and (71) into equation (69), equation (72) is obtained.

$$d(PhO\cdot)/dt = k_r(Mn_y^{III--})_o \exp(-k_e t) \qquad (72)$$

Integrating equation (72) gives equation (73).

$$A_{pho.} = \mathcal{E}_p k_r (Mn_y^{III--})_o (1 - \exp(-k_e t))/k_e \qquad (73)$$

where $\mathcal{E}_p$ = extinction coefficient of 2,4,6-tri-t-butylphenoxyl at 400 nm,

$A_{pho.}$ = absorbance of 2,4,6-tri-t-butylphenoxyl at 400 nm at time t.

(iv) <u>Determination of rate constants</u>

A value of $k_e$ was obtained for each concentration of base from the slope of a plot of equation (68) (see Figure 29). A plot of $k_e$ versus

base concentration gives a slope of $2k_7 + k_8K(PhOH)$ and an intercept of $k_9(PhOH)$ (see equation (67)). Figure 30 is such a plot. The values of $K$ and $k_7$ have been determined in Sections IV and V respectively, $(PhOH)$ is a known quantity, thus, $k_8$ and $k_9$ can be evaluated. The values of $k_8$ and $k_9$ were found to be 2.0 $M^{-1}sec^{-1}$ and $7.5 \times 10^{-2}$ $M^{-1}sec^{-1}$ respectively.

The rate constant $k_e$ was also plotted against concentration of 2,4,6-tri-t-butylphenol (see equation (67) and Figure 31) to check the values of $k_8$ and $k_9$ obtained above. From this plot, $k_9 + k_8K(OH^-)$ and $2k_7(OH^-)$ were found to be 8.3 $\times 10^{-2}$ $M^{-1}sec^{-1}$ and 2.5 $\times 10^{-4}$ $sec^{-1}$ respectively. Using the values of $k_8$ and $k_9$ obtained above, $k_9 + k_8K(OH^-)$ and $2k_7(OH^-)$ were calculated and found to be 8.4 $\times 10^{-2}$ $M^{-1}sec^{-1}$ and 1.7 $\times 10^{-4}$ $sec^{-1}$ respectively. These values agree quite well with those calculated above.

For each run, the value of $k_e$ obtained from a plot of equation (70) was used to calculate the term $1-\exp(-k_e t)$ in equation (73). Then, $A_{pho.}$ was plotted against $1-\exp(-k_e t)$, and such a plot was found to be linear up to about 60 % of reaction. Figure 32 is a typical plot of equation (73). From each such plot a value of $k_r$ was calculated. Then a plot of $k_r$ versus base concentration (see equation (70) and Figure 33) was done to compare the values of $k_8$ and $k_9$ obtained from this plot with the values obtained previously. The values of $k_8$ and $k_9$ obtained from this plot were found to be 2.7 $M^{-1}sec^{-1}$ and 6 $\times 10^{-2}$ $M^{-1}sec^{-1}$, respectively. Although

Figure 32. Absorbance versus $(1 - \exp(-k_e t))$ for 2,4,6-tri-t-butylphenoxyl.

$(Mn^{III}) = 5.6 \times 10^{-4}$ M

$(PhOH) = 2.50 \times 10^{-2}$ M

$(TMA) = 2.65 \times 10^{-2}$ M

Temperature = $25^{\circ}$

Figure 33. Rate constant, $k_r$, versus concentration of base.

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Figure 34. Rate constant, $k_r$, versus concentration of 2,4,6-tri-t-butylphenol.

134
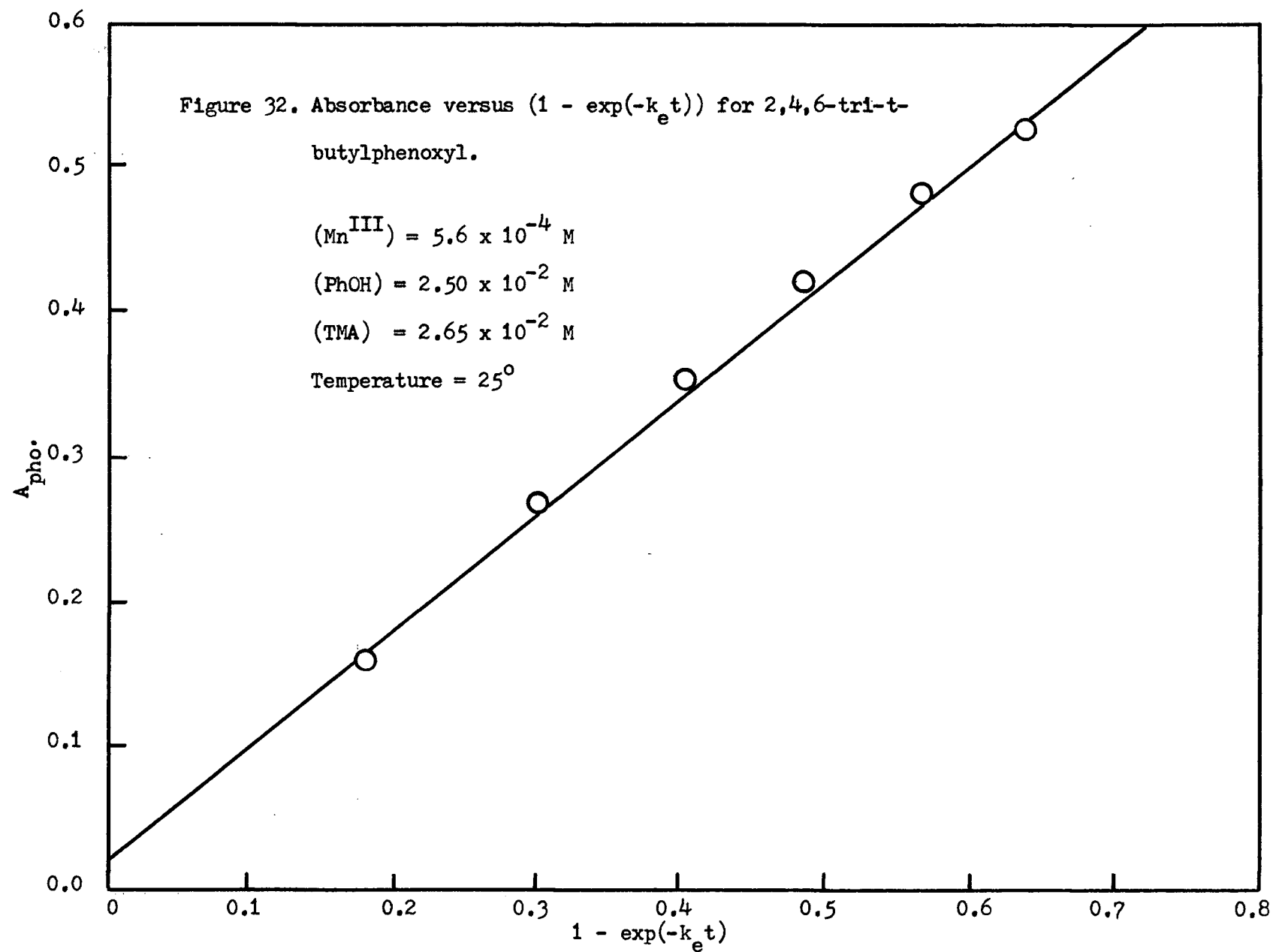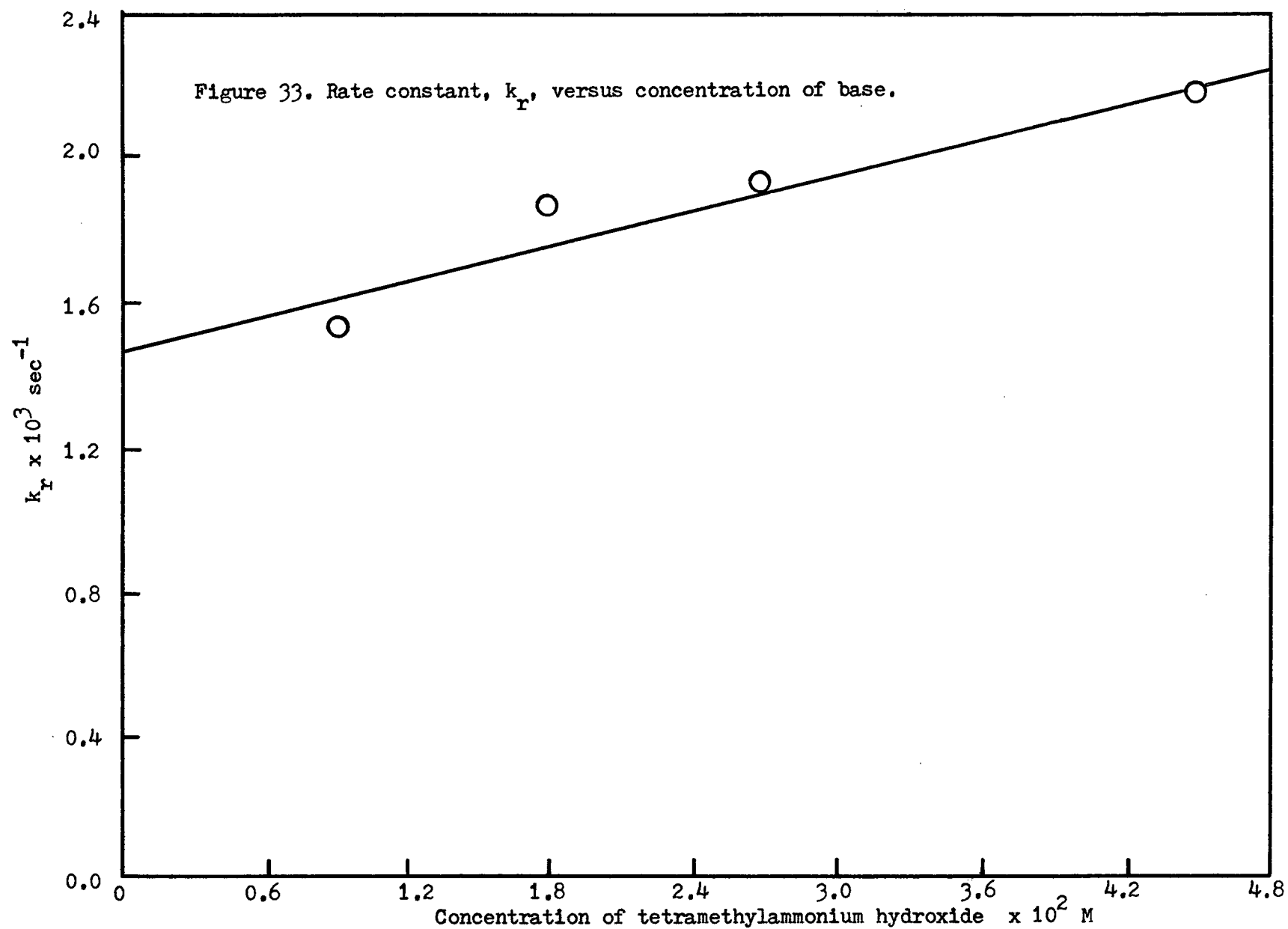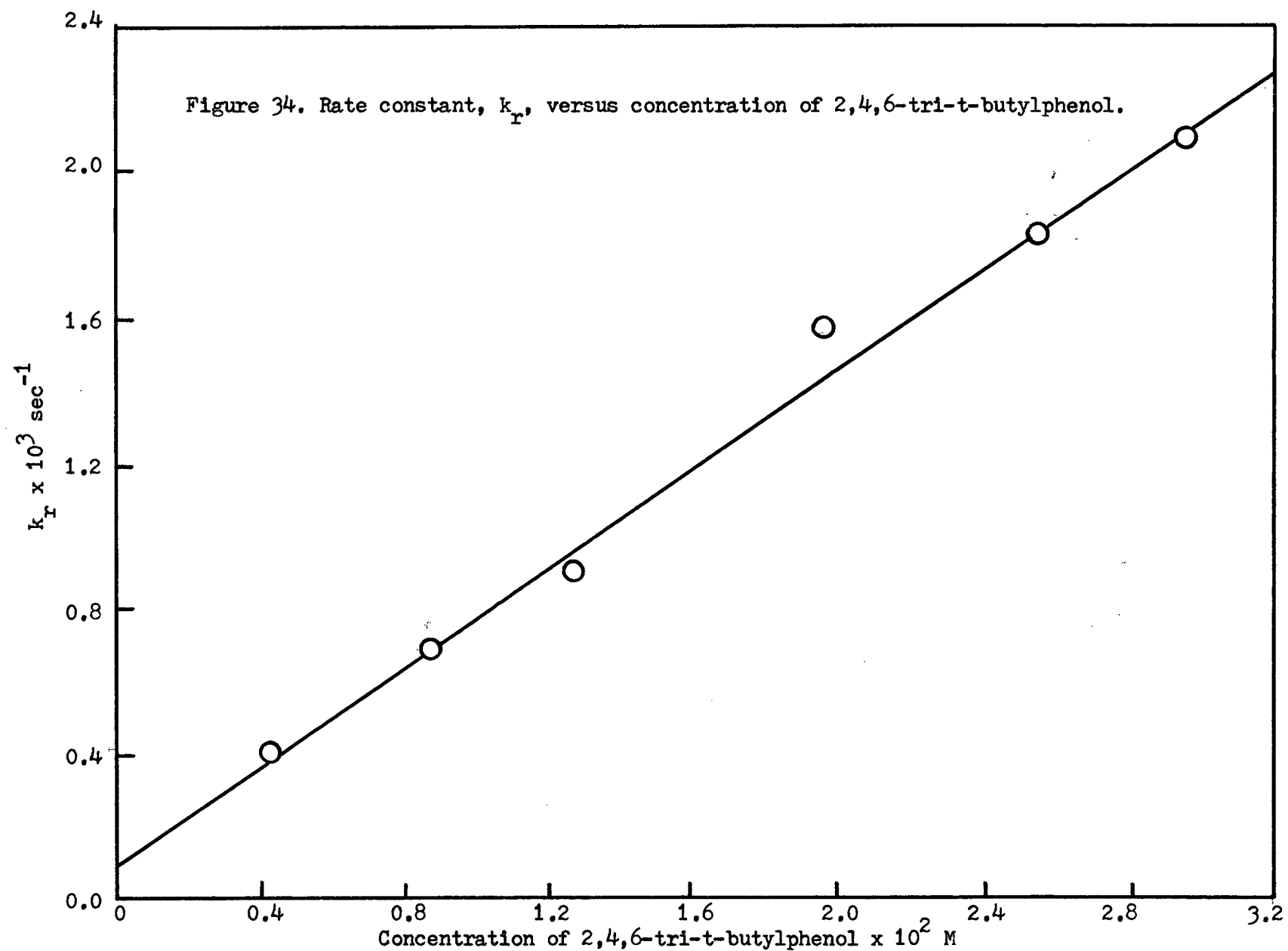
these values do not agree well with those obtained earlier they are of the correct order of magnitude.

A plot of $k_e$ versus concentration of 2,4,6-tri-t-butylphenol was also made (see Figure 34). The slope of this plot gives a value of $k_8 + k_9K(OH^-)$ = 7.2 x $10^{-2}$ $M^{-1}sec^{-1}$, which is slightly lower than the value of 8.4 x $10^{-2}$ $M^{-1}sec^{-1}$ obtained previously.

## (v) Kinetic isotope effect

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex was carried out in methanol-O-d in the presence of different concentrations of sodium deuteroxide at $25^{\circ}$. The values of the different rate constants were obtained using equations (67) and (68). (The value of $k_7$ was obtained from the decomposition of the $Mn^{III}$ complex in methanol-O-d in different concentrations of sodium deuteroxide at $25^{\circ}$). Oxidation of the same phenol with the same oxidant in methanol in the presence of different concentrations of sodium hydroxide was also carried out at $25^{\circ}$ and the values of the rate constants were obtained for comparison. The results are summarised in Table XXVII.

TABLE XXVII

Rates for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex

in methanol and methanol-O-d in the presence of base at $25^{\circ}$

| Solvent | Base | $k_8(M^{-1}sec^{-1})$ | $k_9(M^{-1}sec^{-1})$ | $k_{8H}/k_{8D}$ | $k_{9H}/k_{9D}$ |
|---------|------|----------------------|----------------------|-----------------|-----------------|
| $CH_3OH$ | NaOH | 10.0 | $9.7 \times 10^{-2}$ | 1.3 | 1.9 |
| $CH_3OD$ | NaOD | 7.5 | $5.0 \times 10^{-2}$ | | |

(vi) Effect of cations on rate constants

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex was done in different hydroxides to determine the effect of cations on the rate constants. For each hydroxide, oxidation was carried out at three different concentrations of base and the values of $k_8$ and $k_9$ were obtained using the procedure described above (Section VIII-v). The results are summarised in Table XXVIII.

TABLE XXVIII

Rates for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex

in the presence of different hydroxides in methanol at $25^{\circ}$

| Base | $k_8(M^{-1}sec^{-1})$ | $k_9(M^{-1}sec^{-1})$ | $k_8/k_9$ |
|---|---|---|---|
| KOH | 10.9 | $14.8 \times 10^{-2}$ | 74 |
| NaOH | 10.0 | $9.7 \times 10^{-2}$ | 103 |
| LiOH | 9.7 | $6.4 \times 10^{-2}$ | 151 |
| $(C_3H_7)_4NOH$ | 11.0 | $6.7 \times 10^{-2}$ | 164 |
| $(n-C_4H_9)_4NOH$ | 7.6 | $7.0 \times 10^{-2}$ | 109 |
| $(CH_3)_4NOH$ | 2.0 | $7.5 \times 10^{-2}$ | 27 |

average $k_8/k_9$ = 104

Base concentration at $10^{-2}$ M; $Mn^{III}$ complex concentration at $10^{-4}$ M;

2,4,6-tri-t-butylphenol concentration at $10^{-2}$ M (about $10^{-4}$ M for ionised

form).

(vii) <u>Effect of substituent on rate constant $k_9$</u>

Oxidation of a number of 4-substituted-2,6-di-t-butylphenols with the $Mn^{III}$ complex was carried out at $25^\circ$ to determine the substituent effect on the rate of oxidation. The concentration of tetramethylammonium hydroxide was kept equal to that of the $Mn^{III}$ complex so that the concentrations of the 4-substituted-2,6-di-t-butylphenoxy anions were negligible and equation (62) represents the only important reaction. (Those 4-substituted-2,6-di-t-butylphenols with $pK_a$ values close to that of $Mn^{III}CyDTA(H_2O)^-$ were not studied. They were found to react too rapidly).

The rate of disappearance of the $Mn^{III}$ complex can be expressed by equation (74).

$$- d(Mn^{III})_{tot}/dt \;=\; k_9(PhOH)(Mn^{III})_{tot} \qquad (74)$$

In the presence of a limited amount of base, $(Mn_y^{III=-})$ is not equal to $(Mn^{III})_{tot}$. But $(Mn_y^{III=-})$ can be expressed in terms of $(Mn^{III})_{tot}$ using equations (60) and (75). Thus, equation (74) can be written as equation (76).

$$(Mn^{III})_{tot} \;=\; (Mn_p^{III-}) \;+\; (Mn_y^{III=-}) \qquad (75)$$

$$- d(Mn^{III})_{tot}/dt \;=\; K_2(OH^-)k_9(PhOH)(Mn^{III})_{tot}/(1 + K_2(OH^-)) \qquad (76)$$

The term $K_2(OH^-)/(1 + K_2(OH^-))$ is a constant for a given concentration of base. Since $(PhOH) \gg (Mn^{III})_{tot}$, equation (76) can be expressed as equation (77).

$$- d(Mn^{III})_{tot}/dt = k_{9a}(Mn^{III})_{tot} \qquad (77)$$

$$k_{9a} = K_2(OH^-)k_9(PhOH)/(1 + K_2(OH^-)) \qquad (78)$$

Integrating equation (77) yields equation (79).

$$\log A_{Mn} - \log A_o = - k_{9a}t/2.303 \qquad (79)$$

where $A_{Mn}$ = total absorbance of the $Mn^{III}$ complex at 500 nm at time t,

$A_o$ = total absorbance of the $Mn^{III}$ complex at 500 nm at time zero.

The value of $k_{9a}$ for each 4-substituted-2,6-di-t-butylphenol was obtained from a plot of equation (79). The value of $K_2(OH^-)k_9/(1 + K_2(OH^-))$ was obtained by dividing the value of $k_{9a}$ by the concentration of the phenol. In order to obtain the value of $k_9$, the value of the term, $K_2(OH^-)k_9/(1 + K_2(OH^-))$, for 2,4,6-tri-t-butylphenol was determined under identical conditions. Since the value of $k_9$ for this compound has already been determined, the factor $K_2(OH^-)/(1 + K_2(OH^-))$ could be calculated and thus, the values of $k_9$ for the other compounds could be evaluated.

The results are shown in Table XXIX. The products obtained were identical to those obtained under acidic conditions (see Section VII-viii). A Hammett plot of log $k_9/k_{9H}$ versus $\sigma_p^-$ gives a $\rho$ value (slope of the plot) of 2.3 (see Figure 35).

TABLE XXIX

Rates of oxidation of some 4-substituted-2,6-di-t-butylphenols with the $Mn^{III}$ complex in methanol in the presence of a limited amount of base at 25°

| Substituent | $k_9(M^{-1}sec^{-1})$ | $\sigma_p^-$ | log $k_9/k_{9H}$[*] |
|---|---|---|---|
| t-Bu | $7.5 \times 10^{-2}$ | -0.197 | -0.545 |
| $CH_3$ | $23.9 \times 10^{-2}$ | -0.170 | -0.042 |
| H | $26.3 \times 10^{-2}$ | 0 | 0 |
| Br | $75.3 \times 10^{-2}$ | +0.232 | +0.457 |
| Cl | $80.8 \times 10^{-2}$ | +0.226 | +0.487 |

[*] $k_{9H}$ is the rate constant for 2,6-di-t-butylphenol.

(viii) Activation parameters

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex was studied at other temperatures so that the values of the activation

Figure 35. Plot of log $k_9/k_{9H}$ versus $\sigma_p^-$.
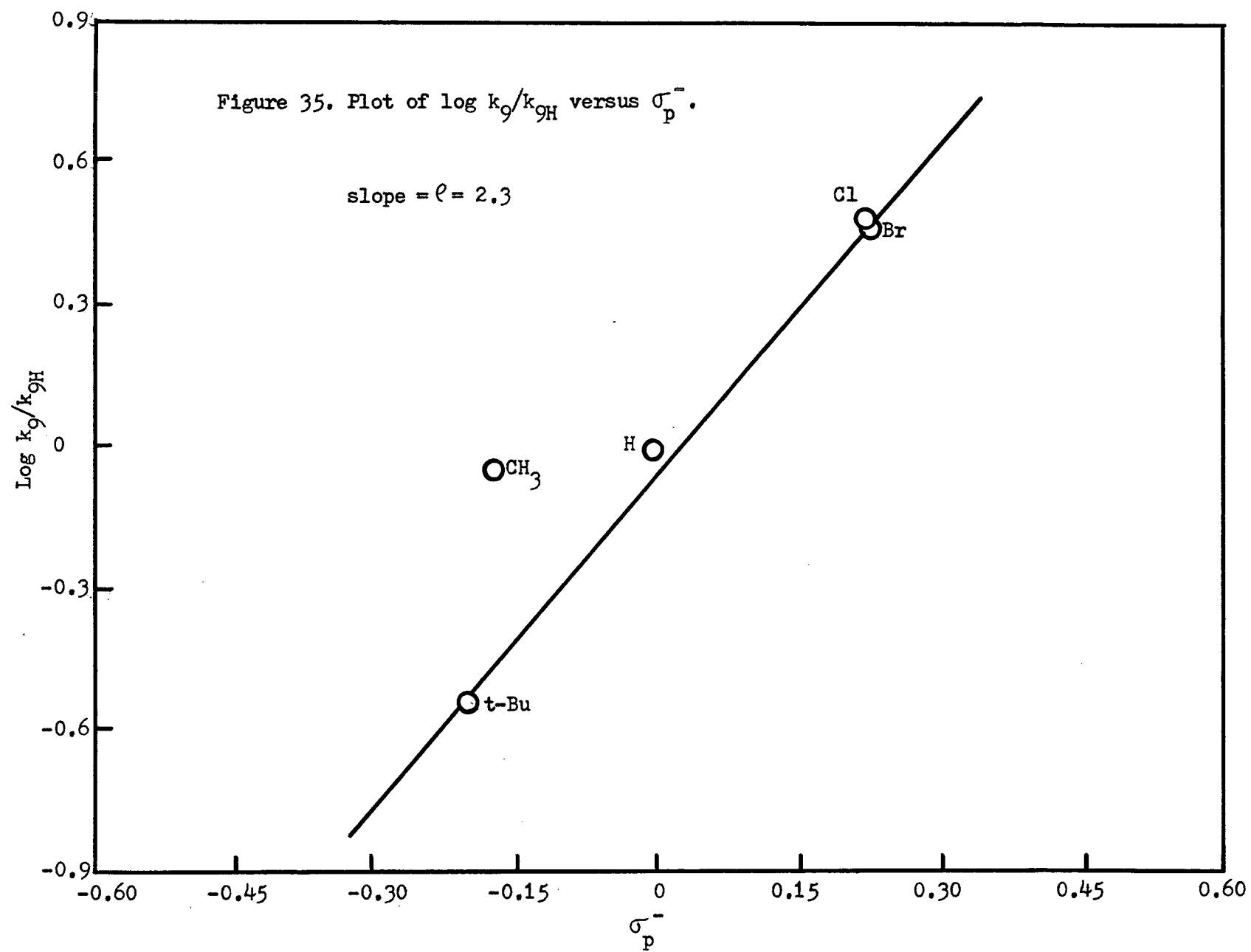
enthalpy and entropy could be determined. The data used in the plots in Figures 36 and 37 were taken from Table XXX. The values of $\Delta H^*$ and $\Delta S^*$ for $k_8$ and $k_9$ were found to be 10.2 Kcal.mole$^{-1}$ and -23 e.u.; 10.2 Kcal. mole$^{-1}$ and -29 e.u. respectively.

## TABLE XXX

### Variation of $k_8$ and $k_9$ with temperature

| Temperature($^\circ$C) | $k_8(M^{-1}sec^{-1})$ | $k_9(M^{-1}sec^{-1})$ |
|---|---|---|
| 25 | 2.0 | 7.5 x 10$^{-2}$ |
| 30 | 2.9 | 11.4 x 10$^{-2}$ |
| 35 | 3.6 | 13.6 x 10$^{-2}$ |
| 40 | 4.9 | 18.6 x 10$^{-2}$ |

(ix) Oxidation of 2,4,6-tri-t-butylphenol with the Mn$^{III}$ complex in methanol in the presence of t-butylamine

The kinetic results of the oxidation of 2,4,6-tri-t-butylphenol with the Mn$^{III}$ complex in methanol in the presence of strong bases and the interesting observations seen in 2,6-di-t-butyl-4-dimethylaminomethylphenol (see Section VII-ix), all indicate that Mn$^{III}$CyDTA(OH)$^{2-}$ is a strong oxidant for unionised phenols. To further support this finding, oxidation of 2,4,6-tri-t-butylphenol with the Mn$^{III}$ complex in methanol in the presence of t-butylamine was carried out. Since t-butylamine is a weaker

Figure 36. Plot of log $k_8/T$ versus $1/T$ for oxidation of 2,4,6-tri-t-butylphenoxy anion with the $Mn^{III}$ complex under basic condition.

$\Delta H^* = 10.2$ Kcal.mole$^{-1}$

$\Delta S^* = -23$ e.u.

Correlation coefficient = -0.9958

Figure 37. Plot of log $k_9/T$ versus $1/T$ for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex under basic condition.

$\triangle H^* = 10.2$ Kcal.mole$^{-1}$

$\triangle S^* = -29$ e.u.

Correlation coefficient $= -0.9890$

144
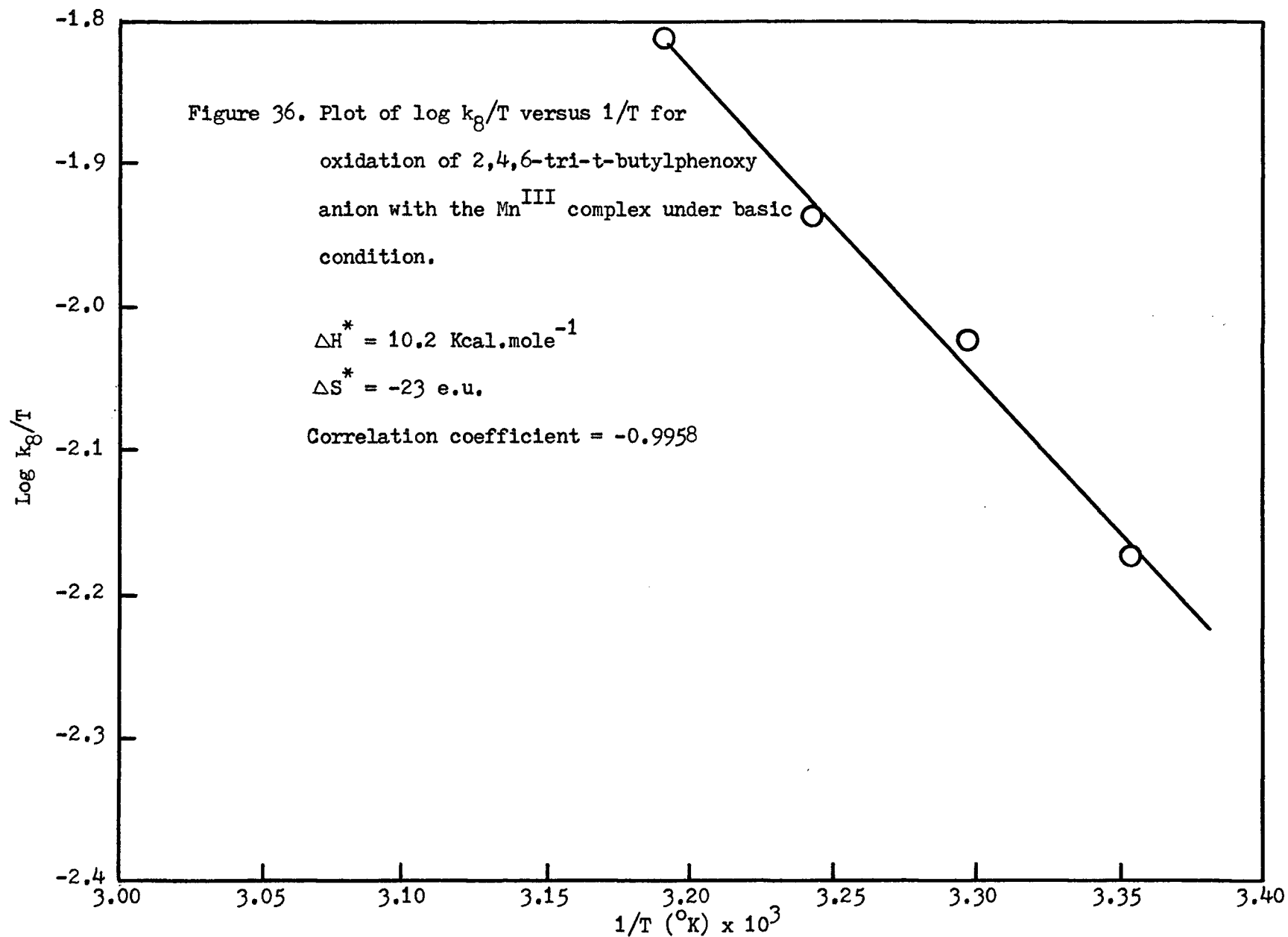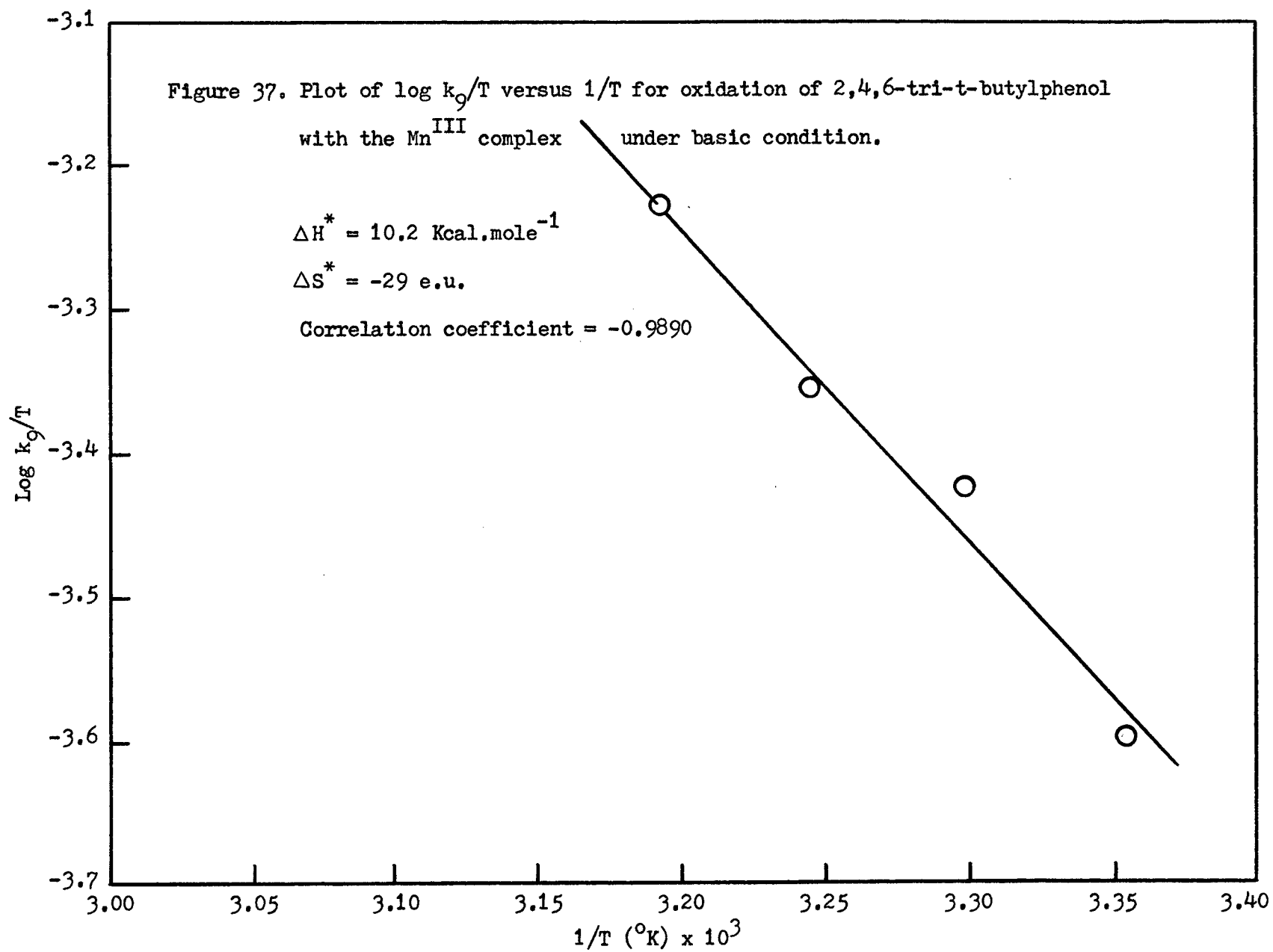
base than the hydroxides the ratio of the concentrations of

$Mn^{III}CyDTA(OH)^{2-}$ and $Mn^{III}CyDTA(H_2O)^-$ can be varied by the addition of

different concentrations of t-butylamine while maintaining the

concentration of 2,4,6-tri-t-butylphenol in its unionised form. A rate

expression (equation (80)) for the disappearance of the $Mn^{III}$ complex

can be derived in a procedure similar to that shown in Section VIII-vii.

$$- d(Mn^{III})_{tot}/dt = k_{9b}(PhOH)(Mn^{III})_{tot} \qquad (80)$$

where $\quad k_{9b} = K_3(\text{t-BuNH}_2)k_9/((\text{t-BuNH}_3) + K_3(\text{t-BuNH}_2)) \qquad (81)$

and $\quad K_3 = (Mn_y^{III})(\text{t-BuNH}_3)/(Mn_p^{III})(\text{t-BuNH}_2) \qquad (82)$

A plot of the values of $k_{9b}$ against the concentration of t-butylamine

is expected to be a curve which flattens off when the concentration of

t-butylamine reaches the point that $Mn^{III}CyDTA(H_2O)^-$ is completely

converted to $Mn^{III}CyDTA(OH)^{2-}$. (Compare with Figure 13 of Section VI).

Such a curved plot is indeed obtained (see Figure 38). The plot in

Figure 38 does not flatten but rises gradually because the reaction shown

in equation (61) becomes important at high concentrations of t-butylamine.

(The values used in the plot in Figure 38 were taken from Table XXXI).

The value of $k_9$ was obtained by extrapolating the linear portion of the

plot to zero concentration of t-butylamine. A value of $7.2 \times 10^{-2} \ M^{-1}sec^{-1}$

Figure 38. Plot of observed rate constant, $k_{9b}$, versus concentration of t-butylamine.

$(Mn^{III}) = 6.0 \times 10^{-4}$ M

$(PhOH) = 4.0 \times 10^{-2}$ M

Temperature = $25^{\circ}$

x-axis: Concentration of t-butylamine x $10^2$ M

y-axis: $k_{9b}$ x $10^2$ $M^{-1}sec^{-1}$
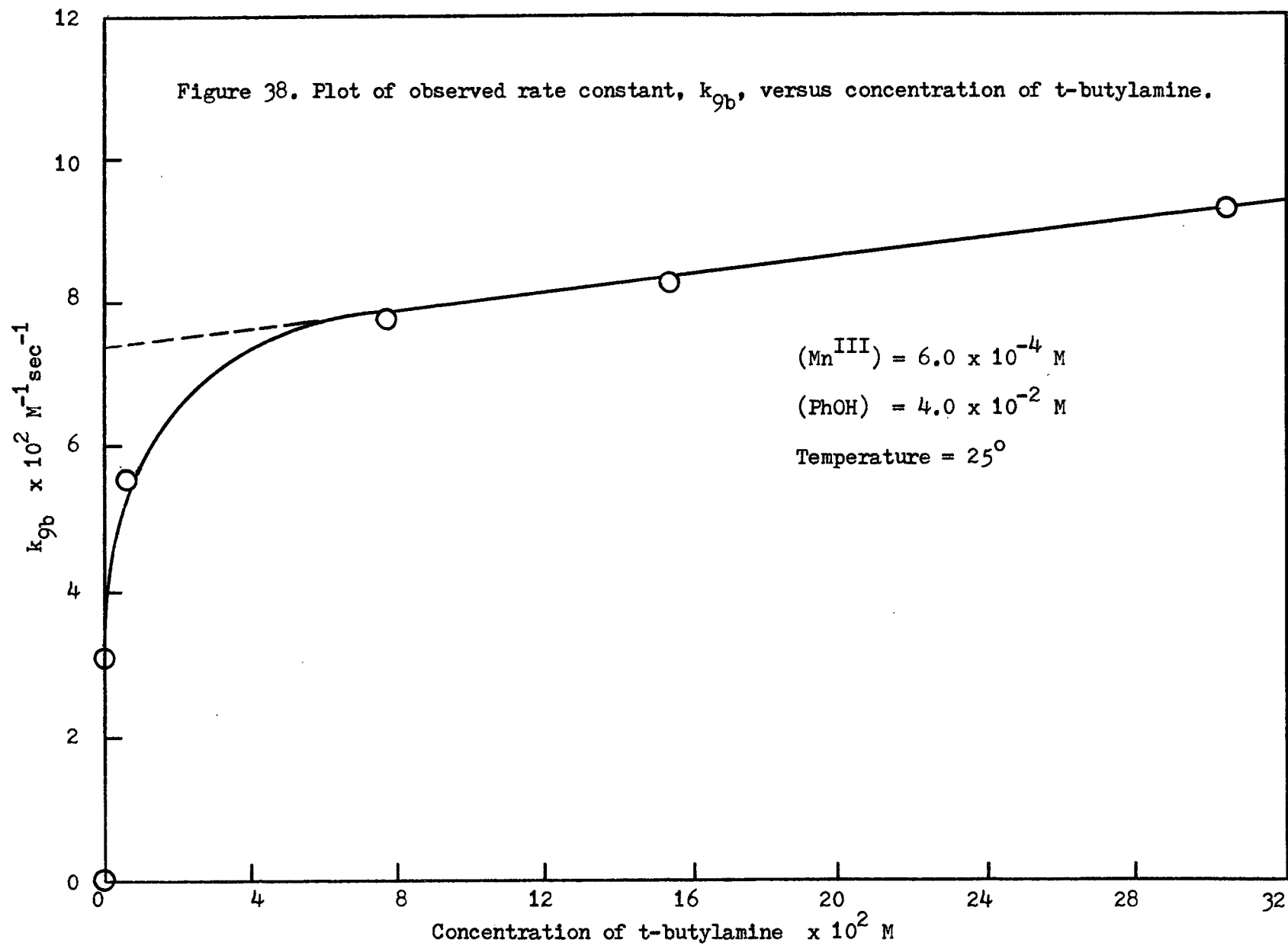
was obtained. This value agrees with those obtained earlier (see Table XXVIII).

TABLE XXXI

Variation of observed rate with concentration of t-butylamine for the oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol at $25^{\circ}$

$(Mn^{III}) = 6.0 \times 10^{-4}$ M $\qquad$ $(PhOH)^{*} = 4.02 \times 10^{-2}$ M

| $(t\text{-BuNH}_2)(M)$ | $k_{9b}(M^{-1}sec^{-1})$ |
|---|---|
| $1.5 \times 10^{-3}$ | $3.04 \times 10^{-2}$ |
| $7.4 \times 10^{-3}$ | $5.55 \times 10^{-2}$ |
| $7.8 \times 10^{-2}$ | $7.74 \times 10^{-2}$ |
| $15.5 \times 10^{-2}$ | $8.26 \times 10^{-2}$ |
| $30.5 \times 10^{-2}$ | $9.31 \times 10^{-2}$ |

* PhOH is used as an abbreviation for 2,4,6-tri-t-butylphenol.

(x) Discussion

The kinetic results of the oxidation of 2,4,6-tri-t-butylphenol agree with a mechanism involving the oxidation of 2,4,6-tri-t-butylphenol and 2,4,6-tri-t-butylphenoxy anion by $Mn^{III}CyDTA(OH)^{2-}$. The former is

probably a hydrogen atom transfer reaction whereas the latter is an electron-transfer reaction. The kinetic isotope effect of $k_{8H}/k_{8D} = 1.3$ is likely due to the replacement of the hydroxide ligand by a deuteroxide ligand. (Taube and co-workers[86,89,93] have found that $Co(NH_3)_5(H_2O)^{3+}$ and $Co(NH_3)_5(OH)^{2+}$ are better oxidants in water than in deuterium oxide whether electron-transfer reactions occur via a 'bridged activated' complex or an 'outer-sphere' mechanism. (An 'outer-sphere' mechanism is one in which the two reactants maintain their own complete coordination shells in the activated complex, and the electron must tunnel through both of these shells. Thus, no bond is broken in this mechanism). The kinetic isotope effects observed by them were near two. No satisfactory reason has been given to account for the slower rates observed when a coordinated water (or hydroxide) ligand is replaced by a deuterium oxide (or deuteroxide) ligand). The kinetic isotope effect of $k_{9H}/k_{9D} = 1.9$ after accounting for the solvent contribution (1.3) is 1.5 which is rather small for a reaction which involves the cleavage of the O-H bond of 2,4,6-tri-t-butylphenol in the rate-determining step. A possible reason for this small kinetic isotope effect is to regard $Mn^{III}CyDTA(OD)^{2-}$ as a stronger oxidant than $Mn^{III}CyDTA(OH)^{2-}$ with respect to hydrogen atom abstraction. Deuteroxide is known to be a stronger base than hydroxide[57-61]. Therefore, if the hydroxy and deuteroxy ligands of the $Mn^{III}$ complex are regarded as analogous to $OH^-$ and $OD^-$ respectively, and their abstractions of hydrogen atom from the O-H group of 2,4,6-tri-t-butylphenol are also

regarded as analogous to proton abstractions by $OH^-$ and $OD^-$, then $Mn^{III}CyDTA(OD)^{2-}$ will be a stronger oxidant than $Mn^{III}CyDTA(OH)^{2-}$. If the above assumptions are correct, then the true kinetic isotope effect of $k_{9H}/k_{9D}$ is greater than the value observed. The above possible reason does not contradict with the fact that $Co(NH_3)_5(H_2O)^{3+}$ and $Co(NH_3)_5(OH)^{2+}$ are better oxidants in water than in deuterium oxide as observed by Taube and co-workers[86,89,93] because the reactions studied by them are electron-transfer reactions and not hydrogen atom transfer reactions. The kinetic isotope effect of $k_{8H}/k_{8D} = 1.3$ is probably true because an electron-transfer reaction is involved.

The ratio of $k_8/k_9$ gives the relative rate of electron-transfer from 2,4,6-tri-t-butylphenoxy anion versus hydrogen atom transfer from 2,4,6-tri-t-butylphenol, to $Mn^{III}CyDTA(OH)^{2-}$. An average value of 104 is obtained (see Table XXVIII).

As can be seen from Table XXVIII, cations seem to affect the values of the two rate constants, $k_8$ and $k_9$. The trend in the metal cations indicates that the larger the cation the larger are the two rates. The values of $k_8$ and $k_9$ for the tetraalkylammonium cations are too random for any generalisation to be drawn. On the whole, the effects are small. Other workers[94-97] have also reported the catalytic effect of cations on electron exchange reactions between two anions. In general, the larger the metal cation the larger is the rate of electron exchange between

two anions, but the change is usually small. The role of cations in an electron exchange reaction between two anions is still not well understood. One proposal[94] is that the electron is actually transferred by the cation which serves as a bridge between the two anions. In this mechanism the polarizability of the cation and its ability to complex with the anions should play a major role in affecting the reaction. The greater polarizability of the larger cations agrees with their generally greater catalytic effect and supports this mechanism.

Electron-withdrawing substituents at the 4-position enhance the rate of oxidation (see Table XXIX). It is difficult to say whether this trend is due entirely to the effect of the 4-substituent on the rate of oxidation or is partially due to the ease of ionization of the O-H group when the 4-substituent is an electron-withdrawing group. The fast rate of reactions of most other 4-substituted compounds prevented a more extensive investigation of 4-substituent effect on reaction rates.

The larger rate of oxidation of 2,4,6-tri-t-butylphenol by $Mn^{III}CyDTA(OH)^{2-}$ compared to its reaction with $Mn^{III}CyDTA(H_2O)^-$ (see Section IX) suggests that an 'inner-sphere'-type mechanism is involved. (The mechanism is not exactly 'inner-sphere' because the hydrogen atom from the phenol is not transferred to the coordination sphere of the oxidant). Taube and co-workers[98,99] have suggested that large values of $k_{OH}/k_{H_2O}$ are to be associated with 'inner-sphere' reactions whereas small values of this ratio are to be associated with 'outer-sphere' reactions. (The two rate constants, $k_{OH}$ and $k_{H_2O}$, refer to the hydroxo- and aquo- complexes

respectively). The ratio of $k_9/k_{3a}$ found in this work is about 360. Some values of relative rate between hydroxo- and aquo- complexes in 'inner-sphere' reactions are shown in Table XXXII.

TABLE XXXII

Values for the relative rate of reduction of $ML_5H_2O^{n+}$ complexes compared to $ML_5OH^{(n-1)+}$ complexes ('inner-sphere' mechanism)

| $ML_5H_2O$ | Reductant | $k_{OH}/k_{H_2O}$ | Reference |
|---|---|---|---|
| $Co(NH_3)_5H_2O^{3+}$ | $Cr^{2+}$ | $3.5 \times 10^6$ | 89 |
| | $Cu^+$ | $3.8 \times 10^5$ | 100 |
| $Fe(H_2O)_6^{3+}$ | $Cr^{2+}$ | $7.7 \times 10^3$ | 101 |
| | $Fe^{2+}$ | $1.3 \times 10^3$ | 102 |
| $Cu(H_2O)_6^{2+}$ | $V^{3+}$ | $9.4 \times 10^3$ | 103 |

# IX. OXIDATION OF 2,4,6-TRI-t-BUTYLPHENOL WITH THE $Mn^{III}$ COMPLEX IN METHANOL*

## (i) Product

2,4,6-Tri-t-butylphenoxyl was produced quantitatively.

## (ii) Analysis of kinetic results

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex was carried out in the presence of an excess amount of 2,4,6-tri-t-butylphenol. Plots of logarithm of absorbance at 500 nm versus time have the features shown in Figure 39. The first 7 % of the reaction gives a curvature in such a plot. From the 7 % to about 60 % of reaction the plot is linear. This linear portion is used in the evaluation of the rate constant. (See Section IX-iii for explanation of curvature in Figure 39). The linear portion of Figure 39 can be expressed by equation (83).

$$- d(Mn^{III})_{tot}/dt = k'_{3a}(Mn^{III})_{tot} \qquad (83)$$

Integrating equation (83) gives equation (84).

$$\log A_{Mn} - \log A_o = - k'_{3a}(Mn^{III})_{tot} \qquad (84)$$

where $A_{Mn}$ = absorbance of the $Mn^{III}$ complex at 500 nm at time t,

$A_o$ = absorbance of the $Mn^{III}$ complex at 500 nm at time zero.

* 2.5 % water (v/v)

Figure 39. Plot of log $A_{Mn}$ versus time for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol.

$(Mn^{III}) = 5.8 \times 10^{-4}$ M

$(PhOH) = 8.6 \times 10^{-2}$ M

Temperature = $25^{\circ}$
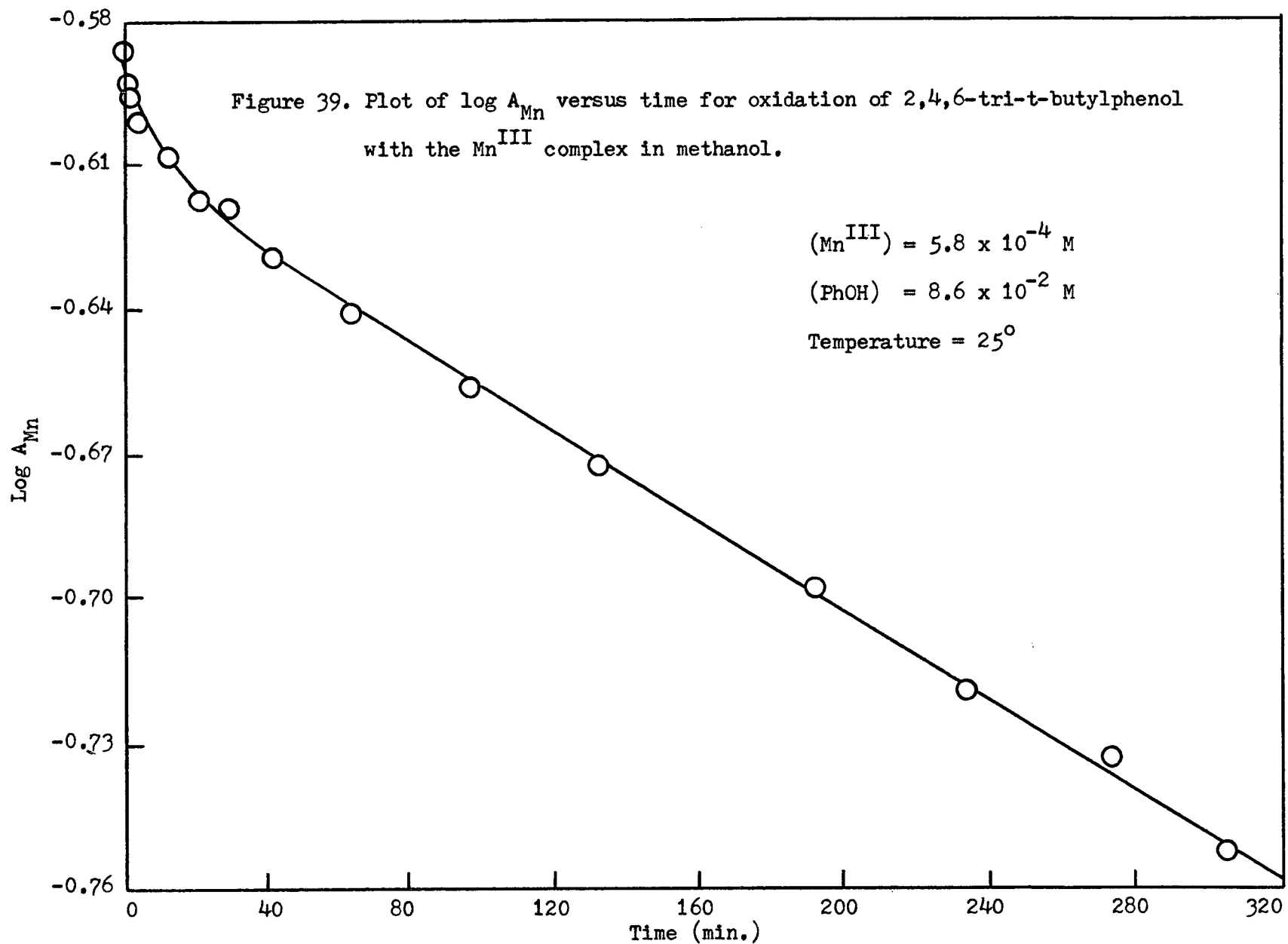
The value of $k'_{3a}$ was found to increase with increase in the concentration of 2,4,6-tri-t-butylphenol (see Table XXXIII and Figure 40).

TABLE XXXIII

Variation of $k'_{3a}$ with concentration of 2,4,6-tri-t-butylphenol at 25°

$$(Mn^{III}) = 5.8 \times 10^{-4} \text{ M}$$

| $(PhOH)^*(M)$ | $k'_{3a}(sec^{-1})$ |
|---|---|
| 0 | $0.2 \times 10^{-5}$ |
| $4.24 \times 10^{-2}$ | $1.1 \times 10^{-5}$ |
| $8.58 \times 10^{-2}$ | $2.1 \times 10^{-5}$ |
| $12.77 \times 10^{-2}$ | $3.3 \times 10^{-5}$ |

* PhOH is used as an abbreviation for 2,4,6-tri-t-butylphenol.

(iii) Mechanism

The following reactions are considered.

$$Mn^{III}_p \xrightarrow{\quad K_a \quad} Mn^{III}_y + H^+ \qquad (85)$$

$$Mn^{III}_y + PhOH \xrightarrow{\quad k_9 \quad} Mn^{II} + PhO\cdot + H^+ \qquad (62)$$

Figure 40. Observed rate constant, $k'_{3a}$, versus concentration of 2,4,6-tri-t-butylphenol.

$$(Mn^{III}) = 5.8 \times 10^{-4} \text{ M}$$

Temperature = $25^{\circ}$

y-axis: $k'_{3a} \times 10^5 \text{ sec}^{-1}$

x-axis: Concentration of 2,4,6-tri-t-butylphenol $\times 10^2$ M

$$Mn_p^{III-} + PhOH \xrightarrow{k_{3a}} Mn^{II} + PhO\cdot + H^+ \qquad (86)$$

Abbreviations used:

$$Mn_p^{III-} = Mn^{III}CyDTA(H_2O)^-$$

$$Mn_y^{III--} = Mn^{III}CyDTA(OH)^{2-}$$

$$PhOH = 2,4,6\text{-tri-t-butylphenol}$$
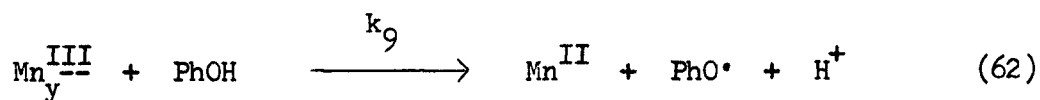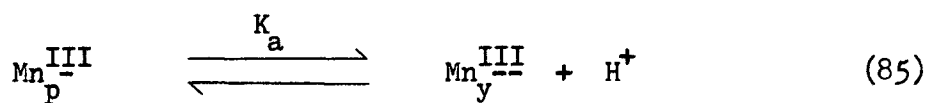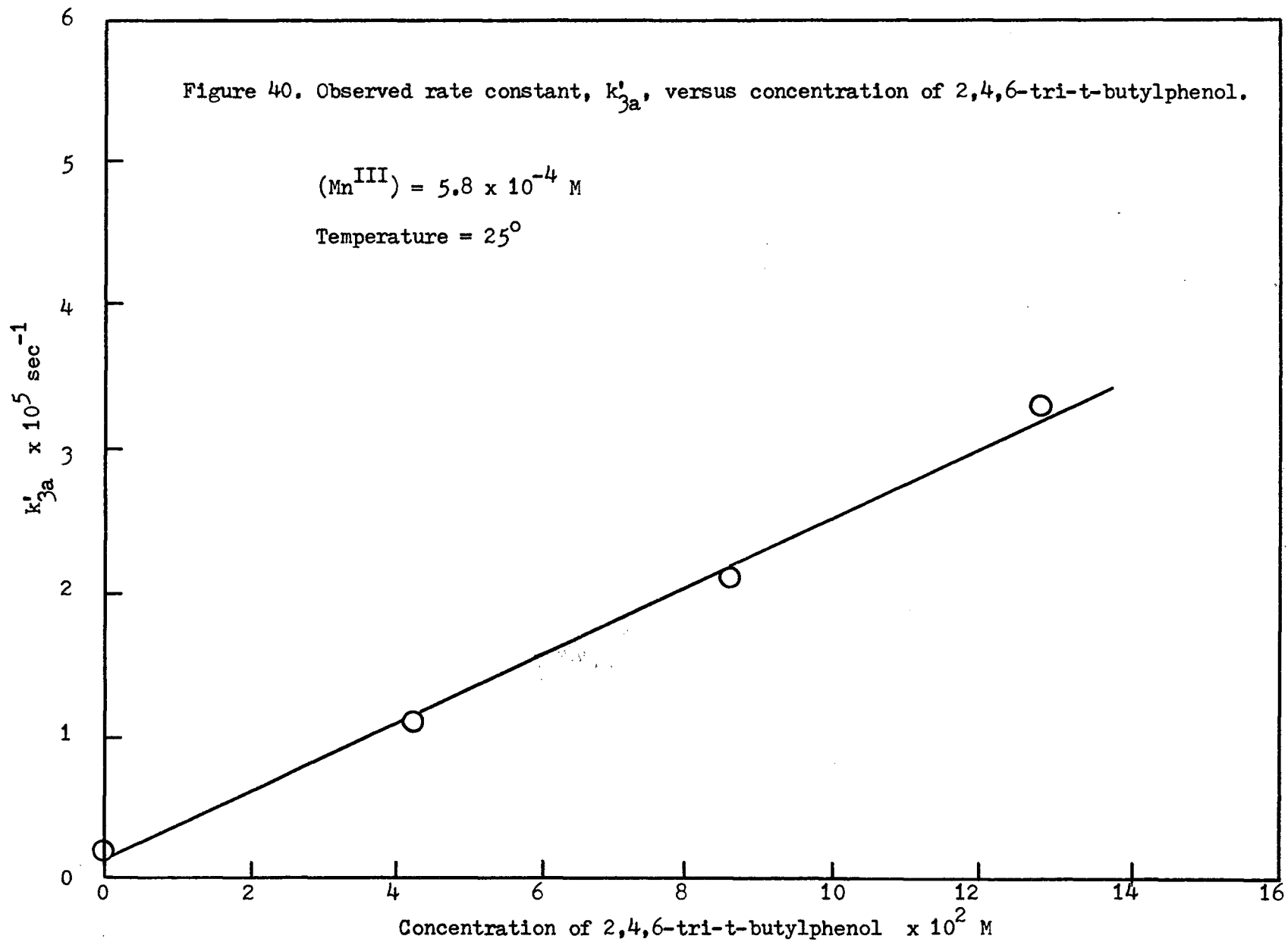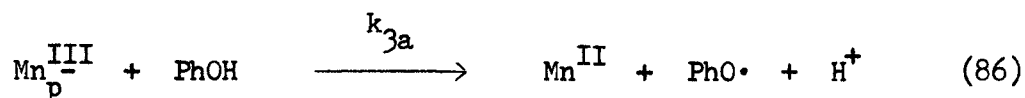
$$PhO\cdot = 2,4,6\text{-tri-t-butylphenoxyl}$$
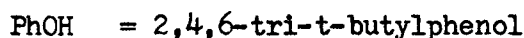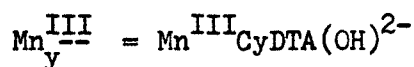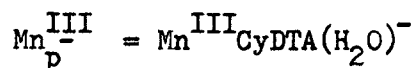
The reaction shown in equation (62) was found to proceed quite rapidly (see Section VIII). Initially, the small concentration of $Mn^{III}CyDTA(OH)^{2-}$ present reacts with 2,4,6-tri-t-butylphenol via reaction (62). As the reaction proceeds, acid is produced and eventually the equilibrium shown in equation (85) lies far to the left; the only important reaction then is that shown in equation (86). As $Mn^{III}CyDTA(OH)^{2-}$ is a more powerful oxidant than $Mn^{III}CyDTA(H_2O)^-$, the initial curvature in Figure 39 is expected. The linear portion of the plot in Figure 39 is due to reaction (86).

The rate of disappearance of the $Mn^{III}$ complex (after reaction (62) becomes unimportant) is given by equation (87).

$$- d(Mn^{III})_{tot}/dt \ = \ k_{3a}(PhOH)(Mn^{III})_{tot} \qquad (87)$$

Since $(Mn^{III})_{tot} = (Mn^{III}_{p^{-}})$ and $(PhOH) \gg (Mn^{III})_{tot}$, equation (87) becomes equation (88) after integration.

$$\log A_{Mn} \ - \ \log A_o \ = \ - \ k_{3a}(PhOH)t/2.303 \qquad (88)$$

Equation (88) is identical to equation (84) with

$$k'_{3a} \ = \ k_{3a}(PhOH) \qquad (89)$$

(iv) Determination of rate constant

A value of $k'_{3a}$ was obtained for each concentration of 2,4,6-tri-t-butylphenol from a plot of $\log A_{Mn}$ versus time (see equation (88) and Figure 39). Then a plot of $k'_{3a}$ versus the concentration of 2,4,6-tri-t-butylphenol was done to obtain an average value of $k_{3a}$ (see Figure 40). An average value of $k_{3a} = 2.4 \times 10^{-4} \ M^{-1}sec^{-1}$ was obtained.

(v) Kinetic isotope effect

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex was carried out in methanol-O-d at $25^{\circ}$. The value of $k_{3a}$ obtained was $4.1 \times 10^{-5} \ M^{-1}sec^{-1}$, giving a kinetic isotope effect of 5.9. Thus, the O-H bond of 2,4,6-tri-t-butylphenol is broken in the rate-determining step of the reaction.

(vi) <u>Substituent effect</u>

Oxidation of some other 4-substituted-2,6-di-t-butylphenols with the $Mn^{III}$ complex in methanol was carried out at $25^o$. The values of $k_{3a}$ for these hindered phenols were obtained using a procedure similar to that of 2,4,6-tri-t-butylphenol. The results are shown in Table XXXIV. The effect observed is small. Figures 41 and 42 are plots of log $k_{3a}/k_{3aH}$ versus $\sigma_p^-$ and $\sigma_p^-$ respectively. The products obtained are identical to those obtained under acidic conditions (see Section VII-viii).

TABLE XXXIV

$\sigma_p$, $\sigma_p^-$ and rates for oxidation of some 4-substituted-2,6-di-t-butyl-phenols with the $Mn^{III}$ complex in methanol at $25^o$

| Substituent | $k_{3a}$ ($M^{-1}sec^{-1}$) | $\sigma_p$ | $\sigma_p^-$ | log $k_{3a}/k_{3aH}$ [*] |
|---|---|---|---|---|
| t-Bu | $2.4 \times 10^{-4}$ | -0.197 | -0.197 | -0.412 |
| $CH_3$ | $4.7 \times 10^{-4}$ | -0.170 | -0.170 | -0.120 |
| H | $6.2 \times 10^{-4}$ | 0 | 0 | 0 |
| Br | $6.0 \times 10^{-4}$ | +0.232 | +0.232 | -0.014 |
| I | $5.8 \times 10^{-4}$ | +0.276 | +0.276 | -0.029 |
| $COC_6H_5$ | $2.5 \times 10^{-4}$ | +0.459 | +0.459 | -0.394 |
| CN | $3.4 \times 10^{-4}$ | +0.628 | +1.000 | -0.261 |
| CHO | $69.0 \times 10^{-4}$ | +0.216 | +1.126 | +1.047 |

[*] $k_{3aH}$ is the rate constant for 2,6-di-t-butylphenol.

Figure 41. Plot of log $k_{3a}/k_{3aH}$ versus $\sigma_p$.

slope $= \rho = -0.07$

Figure 42. Plot of log $k_{3a}/k_{3aH}$ versus $\sigma_p^-$.

slope = $\rho$ = -0.33
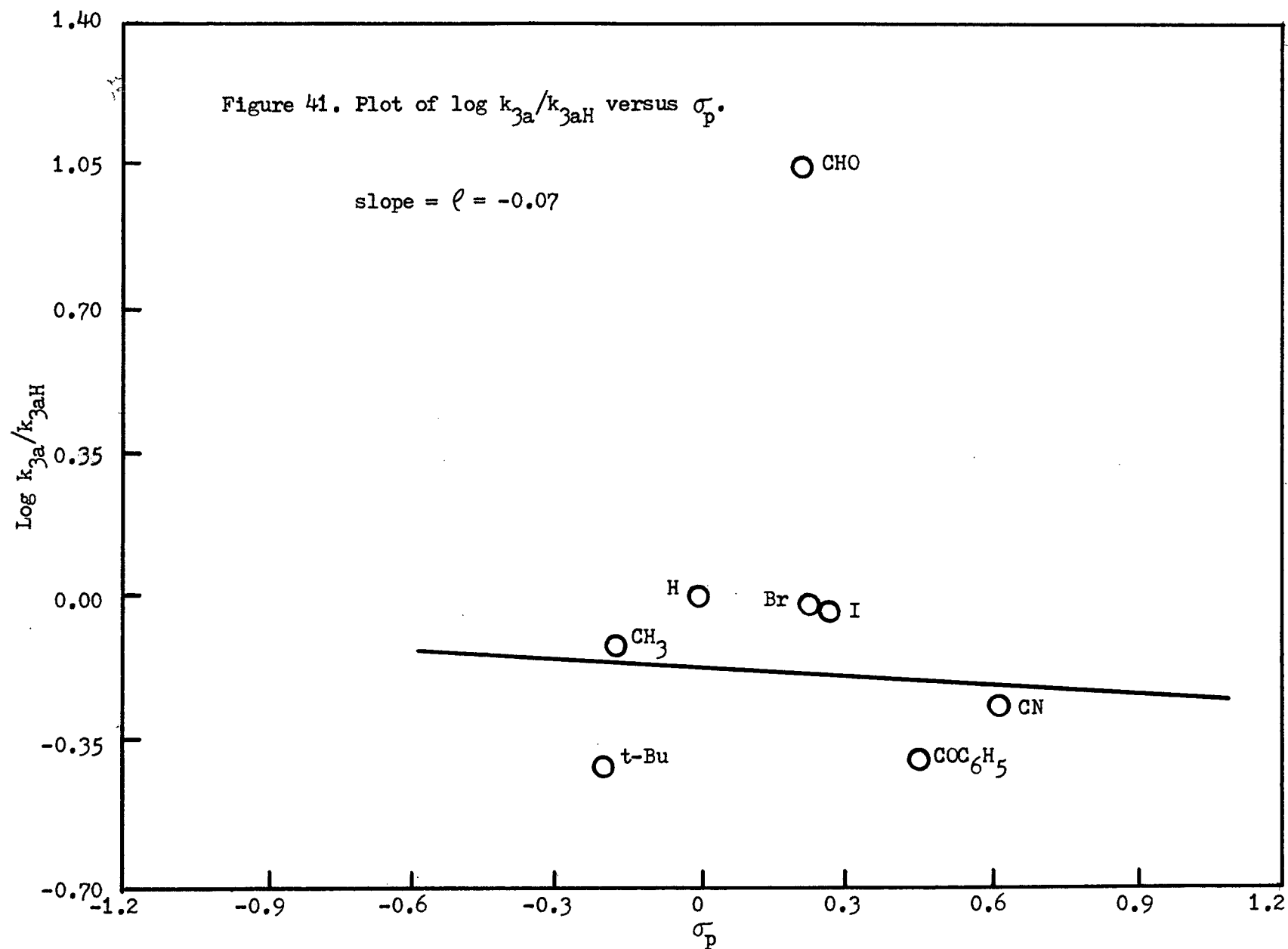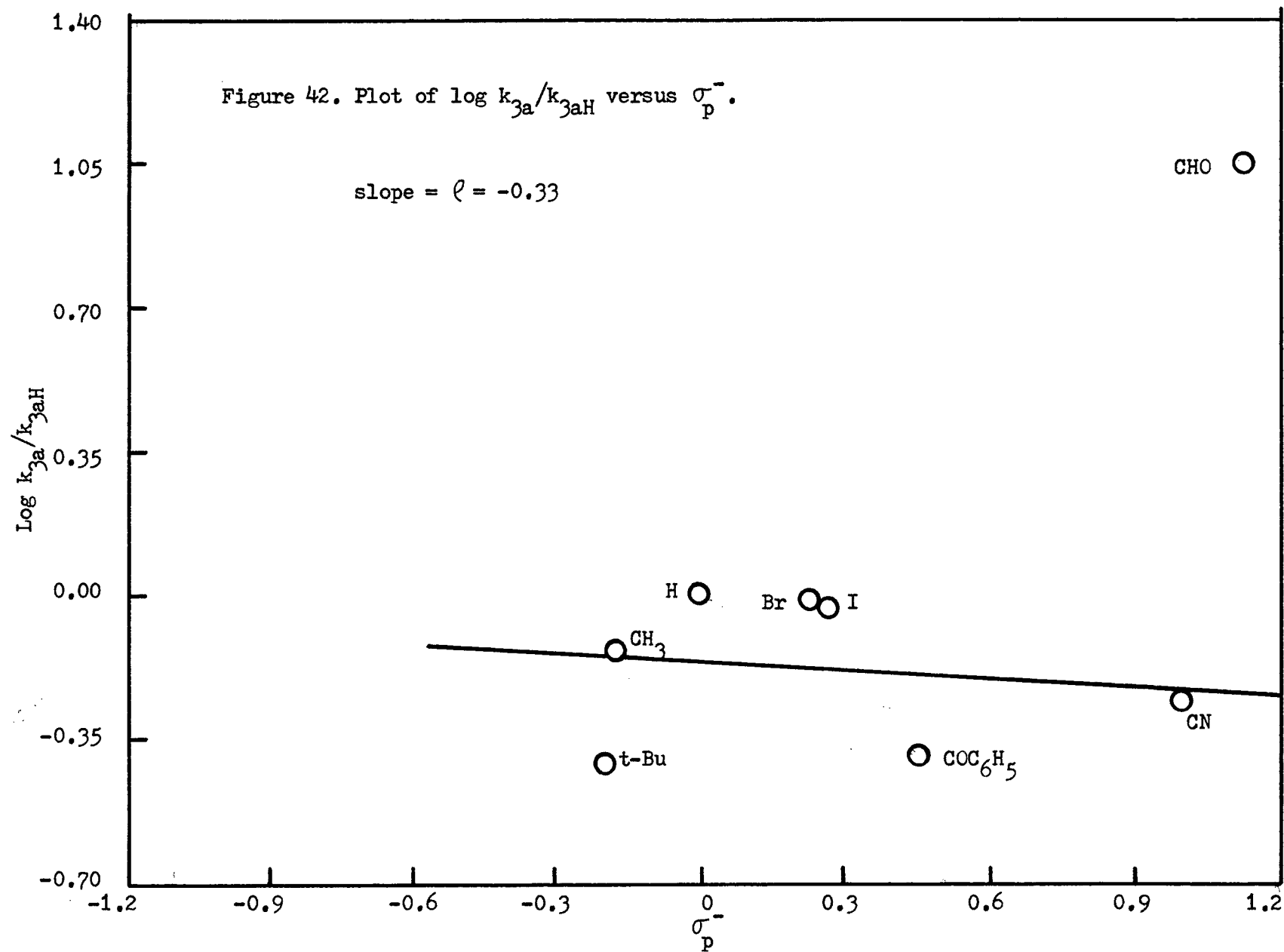
(vii) <u>Activation parameters</u>

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol was carried out at three other temperatures in order to evaluate the values of activation enthalpy and entropy. The values of $\Delta H^*$ and $\Delta S^*$ were found to be 10.9 Kcal.mole$^{-1}$ and -38.6 e.u. respectively. The data in Figure 43 were taken from Table XXXV.

TABLE XXXV

<u>Variation of $k_{3a}$ with temperature</u>

| Temperature($^{o}$C) | $k_{3a}$($M^{-1}$sec$^{-1}$) |
|---|---|
| 25 | $2.4 \times 10^{-4}$ |
| 35 | $3.9 \times 10^{-4}$ |
| 45 | $7.7 \times 10^{-4}$ |
| 50 | $10.7 \times 10^{-4}$ |

(viii) <u>Discussion</u>

The kinetic isotope effect of 5.9 indicates that the oxidation of 2,4,6-tri-t-butylphenol with $Mn^{III}CyDTA(H_2O)^-$ goes via a hydrogen atom abstraction mechanism. The O-H bond of the reductant is cleaved in the rate-determining step of the reaction. An 'inner-sphere' mechanism is probably involved and the hydrogen atom of the reductant forms a bridge

Figure 43. Plot of log $k_{3a}/T$ versus $1/T$ for oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex in methanol.

$\Delta H^* = 10.9$ Kcal.mole$^{-1}$

$\Delta S^* = -38.6$ e.u.

Correlation coefficient $= -0.9941$

Log $k_{3a}/T$

$1/T$ ($^\circ K$) $\times 10^3$
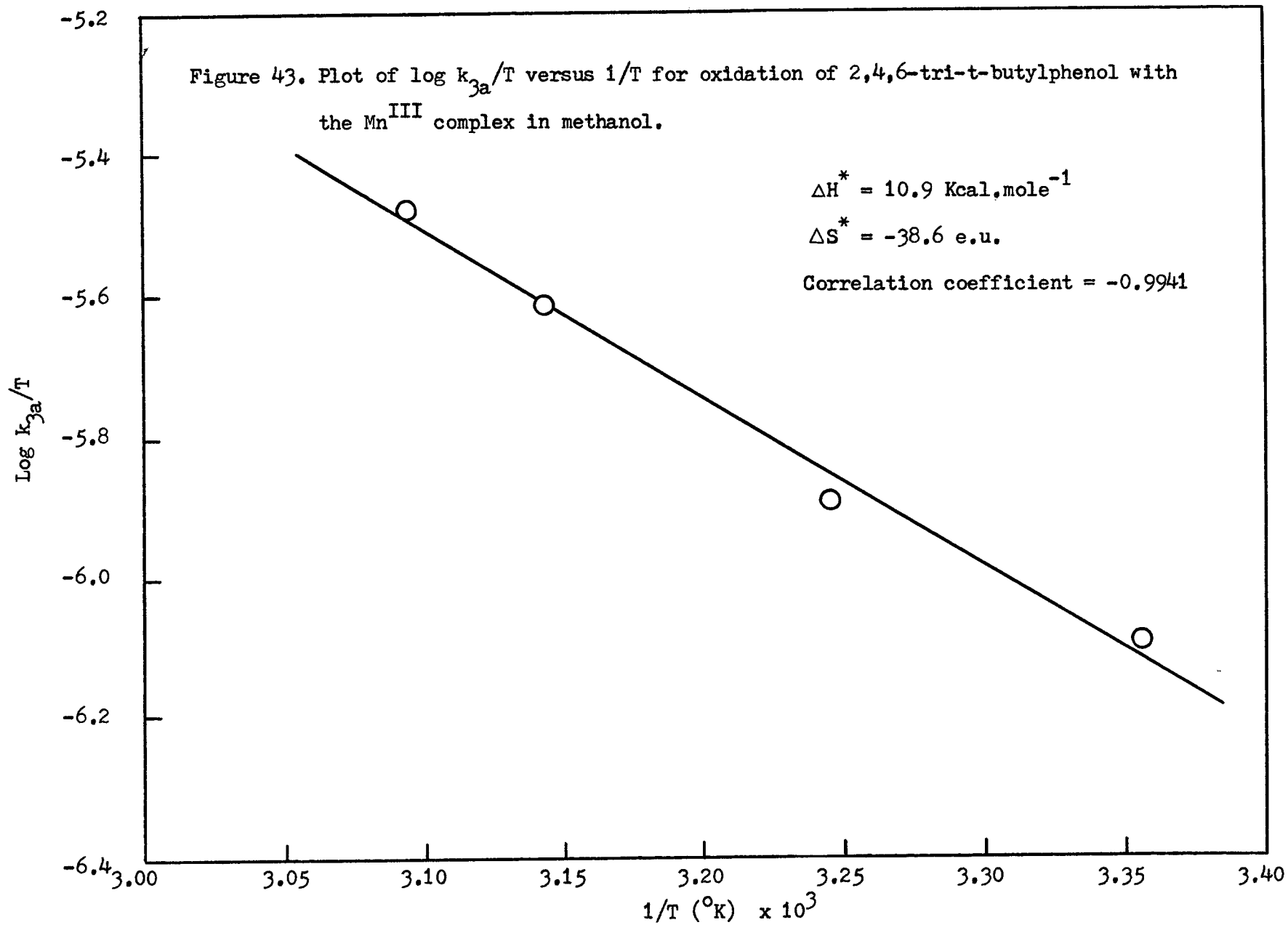
between the two reactants (see Section VII-ix).

The small substituent effect observed suggests the presence of an activated complex which has radical character in the O-H bond of the reductant. The activated complex may be pictured as XXXXIV. Such an activated complex is stabilised by both electron-withdrawing and electron-donating groups and the effect is usually small. (Compare with Section VII-ix). Again, the 4-CHO compound has an anomalously high rate compared with the other hindered phenols. (A similar anomalously high rate for this compound was also observed in acidic condition (see Section VII-ix)). Elemental analysis, melting point and nmr spectrum (see page 20) show that the compound used is 3,5-di-t-butyl-4-hydroxybenzaldehyde.

$$Mn^{III}CyDTA(H_2O)^- \cdots\cdots H\cdots O \text{—ring—} R$$
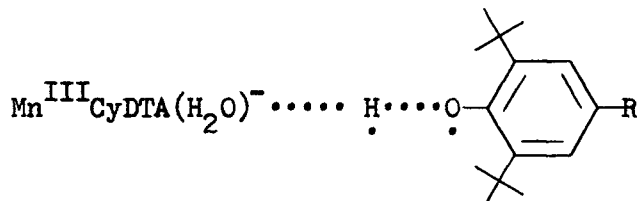
XXXXIV

The relative oxidising power of the three oxidants, $HMn^{III}CyDTA(H_2O)$, $Mn^{III}CyDTA(H_2O)^-$ and $Mn^{III}CyDTA(OH)^{2-}$, with respect to 2,4,6-tri-t-butyl-phenol as the reductant is 458 : 1 : 312.

## X. OXIDATION OF 2,4,6-TRI-t-BUTYLPHENOL WITH THE $Mn^{III}$ COMPLEX IN DIMETHYL SULFOXIDE (DMSO) IN THE PRESENCE OF BASE

### (i) Product

2,4,6-Tri-t-butylphenoxyl was produced quantitatively.

### (ii) Analysis of kinetic results

Oxidation of 2,4,6-tri-t-butylphenol with the $Mn^{III}$ complex was carried out in 95 % DMSO and 5 % water mixed solvent (v/v) in the presence of tetramethylammonium hydroxide. The concentration of the base used was kept lower than that of the $Mn^{III}$ complex for three reasons: (1) to ensure that all the base was used up in ionising the $Mn^{III}$ complex to its yellow form, $Mn^{III}CyDTA(OH)^{2-}$; (2) to ensure that 2,4,6-tri-t-butylphenol remains unionised; (3) excess base tends to decompose the $Mn^{III}$ complex and thereby complicates the kinetics involved.

Oxidation was followed spectrophotometrically by monitoring the change in absorbance at 400 nm (due to the formation of 2,4,6-tri-t-butylphenoxyl). The absorbance of the $Mn^{III}$ complex was too weak to be detected in the narrow concentration range studied (less than $4 \times 10^{-4}$ M).

The following reactions are considered.

$$Mn^{III}_p{}^- + OH^- \underset{}{\overset{K_{2a}}{\rightleftharpoons}} Mn^{III}_y{}^{--} + H_2O \qquad (90)$$

$$Mn_y^{III=-} + PhOH \xrightarrow{k'_{9b}} Mn^{II} + PhO\cdot + H^+ \qquad (91)$$

$$Mn_p^{III-} + PhOH \xrightarrow{k_{3b}} Mn^{II} + PhO\cdot + H^+ \qquad (92)$$

Abbreviations used:

$$Mn_y^{III=-} = Mn^{III}CyDTA(OH)^{2-}$$

$$Mn_p^{III-} = Mn^{III}CyDTA(H_2O)^-$$

PhOH = 2,4,6-tri-t-butylphenol
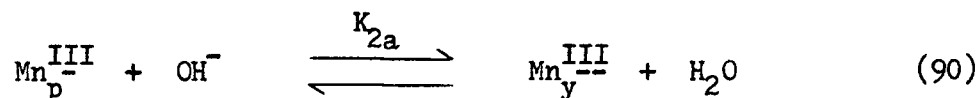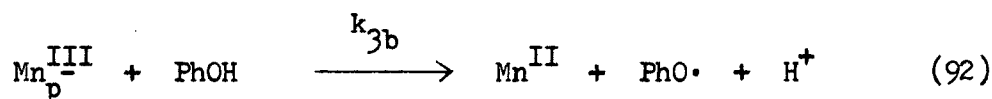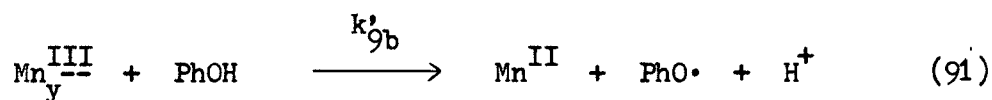
PhO· = 2,4,6-tri-t-butylphenoxyl
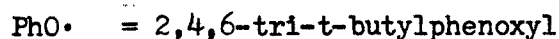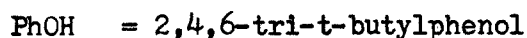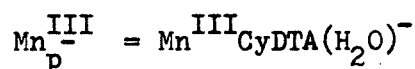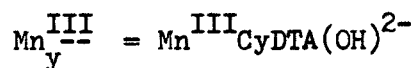
Reaction (92) can be ignored because in the absence of base no detectable reaction between 2,4,6-tri-t-butylphenol and $Mn^{III}CyDTA(H_2O)^-$ was observed in a few hours. Reaction (91) is the rate-determining step. Thus, the rate of formation of 2,4,6-tri-t-butylphenoxyl is given by equation (93).

$$d(PhO\cdot)/dt = k'_{9b}(Mn_y^{III=-})(PhOH) \qquad (93)$$

Assuming all the base was used up in converting $Mn^{III}CyDTA(H_2O)^-$ to $Mn^{III}CyDTA(OH)^{2-}$, the initial concentration of $Mn^{III}CyDTA(OH)^{2-}$ would be equal to the concentration of base added (see Section X-iii). Equation (93)

can be written as equation (94).

$$dx/dt = k'_{9b}(b - x)(p - x) \qquad (94)$$

where  x = concentration of 2,4,6-tri-t-butylphenoxyl at time t,

   b = concentration of tetramethylammonium hydroxide added,

   p = concentration of 2,4,6-tri-t-butylphenol added.

Integrating equation (94) gives:

$$\log (p - x)/(b - x) = k'_{9b}t + \log b/p \qquad (95)$$

The value of x at time t was calculated from the absorbance at 400 nm using an extinction coefficient value of 1989 (measured in this work). The value of the rate constant, $k'_{9b}$, was determined from the slope of a plot of log (p - x)/(b - x) versus t. Figure 44 is a typical plot of equation (95). The values of $k'_{9b}$ obtained for the various concentrations of reactants are summarised in Table XXXVI. An average value of $k'_{9b} = 450 \pm 70$ $M^{-1}sec^{-1}$ was obtained.

Figure 44. Plot of log (p -x)/(b - x) versus time for oxidation of 2,4,6-tri-t-butylphenol with the Mn$^{III}$ complex in DMSO in the presence of base.
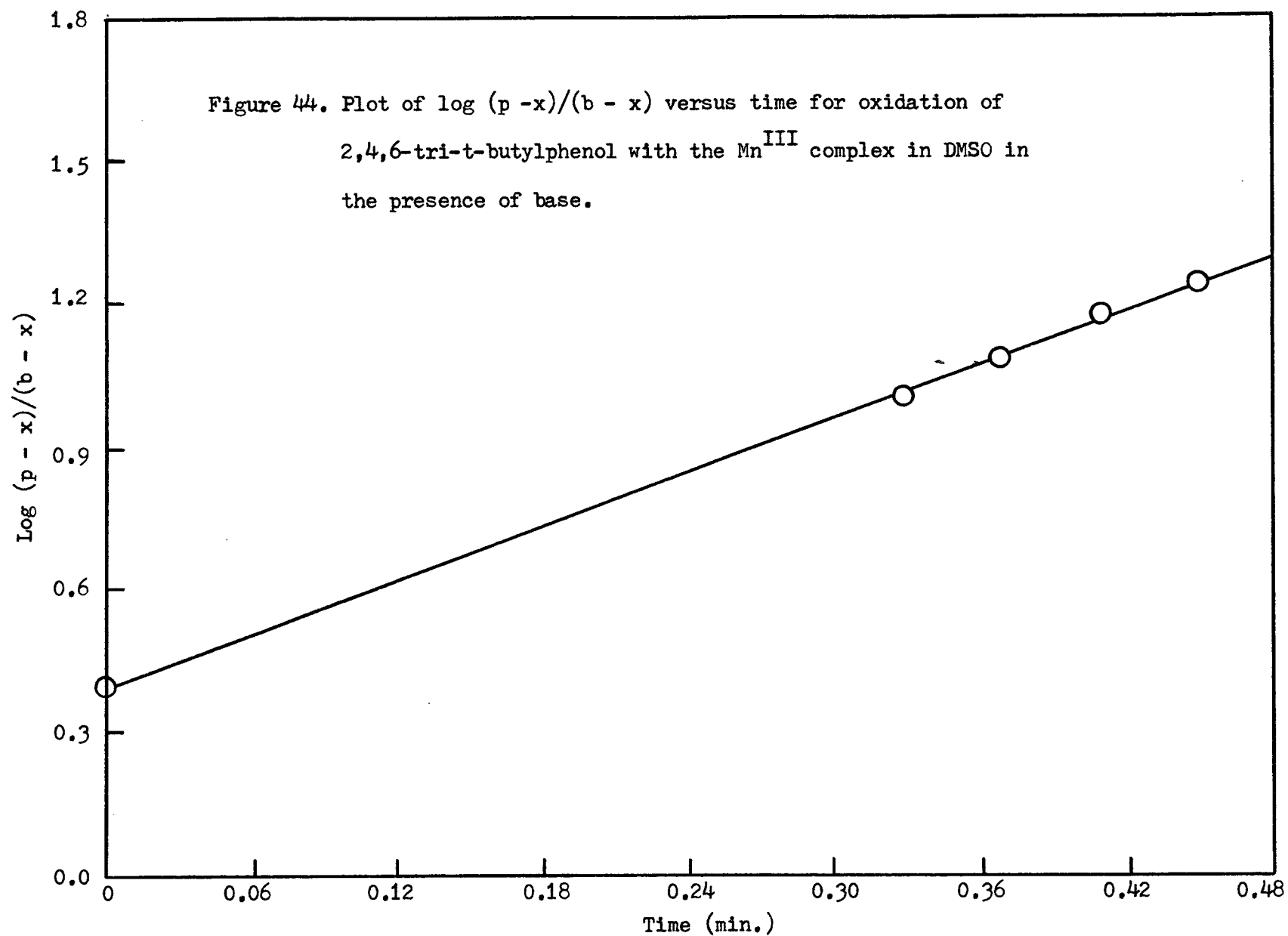
TABLE XXXVI

$\underline{\text{Values of } k'_{9b} \text{ at } 25^{\circ}}$

$(\text{TMA})^* = 1 \times 10^{-4}$ M

| $(\text{Mn}^{III})(\text{M})$ | $(\text{PhOH})^{**}(\text{M})$ | $k'_{9b}(\text{M}^{-1}\text{sec}^{-1})$ |
|---|---|---|
| $2.50 \times 10^{-4}$ | $2.22 \times 10^{-4}$ | 540 |
| $2.50 \times 10^{-4}$ | $2.60 \times 10^{-4}$ | 460 |
| $2.50 \times 10^{-4}$ | $3.07 \times 10^{-4}$ | 400 |
| $2.50 \times 10^{-4}$ | $3.32 \times 10^{-4}$ | 470 |
| $3.25 \times 10^{-4}$ | $2.22 \times 10^{-4}$ | 520 |
| $2.09 \times 10^{-4}$ | $2.22 \times 10^{-4}$ | 410 |
| $1.70 \times 10^{-4}$ | $2.22 \times 10^{-4}$ | 360 |

average $k'_{9b}$     $450 \pm 70$

\* TMA = tetramethylammonium hydroxide

\*\* PhOH = 2,4,6-tri-t-butylphenol

(iii) Discussion

In the derivation of equation (95) it was assumed that the concentration of $\text{Mn}^{III}\text{CyDTA}(\text{OH})^{2-}$ was equal to that of the base added.

This assumption was based on the following facts: (1) the $pK_a$ value of $Mn^{III}CyDTA(H_2O)^-$ in water was found to be $8.1$[41] and the extrapolated $pK_a$ value of 2,4,6-tri-t-butylphenol in water[104] was estimated to be 12.2 ($pK_a$ values of 2,4,6-tri-t-butylphenol in 50 % ethanol, methanol and DMSO were found to be 14.75, 17.40 and 12.28 respectively)[104-106]. Therefore, $Mn^{III}CyDTA(H_2O)^-$ will ionise before 2,4,6-tri-t-butylphenol does in a limited concentration of base; (2) it was found (in this work) that both the $Mn^{III}$ complex and 2,4,6-tri-t-butylphenol were completely ionised in the presence of an equimolar amount of base in 95 % DMSO solvent. For example, when $1.0 \times 10^{-3}$ M of base was added to a solution of $1.0 \times 10^{-3}$ M of the $Mn^{III}$ complex, the complex was quantitatively converted to its yellow form.

It was observed that when the base was kept at a fixed limiting concentration, the amount of 2,4,6-tri-t-butylphenoxyl produced was the same for all concentrations of the $Mn^{III}$ complex and 2,4,6-tri-t-butyl-phenol, in agreement with the reaction path proposed.

Only a narrow range of concentration variation could be studied because oxidation occurred too rapidly at higher concentrations of reactants. Even in the narrow concentration range studied only the last 20 % of the reaction could be followed. Lower concentrations of reactants make spectrophotometric measurement impossible.

Comparing the value of $k'_{9b}$ with that of $k_9$ in Section VIII, it can

be seen that the oxidation of 2,4,6-tri-t-butylphenol with

$Mn^{III}CyDTA(OH)^{2-}$ is about 6000 times faster in DMSO than in methanol.

The substrate is a neutral molecule and the medium effect on its activity

is probably small. The high rate in DMSO solvent is presumably due to the

increase in reactivity of $Mn^{III}CyDTA(OH)^{2-}$.

The value of the rate constant, $k_{3b}$, for the oxidation of 2,4,6-tri-

t-butylphenol with $Mn^{III}CyDTA(H_2O)^-$ in 95 % DMSO was found to be

$1 \times 10^{-5}$ $M^{-1}sec^{-1}$. Thus, $Mn^{III}CyDTA(OH)^{2-}$ is $4.5 \times 10^7$ times as powerful

as $Mn^{III}CyDTA(H_2O)^-$ as an oxidant of 2,4,6-tri-t-butylphenol. This high

ratio of $k'_{9b}/k_{3b}$ (= $4.5 \times 10^7$) suggests an 'inner-sphere' mechanism is

involved in the oxidation reaction (see Section VIII-x).

## XI. OXIDATION OF 2,4,6-TRI-t-BUTYLPHENOL WITH POTASSIUM FERRICYANIDE IN METHANOL*

Oxidation of 2,4,6-tri-t-butylphenol with potassium ferricyanide in methanol was carried out under three conditions: (1) in the presence of base; (2) without acid or base; (3) in the presence of acid. Unfortunately, no kinetic data could be obtained because, in the presence of base (sodium hydroxide), the potassium ferrocyanide formed in the reaction precipitated; there was no observable reaction in the absence of base and acid; and the reaction occurred instantaneously in the presence of hydrochloric acid. However, it was observed that potassium ferricyanide was not consumed completely even when oxidation was carried out in the presence of a large excess of hydrochloric acid and 2,4,6-tri-t-butylphenol. This observation indicated a reversible reaction of the type shown in equation (96). Further investigations (as described below) confirm the presence of a reversible reaction.

$$\text{Ferricyanide}^{**} + \text{PhOH} \rightleftharpoons \text{Ferrocyanide}^{**} + \text{PhO} \cdot + \text{H}^+ \qquad (96)$$

** these species may be protonated.

PhOH = 2,4,6-tri-t-butylphenol

PhO· = 2,4,6-tri-t-butylphenoxyl

* 2.5 % water (v/v)

A. <u>Equilibrium measurements</u>

a. <u>Methods</u>

All solutions used were flushed with high purity nitrogen and transferred with syringes equipped with Chaney adapters. The values of the equilibrium constant, $K_p$ (defined in equation (97)), were determined at $25^\circ$ in two ways: (i) from reaction between 2,4,6-tri-t-butylphenol and potassium ferricyanide in the presence of hydrochloric acid; (ii) from reaction between 2,4,6-tri-t-butylphenoxyl and potassium ferrocyanide in the presence of hydrochloric acid.

(i). To a 3 ml. aliquot of a known concentration of 2,4,6-tri-t-butylphenol in methanol in a 1 cm. cell which was capped with a silicon rubber disc was added 0.050 ml. of hydrochloric acid of known concentration followed by 0.025 ml. of potassium ferricyanide of known concentration. The cell was shaken briefly to mix the reactants well. This cell was then put in the sample cell holder of a Bausch and Lomb Spectronic 505 spectrophotometer and in the reference cell holder was placed a similar cell containing 3 ml. methanol. Spectra from 300 nm to 450 nm region were recorded at short time intervals for the first five minutes. (It was found that the peak at 400 nm (due to formation of 2,4,6-tri-t-butyl-phenoxyl) reached a maximum value instantaneously and then decreased with time. The decrease in absorbance at 400 nm was rather rapid at high concentrations of acid. Therefore, extrapolations to zero time were

needed to obtain the instantaneous absorbance at 400 nm. The peak at

420 nm (due to ferricyanide) also decreased with time, but the

instantaneous decrease was most drastic. A similar extrapolation to zero

time method was used to obtain the instantaneous absorbance at 420 nm).

A spectrum of an identical solution but without 2,4,6-tri-t-butylphenol

was recorded to obtain the absorbances of potassium ferricyanide at 400 nm

and 420 nm. The extinction coefficients of potassium ferricyanide at

these two wavelengths in a given acid concentration were then calculated.

Thus, for each reaction the amount of potassium ferricyanide* left could

be calculated from the absorbance at 420 nm and the amount of 2,4,6-tri-

t-butylphenoxyl* formed could be calculated from the absorbance at 400 nm

(after correcting for contribution from potassium ferricyanide) using

an extinction coefficient of 1955 (see Section IV-iii).


* initial concentrations calculated because absorbances at 400 nm and

420 nm decreased with time due to the formation of a fluffy blue solid

which precipitated out. This fluffy blue solid was not sensitive to

oxygen, it was insoluble in water and aqueous acids, but decomposed by

aqueous potassium hydroxide to a brown solid. This blue solid was

probably prussian blue - $KFe^{III}(Fe^{II}(CN)_6)$ or $KFe^{II}(Fe^{III}(CN)_6)$.

Prussian blue is insoluble in water and aqueous acids, but decomposes

in aqueous potassium or sodium hydroxide to form brown ferric hydroxide.

(ii). To a 3 ml. aliquot of methanol containing a known concentration of 2,4,6-tri-t-butylphenol and hydrochloric acid in a 1 cm. cell which was capped with a silicon rubber disc was added 0.050 ml. of a known concentration of 2,4,6-tri-t-butylphenoxyl (see Section IV-iii for method used to generate 2,4,6-tri-t-butylphenoxyl) followed by 0.025 ml. of potassium ferrocyanide. The cell was shaken briefly to mix the reactants well. Spectra from 350 nm to 450 nm region were recorded at short time intervals in the first five minutes. The concentration of potassium ferricyanide formed and the concentration of 2,4,6-tri-t-butylphenoxyl left were calculated from the absorbances at 420 nm and 400 nm respectively (see (i)).

b. Analysis of results

It was found that the values of $K_p$ (see equation (97)) were constant for a given concentration of acid (see Table XXXVII) and the values of $K_p$ derived from the two methods agreed well (see Tables XXXVII and XXXVIII). But the values of $K_p$ were found to vary proportionately with acid concentration (see Table XXXIX).

$$K_p = (Fe^{II})_{tot}(PhO\cdot)/(Fe^{III})_{tot}(PhOH) \qquad (97)$$

$(Fe^{II})_{tot}$ = total concentration of ferrocyanides (unprotonated + protonated forms),

$(Fe^{III})_{tot}$ = total concentration of ferricyanides (unprotonated + protonated forms),

(PhOH) = 2,4,6-tri-t-butylphenol,

(PhO·) = 2,4,6-tri-t-butylphenoxyl.

TABLE XXXVII

$K_p$ at constant acid concentration at $25°$ (determined by method (i))

| (PhOH)(M) | (PhO·)(M) | $(Fe^{III})_{tot}$(M) | $(Fe^{II})^a_{tot}$(M) | $K_p$ |
|---|---|---|---|---|
| $1.00 \times 10^{-2}$ | $1.43 \times 10^{-4}$ | $5.53 \times 10^{-4}$ | $1.43 \times 10^{-4}$ | $3.7 \times 10^{-3}$ |
| $1.97 \times 10^{-2}$ | $1.87 \times 10^{-4}$ | $4.87 \times 10^{-4}$ | $1.87 \times 10^{-4}$ | $3.7 \times 10^{-3}$ |
| $2.98 \times 10^{-2}$ | $2.24 \times 10^{-4}$ | $4.39 \times 10^{-4}$ | $2.24 \times 10^{-4}$ | $3.8 \times 10^{-3}$ |
| $4.95 \times 10^{-2}$ | $2.76 \times 10^{-4}$ | $4.03 \times 10^{-4}$ | $2.76 \times 10^{-4}$ | $3.8 \times 10^{-3}$ |
| $4.95 \times 10^{-2}$ | $1.97 \times 10^{-4}$ | $2.05 \times 10^{-4}$ | $1.97 \times 10^{-4}$ | $3.9 \times 10^{-3}$ |
| $4.95 \times 10^{-2}$ | $2.44 \times 10^{-4}$ | $2.85 \times 10^{-4}$ | $2.44 \times 10^{-4}$ | $4.2 \times 10^{-3}$ |
| $5.00 \times 10^{-2}$ | $1.13 \times 10^{-4}$ | $6.53 \times 10^{-4}$ | $1.13 \times 10^{-4}$ | $3.9 \times 10^{-3}$ |

average $K_p$ = $3.9 \times 10^{-3}$

(HCl) = $1.63 \times 10^{-2}$ M

a put equal to (PhO·)

## TABLE XXXVIII

<u>$K_p$ at constant acid concentration at $25°$ (determined by method (ii))</u>

| (PhOH)(M) | (PhO·)(M) | $(Fe^{III})_{tot}$(M) | $(Fe^{II})_{tot}^*$(M) | $K_p$ |
|-----------|-----------|------------------|-------------------|-------|
| $5.01 \times 10^{-2}$ | $0.40 \times 10^{-4}$ | $0.99 \times 10^{-4}$ | $5.51 \times 10^{-4}$ | $4.4 \times 10^{-3}$ |
| $5.01 \times 10^{-2}$ | $0.17 \times 10^{-4}$ | $0.56 \times 10^{-4}$ | $5.83 \times 10^{-4}$ | $3.8 \times 10^{-3}$ |
| $5.01 \times 10^{-2}$ | $0.75 \times 10^{-4}$ | $2.10 \times 10^{-4}$ | $4.42 \times 10^{-4}$ | $3.2 \times 10^{-3}$ |
| $5.01 \times 10^{-2}$ | $0.89 \times 10^{-4}$ | $1.92 \times 10^{-4}$ | $4.63 \times 10^{-4}$ | $4.3 \times 10^{-3}$ |

average $K_p$ = $3.9 \times 10^{-3}$

(HCl) = $1.63 \times 10^{-2}$ M

* calculated from the difference between the concentration of
ferrocyanide added and the concentration of ferricyanide formed.

TABLE XXXIX[*]

## Variation of $K_p$ with acid concentration at 25°

| (HCl)(M) | $K_p$ | $(K_p/(H^+))(M)$ |
|---|---|---|
| $1.63 \times 10^{-3}$ | $1.9 \times 10^{-4}$ | $1.2 \times 10^{-1}$ |
| $1.63 \times 10^{-2}$ | $3.9 \times 10^{-3}$ | $2.3 \times 10^{-1}$ |
| $3.51 \times 10^{-2}$ | $1.5 \times 10^{-2}$ | $4.3 \times 10^{-1}$ |
| $5.09 \times 10^{-2}$ | $2.2 \times 10^{-2}$ | $4.3 \times 10^{-1}$ |
| $6.55 \times 10^{-2}$ | $3.0 \times 10^{-2}$ | $4.6 \times 10^{-1}$ |
| $1.01 \times 10^{-1}$ | $5.0 \times 10^{-2}$ | $5.0 \times 10^{-1}$ |

* determined by method (i)

c. Discussion

The oxidant involved is likely to be a protonated form of ferricyanide because, in the absence of acid there is no noticeable reaction between ferricyanide and 2,4,6-tri-t-butylphenol. Ferrocyanide formed is likely to be protonated too because unprotonated ferrocyanide is not soluble in methanol. (Under basic conditions ferrocyanide precipitates immediately when 2,4,6-tri-t-butylphenol is oxidised with potassium ferricyanide in methanol). Oxidation of 2,4,6-tri-t-butylphenol with potassium ferricyanide under acidic conditions occurs instantaneously and that the reaction is

reversible is shown by the results obtained (see Tables XXXVII to XXXIX).

In order to solve the various equilibria involved the values of the ionization constants of ferrocyanic acid ($H_4Fe(CN)_6$) and ferricyanic acid ($H_3Fe(CN)_6$) must be known. Several attempts[107-110] to measure these ionization constants have been made, but only the first two ionization constants of ferrocyanic acid were obtained ($K_1 = (6.7 \pm 0.3) \times 10^{-5}$; $K_2 = (6 \pm 2) \times 10^{-3}$)[110]. The values of the other ionization constants were considered to be larger than $0.1$[110]. The lack of data on the ionization constants of these two acids prevent a detailed analysis of the equilibrium shown in equation (96).

## XII. ATTEMPTS TO SYNTHESIZE 3,5,7-TRI-t-BUTYLTROPOLONE

Several attempts to synthesize 3,5,7-tri-t-butyltropolone (XXXXV) by various methods were made because it was thought that the oxidation of this compound with the $Mn^{III}$ complex would yield a radical analogous to 2,4,6-tri-t-butylphenoxyl (see equation (98)). Unfortunately, all attempts failed to give 3,5,7-tri-t-butyltropolone. The methods used are described below.



$$(98)$$

XXXXV
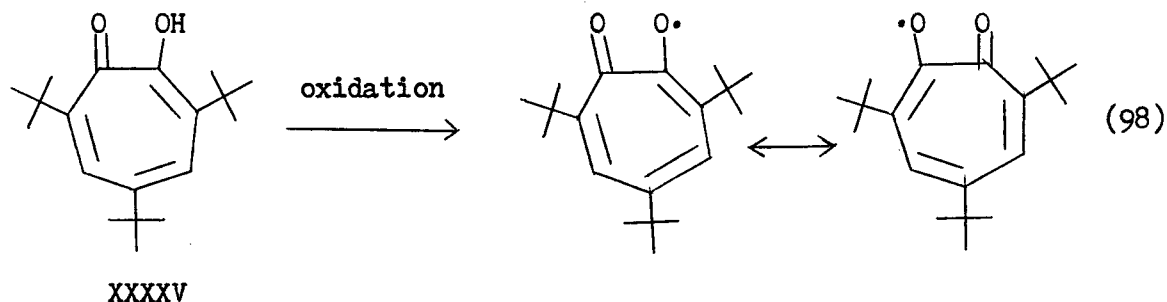
### (a) Reaction of 3,5,7-tribromotropolone with t-butyl lithium

A sample of 2.5 g of 3,5,7-tribromotropolone (6 mmoles) was dissolved in 30 ml. of dry benzene in a 250 ml. three-necked flask. (The compound 3,5,7-tribromotropolone was synthesized by bromination of tropolone according to the method of Takase)[111]. High purity nitrogen was bubbled into the benzene solution through one neck of the flask and a second neck with a glass tube dipping into a beaker of water formed the outlet. The third neck was stoppered with a rubber cap. The benzene solution was stirred with a bar magnet while nitrogen was bubbled in.

Small aliquots of t-butyl lithium were syringed into the reaction flask by means of a 5 ml. syringe. The total volume of t-butyl lithium added varied from 11 ml. (22 mmoles) to 20 ml. (40 mmoles). The reaction mixture was stirred at room temperature for 5 to 22 hours. Then, the reaction mixture was poured into 200 ml. of benzene-water (1 : 1) acidified with hydrochloric acid. The dark benzene layer was flash-evaporated to dryness. A dark solid was obtained that could not be recrystallised from acetone, alcohols or benzene. Analytical data and nmr spectrum showed that it was not the desired compound.

(b) Reaction of tropolone with t-butyl alcohol

A 1 g sample of tropolone (from Aldrich Chemical Company) was dissolved in 10 ml. of t-butyl alcohol in a 50 ml. round-bottomed flask and 0.1 ml. of concentrated sulphuric acid was added to the solution. The reaction mixture was refluxed at about $150^\circ$ for 24 hours. Starting material was recovered at the end of the reaction.

(c) Reaction of tropolone with t-butyl chloride

A 2 g sample of tropolone was dissolved in 20 ml. of glacial acetic acid containing 4.4 g of sodium acetate in a 50 ml. round-bottomed flask. Then, 6.6 ml. of t-butyl chloride was added to the mixture and the contents refluxed at about $110^\circ$ for four hours. Sodium chloride and the starting material were obtained.

## XIII. SUGGESTIONS FOR FURTHER WORK

Further work on: (1) the determination of the ionization constants of ferrocyanic acid ($H_4Fe(CN)_6$) and ferricyanic acid ($H_3Fe(CN)_6$); (2) the synthesis of 5-substituted-3,7-di-t-butyltropolones, are needed.

(1). Several attempts[107-110] to measure the ionization constants of ferrocyanic and ferricyanic acids have been made, but only the first two ionization constants were obtained. The values of the other ionization constants were considered larger than $0.1$[110]. A titrimetric method was used in all these attempts and it is not surprising that the values of the other ionization constants could not be determined, as they are larger than 0.1. A preliminary investigation (this work) indicates that a spectrophotometric method may yield the values of all the ionization constants (the absorbance of potassium ferricyanide at 420 nm in sulfuric acid or perchloric acid up to 10 M acid varies with the acidity of the medium and a study of the variation of absorbance with acidity of the medium may give the ionization constant values). A detailed investigation on the variation of absorbance of potassium ferricyanide and potassium ferrocyanide with acidity in both aqueous and non-aqueous (or mixed) solvents needs to be done and the results compared. Knowing the ionization constants, the equilibrium between 2,4,6-tri-t-butylphenol, ferricyanide and 2,4,6-tri-t-butylphenoxyl, ferrocyanide, can be studied in details.

(2). The series of 5-substituted-3,7-di-t-butyltropolones has not yet

been prepared. Convenient methods of preparing these compounds are needed because they offer a new field of study analogous to that of hindered phenols.

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APPENDIX

An alternative mechanism involving a chloro-complex formation

between the chloride ion and the $Mn^{III}$ complex instead of protonation of

the $Mn^{III}$ complex (see equation (32)) was ruled out on two pieces of

evidence: (1) the spectrum of the $Mn^{III}$ complex in methanol in the

presence of hydrochloric acid is identical to that of the same complex in

methanol in the presence of an equivalent amount of perchloric acid.

Therefore, the spectrum B in Figure 6 is not that of a chloro-complex;

(2) the rate of oxidation of methanol by the $Mn^{III}$ complex is barely

affected by the chloride ion concentration (see Table XXXX).

TABLE XXXX

Variation of $k_b$ with concentration of chloride ion* at $25^o$

$(Mn^{III}) = 5.9 \times 10^{-4}$ M  $(H^+) = 1.63 \times 10^{-2}$ M

| $(ClO_4^-)(M)$ | $(Cl^-)(M)$ | $k_b(sec^{-1})$ |
|---|---|---|
| $1.63 \times 10^{-2}$ | 0 | $1.14 \times 10^{-3}$ |
| $1.30 \times 10^{-2}$ | $0.33 \times 10^{-2}$ | $1.30 \times 10^{-3}$ |
| $0.82 \times 10^{-2}$ | $0.81 \times 10^{-2}$ | $1.52 \times 10^{-3}$ |
| $0.33 \times 10^{-2}$ | $1.30 \times 10^{-2}$ | $1.49 \times 10^{-3}$ |
| 0 | $1.63 \times 10^{-2}$ | $1.54 \times 10^{-3}$ |

\* Variation of chloride ion concentration was obtained by mixing

different volumes of 1 N HCl with different volumes of 1 N $HClO_4$ with

the total volume of the mixture being maintained at 1 ml.

(In the presence of $1.63 \times 10^{-2}$ M of HCl in water the value of $k_b$ was

found to be $2.96 \times 10^{-5}$ $sec^{-1}$ at $25^{\circ}$).