A STUDY OF THE MECHANISMS OF PERMANGANATE OXIDATION OF 2,2,2-TRIFLUORO-1-PHENYLETHANOL AND CYANIDE ION.

by

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B.Sc., Sir George Williams College, 1954.

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We accept this thesis as conforming to the

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DOCTOR OF PHILOSOPHY

of

RONALD VAN DER LINDEN

B.Sc. Sir George Williams College, 1954

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PUBLICATIONS

1. R. Stewart and R. Van der Linden
"The Deuterium Isotope Effect in the Permanganate Oxidation of Aromatic Trifluoromethyl Alcohols" Tetrahedron Letters, **1960,** 28.

2. R. Stewart and R. Van der Linden
"The Acidity of Some Fluoro Alcohols and Ketones". Can. J. Chem. **38,** 399 (1960).

A STUDY OF THE MECHANISM OF PERMANGANATE OXIDATION OF 2, 2, 2-TRIFLUORO-1-PHENYLETHANOL AND CYANIDE ION

ABSTRACT

The mechanism of permanganate oxidation of two very different substrates have been examined. Firstly, in an attempt to elucidate the mechanism of permanganate oxidation of alcohols, a number of meta and para substituted 2, 2, 2-trifluoro-1-phenylethanols have been prepared and the kinetics of permanganate oxidation studied over a pH range of 1 to 13.3. Secondly, the reaction between permanganate and cyanide ion has been examined over the pH range 3 to 14.6.

The reaction between permanganate and 2, 2, 2-trifluoro-1-phenylethanol in aqueous alkaline solution was shown to give manganate and trifluoroacetophenone (hydrated form) in almost quantitative yield under kinetic conditions, and is therefore represented by the equation,

$$2MnO_4^- + C_6H_5CHOHCF_3 + 2OH^- \longrightarrow 2MnO_4^= + C_6H_5COCF_3 + 2H_2O$$

The kinetics of the oxidation, the high deuterium isotope effect $k_H/k_D = 16/1$, the thermodynamics and positive salt effect observed for the reaction indicate a mechanism which involves a primary ionization step to give the anion of the alcohol, and then a rate controlling bimolecular step between permanganate and the alkoxide ions to give the products.

A hydride ion transfer mechanism is somewhat invalidated in view of the observation that the rate constants obtained for the oxidations of the various phenyl substituted alcohols in alkaline solution are relatively insensitive to the nuclear substitutions. A number of mechanisms involving termolecular steps are considered to account for this latter observation.

Kinetics and oxygen^{18} tracer experiments have been performed in an attempt to elucidate the mechanism of the alkaline permanganate oxidation to cyanide. The reaction is represented by the equation,

$$2MnO_4^- + CN^- + 2OH^- \longrightarrow 2MnO_4^= + NCO^- + H_2O$$

Two routes are indicated for the production of cyanate. A process which predominates at low reactant concentrations and higher basicities involves a rate determining bimolecular reaction between permanganate and cyanide ions to give a Mn(V) species and cyanate ion. A second route was indicated by the changing kinetics at higher reactant concentrations and lower basicities, and by the observation that only 15 - 20% of oxygen^{18} was transferred from permanganate to the substrate. A mechanism is considered which involves cyanogen as an intermediate.

GRADUATE STUDIES

Field of Study: Physical Organic Chemistry

Inorganic Chemistry ..... H. C. Clark
Polymer Chemistry ..... B. A. Dunell
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ABSTRACT

The mechanisms of permanganate oxidation of two very different substrates have been examined. Firstly, in an attempt to elucidate the mechanism of permanganate oxidation of alcohols a number of meta and para substituted 2,2,2-trifluoro-1-phenylethanols have been prepared and the kinetics of permanganate oxidation studied over a pH range of 1 to 13.3. Secondly, the reaction between permanganate and cyanide ion has been examined over the pH range 3 to 14.6.

The reaction between permanganate and 2,2,2-trifluoro-1-phenylethanol in aqueous alkaline solution was shown to give manganate and trifluoroacetophenone (hydrated form) in almost quantitative yield under kinetic conditions and is therefore represented by the equation,

$$2MnO_4^- + C_6H_5CHOHCF_3 + 2OH^- \longrightarrow 2MnO_4^= + C_6H_5COCF_3 + 2H_2O$$

The trifluorophenylethanols are more acidic than the normal hydrogen containing secondary alcohols and their pKas as determined spectrophotometrically showed the following order of decreasing acidity for substitution into the phenyl ring m-NO_2 > m-Br > H > p-CH_3 > p-MeO. The rate of reduction of permanganate was followed iodometrically and the rate expression which fits the kinetic data for the alkaline catalyzed oxidation is the following:

$$V = \frac{k\ Ki}{Kw}[\text{Alcohol}][MnO_4^-][OH^-]$$

The rate of oxidation of the p-CH_3, m-Br and unsubstituted trifluorophenylethanols-1-d by permanganate was found in each case to be 16 times slower than the rate of oxidation of the corresponding protio compounds in alkaline solution. This latter result, the kinetics, i.e., the close similarity between the ionization type rate curves and the calculated ionization curves for the alcohols, the thermodynamics and positive salt effect indicate a mechanism which involves a primary ionization step to give the anion of the alcohol and then a rate controlling bimolecular step where permanganate abstracts a hydride ion from the anion.

This mechanism is somewhat invalidated in view of the observation that the rate constants obtained for oxidation of the various substituted alcohols in alkaline solution are relatively insensitive to nuclear substitution. A plot of Hammett σ values versus the log of the rate constants appears to give a smooth curve.

A number of mechanisms involving termolecular steps are considered to account for this latter observation and the large deuterium isotope effect is discussed in the light of present theories.

Kinetic and oxygen^{18} tracer experiments have been performed in an attempt to elucidate the mechanism(s) of permanganate oxidation of cyanide.

A mechanistic interpretation is attempted using the data

obtained in basic solution above pH 12 to 14.6 where the oxidation is represented by the equation,

$$2MnO_4^- + CN^- + 2OH^- \rightarrow 2MnO_4^= + NCO^- + H_2O$$

From pH 12 to 6 the reaction was found to be complex and unstoichiometric yielding cyanate, carbon dioxide, cyanide ion and finally cyanogen at pH 9 to 6.

The rate of reduction of permanganate as followed iodometrically and spectrophotometrically, is found to be markedly dependent on the pH of the medium and reactant concentration. The observation that the rate is negligible in acid solution but rapid in basic media suggests cyanide ion and not hydrocyanic acid molecule to be the primary reactive species.

At pH greater than 12 two parallel processes are indicated which have been designated as Reaction A and Reaction B. Reaction A appears at low reactant concentrations < 0.0004 M cyanide and higher hydroxyl ion concentrations $>$ pH 13. The rate of Reaction A is represented by the kinetic expression

$$-\frac{d[MnO_4^-]}{dt} = k_2[MnO_4^-][CN^-]$$

where k_2 is independent of hydroxyl ion concentration and is insensitive to the effect of manganate and barium ions. A positive salt effect is observed and labeling experiments using permanganate enriched in oxygen[18] showed that the oxygen introduced into the

product cyanate comes mainly from the oxidant (70%-80% oxygen[18] transferred). These observations suggest a mechanism which involves a rate determining bimolecular reaction between permanganate and cyanide ions to yield a Mn V species and cyanate ion.

The possibility that a second parallel process Reaction B was occurring was indicated by the changing kinetics at higher reactant concentrations and lower basicities, by the non-linear Arrhenius plots and the observation that only 15%-25% oxygen[18] transfer from permanganate to substrate had occurred at pH 13. The rate of this latter process can be tentatively represented by the kinetic expression

$$-\frac{d\left[MnO_4^-\right]}{dt} = \frac{k_3\left[MnO_4^-\right]\left[CN^-\right]^2}{\left[OH^-\right]}$$

A mode of oxidation is suggested which appears to fit these results. Permanganate, cyanide ion and a hydrocyanic acid molecule are reacted to produce a reactive species which undergoes further oxidation by permanganate to yield cyanogen. Cyanogen hydrolysis results in cyanate where oxygen is derived from the solvent.

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ACKNOWLEDGEMENTS

I would like to thank Dr. R. Stewart for his very helpful and patient direction during the course of this work.

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INTRODUCTION

The diversity with which potassium permanganate oxidizes organic and inorganic molecules has become well known. The organic functional group and reaction medium profoundly affect the mechanism by which the interchange of electrons, atoms, or both, takes place.

Various valency changes can occur with the permanganate ion on reduction.

$MnO_4^- \longrightarrow MnO_4^=$ 1 electron change.

$MnO_4^- \longrightarrow MnO_4^{\equiv}$ 2 electron change.

$MnO_4^- \longrightarrow MnO_2$ 3 electron change.

$MnO_4^- \longrightarrow Mn^{++}$ 5 electron change.

This multistage reduction of the permanganate ion creates the opportunity for the various oxidation processes which are observed. Some of the elementary steps which permanganate might undergo would be the following:

1. Simple electron interchange with no net reduction

$$Mn^*O_4^- + MnO_4^= \xrightleftharpoons{K=1} Mn^*O_4^= + MnO_4^-$$

2. Transfer of electrons or atoms or both from substrate to permanganate.

(a) Electron abstraction.

$$R + MnO_4^- \longrightarrow R\cdot + MnO_4^=$$

(b) Hydrogen atom abstraction.

$$RH + MnO_4^- \longrightarrow R\cdot + H^+ + MnO_4^=$$

(c) Hydride ion abstraction.

$$RH + MnO_4^- \longrightarrow R^+ + HMnO_4^=$$

3. Transfer of an oxygen atom from permanganate to the substrate.

$$R + O{=}MnO_3^- \longrightarrow RO + MnO_3^-$$

R or RH might be an ion or a neutral molecule. Other oxidizing species should be considered as the reactive entities in acid permanganate oxidations as well as permanganate ion itself. Evidence for each of these modes of oxidation can be observed when a survey of investigations on permanganate oxidation of organic compounds is made.

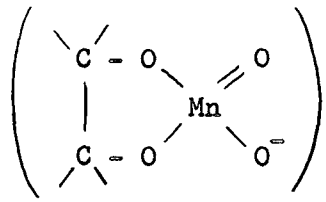
Many of these steps might be seen in the light of Taube's recent work (1) on the redox reactions of complex ions such as

$$(NH_3)_5\ Co\ X^{++} + Cr^{++} + 5H^+ \longrightarrow CrX^{++} + Co^{++} + 5NH_4^+$$

wherein he obtained evidence for the formation of a bridged structure for the activated complex. Thus oxidant and reductant are postulated to form bonds to the common group X, i.e. where X could be Cl^-, OH^-, H_2O, etc.

$$\left((NH_3)_5\ Co\text{--}X\text{--}Cr\right)^{+4}$$

For permanganate oxidation of potassium oleate in alkaline solution a bridged activated complex of this type must be formed since oxygen atoms are introduced into the substrate (2).



Another type of complex postulated by Taube is the outer sphere activated complex as against the previous examples which involves the inner coordination sphere. Sheppard and Wahl postulated this type of complex for the fast electron interchange between permanganate and manganate (3).

$$(MnO_4^{-} --- K^{+} --- MnO_4^{=})$$

whereby a loose type of complex is formed providing a lower energy path for the electron interchange.

Thus a range of intermediates might be visualized which involves varying degrees of bond breaking and bond formation in the activated complex prior to atomic or electronic rearrangement at the bridge or elsewhere in the activated complex. Many of these concepts are difficult to identify experimentally since exchange rates of isotopically labeled molecules are sometimes very rapid.

The possibility of the transfer of one or two electrons simultaneously has been the subject of much contraversy in the past. Permanganate has been designated as a mixed 1 and 2 equivalent oxidizing agent on the basis of the products produced when hydrazine (4) (5) and sulphurous acid (6) are oxidized by this reagent. It now appears as if two electrons can be transferred more or less in one step if it occurs concurrently with atom

transfer (7). Otherwise, a prohibitive activation energy would be required in order for electron transfer to occur. One equivalent oxidations can presumably take place with or without atom transfer.

A. The Oxyanions of Manganese in Alkaline Solution.

The purple, tetrahedral permanganate ion is known to decompose in alkaline solutions according to the equation

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^= + 2H_2O + O_2$$

A study of this reaction has led to many ideas regarding MnO_4^- oxidations in general and the presence of reactive intermediates which might conceivably cause oxidation if an oxidizable substrate were present.

The rate of this reaction was first studied by Ferguson, Lerch and Day (8) under various conditions of temperature and concentration of alkali but no mechanistic interpretations were made. Later Stamm suggested that the equilibrium (9)

$$MnO_4^- + OH^- \rightleftharpoons \cdot OH + MnO_4^=$$

occurred in alkaline solution with oxidation of an oxidizable substrate taking place by free hydroxy radicals.

Duke found the decomposition reaction to be greatly

increased by addition of barium ions which precipitated manganate ions as insoluble barium manganate. This worker postulated a rapid equilibrium

$$MnO_4^- + H_2O \longrightarrow MnO_4^{-2} + H^+ + \cdot OH$$

since he believed that a reaction between the like charged ions permanganate and hydroxyl ion is unlikely (10).

Kinetic studies on the alkaline decomposition of permanganate have been made by Symons who followed (11) the rate of decrease of permanganate spectrophotometrically and by the rate of evolution of oxygen gas. This worker studied the reaction over a wide range of permanganate and alkali concentration at 25°. He presented a series of reactions which appears compatible with his kinetic results and involves a series of electron and proton transfer steps;

$$MnO_4^- + OH^- \rightleftharpoons \cdot OH + MnO_4^=$$

$$\cdot OH + OH^- \rightleftharpoons \cdot O^- + H_2O$$

$$MnO_4^- + \cdot OH + \cdot O^- \rightleftharpoons MnO_4^= + HO_2^-$$

$$MnO_4^- + HO_2^- \rightleftharpoons MnO_4^= + HO_2^{\cdot}$$

$$HO_2^{\cdot} + OH^- \rightleftharpoons O_2^- + H_2O$$

$$MnO_4^- + O_2^- \longrightarrow MnO_4^= + O_2$$

Symons believes that the usual mode of oxidation of alkaline permanganate solutions is by attack of the substrate by hydroxyl radicals or hydroxy radical ions, but this conclusion is doubted by other workers (12). Evidence for the presence of

radicals in the alkaline decomposition of permanganate has been shown by Symons by initiating polymerization of acrylonitrile and styrene in alkaline solutions greater than 3 M (13) whereas in less basic solution only oxidation occurred.

Potassium manganate (Mn $\overline{\underline{VI}}$) and potassium hypomanganate (Mn $\overline{\underline{V}}$) have been made by various methods. Their anions are stable in respectively 1M and 8 M alkaline solutions and their U V spectra are known (14). In dilute alkali both these species disproportionate to the stable permanganate ion and manganese dioxide possibly via the $HMnO_4^-$ and $HMnO_4^=$ ions.

The characteristic green colour of the manganate ion can be seen to accumulate in many oxidation mixtures of permanganate and is an indication of its weaker oxidizing action. The hypomanganate anion is sky-blue in colour and has been transiently observed when hydrogen peroxide reacts with alkaline permanganate solutions (14).

When solutions of hypomanganate and permanganate are mixed the rapid reaction

$$MnO_4^{\equiv} + MnO_4^- \longrightarrow 2MnO_4^=$$

takes place (15). It is now generally believed that Mn $\overline{\underline{V}}$ species can occur as reaction intermediates where Mn $\overline{\underline{VII}}$ is reduced even though the final oxidation state of manganese in the reaction mixture is Mn $\overline{\underline{VI}}$.

The stable isotope of oxygen O^{18} has made many useful

contributions to the study of MnO_4^- oxidations in neutral or alkaline solutions. It can be introduced into permanganate by equilibrating with H_2O^{18} in slightly acid solution for a few hours at 100° (16). The corresponding exchange at room temperature under neutral or alkaline solution is slow and thus a means of tracing the route of the oxygen atoms in many oxidation mixtures becomes possible.

On the other hand, the manganate ion is labile to substitution. Symons found that when H_2O^{18} enriched water was equilibrated with alkaline manganate solutions, slow exchange takes place possibly via the protonated manganate ion and S_{N_2} substitution by hydroxyl ion (17).

?

$$MnO_4^{=} + H^+ \rightleftharpoons H\overset{*}{O}MnO_3^- + HO^- \rightleftharpoons MnO_4^{=} + \overset{*}{O}H^-$$

If permanganate is present in this mixture some O^{18} could end up in the permanganate ion presumably via the fast electron interchange between permanganate-manganate. This exchange is not hydroxyl ion dependent (3) and has a half life of 1-2 sec. (18).

B. Permanganate Oxidation of Various Substrates.

1. Oxidation by Acid Permanganate Solutions.

In strongly acid solution permanganate is reduced to the Mn $\underline{\underline{II}}$ stage. In the studies of the mechanism of acid permanganate

oxidations many reactive manganese species have been considered as the effective oxidizing agent in this media.

Permanganate ion is the first possibility as exemplified in the second order kinetics observed for the formic acid - permanganate reaction (19). Mn $\overline{IV}$ has been directly implicated as the active species (20) whereas other workers (21) postulate OH radicals produced in the reaction between Mn $\overline{IV}$ and water, as the active entity. Reactions of the latter type are characterized by induction periods, resulting in sigmoid reaction-time curves. The manganese species (22) MnO^{2+}, MnO^{+}, MnO_3^{-2}, MnO_3^{+}, have also been considered as the effective oxidizing agents. For details the reader is directed to reviews on the subject (23) (24).

2. Permanganate Oxidation of Inorganic Substrates.

Though little kinetic or mechanistic work has been done on this type of system, the present indication is that these systems are very complex.

As already indicated permanganate is designated as a mixed 1 and 2 equivalent oxidizing agent (4), from the number of products produced and the variable stoichiometry found under varying reactant concentrations and which leads to great difficulties in determining the kinetics of many inorganic reactions.

Possibly an exception to this statement is the recent work by Webster and Halpern (25) on the homogeneous permanganate-hydrogen reaction. These workers have studied the reaction over a wide range of pH and found that the rate of reaction follows the

expression,

$$-\frac{d\left[MnO_4^-\right]}{dt} = k_2\left[MnO_4^-\right]\left[H_2\right]$$

A mechanism involving hydrogen atoms was thought inconsistent with the observed activation energy and therefore, processes involving Mn V intermediates were postulated.

Hydride ion transfer to MnO_4^- or

$$MnO_4^- + H_2 \longrightarrow MnO_4^{\equiv} + 2H^+$$

Oxygen transfer from MnO_4^-

$$MnO_4^- + H_2 \longrightarrow MnO_3^- + H_2O$$

Kinetics for the Ag^+ catalyzed reaction was also obtained and a mechanism postulated. Oxidation of hydrazine by permanganate is an example of a more complex reaction. Abel (26) discussed a mode of decomposition of hydrazine via electron donating and accepting steps to N_2 and NH_3.

Thus:

$$N_2H_4 \longrightarrow NH_2^- + NH_2 - e$$

$$N_2H_4 + e \longrightarrow NH_2^- + NH_2$$

It is difficult to believe an electron rich molecule which has sufficient electrons available to form a stable molecular species

would accept another electron. Higginson, Sutton and Wright (5) indicated a number of steps are possible for the transformation.

$$N_2H_4 \xrightarrow{-2e} N_2H_2 \longrightarrow N_2$$

$$N_2H_4 \xrightarrow{-1e} N_2H_3 \nearrow 2N_2H_3 \longrightarrow N_4H_6 \rightarrow \tfrac{1}{2}N_2 + NH_3$$

$$N_2H_4 \xrightarrow{-1e} N_2H_3 \searrow N_2H_3 \xrightarrow{-1e} NH_2 \longrightarrow N_2$$

The stoichiometry of the reaction between permanganate and hydrogen peroxide in alkaline solution can be represented by the equation -

$$2MnO_4^- + 3H_2O_2 \longrightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

Fournat and Myat (27) attempted a kinetic study of the reaction by following the rate of evolution of oxygen gas. They observed the presence of a fast homogeneous reaction at high reactant concentrations and a slower heterogeneous reaction involving precipitated manganese dioxide. For the homogeneous reaction a number of intermediates are postulated such as $\cdot HO_2$ and $\cdot HO$. For their work they obtained the kinetic expression

$$\frac{d[O_2]}{dt} = 27\left[H_2O_2\right]^{1/2}\left[MnO_2^-\right]^{3/2} + 166\left[H_2O_2\right]^{1/2}\left[MnO_4^-\right]^{3/2}$$

and indicated that they were not able to devise a mechanism which would fit the data.

Pode and Waters (14) postulated a mode of oxidation by

strongly alkaline permanganate involving one electron steps

$$MnO_4^- + O_2H^- \longrightarrow MnO_4^= + HO_2^\cdot$$

$$MnO_4^- + HO_2^\cdot \longrightarrow MnO_4^= + H^+ + O_2$$

$$MnO_4^{-2} + O_2H^- \longrightarrow MnO_4^{\equiv} + HO_2^\cdot \text{ etc.}$$

since each of these oxyanions of manganese can be identified spectrophotometrically as the reduction takes place.

Hydroxylamine has been oxidized by permanganate to give a number of products in alkaline solution. NO_2^-, N_2O, N_2 were observed in the reaction mixtures (28). Permanganate can also oxidize many other inorganic species such as $SO_3^=$, Cl^-, NO_2^-, $AsO_3^=$, some quantitatively, but little work has been done in the field of kinetics and mechanism.

One of the first attempts (29) to trace the route of oxygen atoms in a permanganate oxidation was done by Halperin and Taube in the oxidation of O^{18} enriched sulphite solutions. No excess O^{18} over normal abundance was found in the precipitated manganese dioxide and led them to conclude that an electron transfer mechanism was present.

3. Permanganate Oxidation of Organic Compounds.

Only the investigations of permanganate oxidations of organic molecules or organic functional groups in neutral or alkaline solution will be reviewed, though very little work has been done, until recently, in the field of kinetics and mechanism

on alkaline permanganate oxidations.

(a) Oxidation of a Tertiary Hydrogen.

The mode of decomposition of permanganate in alkaline solution has been mentioned in a preceding section. Kenyon and Symons (30) attempted to correlate the production of reactive intermediates such as $\cdot OH$, $\cdot O^-$, in the decomposition, with the rapid and nearly quantitative conversion of branched chain carboxylic acids to their corresponding hydroxy acids in strongly alkaline solution, i.e. 3 M. When dilute alkali was used the reaction was slow leading to extensive degradation of the acid. In strongly alkaline solution, if the original acid is optically active, a racemic product is obtained whereas on oxidation by dilute manganate solutions complete retention of activity is obtained.

On the basis of the evidence given the authors state that "It is postulated that for reactions with permanganate, the active oxidant is the free hydroxy radical or the O^- radical ion".

Thus for the branched chain carboxylic acids with a tertiary hydrogen they postulate a H atom abstraction.

$$RR^1CH\,(CH_2)_n\,CO_2^- + \cdot OH \longrightarrow RR^1\dot{C}\,(CH_2)_n\,CO_2^- + H_2O$$

$$RR^1\dot{C}\,(CH_2)_n\,CO_2^- + \cdot OH \longrightarrow RR^1COH\,(CH_2)_n\,CO_2^-$$

A hydride ion transfer to the manganate ion is postulated for the other reaction producing a zwitterion type intermediate which can be stabilized by the carboxylate group. These

results have been questioned recently (31).

(b) Oxidation of Benzaldehyde in Alkaline Solution.

The permanganate oxidation of aromatic aldehydes in dilute alkali was studied by Wiberg and Stewart (32). The rate of reaction is given by the expression

$$-\frac{d[MnO_4^-]}{dt} = k\,[RCHO][MnO_4^-]\,[OH]^{1/2}$$

A kinetic isotope effect was not observed for the reaction when deuterium replaced the hydrogen in the substrate and no excess O^{18} was introduced into the substrate when permanganate enriched in O^{18} was used as oxidant indicating that the oxygen introduced into the benzoic acid came from the solvent. A chain mechanism has been suggested which is initiated by·OH even though the conditions for production of radicals was much lower than that proposed by Symons.

(c) Oxidations Involving a Transfer of Oxygen.

(i) Oxidation of aromatic aldehydes in neutral solution.

Although previous investigations of the aromatic aldehyde oxidation had been made, the first detailed study of the mechanism in neutral and basic solution was undertaken by Wiberg and Stewart (32). In neutral solution the reaction was found to

have the following characteristics:

(a) The rate is proportional to the first power of permanganate and aldehyde concentrations.

(b) When permanganate enriched in O^{18} is used as oxidant most of the oxygen introduced into the aldehyde comes from the permanganate.

(c) When deuterium replaces the α hydrogen a seven fold decrease in rate is observed indicating that a C-H bond is broken in the rate determining step.

(d) A linear free energy relation is obtained for the oxidation with a small $-\rho$ value. The reaction is found to be general acid catalyzed.

A mechanism which was postulated and fits the data is as follows:

$$RCHO + H_3O^+ \overset{K_1}{\rightleftharpoons} R\overset{+}{C}HOH + H_2O$$

$$R\overset{+}{C}HOH + MnO_4^- \overset{K_1}{\rightleftharpoons} R-\underset{H}{\overset{OH}{C}}-OMnO_3$$

$$R-\underset{O-MnO_3}{\overset{OH}{C}}-H + :B \xrightarrow{k_2} RCO_2H + HB^+ + MnO_3^-$$

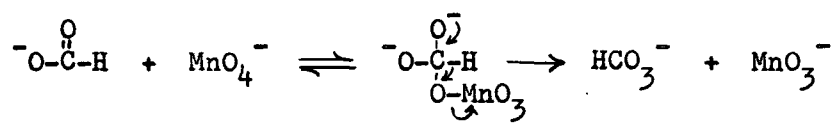
$$3MnO_3^- + H_2O \xrightarrow{fast} 2MnO_2 + MnO_4^= + 2OH^-$$

(ii) Oxidation of Formate ion.

Early work (33) (34) on the oxidation of formic acid in alkaline or neutral solution had shown that the reaction was bimolecular, independent of pH and showed a primary salt effect. Thus a reaction between formate and permanganate ions was postulated.

$$HCO_2^- + MnO_4^- \longrightarrow CO_2 + MnO_3^- + OH^-$$

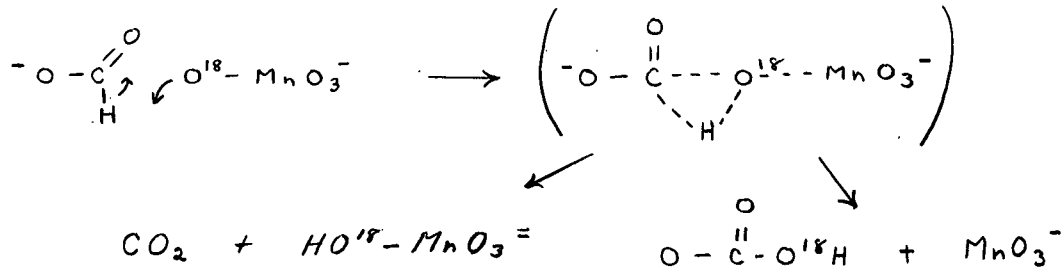
Wiberg and Stewart (35) using labeling techniques have shown that the reaction has a deuterium isotope effect $k_H/k_D = 7.4$ and there was a definite amount (8 - 30%) of O^{18} found in the CO_2 when permanganate labeled with O^{18} is used as oxidant. Though the data are difficult to interpret, a number of possibilities were suggested one of which is:



The objection to this proposal was the observation that the reaction between permanganate and the uncharged formic acid molecule is much slower and an intermediate of the type postulated should form more easily with the latter species.

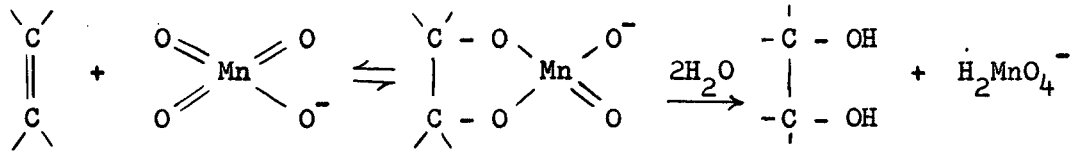
Another possibility leading to the formation of an intermediate in which both the carbon and hydrogen of the formate may be bonded to the oxygen of the permanganate. This could

lead to labeled and unlabeled carbonate depending on which bond was broken.



(iii) Oxidation of Olefins.

Since Boeseken (36) postulated the stereochemical reaction scheme in 1922 for the permanganate oxidation of olefins to a cis-glycol,



many authors have discussed this mode of oxidation and postulated other reaction schemes.

No direct evidence for Boeseken's intermediate was available until Wiberg and Saegebarth (2) applied the O^{18} labeling technique. These workers, using O^{18} enriched permanganate oxidized potassium oleate to the diol and found that up to 1.5 atoms of oxygen can be transferred from permanganate to each

olefin molecule. Thus Boesken's intermediate must have two C-O-Mn bonds which can hydrolyze between the manganese and oxygen atoms.

PART I

INTRODUCTION TO THE STUDY OF PERMANGANATE OXIDATION OF ALCOHOLS

Limited use has been made of permanganate oxidations of alcohols in preparative organic chemistry. Tertiary alcohols are relatively inert to oxidation indicating the relative stability of the C - C single bond to this reagent. Secondary alcohols can be oxidized to their corresponding ketones but these ketones usually suffer from degradation by the oxidant resulting from enolization when an α - hydrogen is present (37). Primary alcohols can be oxidized more readily to the aldehyde but this stage is oxidized very quickly to the more stable acid.

Some mechanistic work has been done in acid solution but little work has been attempted in neutral or basic solution. Merz, Stafford and Waters (20) investigated the system isopropyl alcohol-hydrogen peroxide-permanganate in acid media. These workers concluded that isopropyl alcohol was oxidized by an induced process which possibly involved Mn^{+4}.

Cullis and Ladbury (37) have studied the oxidation of benzyl alcohol, 1-and 2-phenylethanols in 52.4% W/V aqueous acetic acid and showed the reactions were initially first order in substrate and MnO_4^-. No attempt was made to interpret their kinetics in terms of a mechanism.

Stewart (38) chose the secondary alcohol benzhydrol to use in his mechanism studies of the oxidation of alcohols by permanganate mainly because it gives a single product benzophenone in high yields which is stable to further attack. He showed that the reaction could be represented by the equation;

$$(C_6H_5)_2\ CHOH + 2MnO_4^- + 2OH^- \longrightarrow (C_6H_5)_2\ C = O + 2MnO_4^= + 2H_2O$$

Manganate accumulates during the oxidation and oxidizes benzhydrol at one-fortieth the rate of permanganate oxidation. By following the rate of decrease of the MnO_4^- ion iodometrically and spectrophotometrically, he found the rate to be proportional to the first power of benzhydrol, permanganate and hydroxyl ion. A positive salt effect is observed indicating a reaction between two similarily charged ions. When benzhydrol-α-d was oxidized an isotope effect was found; $k_H/k_D = 6.6$. When MnO_4^- enriched in O^{18} was used as oxidant no excess O^{18} was found in the product benzophenone.

These observations led to a mechanism involving a hydride ion transfer from the benzhydrylate ion to the permanganate ion.

$$(C_6H_5)_2\ CHOH + OH^- \overset{K}{\rightleftharpoons} (C_6H_5)_2\ CHO^- + H_2O$$

$$(C_6H_5)_2\ \overset{H}{\overset{|}{C}}-O^- + MnO_4^- \xrightarrow{slow} (C_6H_5)_2\ C=O + HMnO_4^=$$

$$HMnO_4^= + MnO_4^- \longrightarrow 2MnO_4^= + H^+$$

The following investigation was undertaken to further

elucidate the mechanisms of alkaline permanganate oxidation of alcohols as presented by Stewart in the previous paper. The main idea underlying the choice of substrate in this study was to find an organic secondary alcohol whose hydroxyl proton was much more acidic than that of benzhydrol. Also, the alcohol must be oxidized nearly quantitatively to the ketone and that this ketone be stable to permanganate. The 2,2,2-trifluoro-1-phenylethanols fitted these requirements well.

EXPERIMENTAL

A. Synthesis, Purification and Identification of the 2,2,2-Trifluoro-1-phenylethanols.

1. Preparation of the substituted trifluoroacetophenones.

(a) Synthesis of p-methyltrifluoroacetophenone.

To a 500 ml. 3 necked round bottom reaction flask, fitted with reflux condensor, mercury seal stirring apparatus and dropping funnel was added magnesium turnings (5 grams, 0.206 moles.). The apparatus was warmed with a small flame and allowed to cool with a calcium chloride drying tube fitted to the condensor top. Thirty-five millilitres of dry ethyl ether was added along with 25 ml. p-bromotoluene (34.7 grams, 0.203 moles.). The reaction was started by heating with steam for 10 minutes after which a further 60 ml. of ether was added. When the Grignard reaction was complete 150 ml. of dry ether was added and trifluoroacetic acid (7.5 grams, 0.066 moles.) in 20 ml. of ether was added dropwise with vigorous stirring over a period of two hours at room temperature. After refluxing for one hour, the reaction mixture was poured into a 10% sulphuric acid-ice mixture from which the organic material was extracted with ether several times. The ethereal solution was dried with magnesium sulphate and then the ether removed under vacuum. The crude material was fractionally distilled and a clear fraction boiling at 69° at 13 mm. was obtained; yield 30 - 50%. A crystalline solid remained in the

distilling flask which was probably di-p-tolyl trifluoromethyl carbinol. The clear liquid gave a 2,4-dinitrophenylhydrazone derivative, m.p. 133-136°; refractive index $1.4710^{25°}$, literature $1.4693^{20°}$(39).

Analysis; Calculated for $C_9H_7OF_3$: C,57.4; H,3.72; F,30.3;
Found: C,57.77; H,3.92; F,26.81.

(b) Synthesis of m-bromotrifluoroacetophenone.

To a Carius tube of approximately 100 ml. volume was added trifluoroacetophenone (20 grams, 0.115 moles.), 0.1 gram of anhydrous ferric chloride and bromine (9 ml., 0.168 moles.). The mixture was cooled in liquid N_2 before sealing the tube and then heated in a furnace for six days at 130°. The reaction mixture was allowed to cool to room temperature before freezing the tube in liquid N_2. The tube was then opened and allowed to stand in a fume hood overnight to remove excess bromine and hydrogen bromide gas. The organic liquid was extracted several times with aqueous sodium bromide to remove the catalyst and remaining bromine. The mixture was then fractionally distilled and gave a small amount of unreacted trifluoroacetophenone, a solid material which precipitated out in the distilling flask, and a clear fraction boiling at 83.5° at 12 mm.; yield 50%. (refractive index $1.5030^{24°}$) The latter compound gave a 2,4-dinitrophenylhydrazone derivative, m.p. 121.5 - 123°.

Analysis; Calculated for $C_8H_4OF_3Br$: C,38.0; H,1.52; F,22.50;
Found: C,38.17; H,1.56; F,20.63;
Calculated for 2,4-dinitrophenylhydrazone derivative
$C_{14}H_8O_4N_4F_3Br$: C,38.6; H,1.85; N,12.9; F,13.18;

Found: C,38.8; H,2.52; N,11.95; F,12.02.

As a further check on the identity of the above liquid, one gram of the liquid was dissolved in 20 ml. of 2 M sodium hydroxide and heated on a steam bath. A gas was evolved presumably fluoroform (40) and on acidification of the solution there precipitated a white solid which on recrystallization from ethanol-water mixture gave a m.p. of 152 - 153°; literature m.p. of m-bromobenzoic acid 154 - 155°. A mixed melting point with m-bromobenzoic acid showed no depression.

(c) Preparation of m-nitrotrifluoroacetophenone.

To a 400 ml. beaker immersed in a salt-ice mixture was added trifluoroacetophenone (27.2 ml., 0.2 moles.). Sixty ml. of concentrated sulphuric acid was added slowly and the temperature of the mixture was kept at 0° or less. Manual stirring was maintained throughout the reaction. Sixteen ml. of the nitrating acid (made up from 12 ml. concentrated nitric acid plus 4 ml. fuming nitric acid and 24 ml. concentrated sulphuric acid) were mixed and added dropwise to the sulphuric acid - ketone mixture, keeping the temperature below 0°. A yellow solid precipitated out of the reaction mixture after part of the nitrating mixture had been added. When no further temperature increase was observed the addition was stopped and the whole mixture poured on to crushed ice. Several ether extractions were made, the ethereal extracts were washed with water, dried with magnesium sulphate and the ether evaporated under vacuum. The resulting yellow oil gave on fractional distillation a pale yellow low melting solid which distilled at 113° at 12 mm.;

yield 75%. The solid gave a 2,4-dinitrophenylhydrazone derivative m.p., 128 - 132°. Alkaline hydrolysis gave m-nitrobenzoic acid which gave no depression of melting point when mixed with an authentic sample.

Analysis; Calculated for $C_8H_4O_3F_3N$: C,43.80; H,1.83; F,26.0; N,6.38;

Found: C,43.36; H,1.88; F,24.32; N,6.62.

Calculated for 2,4-dinitrophenylhydrazone derivative $C_{14}H_8O_5N_5F_3$: C,42.2; H,2.00; N,17.56; F,14.30;

Found: C,43.10; H,2.76; N,17.04; F,13.42.

(d) Synthesis of p-methoxytrifluoroacetophenone.

This compound was prepared and purified in a similar manner to p-methyltrifluoroacetophenone except the starting material was p-bromoanisol. B.pt. 64° at 0.5 mm.; N_D^{23} = 1.5051. Gave a 2,4-dinitrophenyhydrazone derivative m.p., 104 - 105° (dec.).

Analysis; Calculated for $C_9H_7F_3O_2$: C,52.9; H,3.5;

Found: C,51.9; H,3.6.

2. Purification of trifluoroacetophenone:

Trifluoroacetophenone was obtained from Columbia Organic Chemicals. The impure yellow liquid was redistilled under vacuum before use and gave a 2,4-dinitrophenylhydrazone derivative, m.p 107 - 108°: literature 106 - 107.5° (41).

3. Preparation of the unsubstituted, m-bromo, and p-methyl 2,2,2-trifluoro-1-phenylethanols and their corresponding 1-deuterio alcohols by reduction of the ketones with lithium aluminum hydride and deuteride.

A typical procedure was carried out as follows:

To a 250 ml. 3 necked round bottomed flask fitted with dropping funnel, reflux condensor and drying tube was added trifluoroacetophenone (13.6 grams, 0.078 moles.) in 40 ml. ether. To this mixture was added slowly lithium aluminum hydride (0.8 grams, 0.0216 moles.) in 30 ml. ether. The reaction mixture was decomposed on a sulphuric acid-ice mixture and the ethereal solution separated. Further extractions with ether were made and the combined ethereal extracts were washed with sodium bicarbonate solution, dried with magnesium sulphate and the ether evaporated under vacuum to give an oil which on fractional distillation under vacuum gave a clear fraction boiling at 82° at 13 mm; refractive index $1.4590^{25°}$, literature $1.4610^{20°}$ (42). The yields of crude product before purification were of the order of 80 - 90%.

4. (a) Preparation of 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol by reduction with aluminum isopropoxide in isopropyl alcohol.

To a 100 ml. round bottomed flask fitted with a vigreux column and arranged at the top for distillation was added m-nitrotrifluoroacetophenone (10 grams, 0.045 moles.) dissolved in 40 ml. of dry isopropyl alcohol and aluminum isopropoxide (8.2 grams,

0.04 moles.). The mixture was heated in a steam bath in order to keep 5 - 10 drops of acetone-isopropyl alcohol mixture distilling off per minute. The presence of acetone was checked in the distillate by means of the 2,4-dinitrophenylhydrazone test. After one hour 12 ml. of isopropyl alcohol was added. After continuing the reaction for another hour, the mixture was poured on to a 3 M HCl - ice mixture. The mixture was extracted with ether, washed with water, dried with magnesium sulphate and then evaporated to remove the solvent yielding a dark coloured oil. Vacuum distillation yielded a yellow viscous oil which came over at 106° at 2 mm. and which crystallized on standing. Recrystallization from benzene-petroleum ether gave pale yellow needle like crystals m.p. 47 - 48°.

(b) Preparation of 2,2,2-trifluoro-1-(p-methoxyphenyl)-ethanol.

This compound was prepared by essentially the same method as described for the m-nitrocarbinol and purified by gas chromatography.

5. Further purification of the 2,2,2-trifluoro-1-phenylethanols.

Great difficulty was encountered in removing the small traces of impurities in the alcohols even after repeated fractional distillation. (The presence of reducing impurities was observed from the kinetic plots; 2 - 5% of the permanganate was quickly reduced before the rate plots become linear.)

The purity of the liquid fluorinated alcohols was checked and samples collected, if necessary, by gas chromatography. An Aerograph Gas Chromatographic instrument using a commercial silicone 5-E column was used for this purpose.

2,2,2-Trifluoro-1-protio and 1-deuterio-1-(m-bromophenyl)-ethanols were found to be sufficiently pure but the protio and deuterio compounds of the p-methyl and the unsubstituted alcohols required fractionation by this method. They were injected by hypodermic syringe and samples collected for the kinetic experiments.

The solid ketone m-nitrotrifluoroacetophenone was dissolved in ether and injected into the Chromatographic instrument. A single peak was observed on the chromatogram except for the sharp ethereal peak with a retention time of a few seconds.

6. Physical properties and analysis of the various 2,2,2-trifluoro-1-phenylethanols and their phenylurethan derivatives.

(a) Physical properties.

$Y\text{-}C_6H_4CHOHCF_3$	Boiling Point or Melting Point	Refractive Index Protio	Refractive Index Deuterio	Melting Point Phenylurethan
p - MeO	80° (0.5 mm)	1.4780 $^{23°}$	-	-
p - CH_3	94.5° (12 mm)	1.4650 $^{24°}$	1.4662 $^{24°}$	104 - 105°
H	82° (13 mm)	1.4590 $^{25°}$	1.4600 $^{25°}$	103 - 104°
m - Br	115° (12 mm)	1.5005 $^{27°}$	1.5016 $^{27°}$	-
m - NO_2	47 - 48°	-	-	102 - 103°

(b) Analysis.

(i) 2,2,2-Trifluoro-1-(p-methylphenyl)-ethanol.

Calculated for $C_9H_9F_3O$: C,56.9; H,4.73; F,30.0;

Found: C,57.07; H,4.99; F,26.57.

Phenylurethan derivative; Calculated for $C_{16}H_{14}F_3O_2N$; C,62.10; H,4.53; F,18.4; N,4.53;

Found: C,62.14; H,4.46; F,16.7; N,5.12.

Found for p-$CH_3C_6H_4CDOHCF_3$: C,57.03; H,4.82.

(ii) 2,2,2-Trifluoro-1-phenylethanol.

Phenylurethan derivative; Calculated for $C_{15}H_{12}F_3O_2N$; C,61.0; H,4.07; F,19.30;

Found: C,61.19; H,4.17; F,19.02;

Calculated for $C_6H_5CDOHCF_3$: C,54.2; H,4.52.

Found: C,55.23; H,4.12.

(iii) 2,2,2-Trifluoro-1-(m-bromophenyl)-ethanol.

Calculated for $C_8H_6F_3BrO$; C,37.65; H,2.35; F,22.4; Br,31.4;

Found: C,37.98; H,2.48; F,19.95; Br,31.64.

Found for m-$BrC_6H_4CDOHCF_3$: C,37.35; H,2.38.

(iv) 2,2,2-Trifluoro-1-(m-nitrophenyl)-ethanol.

Calculated for $C_8H_6F_3O_3N$; C,43.50; H,2.72; F,25.8; N,6.34;

Found: C,43.73; H,3.15; F,23.67; N,6.37.

Phenylurethan derivative; Calculated for $C_{15}H_{11}O_4F_3N$; C,53.0; H,3.24; F,16.78; N,8.23;

Found: C,53.12; H,3.56; F,16.31; N,8.35.

(v) 2,2,2-Trifluoro-1-(p-methoxyphenyl)-ethanol.

Calculated for $C_9H_9F_3O_2$; C,52.4; H,4.4;

Found: C,52.2; H,4.6.

7. Isotopic purity and functional group analysis by I.R. spectroscopy for the 2,2,2-trifluoro-1-phenylethanols.

In order to check the isotopic purity of the deuteriated alcohols, the infrared spectra of the carbon tetrachloride solutions of the three pairs of protio-deuterio compounds were taken. The absence of the C-H stretching peak at 2895 cm^{-1} and the presence of a new peak at a lower frequency, 2150 cm^{-1}, indicated their isotopic purity. The 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol was dissolved in chloroform and the spectrum obtained. The presence of an hydroxyl absorption peak at 3560 cm^{-1} and the absence of a carbonyl peak at approximately 1700 cm^{-1} was also observed for the 2,2,2-trifluoro-1-phenylethanols.

B. Kinetic Experiments.

1. Reagents used in the kinetic experiments.

(a) 2,2,2-trifluoro-1-phenylethanols.

Aqueous solutions of the alcohols as prepared and purified by the previous methods were made by weighing given quantities into volumetric flasks. No attempt was made to find maximum solubility of these fluorinated phenylethanols in water at room temperature. Solution molarities were; p-methyl-0.004 M ; unsubstituted - 0.009 M ; m-bromo-0.0035 M ; m-nitro-0.005 M.

(b) Potassium permanganate and sodium hydroxide solutions were made up and standardized as given in Part II of the thesis (experimental section). Reagent grade potassium sulphate, potassium nitrate and dipotassium hydrogen phosphate were used.

2. Kinetic method.

An iodometric method for following the rate of disappearance of the permanganate ion was found suitable for following the oxidation of 2,2,2-trifluoro-1-phenylethanol to trifluoroacetophenone.

A typical kinetic run was carried out as follows:

To a 250 ml. volumetric flask was added 30 ml. 2 M sodium hydroxide, 50.9 ml. 0.003 M, 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol solution and the mixture brought up to the mark with boiled distilled water. Eight 25 ml. aliquots of this solution were pipetted into 125 ml. glass stoppered erlenmeyers and brought to a temperature of 25.2 $\pm$ 0.05° in a constant temperature bath. To each of these solutions was added 4.87 ml. of 0.00627 M potassium permanganate solution from a fast delivery pipette (tip removed)

with manual stirring and the timer started. After a given time interval the reaction was quenched with an acidified potassium iodide solution and the resulting iodine immediately titrated with thiosulphate solution from a 5 ml. capacity microburette using the starch indicator end point. Overall concentrations used here were; sodium hydroxide, 0.2 M, $[\text{Alcohol}]_o = 5.1 \times 10^{-4}$ m/l, $[MnO_4^-]_o = 2\ [\text{Alcohol}]_o$.

For the reaction in weakly basic solution pH less than 11.7 a 2:3 ratio of permanganate to alcohol was used. Dipotassium hydrogen phosphate was used as buffer with addition of concentrated acid or base to vary the pH. Potassium nitrate was used in these experiments to maintain the ionic strength at 0.2. Potassium sulphate was used as the inert electrolyte to determine the effect of salt concentration on the rate of reaction. Use of this kinetic method and its limitations has been dealt with in another section. Series of experiments were run using the same solutions to make the results self consistent though good precision (3%) in the rate constants was obtained when results were repeated from time to time using newly prepared solutions.

3. Trifluoroacetophenone analysis in the oxidation mixture.

Attempts to extract the ketone from aqueous solution quantitatively under the low kinetic concentrations used with ethyl ether were unsuccessful, though a positive 2,4-dinitrophenylhydrazone test could be obtained and a melting point taken. Thus a spectrophotometric study in the ultraviolet was undertaken

using the Beckman DU spectrophotometer.

Trifluoroacetophenone and 2,2,2-trifluoro-1-phenylethanol were shown to have a benzene-like spectra in the U V. The extinction coefficients at a wavelength of 260 mμ were respectively 438 and 204.

Method of Analysis.

To a 125 ml. glass stoppered erlenmeyer were added 40 ml. H_2O, 2.3 ml. of 2.18 M NaOH solution (resulting solution, 0.1 M), 2.8 ml. of 0.00728 M 2,2,2-trifluoro-1-phenylethanol solution and finally 5 ml. of 0.00824 M permanganate solution with stirring. Manganate was observed to accumulate and after one hour the manganate was reduced with a few drops 30% H_2O_2 and the solution made slightly acidic before filtering off the MnO_2 to obtain a clear solution. The optical density at 260 mμ was measured in a one cm. absorption cell and the concentration of trifluoroacetophenone calculated.

4. A spectrophotometric method for determining the pKas of the various substituted and unsubstituted 2,2,2-trifluoro-1-phenylethanols.

A difference in the ultraviolet spectra of the trifluoro-1-phenylethanols was observed when the spectra were taken in neutral or alkaline solution. This spectral difference was attributed to an ionization equilibrium between the unionized and ionized trifluoro-1-phenylethanols. Table IX lists the pKas,

maximum wavelengths and extinction coefficients for the various compounds investigated in their ionized or undissociated forms.

Sample pKa determination for 2,2,2-trifluoro-1-phenylethanol.

Ten ml. of 0.00708 M 2,2,2-trifluoro-1-phenylethanol solution plus 10 ml. of 0.02 M phosphate buffer (made up with 0.02 M disodium hydrogen phosphate solution plus 1 N potassium hydroxide or 1 N sulphuric acid to give the approximate pH desired) was diluted to 25 ml. in a volumetric flask. The optical density of the solution was measured at 260 mμ on the Beckman DU Spectrophotometer and then the pH of the remaining solution was determined using a Beckman Model G pH meter. (The Beckman pH meter was standardized against pH = 10.00 buffer). A number of solutions were prepared at various pHs for the alcohol and the above process repeated. The pKa was calculated using the equation

$$pK = pH + \log \frac{(HA)}{(A^-)}$$

A typical series of calculations are as follows:

pH	D_{260}			
7.5	0.564	$D_{HA}^{(b)} = 0.567$		
8.9	0.570			
11.27	0.533		$pKa^{(c)}$ = 11.27 + 0.67	= 11.94
11.83	0.475		= 11.83 + 0.05	= 11.88
11.83	0.484		= 11.83 + 0.12	= 11.95
12.21	0.431		= 12.21 - 0.36	= 11.85
13.6[a]	0.375	$D_{A^-}^{(b)} = 0.372$		
13.8[a]	0.372			

Mean.....11.90

(a) 0.4 N and 0.6 N in sodium hydroxide respectively, pH calculated directly from hydroxyl ion concentration.

(b) D_{HA} is expected optical density at 260 mμ for 0% ionization, D_{A^-} for 100% ionization based on pKa = 11.9.

(c) Sample calculation - $pKa = pH + \log \frac{(HA)}{(A^-)}$

$$= 11.27 + \log \frac{0.533 - 0.372}{0.567 - 0.533}$$

$$= 11.27 + 0.67 = 11.94$$

RESULTS

A. Stoichiometry and Product Analysis.

The reaction between aqueous alkaline permanganate and 2,2,2-trifluoro-1-phenylethanol can be shown to be nearly quantitative under kinetic conditions and showed the following stoichiometry.

$$2MnO_4^- + C_6H_5CHOHCF_3 + 2OH^- \longrightarrow 2MnO_4^= + C_6H_5COCF_3 + 2H_2O$$

Below pH 12 manganate disproportionates and the stoichiometry becomes

$$2MnO_4^- + 3C_6H_5CHOHCF_3 + 2H^+ \longrightarrow 2MnO_2 + 3C_6H_5COCF_3 + 4H_2O$$

1. Trifluoroacetophenone analysis.

A spectrophotometric method was found suitable to analyze for trifluoroacetophenone. This ketone was shown to be present in 95% yield when permanganate oxidized 2,2,2-trifluoro-1-phenylethanol in 0.1 M sodium hydroxide solution under kinetic concentrations. (See experimental section). Similar results were obtained for the deuterio alcohol and for the oxidation in slightly basic solution i.e. pH = 11. Trifluoroacetophenone was found to be resistant to alkaline permanganate oxidation and to basic hydrolysis in dilute sodium hydroxide over long periods of time at room temperature.

2. Oxidizing power of the reaction mixture.

When the oxidation reaction is carried out in the presence of barium ions under kinetic concentrations, a clear solution results after a few hours in alkaline solution due to precipitation of the manganate as insoluble barium manganate. The final oxidizing power of this solution as determined iodometrically is within 5% of that expected from the amount of permanganate originally present. Similar results are obtained in the absence of Ba^{++} though small amounts of permanganate are difficult to observe when the green manganate ion is present in excess.

3. Evidence for a hydrated ketone.

The observation that the extinction coefficients in the ultraviolet spectrum of trifluoroacetophenone in aqueous solution at the maximum of 260 mμ gave a rather small value is surprising in as far as acetophenone is known to have an extinction coefficient of 12,500 in the same medium. The low value for trifluoroacetophenone was thought to be due to an immediate hydration of the carbonyl function in aqueous solution destroying the chromophoric group. To test this idea a sample of the ketone was dissolved in spectroscopically pure cyclohexane and the U V spectrum taken. The extinction coefficient at a λ maximum of 253 mμ was found to be 13,300. If trifluoroacetophenone is dissolved in ethyl alcohol a high extinction coefficient (4000)

at 253 mμ is observed five minutes after combining solute and solvent. After 100 minutes this value has dropped to 500 indicating the slow formation of another species. It appears, therefore, as if the stable forms of trifluoroacetophenone in aqueous or alcoholic solutions are respectively the hydrated ketone and the hemiketal.

Similar observations have been made by other investigators (43) working with fluorinated organic compounds which have the highly electronegative fluorine atoms substituted alpha to a carbonyl function.

4. Oxidation by manganate.

The measurement of the rate of manganate oxidation of the 2,2,2-trifluoro-1-phenylethanols was undertaken, although manganate is observed to accumulate during permanganate oxidation of these secondary alcohols in alkaline solution.

Alkaline manganate solutions were prepared by the method of Waters (14). The iodometric method was used to follow the rate of oxidation of trifluoro-1-(m-bromophenyl)-ethanol and the corresponding 1-deuterio compound in essentially the same manner as for permanganate oxidations. Linear second order rate plots

were obtained using the expression –

$$k_2 = \frac{1}{[\text{Alcohol}]_o \times t} \cdot \frac{V_o - V_t}{V_t - \frac{1}{2}V_o}$$

and k_2 obtained from the plots.

Kinetic data for manganate oxidation of trifluoro-1-(m-bromophenyl)-ethanols. $[MnO_4^-]_o = [\text{Alcohol}]_o = 5.82 \times 10^{-4}$ M.

	$m\text{-}BrC_6H_4CHOHCF_3$ k_2, l.mole^{-1}sec.$^{-1}$	$m\text{-}BrC_6H_4CDOHCF_3$ k_2, l.mole^{-1}sec.$^{-1}$	k_H/k_D
$[OH^-] = 0.2$ M	0.0906	0.0068	13.3
$[OH^-] = 0.6$ M	0.107		

The results show that manganate oxidation occurs eightly times slower than the permanganate oxidation of trifluoro-1-phenyl-ethanols and also that these secondary alcohols show a high deuterium isotope effect on oxidation by manganate. Increasing the alkalinity from 0.2 M in hydroxyl ion to 0.6 M in hydroxyl ion, should cause a decrease in rate if oxidation is occurring by the permanganate ion through disproportionation. This was not observed.

B. Kinetics.

1. Reaction Order.

An integrated rate expression for a second order reaction was derived by Stewart (32) for permanganate oxidation in alkaline solutions where thiosulphate is used in an iodometric titration and where stoichiometric concentration of reactants are present throughout the oxidation.

For the reaction when manganate accumulates, the molar ratio of permanganate to 2,2,2-trifluoro-1-phenylethanol is 2:1 and the integrated rate expression becomes -

$$k_2 = \frac{1}{\left[C_6H_5CHOHCF_3\right]_o t} \times \frac{V_o - V_t}{V_t - 4/_5V_o} \qquad (1)$$

where V_o = the initial volume of thiosulphate

V_∞ = $4/_5V_o$, the final volume (usually calculated)

V_t = volume used at time t.

$\left[C_6H_5CHOHCF_3\right]_o$ = m./l. at t = o.

When manganate disproportionates at lower alkalinities the ratio of 2:3 is used and the relation

$$k_2 = \frac{1}{\left[C_6H_5CHOHCF_3\right]_o t} \times \frac{V_o - V_t}{V_t - 2/_5V_o} \qquad (2)$$

is applied to the rate data. Equations (1) and (2) were used in this kinetic study except where indicated. When the appropriate expression either $V_o-V_t/V_t-4/_5V_o$ or $V_o-V_t/V_t-2/_5V_o$ was plotted

against time linear plots were obtained in most cases indicating that the reaction is second order. Second order rate constants were calculated from the slopes obtained in this way.

In order to show whether the rate of reaction was proportional to the first power of 2,2,2-trifluoro-1-phenylethanol and permanganate, the molar ratio of reactants was varied from 1:2 to a 1:1 and a 1:4 ratio. Stewart found that the integrated rate expression for the 1:1 molar ratio was

$$k_2 = \frac{4.61}{\left[C_6H_5CHOHCF_3\right]_o \, t} \cdot \log \frac{V_t - 3/_5 V_o}{V_t - 4/_5 V_o} \qquad (3)$$

and for the 1:4 molar ratio

$$k_2 = \frac{-2.30}{\left[C_6H_5CHOHCF_3\right]_o \, t} \cdot \log \frac{V_t - 9/_{10} V_o}{V_t - 4/_5 V_o} \qquad (4)$$

Applying the relations (3) and (4) to the rate date for the oxidation of the protio and deuterio, trifluoro-1-phenylethanols under the various conditions given, linear second order rate plots were obtained when time was plotted against the logarithmic functions. The rate constants were obtained from these plots (Figure 1). The observation (Table I) that the rate constants are insensitive to variations in reactant concentrations shows that the reaction is in agreement with the rate expression -

FIGURE 1

Typical kinetic plots for the alkaline permanganate oxidation of 2,2,2-trifluoro-1-phenylethanols.

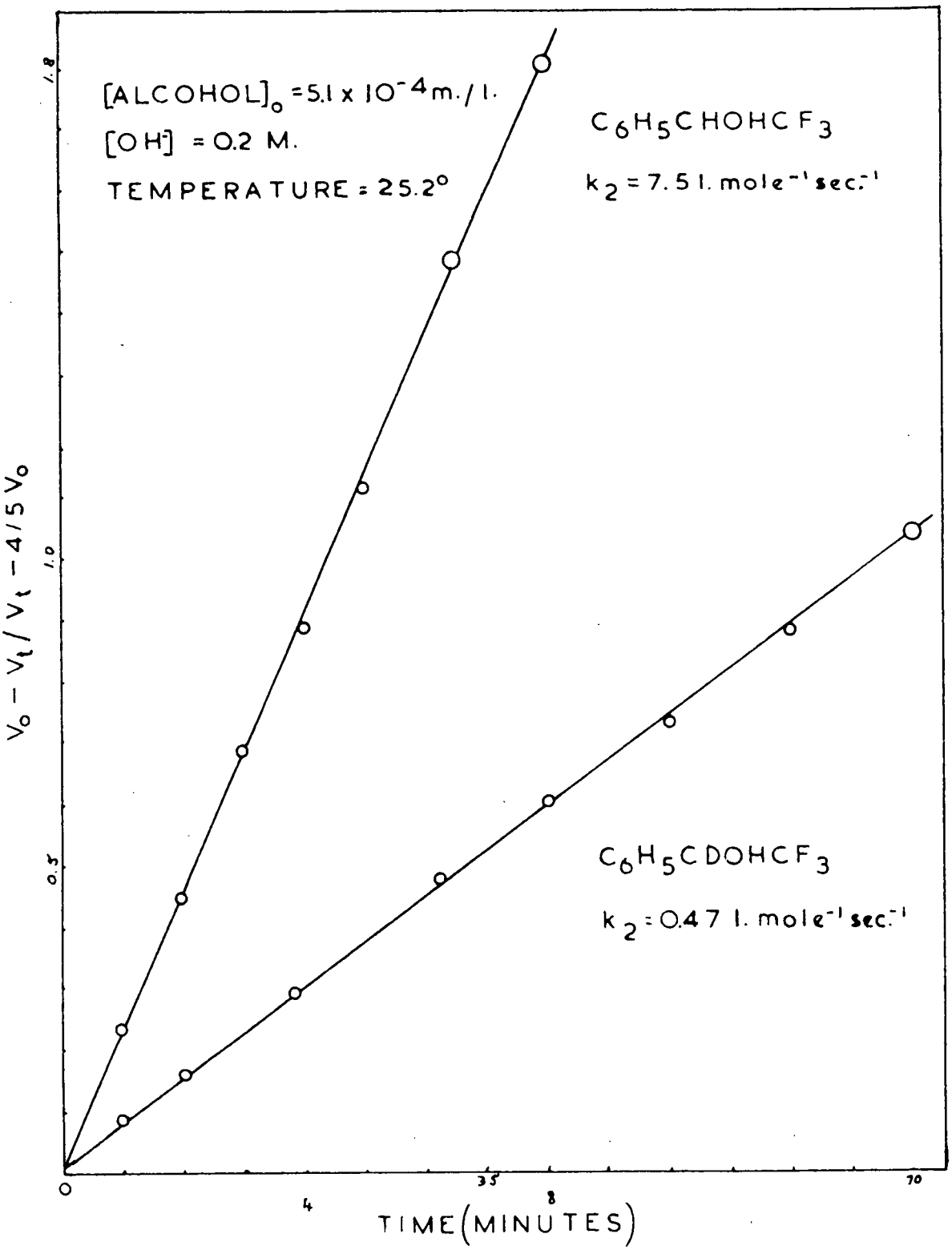


TABLE 1

Rate constants as a function of reactant concentration for the protio and deuterio 2,2,2-trifluoro-1-phenylethanols.

$[MnO_4^-]_o$ - M	$[C_6H_5CHOHCF_3]_o$ - M	$[C_6H_5CDOHCF_3]_o$ - M	k_2[a], l. mole^{-1}sec.$^{-1}$	
7.38×10^{-4}	7.38×10^{-4}		7.6	3
7.38×10^{-4}	1.84×10^{-4}		8.1	4
7.38×10^{-4}	3.69×10^{-4}		8.0	1
10.20×10^{-4}	5.10×10^{-4}		7.5	1
13.50×10^{-4}		13.50×10^{-4}	0.50	3
13.50×10^{-4}		6.74×10^{-4}	0.50	1
13.50×10^{-4}		3.36×10^{-4}	0.54	4
10.20×10^{-4}		5.10×10^{-4}	0.47	1
10.20×10^{-4}		10.20×10^{-4}	0.49	3

(a) Rate constants obtained using equations (1), (3) or (4).

$[NaOH] = 0.2$ M; Temperature $25.2 \pm 0.05°$.

$$-\frac{d[MnO_4^-]}{dt} = k_2 [Alcohol][MnO_4^-]$$

2. Rate of reaction as a function of hydroxide ion concentration.

The rate of reaction is found to change markedly with increasing alkalinity at a constant ionic strength (e.g. a 2500 increase in rate is observed in proceeding from pH = 9 to a pH = 13 solution indicating the oxidation to be a base catalyzed reaction. A plot (Figure 2) of k_2 versus $[OH^-]$ shows a sharp increase in rate at low pH with a leveling off at higher alkalinities indicating the presence of a limiting concentration of a reactive species. The reaction is not simple first order in hydroxide ion as was the case for the benzhydrol-permanganate reaction since a plot of this type would be linear.

3. Influence of ionic strength.

Brönsted, Debye and Hückel developed an equation for predicting the effect of ionic strength on the rate of ionic reactions in dilute solutions (less than 0.01 M).

$$\log k = \log k_o + Z_A Z_B \sqrt{\mu} \qquad (5)$$

The equation predicts a linear relationship if log k is plotted against the square root of the ionic strength with a slope

proportional to the product of $Z_A Z_B$. Thus for a reaction between like singly charged ions, the equation predicts a line of slope +1.

By increasing the amounts of potassium sulphate added initially to the permanganate - 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol reaction mixture at 0.01 M sodium hydroxide, an increase in rate is observed, i.e., a positive salt effect. A plot of log k_2 versus $\sqrt{\mu}$ (Figure 3) for the reaction gives a curve with an approximate slope of 0.5. This result is not unexpected since the ionic strength used in the experiment is in a region where equation (5) is not expected to hold.

Harty and Rollefson (44) have more recently developed a relationship for studying ionic reactions in more concentrated solutions,

$$\log k = \log k_o + \frac{1.02\ Z_A Z_B}{B + 1/\sqrt{\mu}} \qquad (6)$$

where log k is plotted against a parameter which depends on both the ionic strength and the particular salt used. The constant B is equal to 3.26 since potassium sulphate is used as the added electrolyte. Thus a plot of log k versus $\frac{1}{3.26 + 1/\sqrt{\mu}}$ for the oxidation gave a straight line with a positive slope of 1.4; (Figure 4).

FIGURE 2

Plots of k_2 versus hydroxyl ion concentration for the permanganate oxidation of various 2,2,2-trifluoro-1-phenylethanols.

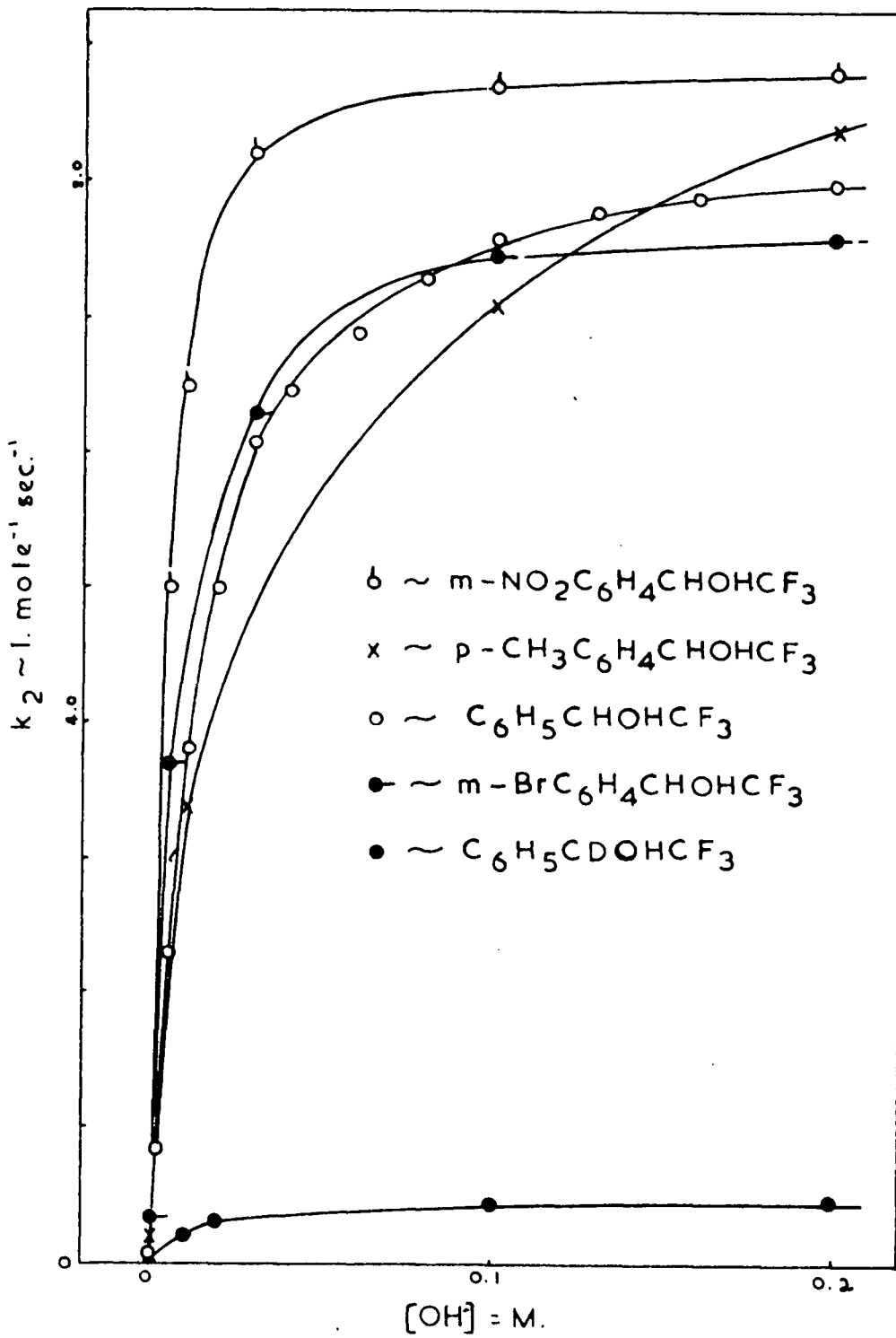


FIGURE 3

Plot of $\log k_2$ versus $\sqrt{\mu}$ for the permanganate: 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol reaction.

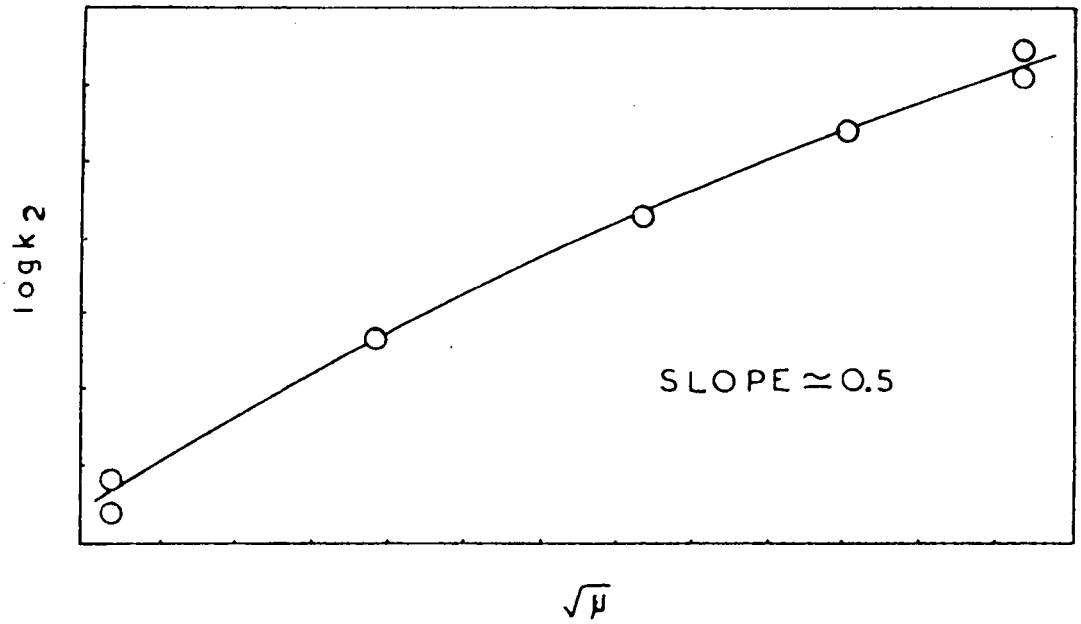


FIGURE 4

Plot of $\log k_2$ versus $\frac{1}{3.26 + 1/\sqrt{\mu}}$

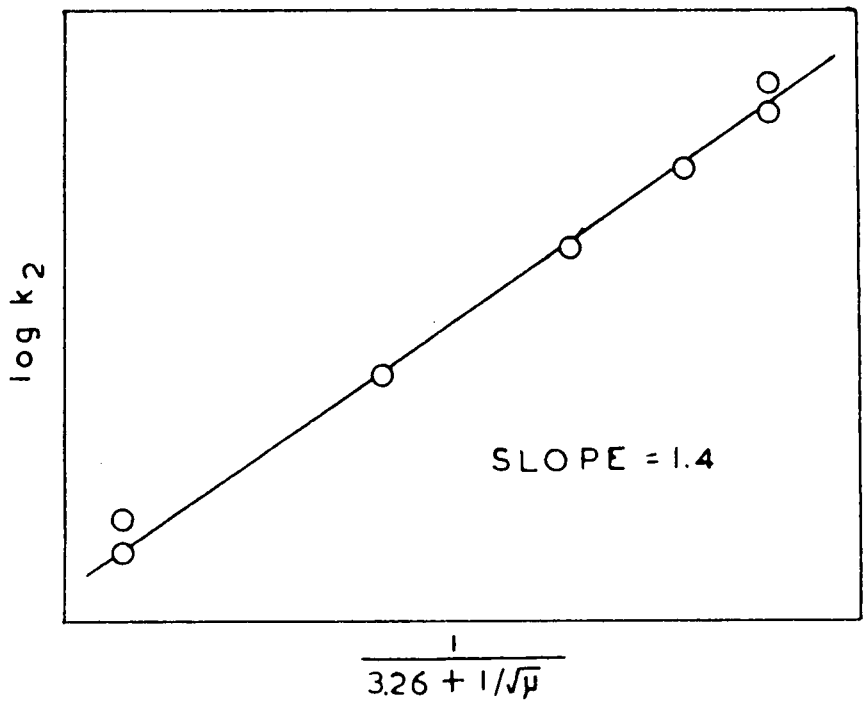


TABLE II

Rate constants as a function of pH for permanganate oxidation of 2,2,2-trifluoro-1-protio and 1-deuterio-1-phenylethanols.

[NaOH] - M	pH	$C_6H_5CHOHCF_3$ k_2, l. mole^{-1}sec.$^{-1}$	$C_6H_5CDOHCF_3$ k_2, l. mole^{-1}sec.$^{-1}$
0.2	13.3	8.0	0.50
0.16	13.21	7.9	-
0.13	13.11	7.8	-
0.1	13.0	7.6	0.47
0.1	13.0	7.5[b]	-
0.08	12.9	7.3	-
0.06	12.78	6.9	-
0.04	12.6	6.5	-
0.03	12.48	6.1	-
0.02	12.3	5.0	0.32
0.01	12.0	3.8	0.23
0.005	11.7	2.3	-
	11.35[a]	0.306	-
	10.9[a]	-	0.013
	10.75[a]	0.361	-
	9.1[a]	0.0053	0.00035
	7.0[a]	0.0039	0.00241

$[\text{Alcohol}]_o = 3.69 \times 10^{-4}$ M, Temperature 25.2 ± 0.05°. (a) Buffered solutions, ionic strength = 0.2. (b) Addition of 0.033 M $Ba(NO_3)_2$ solution.

TABLE III

Rate constants as a function of pH for permanganate oxidation of the phenyl substituted 2,2,2-trifluoro-1-phenylethanols.

pH	$m\text{-}NO_2C_6H_4CHOHCF_3$ k_2, l. mole^{-1}sec.$^{-1}$	$m\text{-}BrC_6H_4CHOHCF_3$ k_2, l. mole^{-1}sec.$^{-1}$	$p\text{-}CH_3C_6H_4CHOHCF_3$ k_2, l. mole^{-1}sec.$^{-1}$
13.3	8.8	7.6	8.4
13.0	8.7	7.4	7.1
12.48	8.2	6.3	-
12.0	6.5	4.7	3.4
11.7	5.0	3.7	-
11.05 (a)	0.84 ?	-	-
10.7 (a)	-	0.30	-
10.4 (a)	0.408	-	-
9.1 (a)	0.019	0.0061	0.0049

$[\text{Alcohol}]_o = 5.1 \times 10^{-4}$ M; Temperature 25.2 ± 0.05°; Ionic strength = 0.2. (a) Buffered solutions, ionic strength = 0.2.

TABLE IV

Rate constant as a function of salt concentration for permanganate oxidation of 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol.

k_2, l. mole^{-1}sec.$^{-1}$	log k_2	μ	$\sqrt{\mu}$	$\frac{1}{3.26 + 1/\sqrt{\mu}}$
4.54	0.657	0.0115	0.107	0.0794
4.45	0.648	0.0115	0.107	0.0794
4.95	0.694	0.0315	0.177	0.112
5.34	0.728	0.0615	0.248	0.137
5.60	0.749	0.0915	0.302	0.152
5.80	0.764	0.1215	0.348	0.163
5.90	0.771	0.1215	0.348	0.163

$[\text{Alcohol}]_o = 5.1 \times 10^{-4}$ M; Temperature = 25.2°, $[\text{NaOH}] = 0.01$ M. Ionic strength varied by use of K_2SO_4.

4. Thermodynamic functions.

The variation of reaction rate with temperature can be utilized to obtain the heat and entropy of activation, respectively $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

The equation

$$k_2 = \frac{kT}{h} \times e^{\left(-\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}\right)}$$

as derived from transition state theory would predict that if log $k_2/T°K$ was plotted against $1000/T°K$ (over a limited temperature range), the slope of the straight line and intercept would give respectively $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

The rate constants were determined at various temperatures over a 25 degree temperature range for the oxidation of 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol, 2,2,2-trifluoro-1-phenylethanol and 2,2,2-trifluoro-1-phenylethanol-1-d at pH 13 where ionization is almost complete and also in more weakly basic solution where the extent of ionization is small. Good linear plots were obtained in all cases when log $k_2/T°K$ was plotted against $1000/T°K$ (Figure 5). The heats and entropies of activation are tabulated in Table V.

5. Deuterium isotope effects.

Investigations using deuterium substituted organic molecules

TABLE V

Thermodynamic data obtained for the oxidation of 2,2,2-trifluoro-1-phenylethanols at various pHs.

$[Y\text{-}C_6H_4CHOHCF_3]_o = 5.1 \times 10^{-4}$ M.

Compound	pH	$\Delta H^{\ddagger}$ kcals./mole	$\Delta S^{\ddagger}$ e.u.
$C_6H_5CHOHCF$	13.0	9.1 ± 0.3	-24.3 ± 1
$C_6H_5CHOHCF_3$	11.0	10.1	-27.9
$C_6H_5CDOHCF_3$	13.0	11.3	-22.4
$C_6H_5CDOHCF_3$	11.0	10.0*	-33.2*
$m\text{-}NO_2C_6H_4CHOHCF_3$	13.0	9.2	-23.8
$m\text{-}NO_2C_6H_4CHOHCF_3$	10.4	9.6	-28.2

* The apparently inconsistent result for the deuteriated compound (compare $\Delta H^{\ddagger}$ values for the protio and deuterio compounds at pH = 13 and 11; respectively $\Delta(\Delta H^{\ddagger})$ = 2.2 kcals. and $\Delta(\Delta H^{\ddagger})$ = -0.1 kcals.) may be partially due to experimental error in determining rate constants at the very slow rates observed at pH 11 and partially due to the difficulty of obtaining exactly reproducible pH 11 measurements. Also a pKa difference between deuterio and protio compounds was observed; the deuterio compound was 0.06 pKa units stronger than the protio compound. This difference though is within the experimental error for the pKa determination. A pKa difference is possibly indicated also by the lower k_H/k_D ratio at pH = 11 (Table VII).

FIGURE 5

Plot of $\log k_2 / T^oK$ versus $1000/T^oK$ for the permanganate : 2,2,2 - trifluoro-1-phenylethanol reaction.

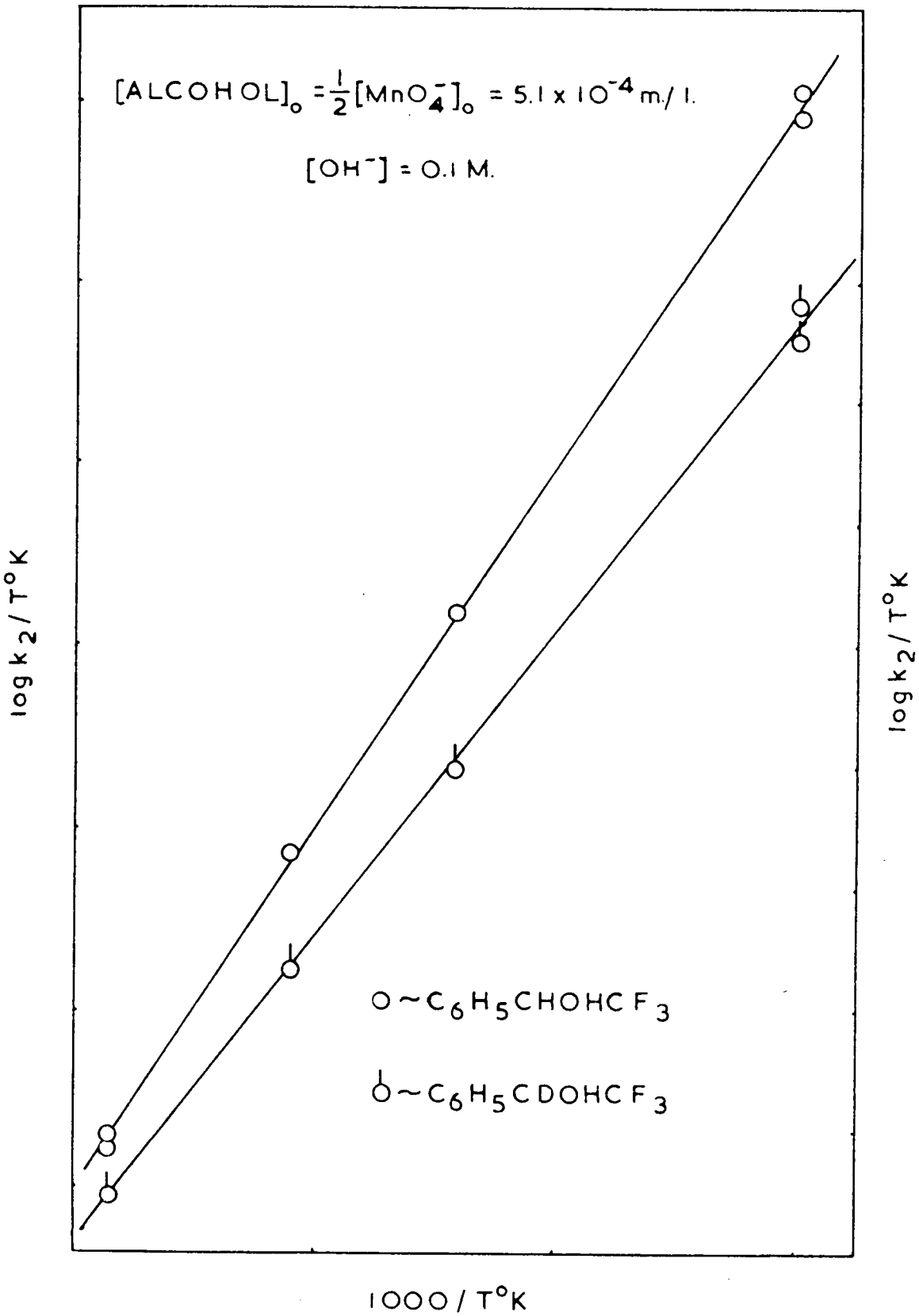


TABLE VI

Table of rate constants for permanganate oxidation of 2,2,2-trifluoro-1-phenylethanols at various temperatures.

Temperature	k_2,[a] l. mole^{-1}sec.$^{-1}$	k_2,[b] l. mole^{-1}sec.$^{-1}$
$[C_6H_5CHOHCF_3]_o = 5.1 \times 10^{-4}$ M		
38.0 ± 0.05°	11.5	0.38
38.0	11.7	-
31.25	7.9	-
25.20	6.2	0.18
12.65	2.8	0.078
12.65	2.9	-
$[C_6H_5CDOHCF_3]_o = 5.1 \times 10^{-4}$ M		
38.0 ± 0.05°	0.88	0.032
31.25	0.56	0.023
25.2	0.38	0.015
12.65	0.16	0.007
12.65	0.15	-

(a) pH = 13; (b) pH = 11; Ionic strength 0.1 K_2HPO_4.

TABLE VI (continued)

Temperature	k_2,[a] l. mole^{-1}sec.$^{-1}$	k_2,[c] l. mole^{-1}sec.$^{-1}$
$[m\text{-}NO_2C_6H_4CHOHCF_3]_o = 5.1 \times 10^{-4}$ M		
38.0 ± 0.05°	12.9	0.84
38.0	12.8	-
25.2	7.0	0.41
25.2	6.8	-
12.65	3.04	0.19
12.65	3.30	-

(a) pH = 13; (c) pH = 10.4; Ionic strength 0.1 K_2HPO_4.

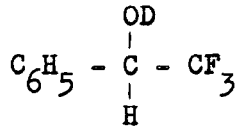
for mechanistic studies have led to detailed information about bond breaking processes. When the substrate 2,2,2-trifluoro-1-phenylethanol is replaced by 2,2,2-trifluoro-1-deuterio-1-phenylethanol in the oxidation by permanganate a large kinetic isotope effect is observed, k_H/k_D = 16/1, at room temperature. At pH 11 a value of 12/1 was observed (Table VII).

When this unusually high value was obtained for the unsubstituted compounds it was felt necessary to prepare other molecules by various methods which were isotopically labeled with deuterium. Thus the p-methyl deuterio and m-bromo deuterio ethanols were made and their rates of oxidation compared with their normal alcohols. In these cases also the ratio of rates of oxidation was found to be 16/1.

When the oxidation is carried out in neutral solution, i.e., uncatalyzed reaction, the high isotope effect of k_H/k_D = 16/1 is still observed even though the reaction is now very slow. If the reaction is carried out in acid solution, pH = 1, the oxidation is still very slow but a very low isotope effect of 1.8 is now observed.

These results indicate that the carbon-hydrogen bond is broken in the rate determining process for the alkali catalyzed and uncatalyzed reaction, i.e., oxidation due to the undissociated species. (The reaction in acid solution appears to involve a different mechanism.)

Further deuterium substitution of the organic molecule such as replacement of the hydroxyl proton by deuterium



can be made to occur indirectly by dissolving the compound in D_2O solution. If the O-D bond is broken in the rate determining step a large isotope effect should be observed. Secondary solvent isotope effects may be observed but these are usually quite small (52). When the rate of oxidation of 2,2,2-trifluoro-1-phenylethanol was measured in 59% D_2O in 0.2 M sodium hydroxide and in 100% H_2O at 25.2° the rate constants were respectively 8.0 l. $mole^{-1}sec.^{-1}$ and 7.7 l. $mole^{-1}sec.^{-1}$.

6. The Hammett relation.

In attempting to obtain information concerning the electronic requirements of the oxidation process, a series of meta and para substituted trifluoro-1-phenylethanols were prepared which had widely separated Hammett σ values. With the use of the Hammett relation (45) $\log k/k_o = \sigma\rho$, a plot was obtained for the reaction using data obtained at 0.2 M sodium hydroxide (Figure 6). Since the alcohols are incompletely ionized (93-99%) (pKa values Table IX) in 0.2 M sodium hydroxide, a small correction for an ionization equilibrium was applied to the rate constants to normalize the results to 100% ionization.

Also included in this section is a Hammett plot for the ionization data. A linear plot was observed (Figure 7) giving a

TABLE VII

Table of k_H/k_D values observed for permanganate oxidation of the various 2,2,2-trifluoro-1-phenylethanols.

$C_6H_5CHOHCF_3$

pH	13.3[a]	13.3[a]	13.0[a]	12.0[a]	13.0[b]
$[\text{Alcohol}]_o \times 10^4$ M	5.1	3.69	3.69	3.69	5.1
Temperature	25.2°	25.2°	25.2°	25.2°	38.0°
k_H, l. mole^{-1}sec.$^{-1}$	7.5	8.0	7.6	3.8	11.6
k_D, l. mole^{-1}sec.$^{-1}$	0.47	0.50	0.47	0.23	0.88
k_H/k_D	16.0	16.0	16.2	16.5	13.2

pH	13.0[b]	11.0[b]	7.0[a]	1.0[b]
$[\text{Alcohol}]_o \times 10^4$ M	5.1	3.69	62.6	15.4
Temperature	12.7°	25.2°	25.2°	25.2°
k_H, l. mole^{-1}sec.$^{-1}$	2.85	0.18	0.00394	0.00096
k_D, l. mole^{-1}sec.$^{-1}$	0.155	0.0153	0.000241	0.00055
k_H/k_D	18.4	12.0	16.0	1.8

(a) Ionic strength 0.2. (b) Ionic strength 0.1.

TABLE VII (continued)

	$m\text{-}BrC_6H_4CHOHCF_3$	$p\text{-}CH_3C_6H_4CHOHCF_3$
pH	13.3[a]	13.3[a]
$[\text{Alcohol}]_o \times 10^4$ M	5.1	5.1
Temperature	25.2°	25.2°
k_H, l. mole^{-1}sec.$^{-1}$	7.6	8.4
k_D, l. mole^{-1}sec.$^{-1}$	0.47	0.52
k_H/k_D	16.2	16.1

(a) Ionic strength 0.2.

ρ value of +0.91.

Though a linear relationship was not realized with the data obtained in the oxidation, the result shows the possibility that a smooth curve does exist. The rate constant for the para-methoxy compound, of the five alcohols studied, was determined at a later date. A kinetic experiment performed at the same time on the unsubstituted alcohol indicated that this later result is reliable. The estimated slopes from the curve (Figure 6) for the p-methoxy and p-methyl compounds and m-nitro and m-bromo compounds are respectively -0.4 and +0.2. The values indicate dual electronic requirements at the reaction site since electron withdrawing and electron donating groups in the aromatic ring have similar effects.

TABLE VIII

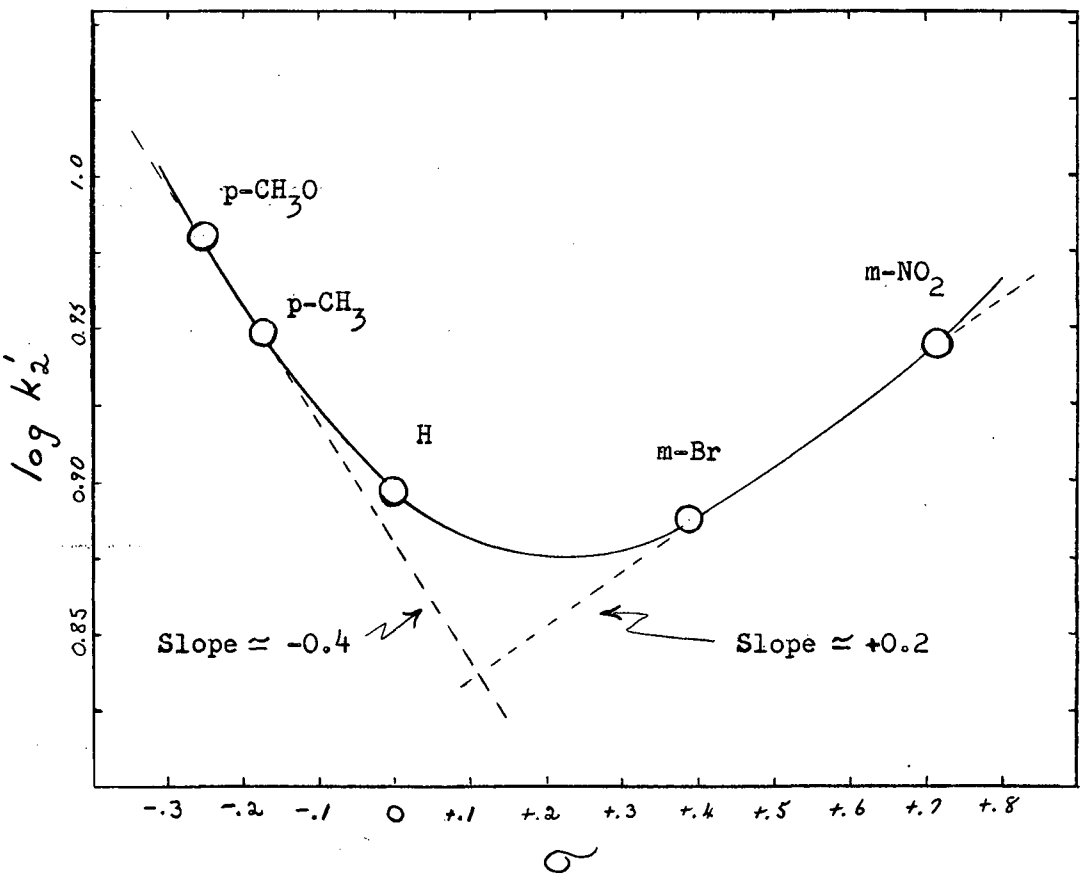
Rate constants used for Hammett relation.

$Y\text{-}C_6H_4CHOHCF_3$	k_2, l. mole^{-1}sec.$^{-1}$	k_2', l. mole^{-1}sec.$^{-1}$
p-CH_3O	8.9 (a)	9.6 (b)
p-CH_3	8.4	8.9
H	7.5	7.9
m-Br	7.6	7.7
m-NO_2	8.8	8.9

(a) Uncorrected rate constants; (b) Values corrected to 100% ionization using values obtained in 0.2 M sodium hydroxide; $[\text{alcohol}]_o = 5.1 \times 10^{-4}$ M. Temperature 25.2°, μ = 0.2.

FIGURE 6

PLOT OF LOG k_2' VERSUS THE HAMMETT σ VALUES FOR PERMANGANATE OXIDATION OF THE VARIOUS SUBSTITUTED 2,2,2-TRIFLUORO-1-PHENYLETHANOLS AT pH 13.3

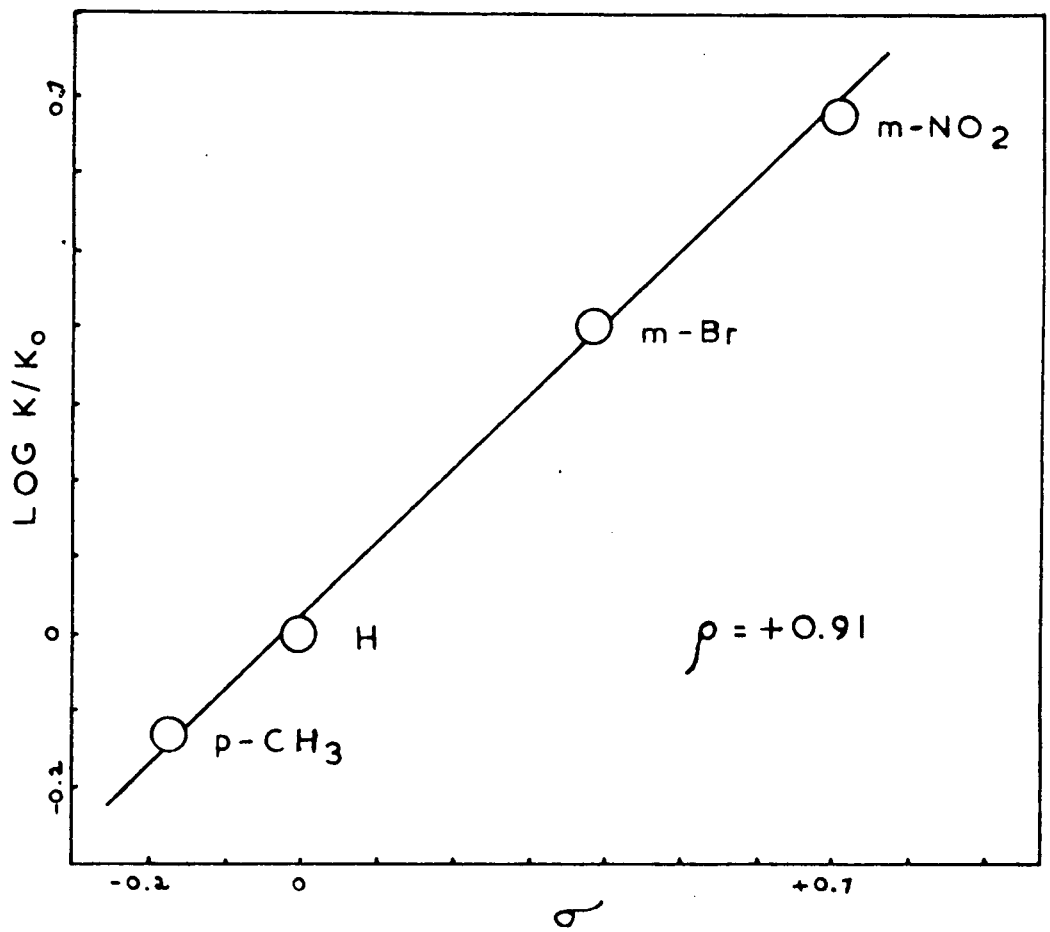


O - RESULTS CORRECTED TO 100% IONIZATION

FIGURE 7

HAMMETT PLOT FOR THE

IONIZATION OF 2,2,2-TRIFLUORO-1-PHENYLETHANOLS.



7. Results from the pKa determinations.

TABLE IX

pKa, maximum wavelengths λ and extinction coefficients ϵ obtained from the ultraviolet spectra of the various substituted and unsubstituted 2,2,2-trifluoro-1-phenylethanols.

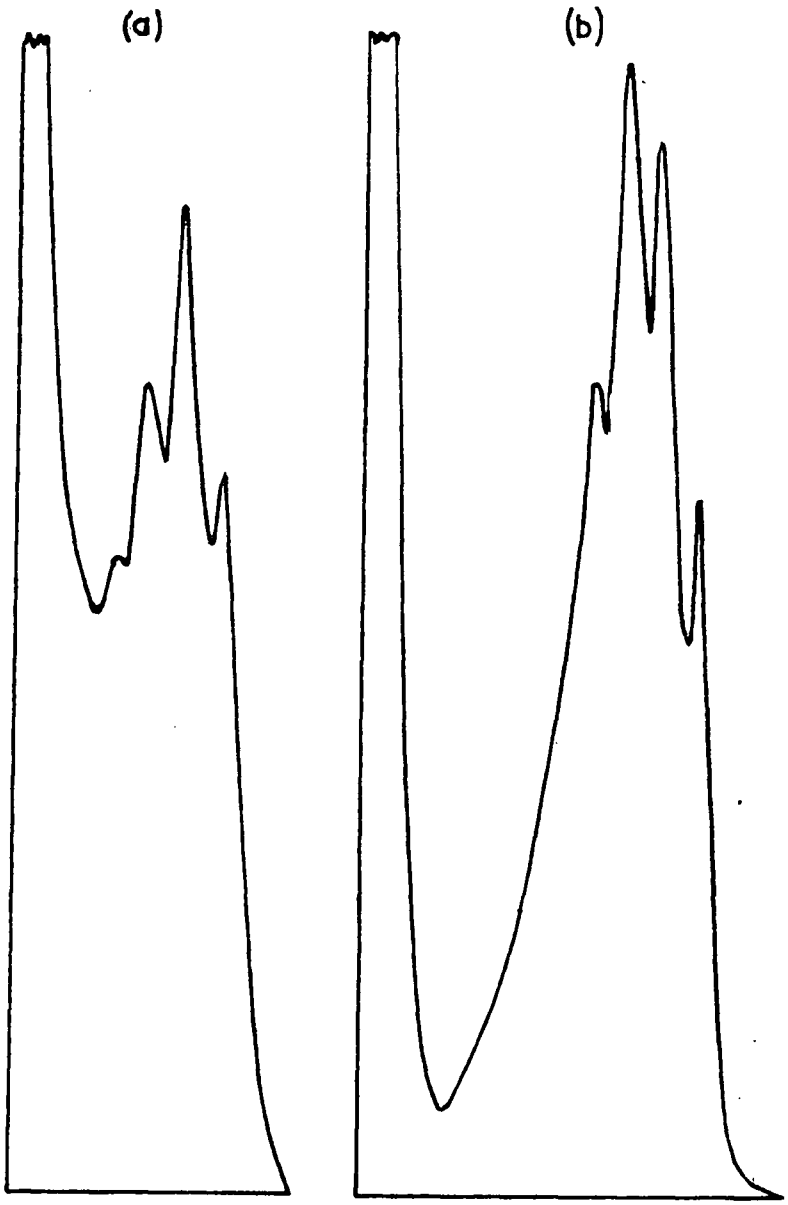
Compound	HA λ maximum	HA ϵ	A^- λ maximum	A^- ϵ	pKa
$m\text{-}NO_2C_6H_4CHOHCF_3$	264	7600	270	7000	11.23 ± 0.06
$m\text{-}BrC_6H_4CHOHCF_3$	274	254	274	162	11.50
	267	340	267	244	
	261	286			
$p\text{-}CH_3C_6H_4CHOHCF_3$	265	156	271	192	12.04
	260	225	262	275	
	254	194	256	230	
$C_6H_5CHOHCF_3$	266	134	262	144	11.90
	260	204	257	194	
	256	216	251	158	
	250	157	247	126	
$C_6H_5CDOHCF_3$	266	140	262	149	11.85
	260	210	257	200	
	256	224	251	165	
	250	163	247	130	
$p\text{-}MeOC_6H_4CHOHCF_3$	278	1130	277	1080	12.24
	272	1320	271	1240	

HA - Spectra of undissociated alcohol.

A^- - Spectra of dissociated alcohol.

FIGURE 8

Ultraviolet spectra of 2,2,2-trifluoro-1-phenylethanol-1-d using a Cary Model 14 Recording Spectrophotometer. [Alcohol] = 0.00268 M.



(a) Spectrum of $C_6H_5CDO^-CF_3$ at pH 13.6.

(b) Spectrum of $C_6H_5CDOHCF_3$ at pH 4.

DISCUSSION

The trifluorophenylethanols are much more acidic than the carbinol, benzhydrol, due mainly to the large inductive electron withdrawing effect of the α-trifluoromethyl group. The order of decreasing acidity for substitution into the phenyl ring m-NO_2 > m-Br > H > p-CH_3 > p-MeO is that expected (See Hammett plot ρ = 0.91). Haszeldine (46) has reported pKa determinations for many fluorinated aliphatic primary and secondary alcohols and found the acidity of the hydroxy proton to depend on the number of adjacent fluorine atoms.

Since the kinetics of oxidation of trifluorophenylethanols by permanganate is first order in permanganate and first order in alcohol, a possible explanation for the base catalysis might be a prior equilibrium step followed by a slow rate determining bimolecular reaction between the alkoxide ion and permanganate ion to form the products,

$$C_6H_5CHOHCF_3 + OH^- \overset{K}{\rightleftharpoons} C_6H_5CHO^-CF_3 + H_2O$$

$$C_6H_5CHO^-CF_3 + MnO_4^- \xrightarrow[\text{slow}]{k} \text{Products}$$

A rate law which fits the mechanism is the following:

$$-\frac{d[MnO_4^-]}{dt} = k[C_6H_5CHO^-CF_3][MnO_4^-] \qquad (7)$$

$$\text{where } K = \frac{[C_6H_5CHO^-CF_3][H_2O]}{[C_6H_5CHOHCF_3][OH^-]}$$

substituting in equation (7) for alkoxide ion

$$\text{Rate} = \frac{kK[C_6H_5CHOHCF_3][OH^-][MnO_4^-]}{[H_2O]} \qquad (8)$$

$$\text{Where } k_{experimental} = \frac{kK[OH^-]}{[H_2O]} = \frac{kKi}{Kw}[OH^-]$$

If the alkoxide ion is the reactive intermediate, a maximum limiting rate should be observed at higher alkalinities where the weak acids are completely ionized. A plot of $k_{experimental}$ versus hydroxyl ion concentration (Figure 2) does show a leveling off at higher basicities with the attainment of maximum rate being in the order of the acidities of the alcohols m-NO_2 > m-Br > H > p-CH_3. The fact that complete leveling in these plots is not observed is due to the incomplete ionization of the alcohols (99.1 to 93%) in 0.2 M NaOH. Essentially, the rate of oxidation becomes independent of hydroxyl ion and dependent only on the alkoxide and permanganate concentrations under these conditions. Thus equation (8) reduces to

$$-\frac{d\left[MnO_4^-\right]}{dt} = k_{exp}\left[MnO_4^-\right]\left[C_6H_5CHOHCF_3\right]$$

$$= k\left[C_6H_5CHO^-CF_3\right]\left[MnO_4^-\right]$$

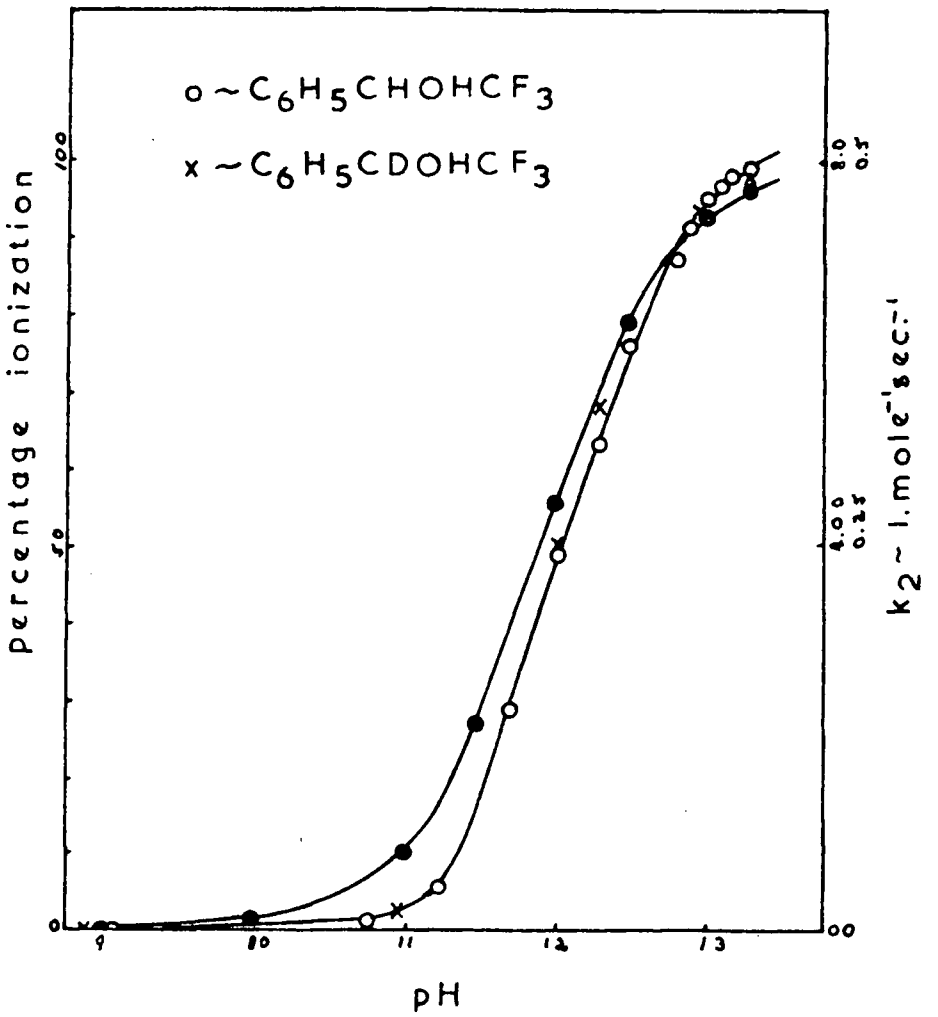
An ionization type curve should be obtained if k_2 is plotted against pH, since k_2 is directly proportional to the ratio of ionized to unionized acid (Figures 9(a) and 9(b)). Good agreement is found between the calculated ionization curve and the experimental oxidation curves. Further, the pKa for each of the weak acids occurs as it should close to the pH corresponding to half the maximum oxidation velocity.

The derived rate expression is in accord with the observed kinetics. These findings are very similar to the results obtained by Stewart for the benzhydrol-permanganate reaction except for the leveling off of the rate at high pH which he was unable to detect owing to the weakness of benzhydrol as an acid. The results support the idea of a prior equilibrium step in the oxidation. The positive salt effect observed is in accord with a rate determining step between two like singly charged ions.

Information about the equilibrium step may be found in the thermodynamics of the process. When the reaction is carried out at lower alkalinities the heat and entropy values obtained would be those of ionization and the rate determining step together. At higher alkalinities where the weak acids would be almost completely ionized, the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ would be those of the rate determining

FIGURE 9(a)

Plot of percentage ionization and k_2 for permanganate oxidation versus pH.

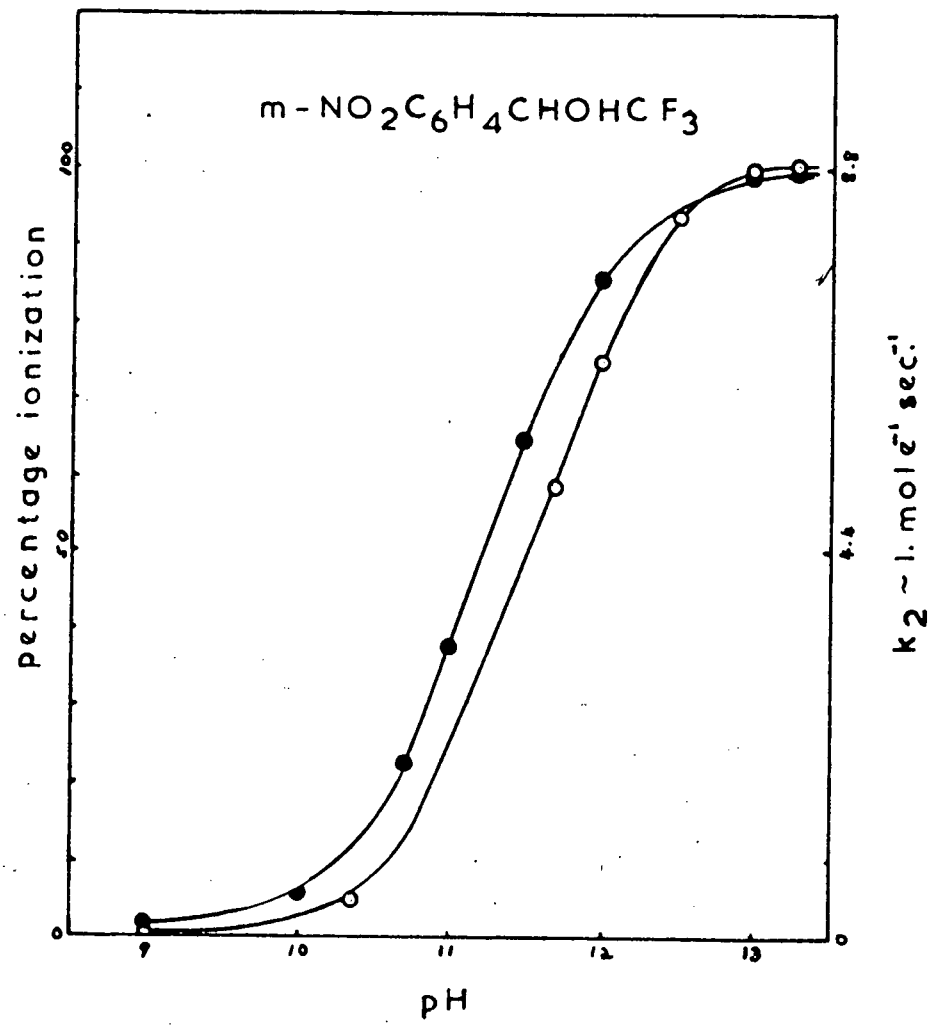


● ~ Theoretical ionization curve.

o, x ~ Experimental rate plots.

FIGURE 9(b)

Plot of percentage ionization and k_2 for permanganate oxidation versus pH.



● ~ Theoretical ionization curve.

o ~ Experimental rate plot.

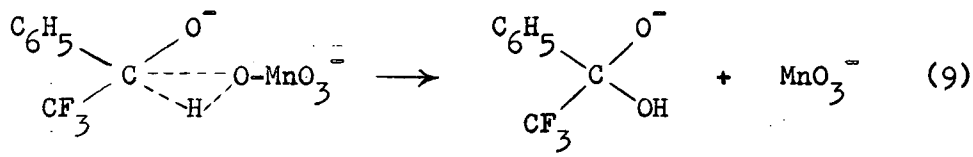
step alone. The difference between the thermodynamic values obtained at p^H = 10.4 and 13.0 for the oxidation of trifluoro-1-(m-nitrophenyl)-ethanol (Table V) are $\Delta(\Delta S^{\ddagger})$ = -5.4 e.u. and $\Delta(\Delta H^{\ddagger})$ = 0.4 kcals/mole $\simeq$ 0 and should result in values for the ionization step alone. The thermodynamics of ionization of weak acids usually involves values of this order (47). Moreover during the measurement of the ionization constants for the alcohols it was observed that temperature changes of a few degrees appeared to have a negligible effect on the degree of ionization showing that $\Delta H_{ion.}$ must be very small.

Although the kinetics, thermodynamic and salt effect data are in agreement with the ideas put forward by Stewart in the benzhydrol oxidation (38), the ρ plot and high value for the isotope effect indicate that the detailed mechanism is possibly more complex than the hydride transfer process suggested for that reaction. A number of possibilites will be considered.

Reactions involving hydroxyl ions and oxidant in a primary step to produce radicals or a chain process would not be consistent with the kinetic data since the rate is found to be independent of hydroxyl ions at higher alkalinities. It is conceivable though that at much higher basicities, i.e. greater than 3 M, where the concentration of radicals is thought to be large other processes might become important. Kinetic evidence would be difficult to obtain under these conditions.

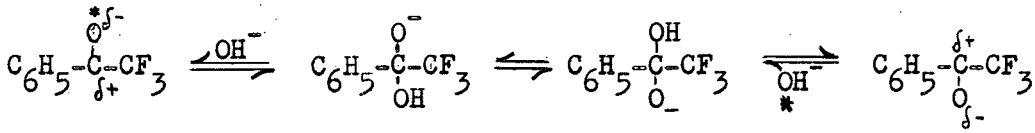
A transition state considered previously for the alkaline permanganate oxidation of benzhydrol and formate ions involved a

triangular transition state whereby the permanganate ion attacks the carbon-hydrogen bond



(9)

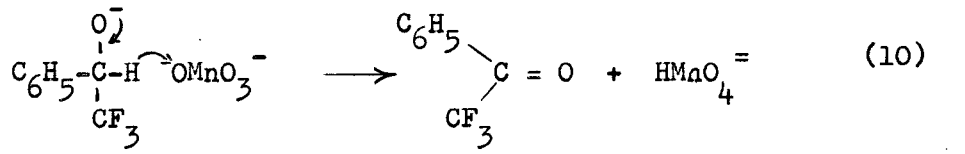
If the ideas of Lewis (48) and Symons (49) regarding isotope effects are correct this triangular transition state reaction (9) can be ruled out. They have pointed out that for such a transition state there should only be a partial loss of the zero point energy in the carbon hydrogen stretching mode and hence a small isotope effect should result. In the present case a large isotope effect is observed. A further test of this mechanism would be difficult here since labeling experiments using permanganate $-O^{18}$ would result in a rapid exchange of oxygen between solvent and ketone via the hydrated species.



No O^{18} was introduced into the substrate when benzhydrol was oxidized with permanganate $-O^{18}$, though the benzhydrol reaction cannot be considered as an unequivocal parallel in view of the results presented herein.

A simple hydride ion transfer to permanganate ion as for the

benzhydrol case seems plausible since part of the driving force for this reaction would be the electron donating ability of the alkoxide ion.



(10)

Though the magnitude of the kinetic isotope effect is larger k_H/k_D = 16/1 than is normally observed, this mechanism is in agreement with the idea that a carbon hydrogen bond is broken in the rate determining step. When the fluorinated alcohols are almost completely ionized in alkaline solution a Hammett plot (45) should apply to the rate determining step alone, with a small or negligible contribution from the ionization equilibrium. Thus if a hydride ion transfer mechanism was taking place one should observe a large effect on the development of charge in the transition state by polar substituents in the phenyl ring, i.e., a large negative ρ value. A p-methoxy substituent should accelerate the process and a p-nitro group retard it. The small ρ values * estimated from the curved Hammett plot indicate the possibility that dual electronic requirements in the transition state are important, i.e., one

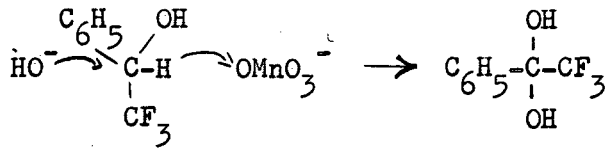
* If dual reactions are taking place one would expect that the estimated values (see results Figure 6) would be small. The actual ρ values in each case will necessarily be much larger than the estimated values in order to give the resulting curve, i.e., -1.0 and +0.8.

process being accelerated by an electron releasing group such as the p-methoxy group and another process which is accelerated by an electron withdrawing group such as the m-nitro group. The negative slope involving the p-methoxy and p-methyl compounds is consistent with a mechanism involving hydride ion transfer to the oxidant. Examples of hydride ion transfer mechanisms in which a Hammett study have been obtained are the Meerwein Ponndorf reaction (50) (a ρ value of +1.296 was obtained from the experimentally determined equilibrium constants for a series of substituted benzophenones) and the Cannizzaro reaction (51) (a value of ρ = 3.633 was observed). Each of these reactions are known to involve a number of steps which contribute to the overall value of ρ and therefore any statement as to the size of the ρ value for hydride ion transfer process might be considered as tentative.

Swain (52) has recently studied the mechanism of formation of ethylene oxide from 2-chloroethanol and has pointed out that it is kinetically impossible to distinguish between a mechanism involving the alkoxide ion as a discrete intermediate and a concerted mechanism involving hydroxyl ion and 2-chloroethanol. Since a similar rapid equilibrium exists in the present case, i.e.,

$$C_6H_5CHOHCF_3 + OH^- \overset{K}{\rightleftharpoons} C_6H_5CHO^- CF_3 + H_2O$$

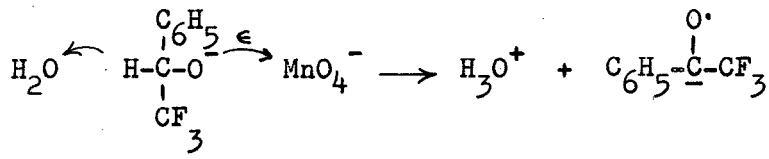
a termolecular process could be envisaged which involves hydroxyl ion, permanganate ion and a trifluorophenylethanol molecule;



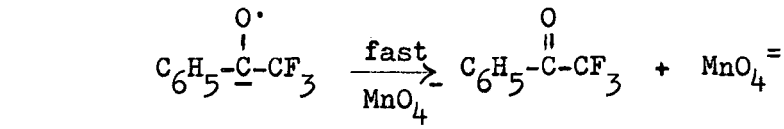
(11)

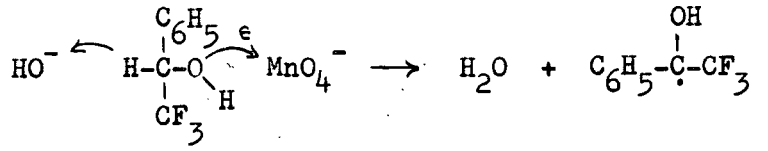
It is conceivable that if the attack by hydroxyl ion on the carbon atom was very important in the transition state while permanganate removes a hydride ion from trifluorophenylethanol, then such a process could be favoured by electron withdrawing groups. The observation that these ketones hydrate readily (53) tends to support these ideas.

If the curvature of the Hammett plot is not considered significant, then a number of mechanisms involving termolecular steps must be considered to explain the relative insensitivity of the rate of oxidation of the various nuclear substituted alcohols. Reaction (11) above fits into this latter category. A number of these processes are:

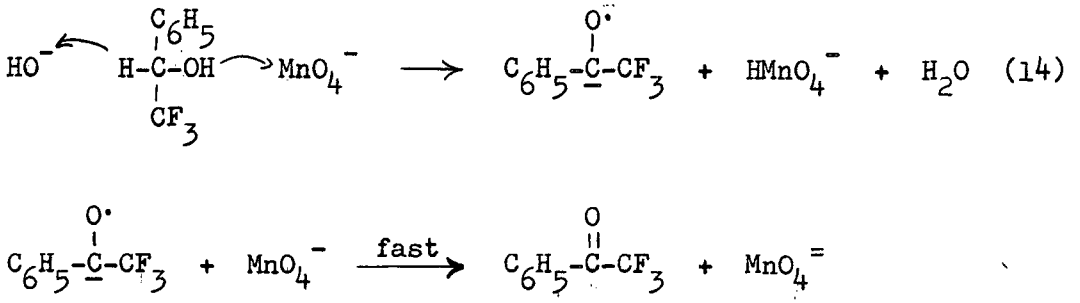


(12)





(13)

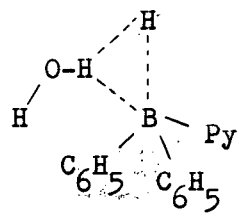


In reaction (12) permanganate acts as an electron abstractor with a water molecule acting simultaneously as a proton abstractor. This mechanism is in agreement with the kinetic and isotopic evidence and since the alkoxide ion is losing both an electron and a proton in the transition state the effect of substituents should be slight.

In reaction (13) hydroxyl ion removes a hydrogen attached to the hydroxyl carbon as a proton while permanganate abstracts an electron from the electron rich oxygen atom to produce a resonance stabilized radical which undergoes a fast reaction with another molecule of permanganate to yield the ketone. If reaction (14) was important a large deuterium isotope effect should be observed if the oxygen-hydrogen bond is broken in the rate determining step. Kinetic experiments run in 60% D_2O indicated that no marked change in rate had occurred, thus eliminating this possibility.

In regards to carbon-hydrogen bond breaking, Wiberg (54) had observed that there was no apparent difference in magnitude of the isotope effect in the removal of hydrogen or deuterium as a proton, a hydride ion or a neutral atom. Recent suggestions (48) (49) however, have indicated that hydride ion mechanisms in general

have small isotope effects. Examples shown to be hydride transfer and give low isotope effects are the Cannizzaro reaction, (55), Meerwein, Ponndorf, Verley reduction, (56), carbonium ion-formic acid reaction (57), and the carbonium ion-alcohol reaction (58). Hawthorne and Lewis (49) have postulated a non linear transition state for the aqueous hydrolysis of diphenylborane-pyridine complex from evidence obtained on labeling substrate and solvent with deuterium in separate kinetic experiments. They observed



a very low isotope effect when the boron-hydrogen bond is broken and a high value when the oxygen-hydrogen bond is broken in the solvent molecule. In contrast, Stewart has observed kinetic isotope effects of 6.6/1 for benzhydrol oxidation; a reaction assumed to involve hydride transfer.

The oxidation of 2,2,2-trifluoro-1-phenylethanol by permanganate in neutral or alkaline solution has shown a deuterium isotope effect whose magnitude, k_H/k_D = 16/1 at room temperature, is unprecedented. Manganate oxidation also shows a high isotope effect. Similar results have been reported privately by Dauben (59) who found large deuterium isotope effects in the oxidation of hydrocarbons by carbonium ions. As indicated above these processes are presumed to proceed via hydride ion transfer mechanisms.

The ratio (ν_H/ν_D) of vibrational stretching frequency for the two bonds is found to be 1.35 from their infrared spectra, a value which is found for many other pairs of organic compounds where hydrogen attached to carbon is replaced by deuterium. Since a good correlation (54) between the difference in vibrational zero point energy for the two bonds and the ratio of rates of chemical reactions involving these bonds has been made, the high isotope ratio observed here appears anomalous.

Consideration of the thermodynamic data for the two species in alkaline solution (Table V) shows a difference only in the heat of activation; the difference is 2.1 kcals. Using the equation $\Delta(\Delta F^{\ddagger}) \approx \Delta(\Delta H^{\ddagger}) = RT \ln k_H/k_D$ a value of k_H/k_D of 14.1 can be calculated, a number which is at least close to the observed ratio. One would normally expect to see the cause of the difference in the observed rates in the enthalpy rather than the entropy term since the activation energy is partially governed by bond strength.

Secondary deuterium isotope effects have been observed when deuterium replaces hydrogen on the carbon atom containing the functional group or α to it. If an equilibrium is involved, the effect is usually very small as compared to kinetic isotope effects though it is conceivable that the pKa difference of the 1-deuterio and 1-protio ethanol may cause an increase or decrease in the concentration of the reactive species at a given pH. (This is a possible explanation for the lowered k_H/k_D ratio at pH 11.). That no major effect occurs is seen from the pKa values for the two species, 11.84 for the 1-deuterio and 11.90 for the 1-protio ethanol. The

experimental oxidation rate versus pH curves indicated the same conclusion.

One explanation for the large isotope effect might be to incorporate the loss in zero point energy for the two bending modes to the loss in zero point energy due to the stretching vibration in forming the transition state. This is possible if one considers that the transition state must be formed at a maximum distance due to electrostatic repulsions between the like charged ions.

Since both permanganate and manganate oxidation yield large kinetic isotope effects, one could consider that the anomalous value observed might be due to some unique effect attributable to the trifluoromethyl group. The unusual physical and chemical properties created by the presence of the trifluoromethyl group is well documented in the literature. The effect on the enhancement of the acidity of the alcohols has already been noted. The trifluoromethyl group is generally a very stable group (60) and especially in the alcohols where dehydrating and halogenating agents have no effect on the molecule (61). This latter effect is the result of carbon-oxygen bond strengthening due to the presence of the adjacent trifluoromethyl group (61). Electron diffraction studies on trifluoroethanol indicates that the carbon-oxygen bond is shortened (61). Hyperconjugative effects have been invoked to explain the hydrolysis of the labile trifluoromethyl group in aromatic compounds (60).

In summary, there are two unusual features of the permanganate oxidation of aryl trifluoromethyl carbinols, viz., the size of the deuterium isotope effect and the effect of aromatic substituents

on the rate. If a simple hydride transfer from alkoxide to permanganate ion is rejected on the basis of the negligible effect of substituents one is forced to conclude that a termolecular process is occurring. The most attractive of these alternatives is that in which a permanganate ion and a water molecule remove an electron and a proton respectively from the alkoxide ion.

PART II

INTRODUCTION TO PERMANGANATE OXIDATION OF CYANIDE ION

Previous attempts to investigate the mechanism of the alkaline permanganate oxidation of cyanide ion have not been made, though a number of workers (62) (63) have shown that the reaction has the following stoichiometry in alkaline solution,

$$2MnO_4^- + CN^- + 2OH^- \longrightarrow NCO^- + H_2O + 2MnO_4^=$$

Drummond and Waters (12) made use of the quantitative nature of the reaction in their attempts to study the response of different organic functional groups to isolated valency changes of manganese. Cyanide has also been used to test the purity of alkaline manganate solutions since its oxidation by manganate is much slower than by permanganate (14).

Adamson (64) attempted to investigate the oxidation of cyanide by ferricyanide ion in weakly basic solution and found the reaction complex. A number of reaction products were reported including ammonia, cyanate and cyanogen polymers which precipitated out of the reaction mixture as a brown material, though a positive test for cyanogen was not obtained. The rate of reaction was followed spectrophotometrically. He found that the rate was slow in acid solution. Though simple kinetic orders were not obtained

Adamson presented the following mode of oxidation,

$$Fe(CN)_6^{-3} + 2CN^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_6^{-4} + (CN)_2^-$$

$$(CN)_2^- + H_2O \xrightarrow{k_3} P + CN^-$$

$$Fe(CN)_6^{-3} + P \longrightarrow Fe(CN)_6^{-4} + Q$$

and considered species P could possibly be the hydrated cyanogen radical $O = \dot{C}NH_2$. The steady state treatment was applied to this mechanism but a fit to the observed kinetics was not obtained though the reaction scheme was considered to be qualitatively correct.

Preliminary work (65) on the permanganate-cyanide reaction indicated that a transfer of oxygen to the product cyanate had taken place when permanganate enriched in O^{18} had been used as oxidant. Thus the work reported herein is an extension of this work as well as a report on the kinetics of the reaction over a pH range from 6 to 14.6.

EXPERIMENTAL

A. Analytical Methods.

Qualitative and semiquantitative methods were used for the analysis of the reaction products produced in the oxidation of aqueous alkaline cyanide solution by permanganate over the pH range 6 to 14.6. Cyanogen, carbon dioxide, cyanate and cyanide ion were identified in varying yields depending on the pH with cyanate being the sole product produced in alkaline solutions above pH = 12.

1. Cyanogen analysis.

A method developed by Rhodes (66) for detecting cyanogen was used. The method involved bubbling N_2 gas through the cooled, acidified reaction mixture after the oxidation and into a series of solutions in test tubes. In this manner the gaseous cyanogen could be displaced from the reaction vessel, washed free of hydrocyanic acid by passing the gas flow through two tubes containing acidified 10% silver nitrate solution, and then passed into two tubes containing 0.5 M sodium hydroxide which can hydrolyze cyanogen quantitatively to cyanide and cyanate (67). Cyanide can then be

$$(CN)_2 + 2OH^- \longrightarrow CN^- + NCO^- + H_2O$$

titrated by a Liebig titration (68). The presence of cyanide ion

was also indicated by the formation of the characteristic Prussian Blue precipitate. Yields of cyanogen were much lower if the permanganate oxidation was carried out at room temperature or if the reaction mixture was allowed to stand for any length of time before acidification due mainly to extensive hydrolysis under these conditions. If the oxidation was carried out at pH 9 at room temperature no cyanogen was found. Also cyanogen was not found when freshly precipitated manganese dioxide was used as the oxidizing agent. Paracyanogen or cyanogen polymer could not be observed when the reaction mixture after oxidation was slightly acidified and the manganese dioxide reduced with sodium bisulphite to obtain a clear solution.

2. Cyanate analysis.

(a) Cyanic acid can be converted quantitatively (69) to carbon dioxide and ammonia by acid hydrolysis and

$$HOCN + H_3O^+ \longrightarrow CO_2 + NH_4^+$$

the latter determined by usual Kjeldahl method. Cyanogen was first removed from the reaction solutions before carrying out the Kjeldahl analysis.

(b) A gravimetric method, found to be reliable, involved the precipitation of cyanate as the silver salt after neutralizing the alkaline reaction mixtures to pH 5. This method cannot be used when the oxidation is carried out below pH 11, since cyanide,

recovered in the reaction mixture is precipitated as silver cyanide.

3. Carbon dioxide analysis.

The total CO_2 content of the reaction mixtures can be determined by using the same technique as for the analysis of cyanogen. N_2 gas is bubbled through the acidified oxidation mixture, then through an acidified 10% silver nitrate solution, into two tubes containing standard barium hydroxide solution. The unneutralized barium hydroxide is then titrated with standard acid. The amount of carbon dioxide which is actually present in the oxidation mixture at a given pH is the total amount minus the amount produced from cyanate hydrolysis.

4. Cyanide analysis.

Cyanide can be conveniently analyzed for by the usual Liebig titration once the reaction mixtures are clear. Below pH 12 where a 2:3 molar ratio of permanganate-cyanide are used the precipitated MnO_2 is filtered off. Above pH 12 where a 2:1 molar ratio is used barium nitrate is added initially to the reaction mixture to precipitate insoluble barium manganate which is removed by filtration to obtain a clear solution.

B. Reagents.

Potassium cyanide:

Baker and Adamsons Reagent chemical was used in most of the experiments. The granular solid was dried under vacuum over calcium chloride and samples weighed into brown bottles and dissolved by the required amount of distilled water which had been previously boiled to remove the dissolved gases. Samples were then standardized against 0.1 M silver nitrate solution by a Liebig titration. Solutions, under these conditions kept their titre for two weeks or more and gave reproducible kinetic results. Potassium cyanide was also weighed accurately into a volumetric flask and the titre, as determined by a Liebig titration agreed to within 0.8% of that calculated from the weight of material. Potassium cyanide was also recrystalized from water and gave similar kinetic results as the solutions prepared in the above manner.

Potassium permanganate:

Solutions were prepared and standardized against sodium oxalate according to the procedure of Vogel (68).

Silver nitrate:

Baker and Adamsons Reagent chemical was used. The material was pulverized, dried at 110° for two hours, and weighed into volumetric flasks.

Potassium hydroxide:

Acculute 1 N (CO_2 free) was used for many experiments.

Sodium hydroxide:

"Analar" Grade pellets were dissolved in water under conditions which caused precipitation of the carbonates. The clear solution was diluted with boiled distilled water to the required concentration and then standardized against hydrochloric acid. Similar kinetic results were obtained whether sodium or potassium hydroxide was used.

Inorganic salts:

Reagent grade potassium sulphate, potassium nitrate, barium nitrate, strontium nitrate, sodium thiosulphate, dipotassium hydrogen phosphate were used as obtained.

Potassium manganate solutions:

Alkaline manganate solutions were prepared by the method of Waters (14). The oxidizing power and alkalinity of the solutions were determined by an iodometric and hydrochloric acid titration methods respectively. A small correction to the alkalinity is required due to disproportionation of manganate. When manganate solutions were diluted, the solution was not allowed to become less basic than 0.01 M sodium hydroxide.

C. Kinetic Methods.

A number of methods were used to follow the rate of alkaline

permanganate oxidation of cyanide. Iodometric and spectrophotometric methods were used to follow the rate of reduction of permanganate. A technique to follow the rate of a fast oxidation reaction was also developed. An argentimetric method was used to follow the rate of oxidation of cyanide.

1. Iodometric method - Typical kinetic run:

Overall conditions: $[KOH] = 0.1$ M; $[CN^-]_o = 0.00024$ M; $[MnO_4^-]_o = 0.0005$ M; $\mu = 0.2\ (K_2SO_4)$; Temperature $25 \pm 0.05°$.

To a 500 ml. volumetric flask was pipetted 55 ml. of 1 M potassium hydroxide solution, 36.3 ml. of 0.5 M potassium sulphate solution and 1.35 ml. of 0.1 M potassium cyanide solution. The flask was made up to the mark with boiled distilled water and the solution mixed thoroughly. Fifty ml. samples were then pipetted into 125 ml. glass stoppered erlenmeyers and the erlenmeyers brought to a temperature of $25 \pm 0.05°$ in a constant temperature bath. The reaction was initiated by introducing 4.73 ml. of 0.00574 M permanganate solution with manual stirring from a rapid delivery pipette. The reaction was quenched at a given time interval with an acidified potassium iodide solution. The liberated iodine was titrated immediately with thiosulphate solution from a 5 ml. capacity microburette. The time and volume of thiosulphate were recorded and in most cases at least eight points were obtained for the kinetic plots. The procedure for following the rate of

manganate oxidation of cyanide was similar except that equimolar concentrations of reactants were used.

2. Spectrophotometric method:

A Beckman DU spectrophotometer was used to measure the change in optical density as permanganate was being converted to manganate. Since their absorption curves overlap at their respective absorption maxima, the reaction was followed at two wavelengths, 522 mμ and 426 mμ for permanganate and manganate respectively.

Typical kinetic method:

Overall conditions: $[KOH] = 0.1$ M; $[CN^-]_o = 1.84 \times 10^{-4}$ M; $[MnO_4^-]_o = 3.67 \times 10^{-4}$ M; Temperature $25 \pm 0.05°$.

Two reaction mixtures were made up in glass stoppered erlenmeyer flasks by addition of 1.88 ml. of 0.0049 M potassium cyanide solution, 5 ml. of 1 M potassium hydroxide solution and 38.4 ml. of boiled distilled water to each flask. Final volume after addition of permanganate solution was 50 ml. This solution and the permanganate solution were brought to a temperature of $25 \pm 0.05°$ in a constant temperature bath. The Beckman DU spectrophotometer, fitted with thermospacers, was brought to the same temperature by means of a pumping system attached to the constant temperature bath. The reaction was initiated by introducing 4.73 ml. of 0.00388 M permanganate solution to the alkaline mixture with stirring and immediately transferring a small portion to the 1 cm. Beckman

cell. In transferring the solution to the Beckman cell, the temperature readings dropped slightly and, therefore, optical density readings were commenced after the solution reached the required temperature (approximately 3 minutes). A series of absorption readings were taken at 522 mμ. A similar process was followed using the second alkaline cyanide solution where absorption readings were taken at 426 mμ at the same time intervals.

3. Argentimetric method:

A typical kinetic method for following the rate of oxidation of cyanide is the following:

Overall conditions: $[KOH] = 0.01$ M; $[CN^-]_o = 5.02 \times 10^{-4}$ M
$[MnO_4^-]_o = 10 \times 10^{-4}$; $\mu = 0.1$;
Temperature $25 \pm 0.05°$.

To a 500 ml. volumetric flask was added 2.26 ml. of 0.1226 M potassium cyanide solution, 4.99 grams of potassium nitrate and 5.49 ml. of 1 M potassium hydroxide solution. The solution was made up to the mark with boiled distilled water and 50 ml. aliquots were pipetted into 125 ml. glass stoppered erlenmeyer flasks. After being brought to a temperature of $25 \pm 0.05°$ in a constant temperature bath 4.92 ml. of 0.0116 M permanganate solution was added to each solution to start the reaction. The reaction was timed and then quenched with 1 drop of 30% hydrogen peroxide and the manganese dioxide filtered off. The clear solution was then titrated for cyanide by

a Liebig titration using 0.05 M silver nitrate solution delivered from a microburette.

4. Fast reaction kinetics:

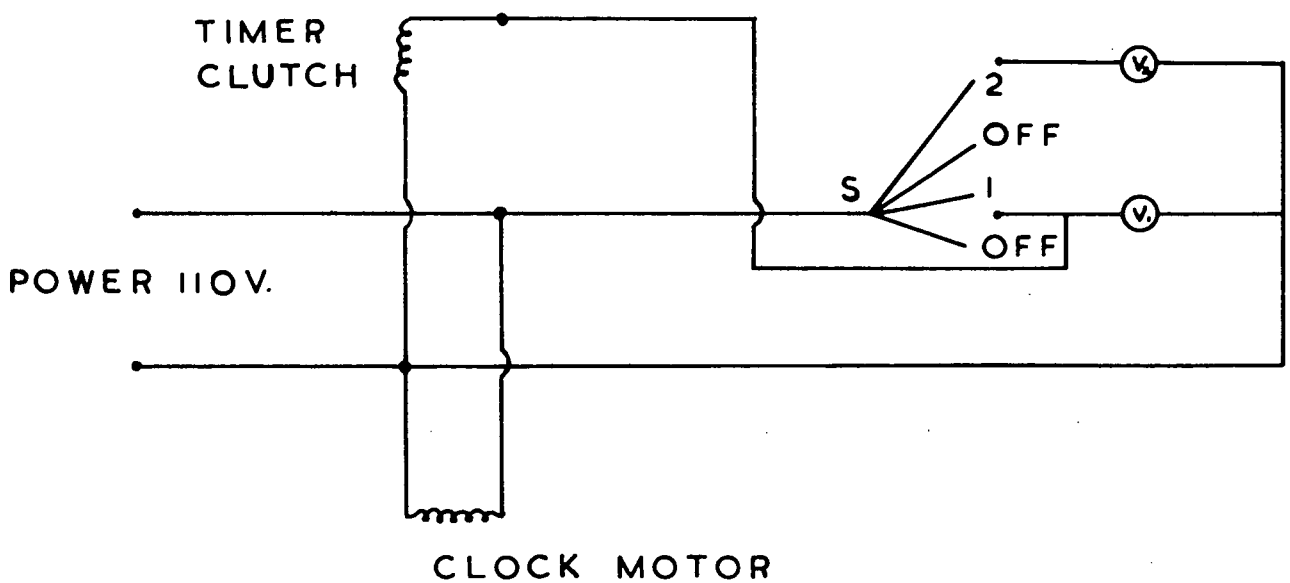
It became apparent that the normal iodometric method in which reactants and quenching mixtures are mixed manually was not suitable for reactions with half lives of around one minute or less. Therefore, an iodometric method was developed which involved the timing of the reaction and introduction of permanganate and quenching solutions under N_2 pressure. Electronic air valves connected to a timer circuit were used to perform this operation.

(i) Description of apparatus:

The circuit was set up as shown in Figure 10. An S-1 Standard timer Model WD-7742-B was used. A switch S and timer were set into a central box. Two air valves, General Controls type K-20-3 were mounted on the constant temperature bath and connected by pressure tubing from the N_2 cylinder to the glass cells I and II. Approximate cell size was 5.5 cms. x 2.5 cms. A 125 ml. glass stoppered erlenmeyer fitted with side arms served as the reaction flask. The reaction mixture was stirred by the use of a polythene bar magnet inserted into the reaction flask. Another bar magnet was wired to the chuck of an air driven stirrer and the assembly and flask were immersed in a constant temperature bath. Glass cells I and II were placed in position as indicated in the diagram. Each cell had two inlets, one for N_2 gas and the other for

FIGURE 10.

WIRING DIAGRAM FOR TIMER CIRCUIT



introducing a pipette. The latter inlet was fitted with tubing and a pinch clamp. The outlet tube consisted of a ball and socket joint for easy manipulation.

(ii) Typical kinetic run using timer circuit.

An alkaline cyanide solution was made up and aliquots taken as in Method C,1. Four ml. of a permanganate solution was pipetted into cell I and the quenching mixture into cell II. The pinch clamps were closed and both cells set in position as given in the diagram (Figure 11).* The reaction was started by switching S to position (1) which opens valve V_1 and starts the timer. The surge of N_2 gas (5 lbs/sq. in.) forces the permanganate solution into the alkaline cyanide solution which was being vigorously stirred by the bar magnet arrangement. The reaction was stopped by turning the switch to position (2). This activates valve V_2 and introduces the acidified-iodide solution as well as stopping the clock. The flask was removed from the bath and titrated in a similar manner. For times over one minute an ordinary timer was used and the mixture quenched in the normal way. In order to quench the strongly alkaline permanganate solution, crushed ice was added to the acid-iodide mixture before quenching to keep the lose of iodine to a minimum. *See Page 125 for Figure 11.

D. Oxygen-18 Tracer Techniques.

1. Oxidation of cyanide with permanganate-O^{18}:

Procedure (a) Silver cyanate obtained under stoichiometric reaction conditions.

A typical experiment was performed as follows: Overall conditions; Volume of solution 55 ml., approximate alkalinity 4 M, $[CN^-]_o$ = 0.0195 M; To a 125 ml. glass stoppered erlenmeyer was added 0.304 grams of potassium permanganate (0.00192 moles ; 1.114% enriched in O^{18}) dissolved in 25 ml. boiled distilled water, 10 ml. of 0.2 M barium nitrate solution and 14 ml. of 15.8 M sodium hydroxide (carbonates removed) solution. The solution was cooled and immediately 5.5 ml. of 0.195 M (0.00107 moles) potassium cyanide solution was pipetted into the stirred alkaline permanganate solution. The reaction mixture was allowed to stand for approximately five minutes at room temperature. The solution was centrifuged and the supernatant liquid filtered through a sintered glass funnel to remove the remaining insoluble barium manganate. The clear alkaline solution was then neutralized to pH 5 with dropwise addition of 4 M nitric acid. The neutralizing mixture was cooled in an ice bath while the solution was vigorously stirred with a magnetic stirring arrangement. Four ml. of 0.5 M silver nitrate solution was added, silver cyanate was allowed to settle and filtered on a sintered glass funnel, washed and then dried over P_2O_5 under vacuum.

Procedure (b) Silver cyanate obtained using a two fold excess permanganate-O^{18}.

When a two fold excess of labeled permanganate was

used, the excess permanganate was reduced with a few drops of 30% hydrogen peroxide after allowing the reaction mixture to stand for two minutes. After filtering and centrifuging the manganese dioxide-barium manganate precipitate, the solution was neutralized and the silver cyanate precipitated as in the previous procedure.

Procedure (c) Silver cyanate obtained under dilute reaction conditions.

Overall conditions; Volume of solution 500 ml. of water; Alkalinity 0.2 M; $[CN^-]_o = 2.2 \times 10^{-3}$ M; $[MnO_4^-]_o = 2.27 \times 10^{-3}$ M. To a 1000 ml. stoppered erlenmeyer was added 0.172 gr./(0.00109 moles) of labeled permanganate dissolved in 300 ml. of water, 5.6 grams of barium nitrate dissolved in 150 ml. of water, then 49 ml. of 2.04 M sodium hydroxide solution. To the vigorously stirred mixture was added 10 ml. of 0.1088 M (0.00109 moles) potassium cyanide solution. The reaction mixture was allowed to stand until the permanganate colour was not observed (approximately 15 minutes) and then the combined silver cyanide-silver cyanate precipitate obtained as before.

2. Determination of oxygen exchange between cyanate and H_2O^{18}:

A typical experiment was performed as follows: A sample of recrystallized potassium cyanate (0.092 grams, 0.00113 moles) was weighed into a 4 ml. stoppered flask and dissolved with 2 ml. of water ($>$ 1.4% enriched in O^{18}). The pH of the solutions as measured on a Beckman Model G pH meter, was varied by addition of

concentrated sodium hydroxide or dilute nitric acid. Solutions were neutralized with nitric acid where necessary. The solution was allowed to stand in a constant temperature bath at 25° for 30 minutes. The solution was transferred to a 5 ml. centrifuge tube and the cyanate precipitated with silver nitrate solution. The precipitate was centrifuged, the liquid decanted and the solid washed with water. The wet precipitate was transferred to a 5 ml. beaker, dried over calcium chloride and then over P_2O_5 under vacuum.

3. O^{18} analysis of silver cyanate:

Two methods were found suitable to convert silver cyanate to carbon dioxide which could be conveniently analyzed for O^{18} content by a Mass Spectral method.

(a) Sulphuric acid method.

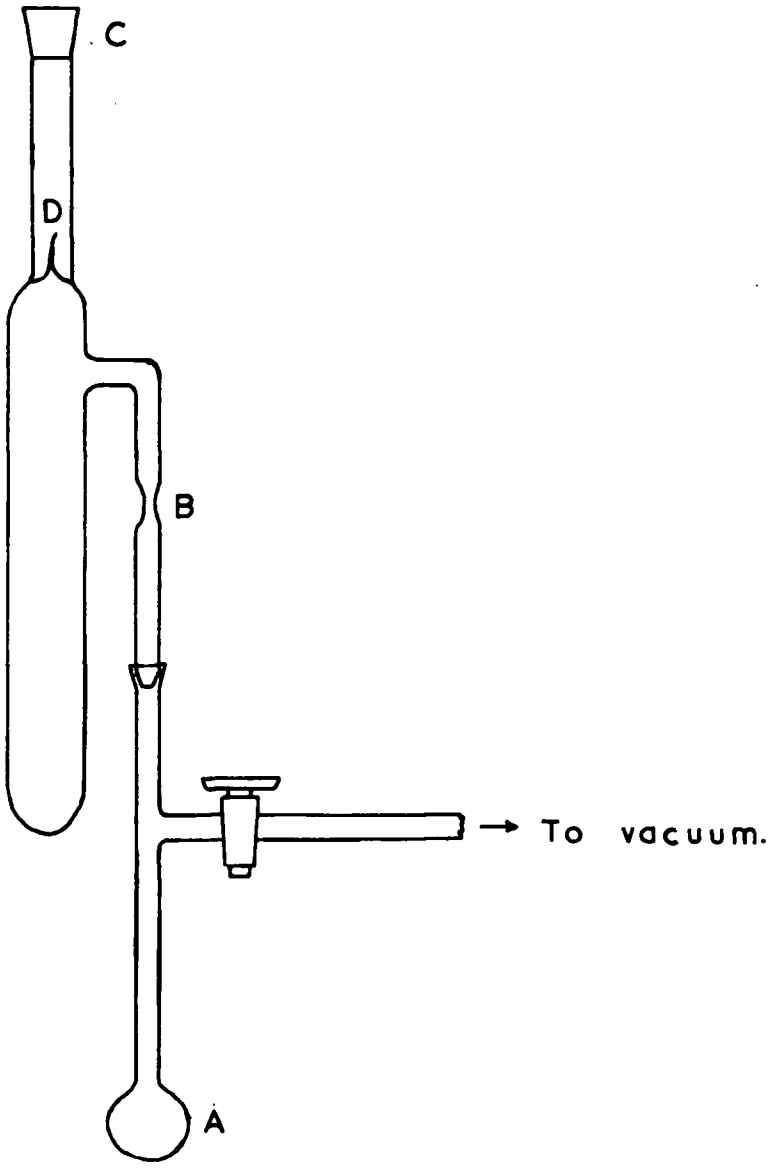
(b) Pyrolysis method.

(a) The sulphuric acid method involved dropping silver cyanate on to concentrated sulphuric acid and collecting the carbon dioxide evolved. The procedure in more detail is given as follows: (Refer to diagram of apparatus, Figure 12) One ml. of concentrated sulphuric acid was frozen by a Dry Ice-acetone mixture in the bulb A, then approximately 0.06 grams of silver cyanate was placed on the cold sulphuric acid. A break seal was fitted to the carbon dioxide generator as in the diagram, the bulb being kept in the Dry Ice-acetone mixture. The system was

FIGURE 12

APPARATUS USED TO COLLECT CARBON DIOXIDE

FROM SILVER CYANATE SAMPLES.



evacuated for a few minutes through the side arm to 0.02 mm. The stopcock on the generator was closed and the mixture allowed to warm to room temperature. A gas was evolved and the break seal closed at B before the silver cyanate had completely decomposed. The break seal could be attached to the gas handling equipment of a mass spectrometer at C and the gas introduced by breaking the glass spiral at D.

The amount of O^{18} found in the silver cyanate can be calculated using the following equation (32); natural abundance of O^{18} = 0.204%.

$$\% \text{ O from permanganate} = \frac{2y - 0.408}{x - 0.204} \times 100$$

$$\text{where } 2y = \frac{I_{mass}{}^{46}}{I_{mass}{}^{44} + I_{mass}{}^{46}}$$

$$x = \% \ O^{18} \text{ in } KMnO_4 = 1.114$$

(b) The pyrolysis method involved decomposing the silver cyanate under a low flame to carbon dioxide.

Attempts to obtain carbon dioxide by heating silver cyanate in the presence of powdered carbon were unsuccessful, but if the silver cyanate precipitate was heated alone under a low flame carbon dioxide was obtained. Thus samples were decomposed using the same apparatus as for the previous method and samples collected and analyzed in a mass spectrometer. Other gases were

produced in the decomposition as observed by scanning the mass spectrum of the gaseous material but unlabeled silver cyanate on decomposition gave the expected normal isotopic abundance for O^{18}.

The amount of O^{18} found in the silver cyanate can be calculated using a similar equation except that now all the oxygen in the carbon dioxide comes from the silver cyanate.

$$\% \, O^{18} \text{ from permanganate} = \frac{y - 0.204}{x - 0.204} \times 100$$

$$2y = \frac{I_{mass}46}{I_{mass}46 + I_{mass}44}$$

$$x = \% \, O^{18} \text{ in } KMnO_4 = 1.114$$

Though similar results were obtained when samples of silver cyanate were subjected to analysis by both methods, this latter method was preferred.

RESULTS

A. Kinetic Results.

The iodometric method was used preferentially to obtain rate data for the alkaline permanganate oxidation of cyanide. An integrated second-order rate expression was applied to the rate data when the hydroxyl ion concentration was 0.01 M or greater and stoichiometric concentration of reactants were used.

$$k_2 = \frac{1}{[CN^-]_o \times t} \times \frac{V_o - V_t}{V_t - 4/5 V_o}$$

where $[CN^-]_o$ - Concentration of cyanide ion at time t = 0.

V_o = Initial volume of thiosulphate.

V_t = Volume of thiosulphate at time t.

V_∞ = 4/5 V_o, Volume of thiosulphate required for complete conversion of permanganate to manganate (usually calculated).

If $V_o - V_t / V_t - 4/5 V_o$ was plotted against time linear plots were obtained over a limited reactant and hydroxyl in concentration range; (See tables of rate constants). Linear second-order rate plots were obtained up to 70% completion of the reaction but most plots were taken to 50% completion. Second order rate constants (k_2, l. mole^{-1} sec.$^{-1}$) were calculated from the slopes of the lines, knowing the initial concentration of cyanide.

Though sufficiently reproducible kinetic results were obtained there are a few difficulties inherent in the iodometric method which should be considered further. The main drawback to this method involves the reduction of all manganese species to the manganous state whereas the valency change in the alkaline oxidation was only from Mn $\overline{VII}$ to Mn $\overline{VI}$. This difficulty could be partially overcome, if 6 to 7 ml. of 0.02 M thiosulphate solution were delivered from the 5 ml. capacity microburette for each titration, the difference between V_o and V_∞ was then sufficient ($\geq$1.30 ml.) to obtain reproducible burette readings. Too dilute a concentration of reactants or titrants leads to erroneous starch-iodine indicator end points. If a series of kinetic experiments were performed such as in the determination of the salt effect or the Arrhenius plots, the same solution (i.e., cyanide, permanganate and alkali) were used to obtain the data in a given series.

For the spectrophotometric method, the extinction coefficients at 522 mμ and 426 mμ were taken from the permanganate and manganate spectra respectively (16).

		λ 522 mμ	λ 426 mμ
$\epsilon_{MnO_4^-}$	-	2370	77
$\epsilon_{MnO_4^=}$	-	387	1370

$$O.D._{522} = 2370\,[MnO_4^-] + 387\,[MnO_4^=]$$

$$O.D._{426} = 77\,[MnO_4^-] + 1370\,[MnO_4^=]$$

Solving for the permanganate concentration

$$\left[MnO_4^-\right] = \frac{O.D._{522} - 0.282\ O.D._{426}}{2248}$$

The integrated second-order rate expression was applied to the rate data

$$k_2 = \frac{1}{2t}\left(\frac{1}{X_t} - \frac{1}{X_o}\right)$$

where X_o is the concentration of permanganate initially and X_t is the concentration of permanganate at time t as calculated from the above equation.

Plots of reciprocal of the permanganate concentration versus time were found to be linear up to approximately 50% reaction and second-order rate constants calculated. The plots become non-linear and variable if the reaction was taken beyond 50% completion

Note: (The contribution of reaction B to k_2 is probably 0 to 10%. The probable error in k_2 is approximately $\pm 5\%$).

TABLE X

Table of second-order rate constants for the permanganate-cyanide reaction under various conditions.

Method	$[CN^-]_o$ - M	$[OH^-]$ - M	μ	k_2, l. mole^{-1}sec.$^{-1}$
S	1.84×10^{-4}	0.1	0.1	3.2
S	2.57×10^{-4}	0.1	0.1	3.2
I	2.44×10^{-4}	0.1	0.1	2.9[a]
I	4.50×10^{-4}	0.1	0.2	4.0[b]
I	2.44×10^{-4}	0.1	0.2	3.9[c]
S	1.74×10^{-4}	0.2	0.2	3.7
I	2.44×10^{-4}	0.2	0.2	3.7[d]
I	2.53×10^{-4}	0.06	0.1	3.0[b]
S	1.84×10^{-4}	0.06	0.1	3.4

I - Iodometric method, S - Spectroscopic method, $[MnO_4^-]_o = 2[CN^-]_o$; Temperature = 25 ± 0.05°; (a) Average of two determinations; (b) Rate constant obtained from the linear portion of the plot; (c) Average of two determinations; (d) Average of three determinations.

TABLE XI

Table of second-order rate constants at various temperatures.

Temperature	0.1 M KOH k_2, l. mole^{-1}sec.$^{-1}$	0.2 M KOH k_2, l. mole^{-1}sec.$^{-1}$
10° ± 0.05	-	1.84
10° ± 0.05	-	1.88
15° ± 0.05	2.30	2.20
15° ± 0.05	2.20	2.16
20° ± 0.05	2.60	2.62
20° ± 0.05	-	2.64
30° ± 0.05	3.50	4.40
35° ± 0.05	4.3	5.80
35° ± 0.05	5.0	5.76

$\left[MnO_4^-\right]_o = 2\left[CN^-\right]_o = 2.44 \times 10^{-4}$ M: Refer to Table X for 25° temperature points.

TABLE XII

Rate constant as a function of ionic strength.

Ionic Strength - μ	k_2, l. mole^{-1}sec.$^{-1}$
0.1	2.90
0.1	2.80
0.133	3.20
0.166	3.40
0.166	3.67
0.200	3.90
0.200	3.90

$[OH^-]$ = 0.1 M; $[CN^-]_o$ = 2.44 x 10^{-4} M; $[MnO_4^-]_o$ = $2[CN^-]$; Potassium sulphate used to vary μ . Temperature 25 $\pm$ 0.05; Iodometric method.

TABLE XIII

Table of second-order rate constants for the permanganate-cyanide reaction under saturated salt (a) conditions.

$[CN^-]_o$ - M	$[OH^-]$ - M	k_2, l. mole^{-1}sec.$^{-1}$
4.04×10^{-4}	0.1 (a)(b)	8.2
2.02×10^{-4}	0.1 (a)(b)	6.4
4.04×10^{-4}	0.2 (b)	8.3
2.02×10^{-4}	0.2 (b)	6.4
4.04×10^{-4}	0.53 (b)	6.0
4.04×10^{-4}	1.55 (b)	6.6
4.04×10^{-4}	2.41	7.8
4.04×10^{-4}	3.36	13.7 ± 10%
4.04×10^{-4}	3.65	20. ± 20%
4.04×10^{-4}	0.03 (b)	165) Initial rates
4.04×10^{-4}	0.03	16.5) taken from the non linear plots

(a) Use of 2 M KNO_3 gave a limiting reaction rate, i.e. further increases in salt concentration did not increase rate of reaction. Iodometric method - Procedure (4). Temperature 25 ± 0.05°.

(b) Ionic strength = 2.0; $[MnO_4^-]_o = 2[CN^-]_o$.

TABLE XIV

Effect of initial amounts of manganate and barium nitrate on the second-order rate constants.

$[CN^-]_o$ - M	$[MnO_4^=]_o$ - M	$[OH^-]$ M	μ	$k_2^{(a)}$, l. mole^{-1}sec.$^{-1}$
1.84×10^{-4}	1.78×10^{-4}	0.1	0.1	2.60
1.84×10^{-4}	3.55×10^{-4}	0.1	0.1	2.60
2.20×10^{-4}	2.13×10^{-4}	0.1	0.1	2.90

$[CN^-]_o$ - M	$[Ba(NO_3)_2]$ - M	$[OH^-]$ M	μ	$k_2^{(b)}$, l. mole^{-1}sec.$^{-1}$
2.53×10^{-4}	0.005 M	0.2	0.215	4.10
2.53×10^{-4}	-	0.2	0.215	3.50[c]
2.53×10^{-4}	0.005 M	0.2	0.215	3.70

(a) Spectrophotometric kinetic method; (b) Iodometric kinetic method; $[MnO_4^-]_o = 2[CN^-]_o$; Temperature 25 ± 0.05°. (c) 0.005 M $Sr(NO_3)_2$ used in this experiment.

of the reaction possibly from light scattering due to precipitation of manganese dioxide caused by disproportionation of manganate.

The rate expression

$$-\frac{d\left[MnO_4^-\right]}{dt} = k_2\left[CN^-\right]\left[MnO_4^-\right]$$

is in agreement with the observed kinetics over a limited reactant and hydroxyl ion concentration range. The second order rate constants k_2, l. mole^{-1}sec.$^{-1}$ obtained by both spectrophotometric and iodometric kinetic methods are in good agreement and indicate that the rate constants, calculated from the rate plots, are reliable. (Table X; Figures 13 and 14).

Observation of Table XIV with reference to Table X indicates that the second-order rate constants are relatively insensitive to additions of initial amounts of manganate ions (Figure 15) and barium ions (Figure 16). Strontium nitrate was used to replace barium nitrate in one experiment in order to keep the ionic strength constant. Addition of initial amounts of manganate to the reaction mixture was possible since this species oxidizes cyanide eighty times slower than permanganate (Figure 17).

Data from Table X and Table XIII indicates that the second order reaction is independent of the hydroxyl ion concentration under constant ionic strength conditions. e.g., a 25 fold change in hydroxyl ion concentration does not change k_2 appreciably.

If increasing amounts of an inert electrolyte (potassium sulphate or potassium nitrate) are added to the reaction mixtures

FIGURE 13

SPECTROPHOTOMETRIC METHOD; SECOND ORDER RATE PLOTS FOR THE PERMANGANATE:CYANIDE REACTION.

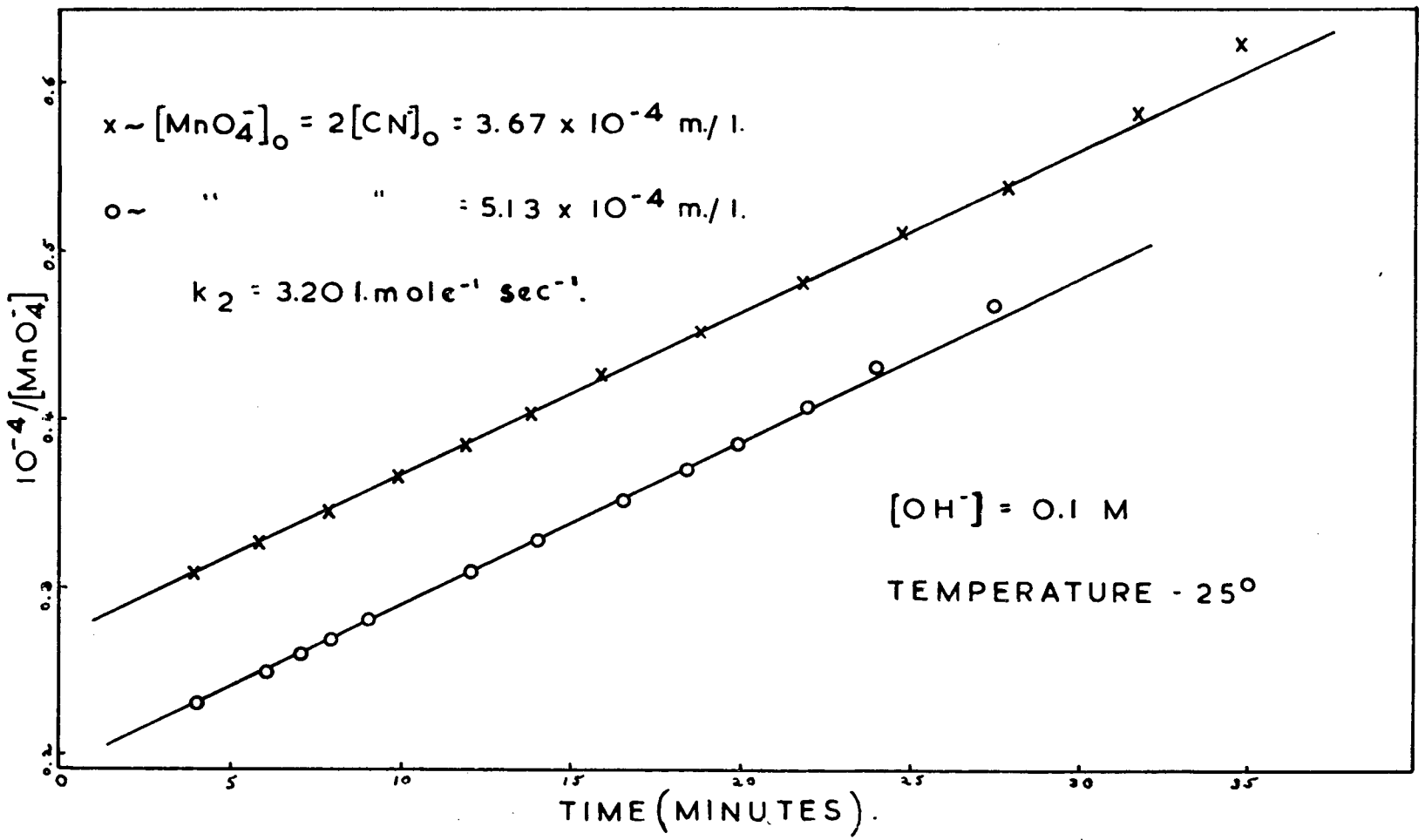


FIGURE 14

VARIATION OF THE SECOND ORDER RATE PLOT WITH REACTANT CONCENTRATION.

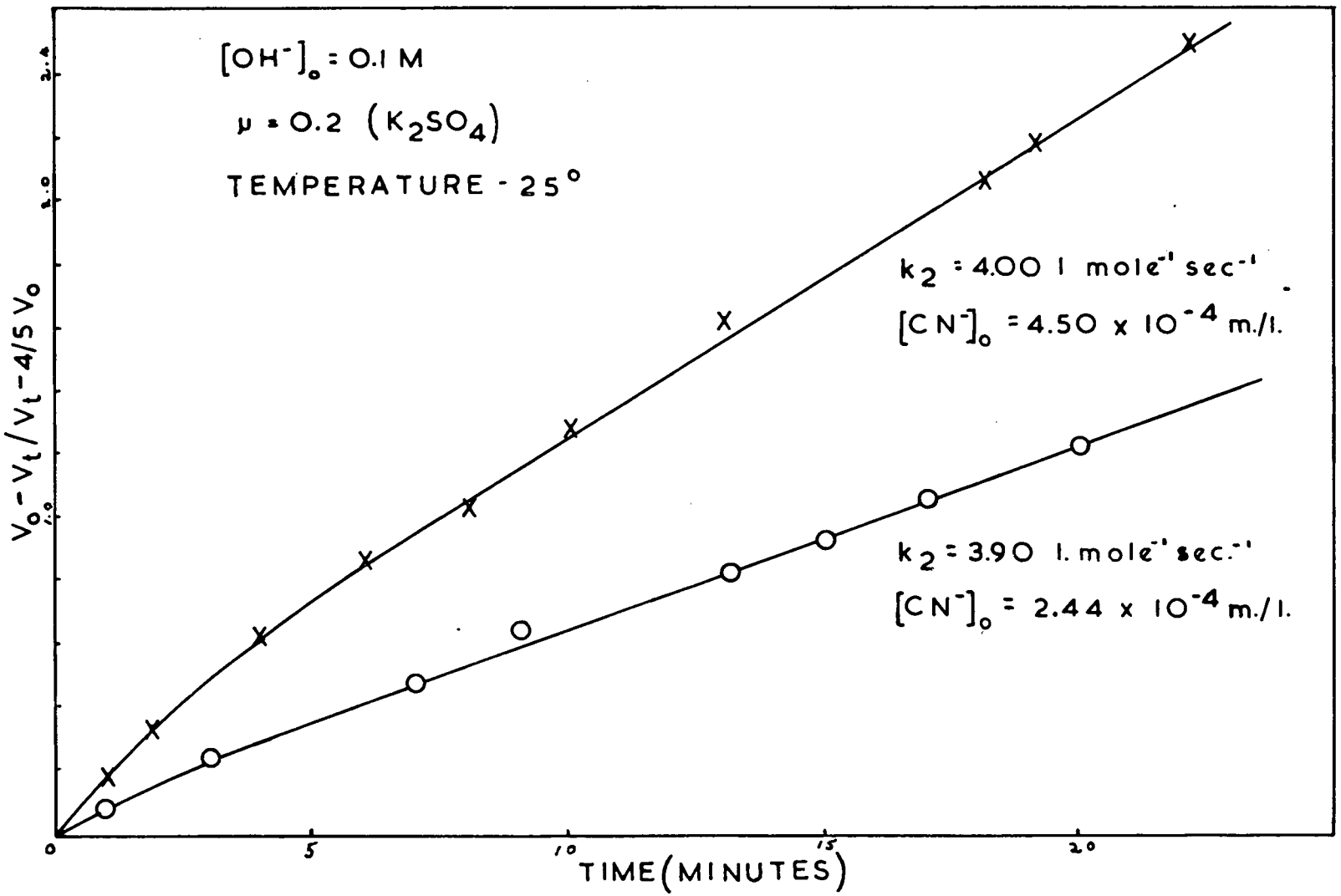


FIGURE 15

EFFECT OF ADDING INITIAL AMOUNTS OF MANGANATE ON THE SECOND ORDER REACTION.

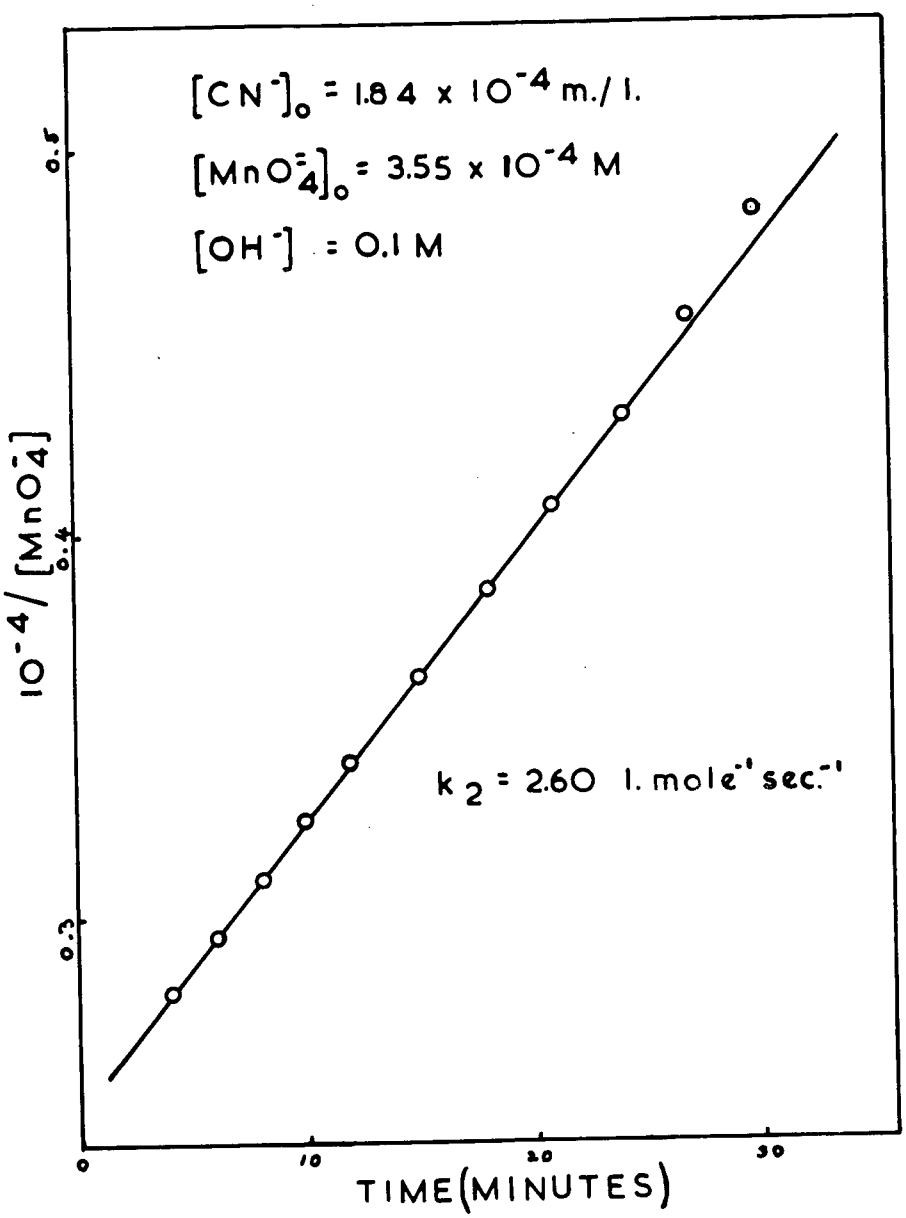


FIGURE 16.

EFFECT OF ADDING INITIAL AMOUNTS OF BARIUM IONS ON THE SECOND ORDER REACTION.

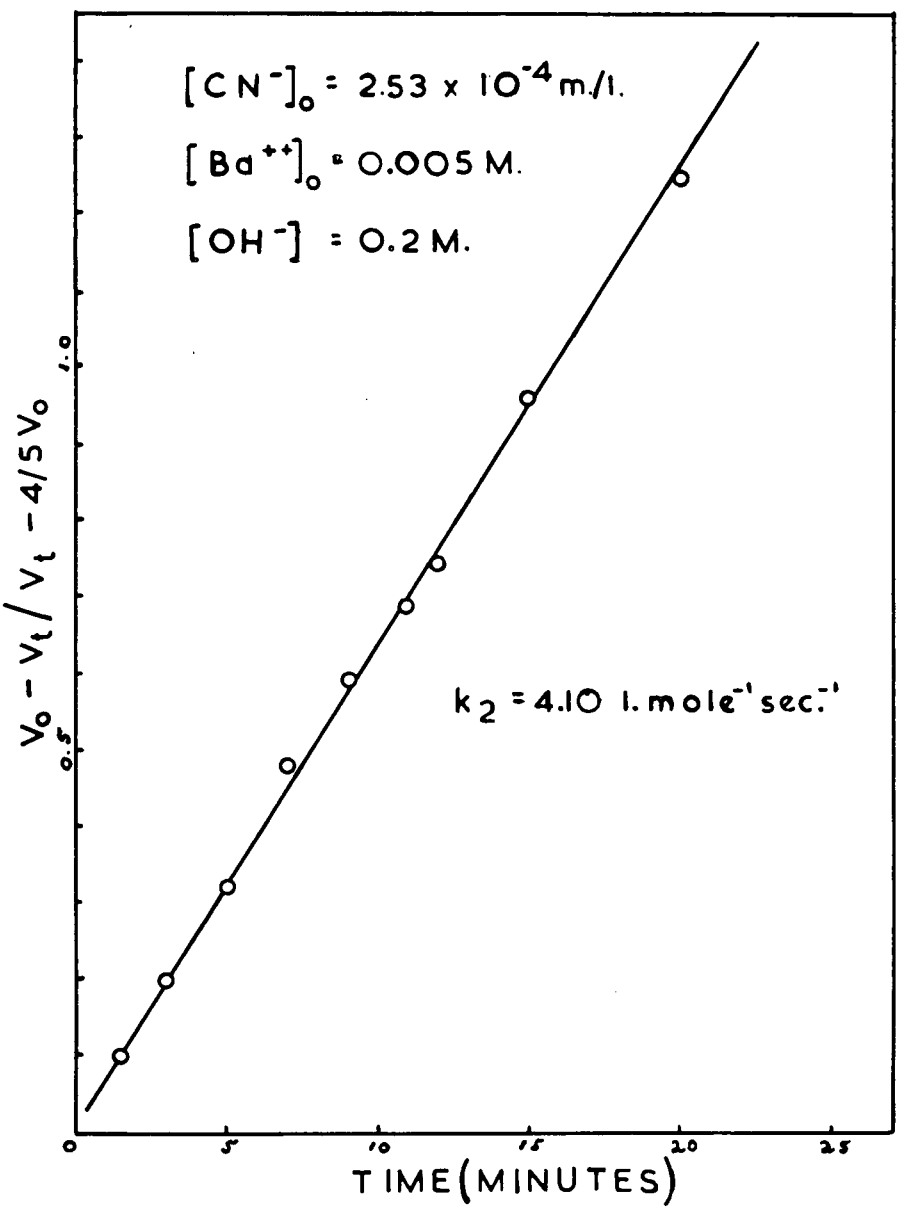


FIGURE 17

SECOND ORDER RATE PLOT FOR THE ALKALINE MANGANATE OXIDATION OF CYANIDE.

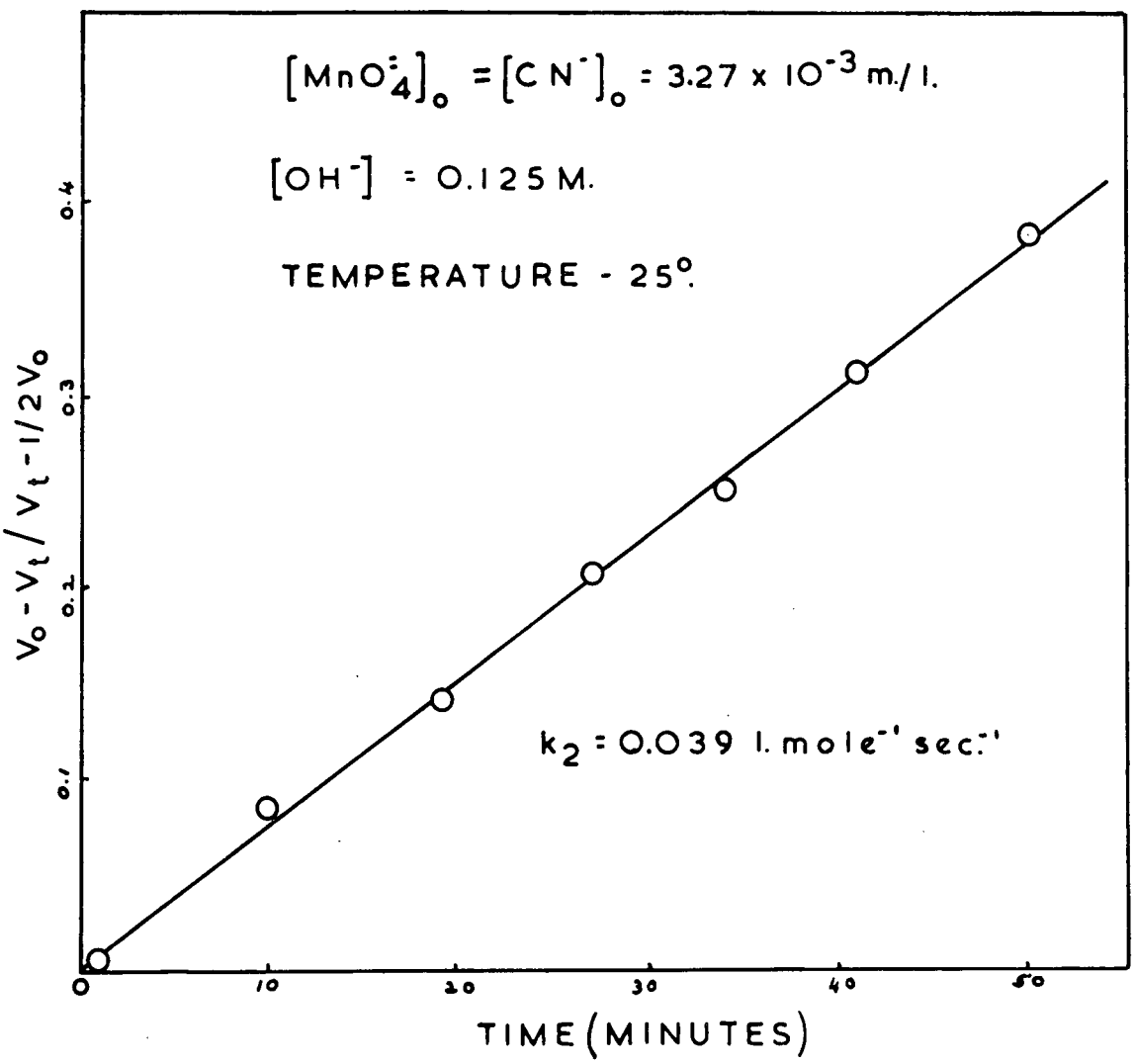


FIGURE 18

PLOT OF LOG k_2 VERSUS $\sqrt{\mu}$ FOR THE ALKALINE PERMANGANATE OXIDATION OF CYANIDE.

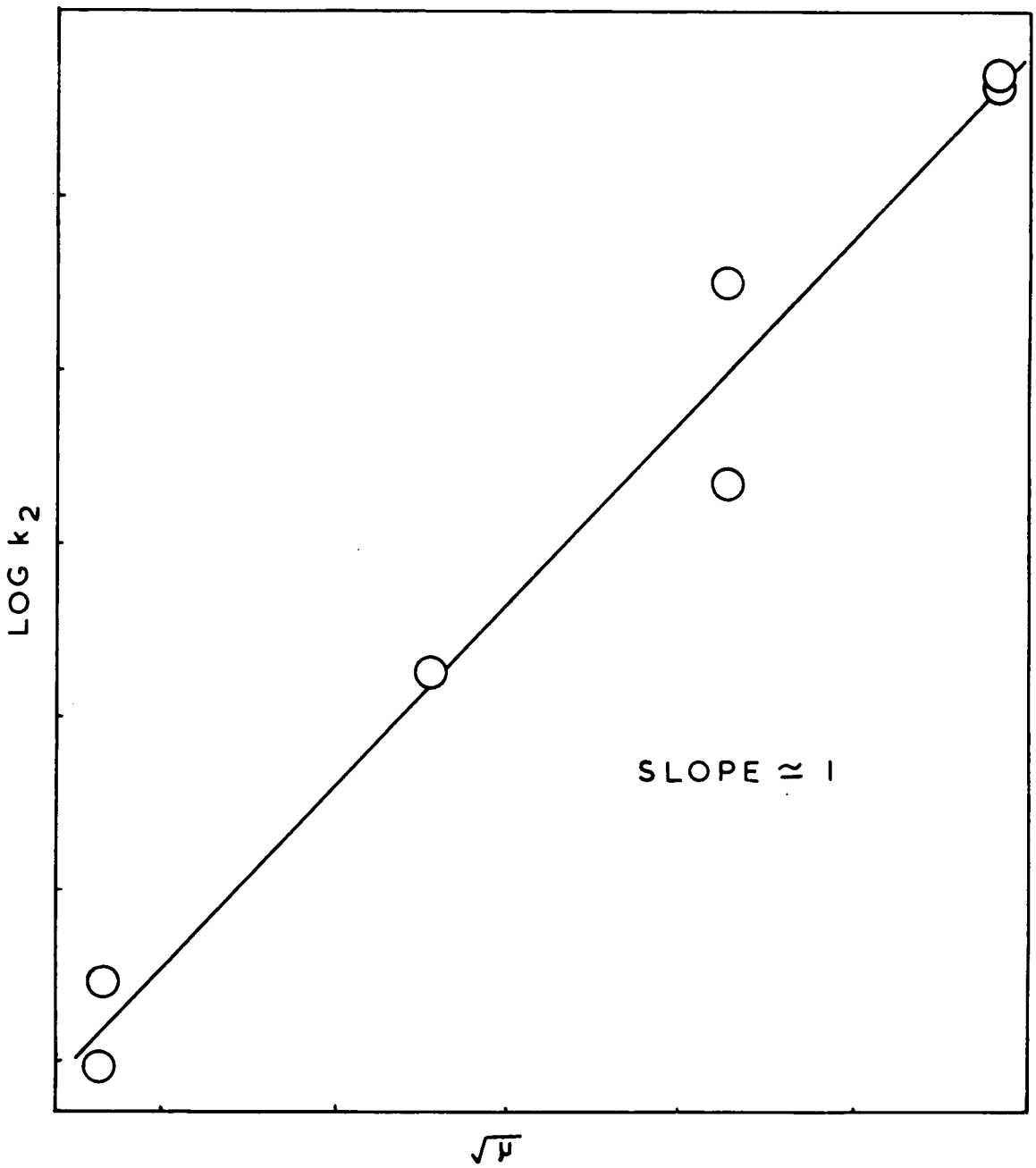


FIGURE 19

PLOT OF LOG k_2 / T°K VERSUS 1000/T°K FOR THE PERMANGANATE : CYANIDE REACTION AT 0.1M KOH.

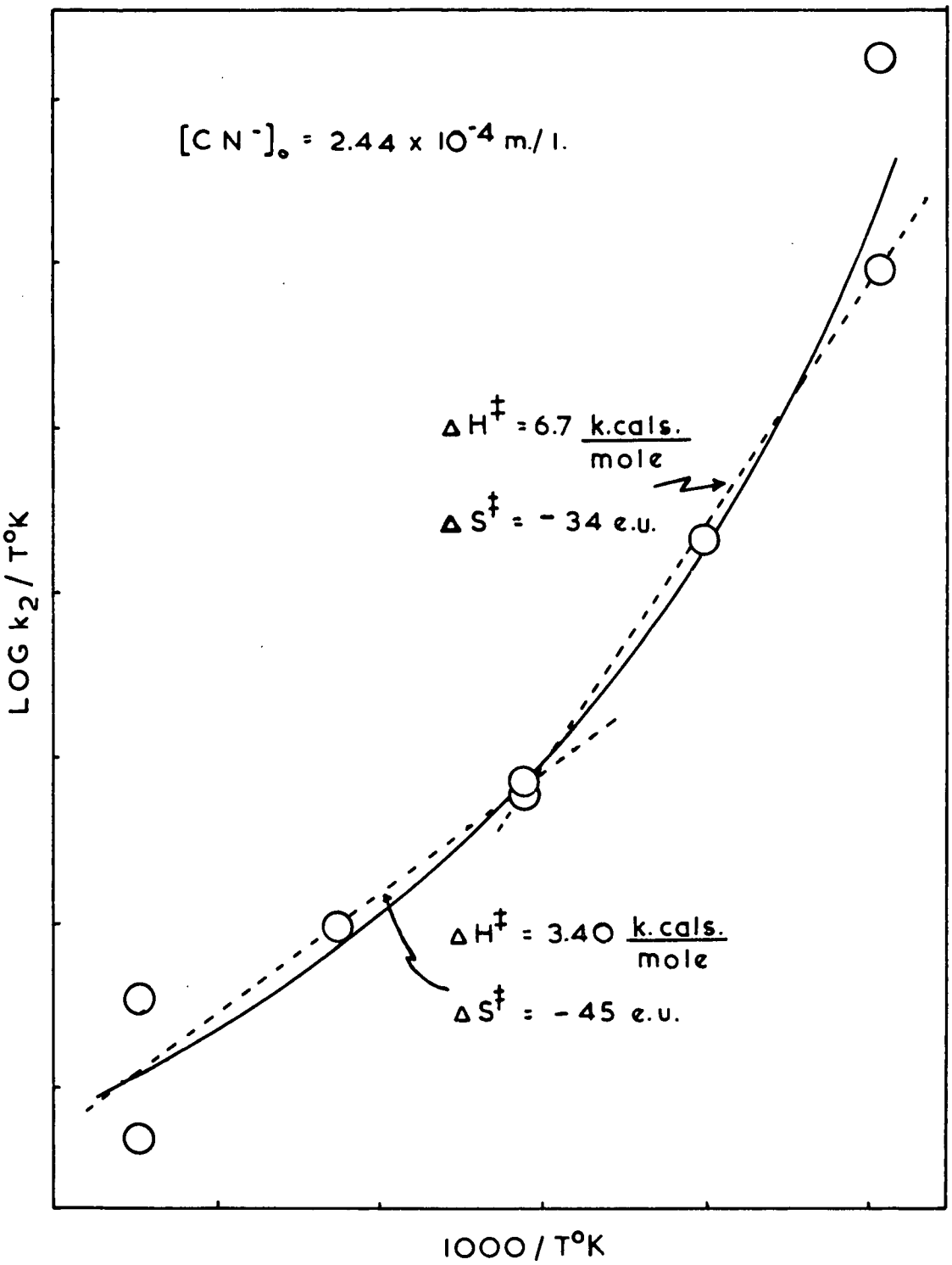


FIGURE 20

PLOT OF LOG k_2 / T°K VERSUS 1000/T°K AT 0.2M KOH

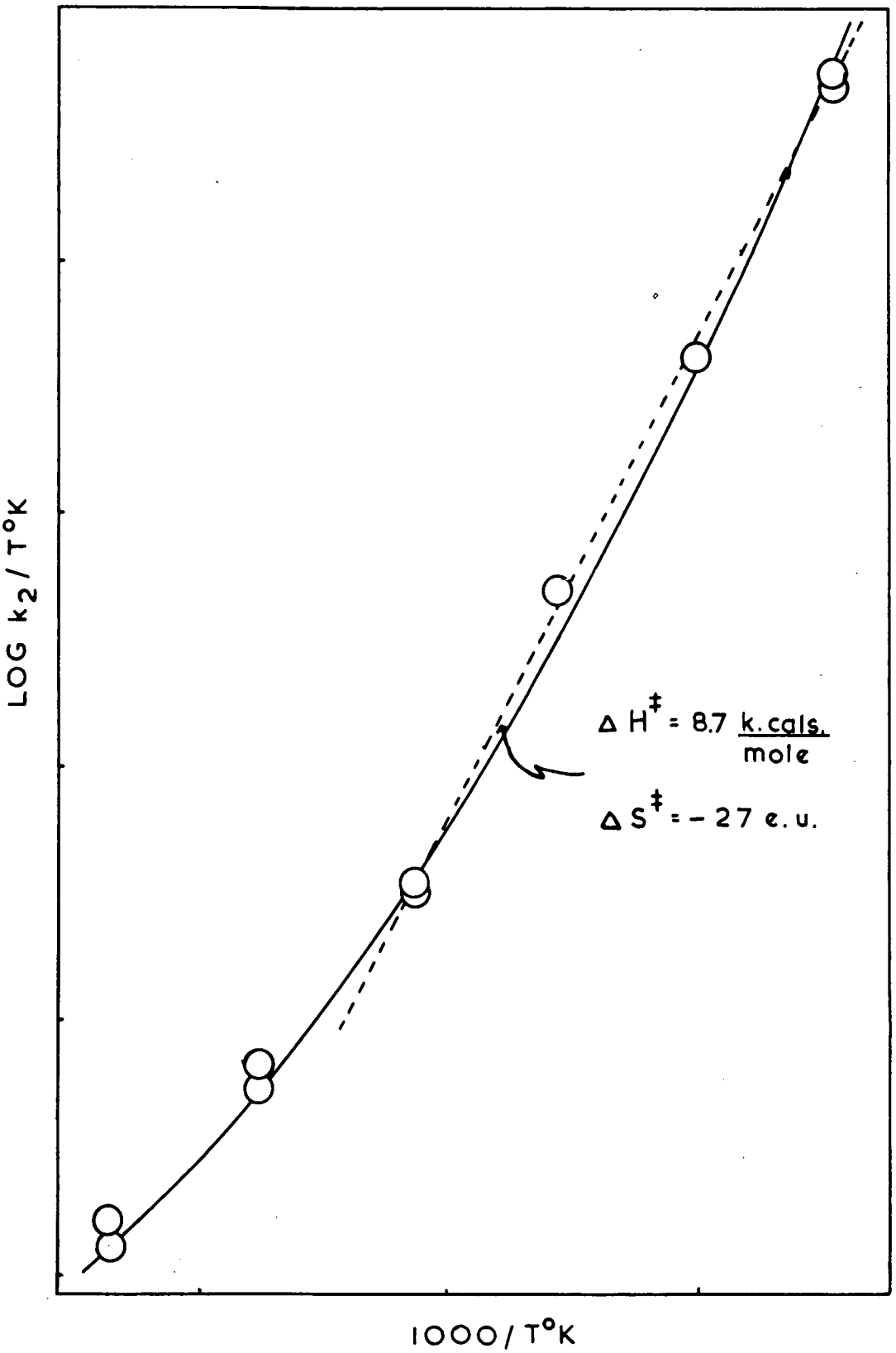


FIGURE 21

VARIATION OF THE SECOND ORDER RATE PLOTS WITH REACTANT CONCENTRATION AT 0.1M NaOH. $[MnO_4^-]_o = 2[CN^-]_o$.

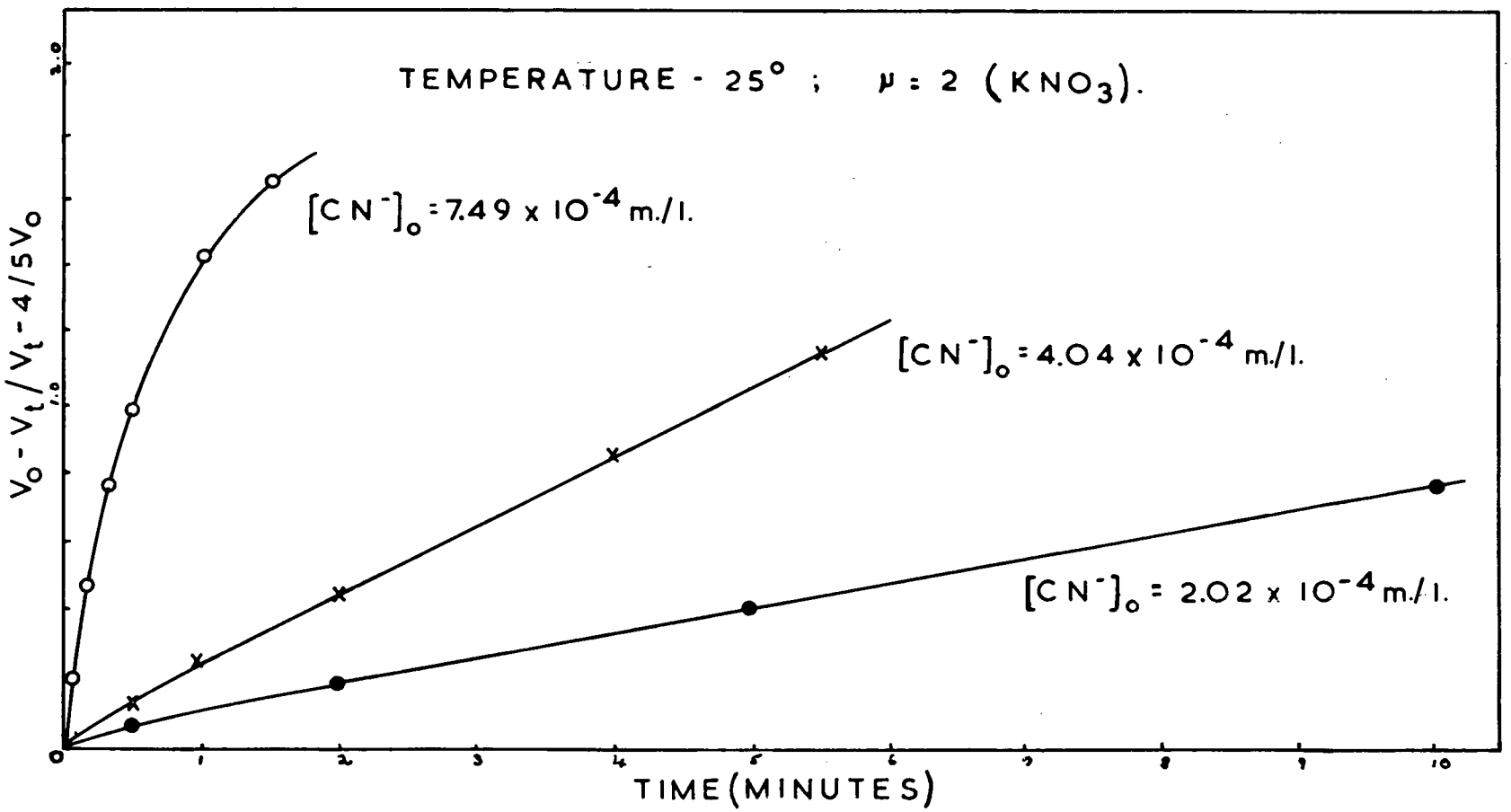
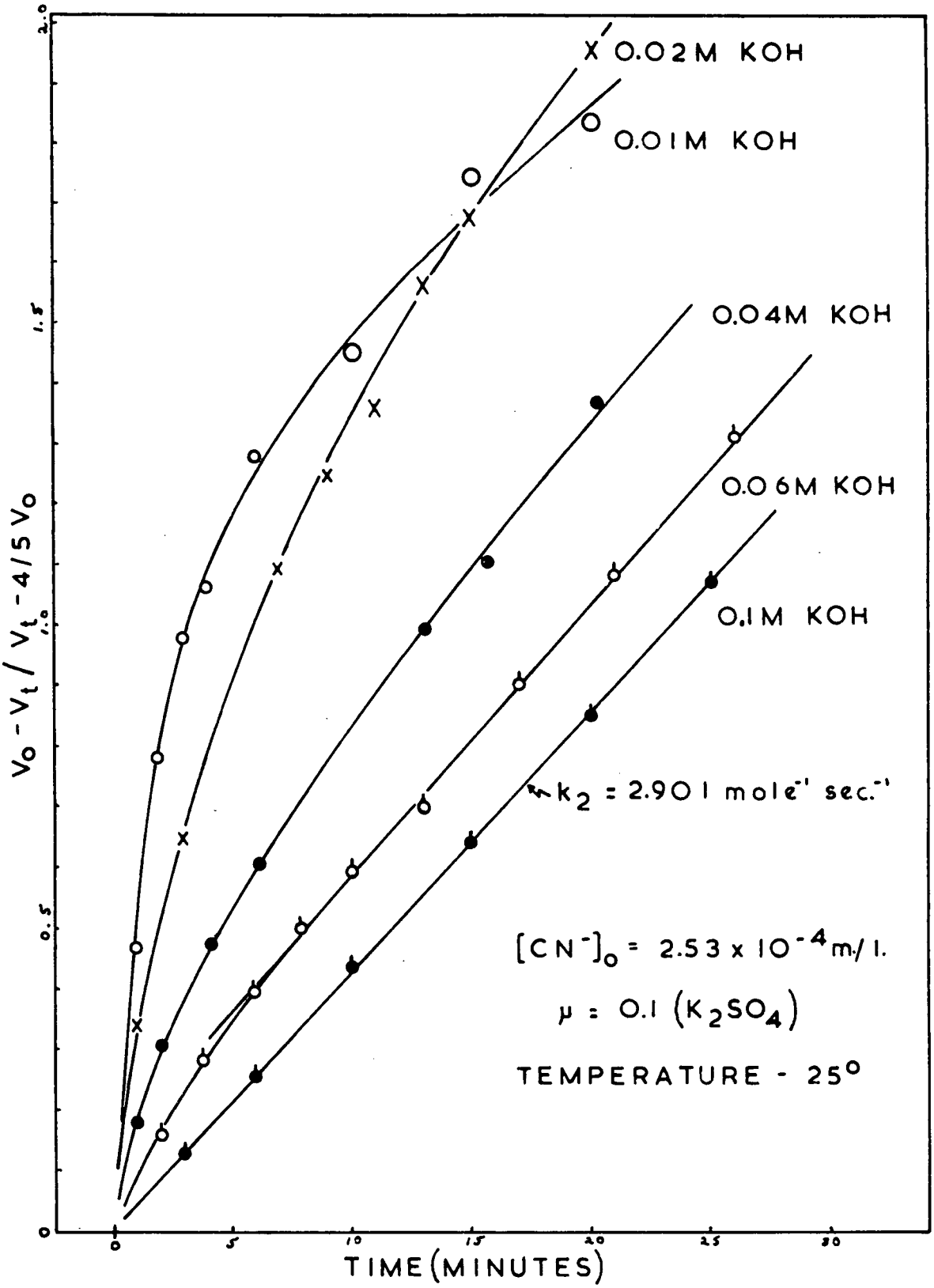


FIGURE 22

VARIATION OF THE SECOND ORDER RATE PLOTS WITH HYDROXYL ION CONCENTRATION. $[MnO_4^-]_o = 2[CN^-]_o$



an increase in rate is observed at 0.1 M potassium hydroxide (Table XII and Table XIII). A primary positive salt effect is observed when log k_2 is plotted against $\sqrt{\mu}$ giving a straight line of slope + 1 (Figure 18). This agreement with the value expected from the Brönsted-Delye-Hückel relationship was surprising since this study was undertaken in a high ionic strength region. This apparent anomalous result will be considered later in the thesis.

In order to determine the thermodynamics of the rate process a temperature study was done at 0.1 M and 0.2 M potassium hydroxide (Figures 19 and 20 and Table XI). When Arrhenius type plots were made, linear plots were not obtained indicating that a more complex process was taking place than was implied by the simple rate expression given previously.

Since a cursory glance at the kinetics indicates the presence of more than one mode of oxidation of cyanide by permanganate, the reaction conditions under which the second order process is observed are summarized as follows:

when (a) $[MnO_4^-]_o = 2[CN^-]_o$ is less than 8×10^{-4} M.

(b) $[OH^-]$ is greater or equal to 0.1 M.

(c) Temperature is 25°.

If second-order rate plots are attempted at higher concentration of reactants at the <u>same alkalinity</u> (Figure 21) or lower alkalinities at the <u>same concentration of reactants</u> (Figure 22), non-linear second-order rate plots are obtained and the rate is found to decrease with time. Under intermediate conditions (Figures 14

and 22) the initial second-order rate plots are non-linear, becoming linear when the concentration of the reactants appears to have been reduced.

The presence of a second mode of oxidation of cyanide is indicated. Its rate appears to be a different function of concentration than the second order process observed at lower concentrations and its rate is inhibited by high hydroxyl ion concentration. In an attempt to separate the two suspected reactions, concentration versus time plots were made for the rate data (Figure 23) which gave non-linear second order kinetics. These curves were smoothed and the slopes $(-d[MnO_4^-]/dt)_{A+B}$ obtained at various times.

Consider two parallel reactions contributing to the overall rate

$$\left(-\frac{d[MnO_4^-]}{dt}\right)_{A+B} = \left(-\frac{d[MnO_4^-]}{dt}\right)_A + \left(-\frac{d[MnO_4^-]}{dt}\right)_B$$

$$\text{where}\left(-\frac{d[MnO_4^-]}{dt}\right)_A = 1/2\ k_2[MnO_4^-]^2$$

$$\text{and}\quad \left(-\frac{d[MnO_4^-]}{dt}\right)_B \propto [MnO_4^-]^n$$

Substituting for reaction A in the above equation and rearranging.

TABLE XV

A typical series of calculations for reaction B.

	Time	$[MnO_4^-]$ m./l.	$\left(-\frac{d[MnO_4^-]}{dt}\right)_{A+B}$
1.	5 sec.	11.57×10^{-4}	0.387×10^{-4}
2.	10 sec.	10.10×10^{-4}	0.236×10^{-4}
3.	20 sec.	8.40×10^{-4}	0.125×10^{-4}
4.	30 sec.	7.45×10^{-4}	0.0735×10^{-4}
5.	45 sec.	6.60×10^{-4}	0.0440×10^{-4}
6.	60 sec.	6.07×10^{-4}	0.0267×10^{-4}
7.	80 sec.	5.70×10^{-4}	0.011×10^{-4}

	$-\frac{1}{2} k_2[MnO_4^-]^2$	$\left(-\frac{d[MnO_4^-]}{dt}\right)_B$	$[MnO_4^-]^3$
1.	0.0427×10^{-4}	0.344×10^{-4}	15.40×10^{-10}
2.	0.0327×10^{-4}	0.203×10^{-4}	10.15×10^{-10}
3.	0.0226×10^{-4}	0.102×10^{-4}	5.93×10^{-10}
4.	0.0178×10^{-4}	0.056×10^{-4}	4.14×10^{-10}
5.	0.0144×10^{-4}	0.030×10^{-4}	2.88×10^{-10}
6.	0.0118×10^{-4}	0.015×10^{-4}	2.24×10^{-10}
7.	0.0104×10^{-4}	0.001×10^{-4}	1.85×10^{-10}

$[CN^-]_o = 7.49 \times 10^{-4}$ M; $[OH^-] = 0.1$ M; $\mu = 2.0$; Temperature 25°;
Under similar conditions at $[CN^-]_o = 2.02 \times 10^{-4}$ M, $k_2 = 6.4$ l. mole^{-1} sec.$^{-1}$.

$$\left(-\frac{d\left[MnO_4^-\right]}{dt}\right)_B = \left(-\frac{d\left[MnO_4^-\right]}{dt}\right)_{A+B} - \tfrac{1}{2} k_2 \left[MnO_4^-\right]^2$$

Therefore if k_2 is known at the same ionic strength and temperature and since reaction A is found to be independent of hydroxyl ion concentration, the rate of reaction A can be subtracted from the overall rate. A typical series of calculation are given in Table XV. A plot of $(-d[MnO_4^-]/dt)_B$ versus $[MnO_4^-]^3$ gives a straight line (Figure 23). This technique was applied to a number of rate plots which gave non-linear second-order kinetics (Figure 24). The results are qualitative (Table XVI) but they do indicate the third-order nature of the reaction.

Thus $$\left(-\frac{d\left[MnO_4^-\right]}{dt}\right)_B = k_3\left[MnO_4^-\right]^3$$

where k_3 = slope of the line = $1.^2$ mole^{-2}sec.$^{-1}$.

TABLE XVI

Table of third order rate constants as obtained from Figures 23 and 24.

$[OH^-]$-M	$[CN^-]$-M	k_3, $1.^2$ mole^{-2}sec.$^{-1}$
0.01 (a)	2.53×10^{-4}	1.6×10^4
0.02 (a)	2.53×10^{-4}	1.1×10^4
0.05 (a)	2.53×10^{-4}	0.5×10^4
0.1 (b)	7.49×10^{-4}	2.5×10^4

TABLE XVI (continued)

(a) Second-order rate constant used here k_2 = 3.00 l. mole^{-1}sec.$^{-1}$; $[CN^-]_o$ = 2.53 x 10^{-4} M; μ = 0.1; Temperature 25°.

(b) μ = 2.0; Temperature 25°.

Observation of Table XVI does indicate that reaction B is inhibited by hydroxyl ions. In order to determine the dependence of rate of reaction B on hydroxyl ion concentration more accurately, another plot using initial rates as obtained from the rate data from pH 12 to 13 was attempted. The initial point of the concentration-time plot was used to obtain $(-\Delta[MnO_4^-]/\Delta t)_{A+B}$ (Table XVII).

TABLE XVII

Date of initial rate as a function of hydroxyl ion concentration.

$[OH^-]$ M	$\left(-\frac{\Delta[MnO_4^-]}{\Delta t}\right)_{A+B}$ (Initial Rate)
0.01	0.034 x 10^{-4}
0.02	0.021 x 10^{-4}
0.04	0.012 x 10^{-4}
0.05	0.0082 x 10^{-4}
0.06	0.0053 x 10^{-4}
0.10	0.0033 x 10^{-4}

$[CN^-]_o$ = 2.53 x 10^{-4} m./l.; μ = 0.1; Temperature 25°

A plot of $(-\Delta[MnO_4^-]/\Delta t)_{A+B}$ versus the reciprocal of the

hydroxyl ion concentration (Figure 25) gives an approximate linear relationship indicating that

$$k_3 \simeq \frac{k_3'}{[OH^-]}$$

The next stage in the investigation of this third-order process was to attempt fast reaction kinetics under pseudo-order reaction conditions, i.e., in this case a ten fold excess cyanide over permanganate. Though the results are only qualitative a plot of log $[MnO_4^-]$ versus time (Figure 26) at 0.03 M NaOH does indicate that over most of the kinetic plot, the rate is first order in permanganate.

In an attempt to determine whether manganate was involved in a prior equilibrium step barium ions were added initially to the kinetic mixture. No marked change in rate was observed at 0.01 M and 0.04 M sodium hydroxide when insoluble barium manganate was precipitated. Also checks were made under various conditions using strontium nitrate to keep the ionic strength constant with no variation in rate being observed. Addition of manganate to the kinetic mixtures initially at low alkalinities pH 12 gave inconclusive results by both spectroscopic and iodometric methods.

The spectrophotometric kinetic method led to marked non-linear second order rate plots only at lower hydroxyl ion concentration, e.g., (0.02 M sodium hydroxide, μ = 0.1) since the permanganate and cyanide concentration used in this method were necessarily lower than those concentrations used in the iodometric method.

FIGURE 23

CONCENTRATION - TIME and THIRD ORDER RATE PLOTS

FOR THE PERMANGANATE - CYANIDE REACTION

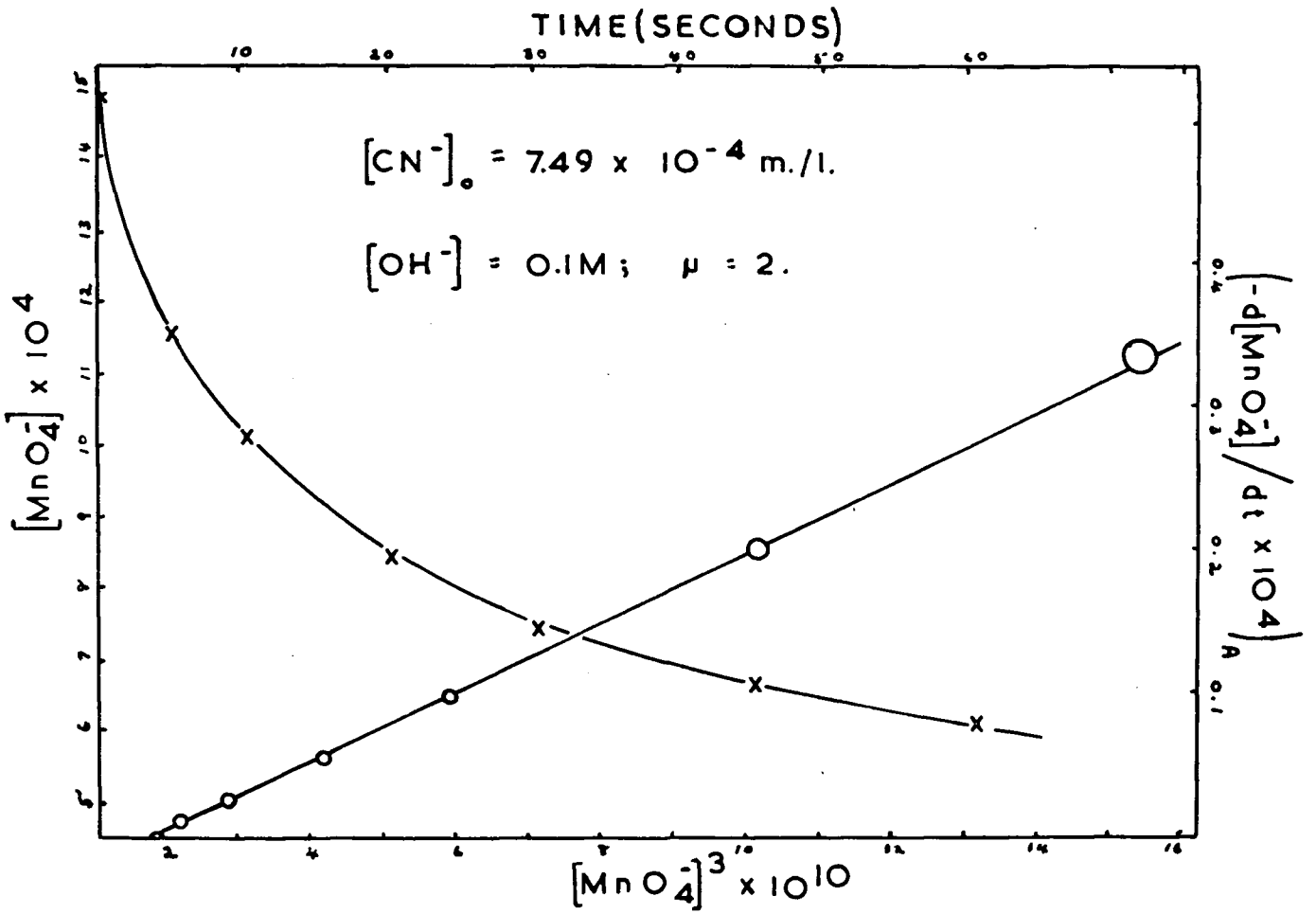


FIGURE 24

THIRD ORDER RATE PLOTS FOR THE PERMANGANATE-CYANIDE REACTION.

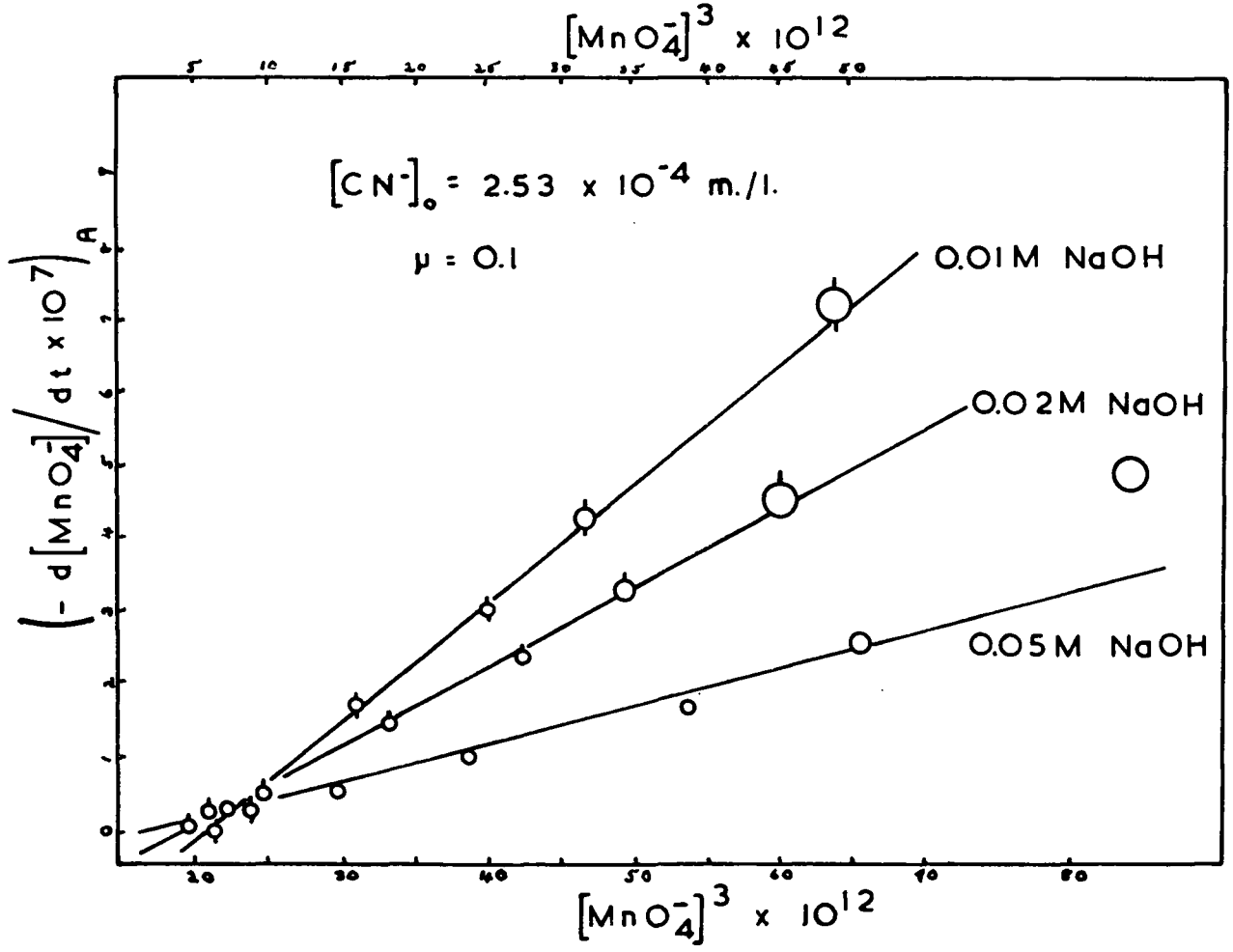


FIGURE 11.

APPARATUS USED TO STUDY RAPID REACTION KINETICS.

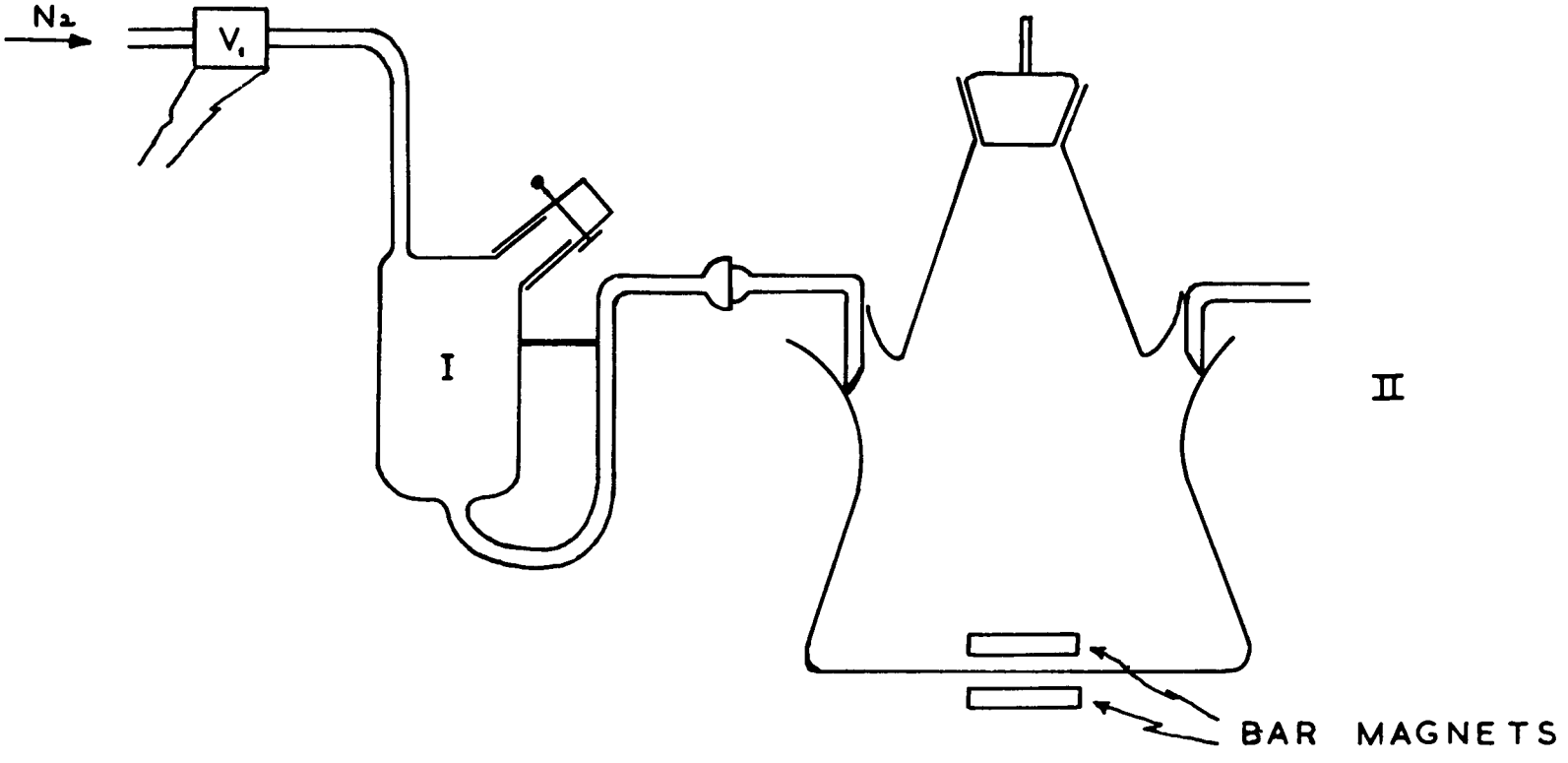


FIGURE 25

PLOT OF INITIAL RATE FOR THE PERMANGANATE -CYANIDE REACTION VERSUS $1/[OH^-]$; pH 12 TO 13.

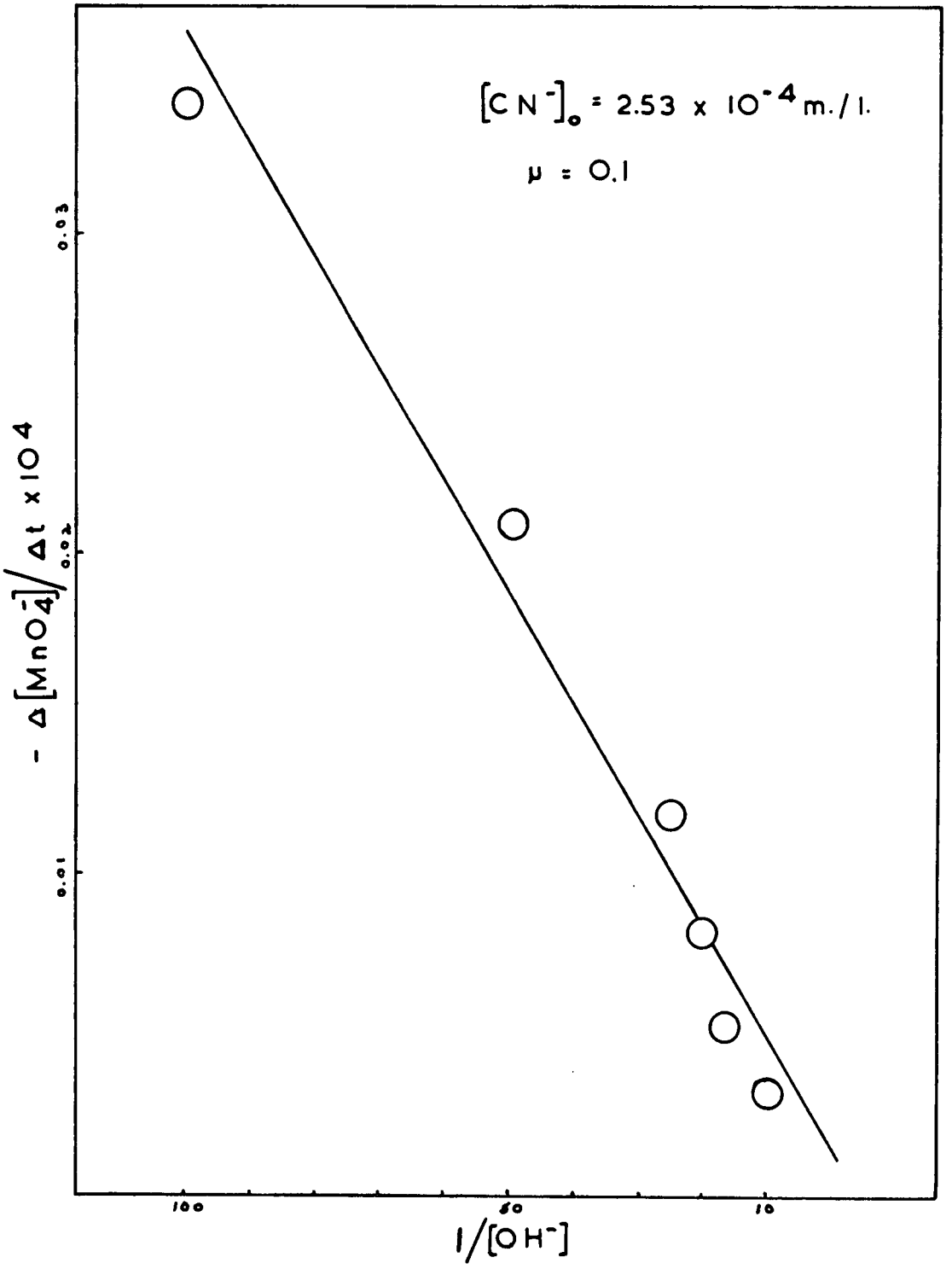
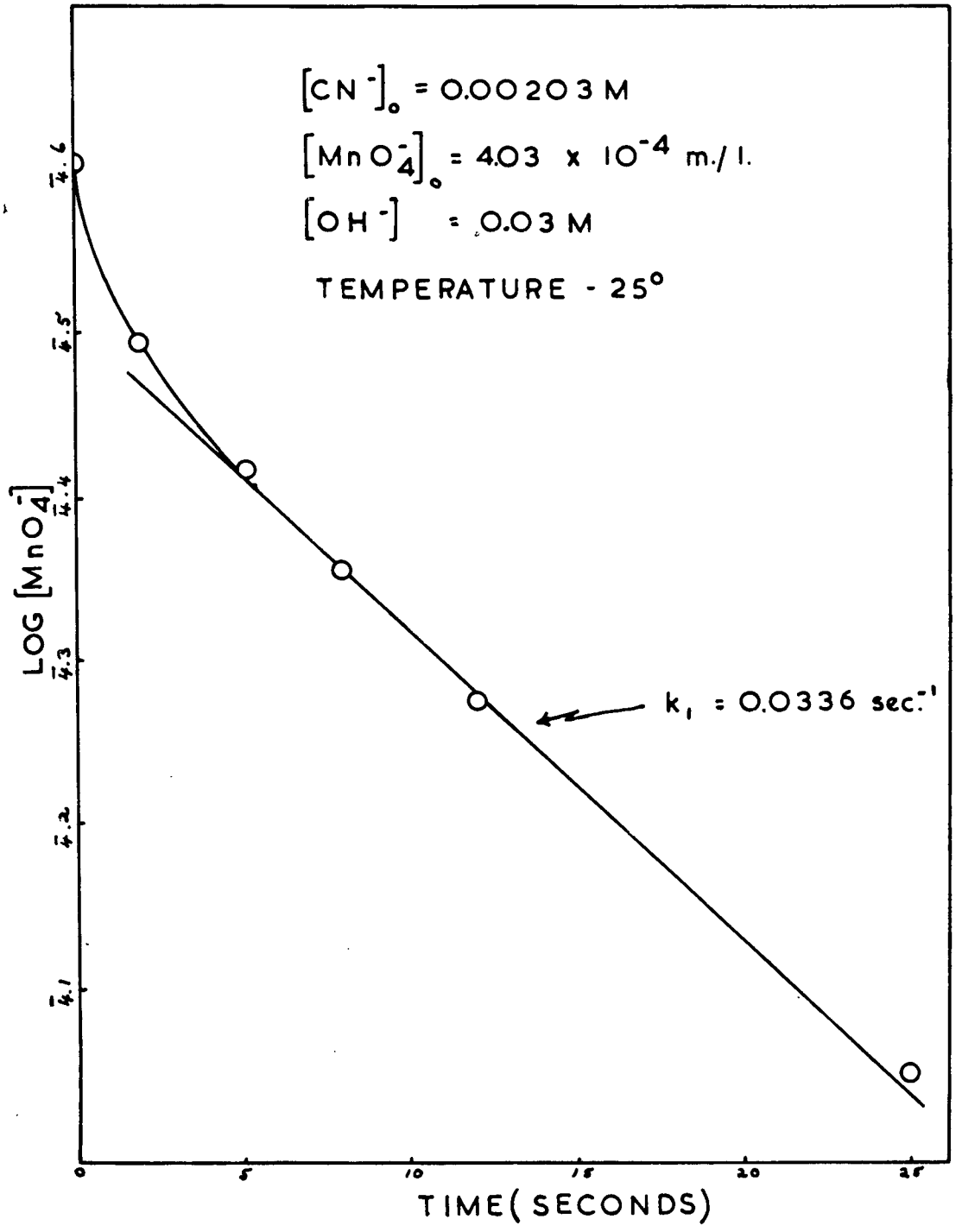


FIGURE 26

PLOT OF LOG $[MnO_4^-]$ VERSUS TIME FOR THE PERMANGANATE-CYANIDE REACTION.



Also observed for the third-order reaction was a ten fold increase in rate (Table XVI) when the ionic strength was varied from 0.1 to 2, as compared to the small change for the second order reaction, i.e., two fold. Another experiment in this connection was performed at 0.03 M sodium hydroxide, $[CN^-]_o = 4.04 \times 10^{-4}$ M when the ionic strength was varied from 0.03 to 2 with a similar increase in rate being observed (Table XIII).

A possible cause for the observed faster reactions at lower alkalinities and higher reactant concentrations was considered. If a deep-seated oxidation was taking place reducing permanganate or permanganate or manganate to lower oxidation states, an excess of cyanide over permanganate should be observed as reaction proceeds. Therefore, the argentimetric method for following the rate of oxidation of cyanide was developed. Observation of the concentration-time plots obtained by both argentimetric and iodometric methods (Figure 27) for the faster process at 0.1 M and 0.01 M sodium hydroxide, indicate that the stoichiometric concentrations (in this case $[MnO_4^-] : [CN^-]$ 2:1 molar ratio) holds throughout a major portion of the plot.

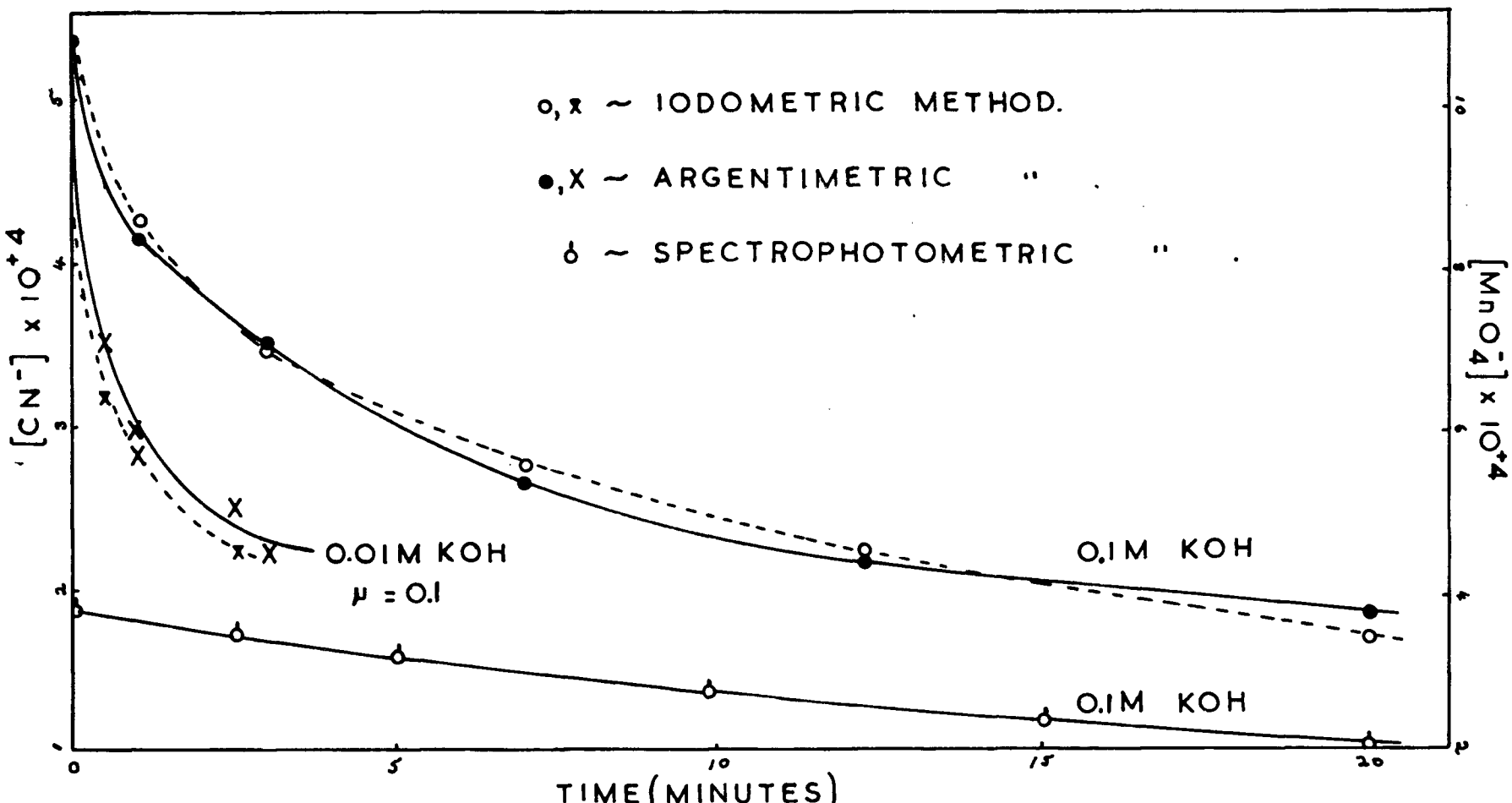
Note: The size of the circles in Figures 24 and 25 represent the relative error in determining the gradient of the concentration time plots. The probable error in determining k_3 is high.

B. Permanganate-Cyanide Reaction at pH < 12

Early in the kinetic study a number of rate plots were obtained for the reaction at low pHs and a few of these plots are presented

FIGURE 27

CONCENTRATION-TIME PLOTS FOR THE ALKALINE PERMANGANATE OXIDATION OF CYANIDE AS OBTAINED BY THE VARIOUS KINETIC METHODS.



(Figure 28). Since the kinetics were more complex than those studied in more basic solution, a relative rate study was undertaken. This was accomplished by measuring the rate of the permanganate-cyanide reaction over a wide pH range stopping the reactions at a given time interval. The extent of the reduction of permanganate was determined in an iodometric titration and $V_o - V_t$ plotted against pH for a number of reaction conditions (Figure 29).

Two important results from this work might be noted -

(a) That the rate of the permanganate-cyanide reaction is negligible in acid solution and increases markedly with increasing basicity.

(b) The maximum rate of the relative rate plots appears at the pKa of HCN (pH = 9).

C. Oxygen-18 Tracer Results.

Observation of Table XVIII does show that a transfer of oxygen has occurred from the oxidizing agent permanganate to the substrate cyanide. The percentage O^{18} transferred appears to depend on the molar ratio and concentration of reactants as well as the alkalinity used in the experiments.

In order to determine whether the product cyanate exchanges its oxygen with the solvent, cyanate was equilibrated with H_2O^{18} ($>$ 1.4% enriched) for 30 minutes at 25° at various acidities, (six experiments were performed over a pH range from 5 to 14.6). In all

experiments a negligible amount of O^{18} (0 to 2%) was found in the cyanate recovered as the silver salt, indicating that cyanate does not exchange its oxygen with the solvent in the time required to perform the oxidation.

The variation in the amount of O^{18} transferred under apparently similar conditions (e.g., 4 M sodium hydroxide) is difficult to explain but it should be pointed out that exchange reactions can serve only to decrease the apparent transfer of O^{18} and, therefore, the maximum percentage transfer at any given pH can be used as a criterion of mechanism.

The O^{18} tracer and kinetic data will be discussed in terms of mechanism further in the paper, but the important features of the tracer data might be itemized as follows:

(a) The maximum percentage O^{18} transferred in any experiment was 82% in 4 M sodium hydroxide at 50°.

(b) A general increase in percentage O^{18} transferred is observed as the alkalinity is increased from 0.04 M to 6 M sodium hydroxide, i.e., four fold increase (Figure 30).

(c) The low percentage O^{18} transferred at 0.1 M sodium hydroxide is not affected when the reaction is carried out at high ionic strength, i.e., $\mu = 4$.

(d) Almost a two fold increase in O^{18} transfer occurred on diluting the reaction mixture by eight fold at 0.4 - 0.5 M sodium hydroxide whereas at 0.02 - 0.04 M sodium hydroxide no change in percentage transfer took place.

In this connection, a tracer study involving equimolar amounts of permanganate and cyanide was undertaken as a sufficient amount of product could only be obtained for O^{18} analysis under dilute reaction conditions if the cyanate and cyanide silver salts were coprecipitated.

(e) No further increase in O^{18} transfer is observed when the reaction is carried out with excess permanganate-O^{18} at 4 M base whereas an approximate two fold increase is observed at 0.1 M sodium hydroxide.

(f) In weakly basic solution $pH < 12$ only a small percentage of the oxygen introduced into cyanate originates from the oxidant.

FIGURE 28

TYPICAL SECOND ORDER RATE PLOTS FOR

THE PERMANGANATE - CYANIDE REACTION AT LOW pH.

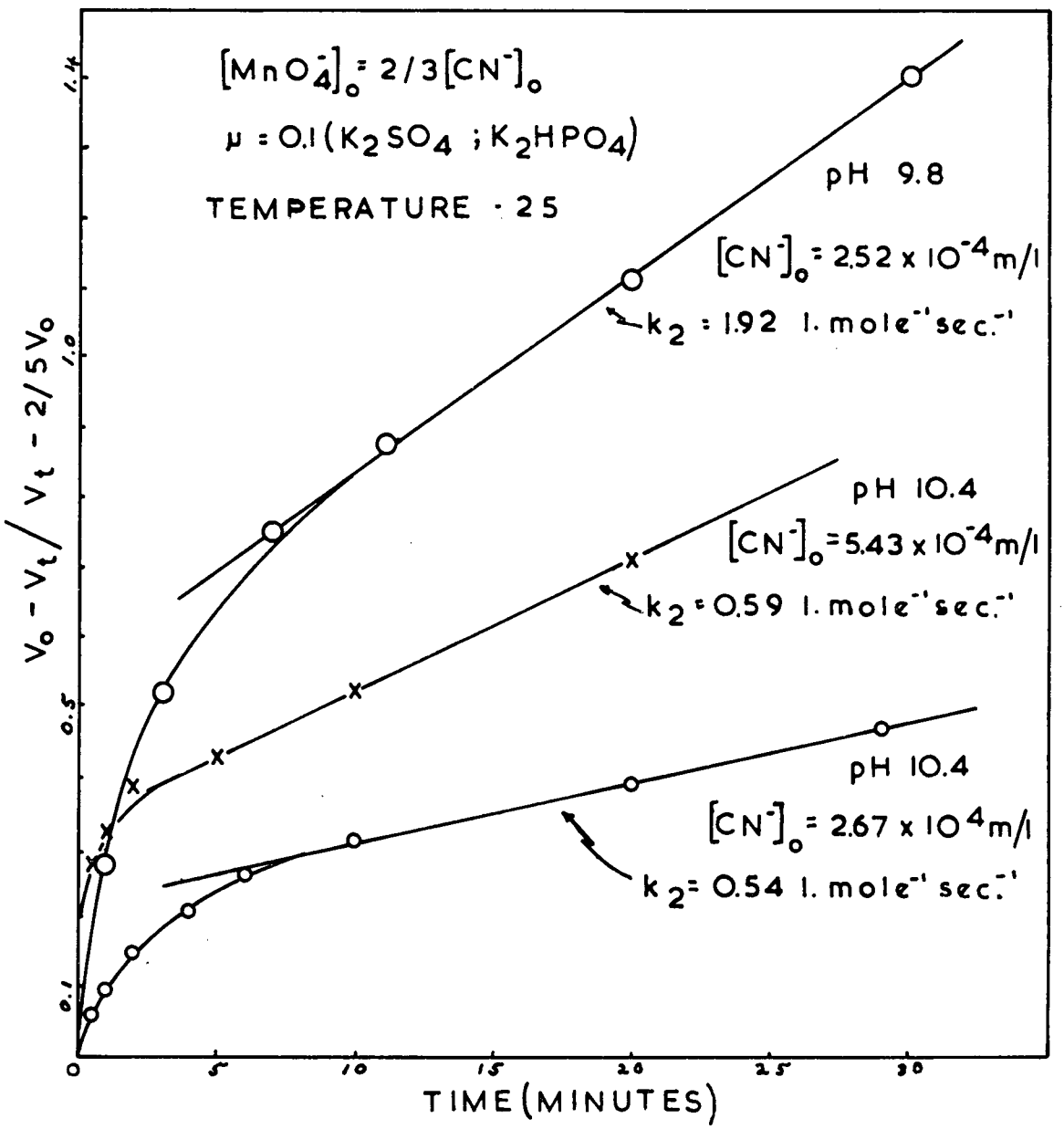


FIGURE 29

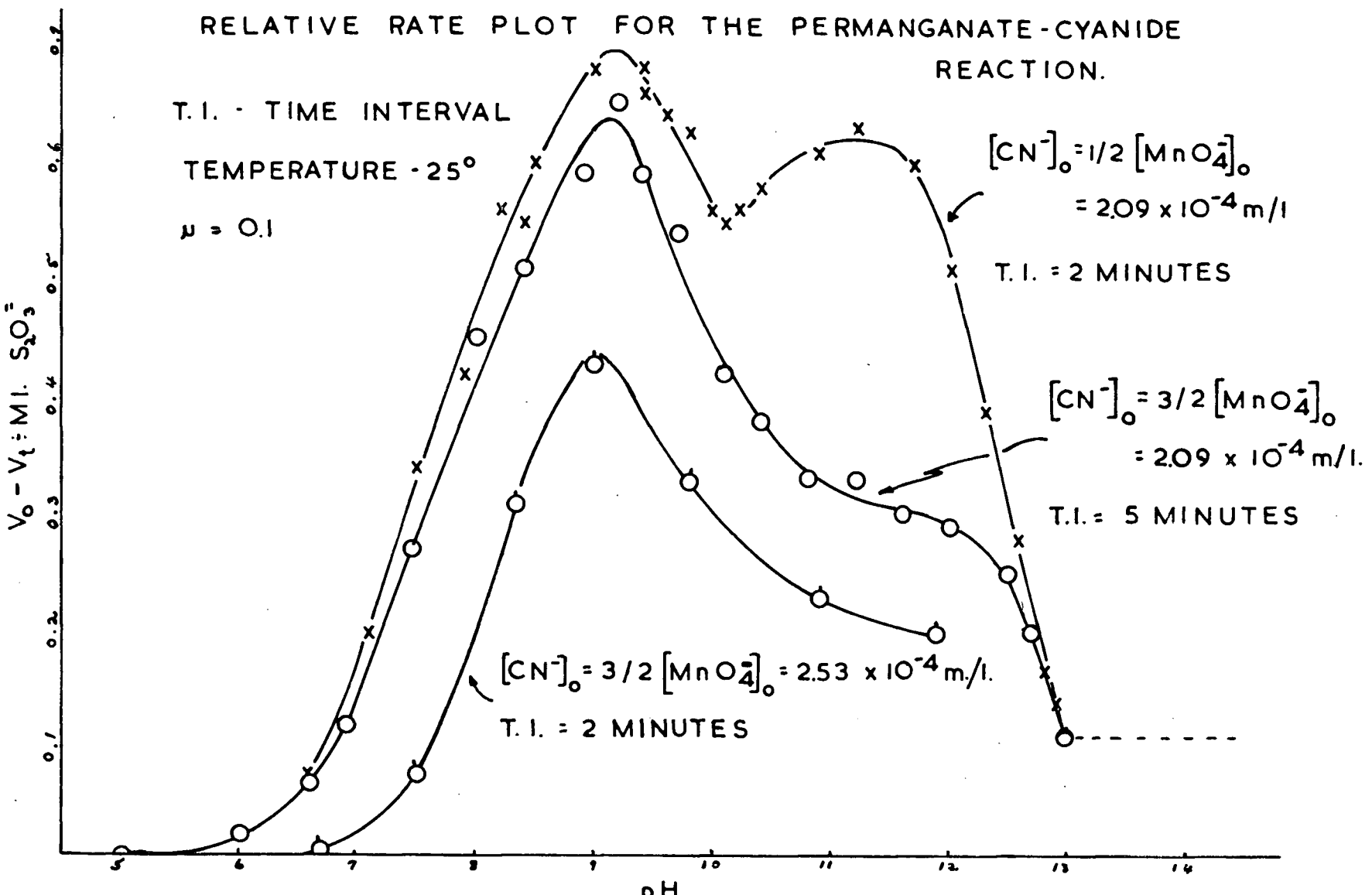

RELATIVE RATE PLOT FOR THE PERMANGANATE-CYANIDE REACTION.
T.I. - TIME INTERVAL
TEMPERATURE - 25°
μ = 0.1
[CN⁻]₀ = 1/2 [MnO₄⁻]₀ = 2.09 x 10⁻⁴ m/l
T.I. = 2 MINUTES
[CN⁻]₀ = 3/2 [MnO₄⁻]₀ = 2.09 x 10⁻⁴ m/l.
T.I. = 5 MINUTES
[CN⁻]₀ = 3/2 [MnO₄⁻]₀ = 2.53 x 10⁻⁴ m./l.
T.I. = 2 MINUTES
V₀ - Vₜ : Ml. S₂O₃⁻⁻
pH
0.1
0.2
0.3
0.4
0.5
0.6
0.7
5
6
7
8
9
10
11
12
13
14

FIGURE 30

PERCENTAGE O^{18} TRANSFERED FROM PERMANGANATE TO CYANIDE VERSUS HYDROXYL ION CONCENTRATION

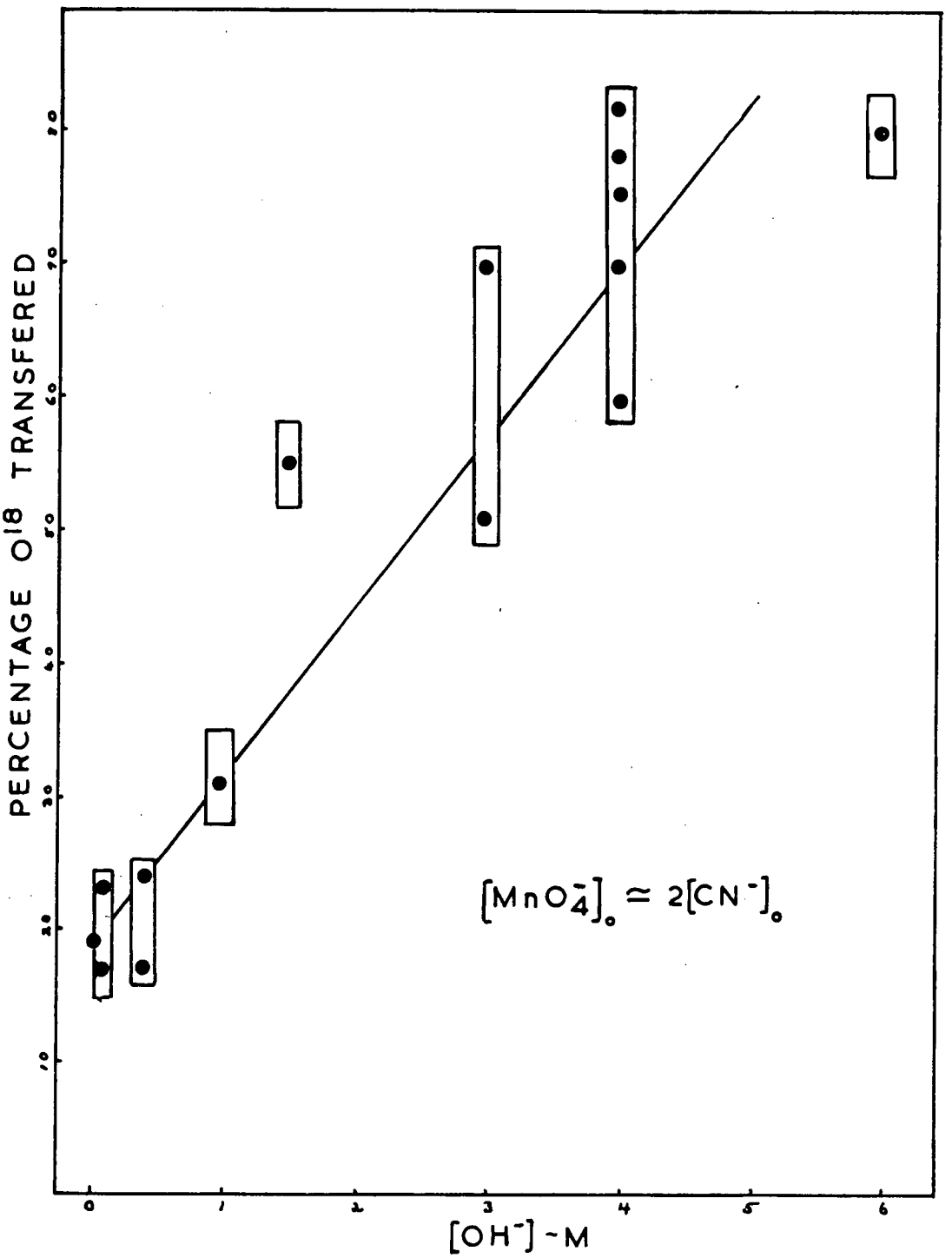


TABLE XVIII

Percentage O^{18} transferred from permanganate to cyanide under various reaction conditions.

Alkalinity	$[MnO_4^-]_o/[CN^-]_o$	% O^{18} transferred (mean)	% O^{18} transferred (maximum) (a)
6 M	2/1 (b)	-	80%
4 M	2/1	70%(c)	78%(d)(e)
3 M	2/1	60%(f)	70%
1.5 M	2/1	-	55%
1 M	2/1	-	31%
0.4 M	2/1	22%(g)	25%
0.1 M	2/1	20%(h)	23%(i)
0.04 M	2/1	-	20%
4 M	4/1	-	71%(j)
0.1 M	4/1	-	49%(j)
0.5 M	1/1	-	47%(k)
0.02 M	1/1	-	16%(k)
pH=11.2	2/3	-	14%
=10	2/3	-	19%
= 8	2/3	-	10%

(a) $[CN^-]_o$ = 0.019 M; CO_2 obtained by pyrolysis of AgOCN.

(b) Approximately 5% excess cyanide used in these experiments.

(c) Average of five determinations. (d) 76% obtained by the

TABLE XVIII (continued)

sulphuric acid method with the same sample. (e) 82% transferred when the reaction was carried out at 50°. (f) Average of two determinations. (g) Average of three determinations. (h) Average of two determinations. (i) 26% transferred under saturated salt conditions, i.e., ionic strength 4 M KNO_3. (j) $[CN^-]_o$ = 0.013 M. (k) $[CN^-]_o$ = 0.0023 M.

TABLE XIX

Analytical data for the permanganate-cyanide reaction.

pH	13	12	11	11	10	10
% OCN^- Kjeldahl Method	94%[a]		84%	85%	42%	37%
% OCN^- as AgOCN	98%[a]	96%				
% CO_2		99%	96%		71%	
% CO_2 produced in the reaction		-	12%		30%	
% CN^- recovered		0%			27%	
% $(CN)_2$	-				-	

pH	9	9	8	7[c]
% OCN^- Kjeldahl Method	35%	35%	30%	12%
% CO_2	51%	49%		46%
% CO_2 produced in the reaction	18%[b]	16%		
% CN^- recovered	41%			46%
% $(CN)_2$	+		11%	28%

Cyanide concentration approximately 0.02 M in the analytical experiments; 3:2 molar ratio of cyanide to permanganate used below pH 12; 1:2 molar ratio used at pH 12 and above; (a) At pH 14.6, 84% silver cyanate recovered. (b) Weighed as barium carbonate. (c) The reaction was very slow at pH 5.

DISCUSSION

The correlation of kinetic, oxygen ^{18} tracer and analytical data which were obtained under various reaction conditions probably constitutes the greatest difficulty in interpreting some of the experimental data. The kinetic data could only be conveniently obtained under low reactant concentration conditions where the rate was relatively slow, whereas oxygen ^{18} tracer and analytical experiments necessitated in most cases considerably higher reactant concentrations.

The main features of the analytical data obtained for the permanganate-cyanide reaction over the pH range 6 to 14.6 are the following: Above pH 12 the sole product of the reaction is cyanate in almost quantitative yield; below pH 12 the reaction becomes increasingly unstoichiometric yielding cyanate, carbon dioxide, cyanide and finally cyanogen which is isolated at pH 9 to 6. Cyanogen is presumably formed at higher basicities in these reaction mixtures but hydrolysis is very rapid at any pH greater than 9. Cyanogen has been reported to be present when permanganate oxidizes potassium cyanide solutions (70). A fair material balance was obtained for the reaction over most of the pH range studied except for nitrogen (Table XIX). The presence of cyanogen in the reaction gives a ready explanation for the production of carbon dioxide through a deep-seated oxidation with permanganate and consequent recovery of cyanide, since cyanogen in known to hydrolyze readily in aqueous solutions to a number of easily oxidizable compounds

(71)(72). As a consequence most of the kinetic and oxygen ^{18} tracer experiments were performed in alkaline solution above pH 12.

The rate of permanganate oxidation of cyanide is found to be markedly dependent on the pH of the medium and on the reactant concentrations. Thus the rate of reaction is negligible in acid solution at pH 6 or less and above pH 7 the rate increases rapidly as the solution becomes more alkaline reaching a maximum rate at pH 9.1. At this point the rate decreases again as the alkalinity is increased and at pH 13 (depending on reactant concentration) the rate levels off and becomes independent of pH except for an ionic strength effect (Figure 29).

An explanation can be found for the broad aspects of this pH dependence by considering the equilibrium:

$$HCN + OH^- \overset{K}{\rightleftharpoons} H_2O + CN^-$$

In acid solution the predominant species is of course the hydrocyanic acid molecule which is presumably unreactive to permanganate. As the alkalinity is increased the rate increases indicating that it is the cyanide ion which is the reactive entity (Figure 29). If cyanide was solely involved an ionization type rate curve should be observed with a maximum rate or leveling of the rate occurring when the weak acid had been completely converted to cyanide ion. As observed this hydroxyl ion independent reaction, Reaction A appears only at higher alkalinities greater than 0.1 M potassium hydroxide and then only if the permanganate-cyanide concentrations are low.

From the evidence obtained it would appear as if a second process Reaction B was superimposed on Reaction A, i.e., two parallel reactions.

Since the experimental evidence for Reaction A is more clearcut, this process will be discussed first.

Route A:

(1) Second-order kinetics are observed over a limited reactant and hydroxyl ion concentration range indicating that the rate expression

$$-\frac{d\left[MnO_4^-\right]}{dt} = k_2\left[MnO_4^-\right]\left[CN^-\right]$$

holds for Reaction A.

(2) A primary positive salt effect was observed indicating that the slow step was between two like singly charged ions presumably permanganate and cyanide ions. This result is surprising in this case in view of the fact that the Brönsted-Debye-Hückel relationship normally holds for reactions carried out under more dilute aqueous conditions. Though the result is qualitatively correct, the close correlation to theory may be the result of an increased contribution from a reaction which is strongly ionic strength dependent (See results on Reaction B).

(3) At constant ionic strength or under saturated salt conditions k_2 is found to be independent of the hydroxyl ion concentration,

i.e., from 0.1 M to 2.4 M sodium hydroxide at low reactant concentrations. The increase in rate (2 and 3 fold) observed at 3.40 and 3.65 M sodium hydroxide is probably not a result of a mechanism change but may be the result of replacing nitrate by hydroxyl ions since the effect of various electrolytes on the activity coefficients of the reacting molecules is difficult to predict under high ionic strength conditions (47).

(4) The rate is not affected by the presence of initial quantities of manganate or barium ions. If an equilibrium was present such as

$$MnO_4^- + CN^- \rightleftharpoons MnO_4^= + CN\cdot$$

an initial concentration of manganate should retard the reaction whereas the presence of barium ions would precipitate barium manganate and thereby increase the rate of reaction.

(5) The oxygen introduced into the product cyanate comes predominantly <u>from</u> the oxidizing agent rather than from the solvent. The maximum percentage O^{18} transferred 80%, occurred when the tracer experiments were carried out at high alkalinities, e.g., 4 M sodium hydroxide. An explanation is necessary at this point. The majority of the kinetic data was obtained in the low hydroxyl ion concentration region 0.1 to 0.2 M potassium hydroxide where a low 15 to 25% O^{18} transfer was observed. The discrepancy between the kinetic and O^{18} results at low base concentrations is probably due to the large

reactant concentration difference which exists between the two series of experiments, e.g., 0.02 M cyanide for the tracer experiments and 0.0004 M cyanide for the kinetic experiments. When the alkalinity is increased in the O^{18} tracer experiments, a gradual increase in percentage O^{18} transfer is observed (Figure 30) whereas k_2 remains essentially constant (Table XIII) for the same increase in base concentration, thus indicating that Reaction A (the second-order process) involves the oxygen transfer mechanism. The changing kinetics at higher reactant concentrations at 0.1 to 0.2 M potassium hydroxide tends to confirm these ideas. In this connection a two fold increase in percentage O^{18} transferred was observed at 0.5 M sodium hydroxide when the reactants were diluted eight fold as would be expected if Reaction A was favoured at the lower reactant concentrations.

(6) Though Arrhenius plots were made using the rate constants obtained at various temperatures under conditions where apparently only one reaction process was present, non-linear plots were observed. Approximate values of $\Delta H^{\ddagger}$ = 8.7 kcals/mole and $\Delta S^{\ddagger}$ = -27 e.u. were obtained for the study at 0.2 M potassium hydroxide. These values are comparable to those observed in other permanganate oxidations and the entropy of activation is reasonable for a reaction between two anions. The significant curvature observed in the plots further indicates the possibility that two processes are present each with a different activation energy.

A mechanism which fits most of the data for Reaction A is the following:

$$MnO_4^- + CN^- \xrightarrow{k_2} \left(NC\cdots O\cdots MnO_3\right)^{=} \rightarrow MnO_3^- + {}^-OCN$$

$$MnO_3^- + MnO_4^- + 2OH^- \xrightarrow{fast} 2MnO_4^{=} + H_2O$$

The evidence for the existence of a Mn V species as a reaction intermediate in permanganate oxidations has already been indicated (see Introduction).

It was observed that as the concentration of hydroxyl ion was decreased in the tracer experiments a greater percentage of the oxygen found in the cyanate originated from the solvent indicating that either a hydroxyl ion dependent exchange was taking place or a change in mechanism had occurred. Since permanganate and cyanate do not exchange their oxygens with the solvent under the reaction conditions, only the presence of manganate could indirectly cause the dilution of the permanganate oxygens via the fast electron interchange. Manganate is known to exchange oxygen with the solvent (17). This latter process should be minimized in the presence of barium ions and further, the manganate-permanganate electron interchange has been found to be insensitive to changes in the hydroxyl ion concentration (3). These considerations lead to the conclusion that it is a mechanism change which results in the low percentage O^{18} being transferred from permanganate in dilute alkali. In this connection, the rate date indicate the presence of two parallel reactions, one Reaction A and another reaction which occurs at higher reactant concentrations and whose rate is inhibited by hydroxyl ions. At present the kinetic and O^{18} tracer data are

consistent with the idea that for the latter process, Reaction B, the oxygen introduced into cyanate is derived from the solvent rather than from the oxidizing agent. The observation that no further increase in percentage O^{18} transfer occurs at 0.02 to 0.04 M potassium hydroxide when the reactants were diluted eight fold is in agreement with the previous statement, although a 49% O^{18} transfer at 0.1 M potassium hydroxide using a two fold excess of permanganate is difficult to explain in the light of the previous discussion.

In attempting to rationalize some of the oxygen transfer data, consideration should be given to a reaction process involving a metastable intermediate leading to the production of cyanate by a number of secondary product determining steps.

$$MnO_4^- + CN^- \xrightarrow[\text{r.d.}]{k_2} \text{INTERMEDIATE} \begin{cases} \xrightarrow{\text{p.d.}} \text{Products} \\ \xrightarrow{\text{p.d.}} \text{Products} \end{cases}$$

Evidence is not available as to whether a metastable ester intermediate is formed between cyanide ion and permanganate ion but certainly an intimate complex must be formed for oxygen transfer to occur. The foregoing might help to explain the tracer experiment performed at 4 M sodium hydroxide using a two fold excess of permanganate over cyanide which results in 71% O^{18} being transferred to the reductant. These reaction conditions should minimize exchange processes.

Mechanisms of the type

$$MnO_4^- + OH^- \rightleftharpoons MnO_4^= + OH^{\cdot} \text{ etc.}$$

have been considered for the initial stage of permanganate oxidations of organic molecules (9)(30). A process of this type can be eliminated on the basis of the O^{18} tracer experiments and the observed kinetics, since the above mechanism predicts an increase in rate with increasing alkalinity as well as the major proportion of the oxygen introduced into a substrate being derived from the solvent. The above process is also known to be highly endothermic (11). High percentage O^{18} transfer was observed even in 6 M sodium hydroxide.

Route B:

Although the kinetic data for Reaction B is of a qualitative nature, certain aspects of this study, the O^{18} tracer experiments and the observation that cyanogen was produced in the reaction at lower pH, might be useful in producing a mode of oxidation which is consistent with many of the observations.

Linear third-order kinetic plots were obtained for some of the rate data. In some instances a much faster decrease in rate with time was observed for the initial portions of the rate plots than would be predicted for a third-order process, thus indicating that more complex processes were occurring. Attempts to determine the order of the reaction with respect to permanganate or cyanide

for Reaction B by pseudo-order kinetics were inconclusive since a log $[MnO_4^-]$ versus time plot attempted was not completely linear (Figure 26).

Thus a choice remains between the following relations;

$$-\frac{d[MnO_4^-]}{dt} = k_3 [MnO_4^-]^3 = \frac{k_3}{2} [MnO_4^-]^2 [CN^-]$$

$$-\frac{d[MnO_4^-]}{dt} = k_3 [MnO_4^-]^3 = \frac{k_3}{4} [MnO_4^-][CN^-]^2$$

Though the kinetics are not definite the dependence of rate on hydroxyl ion concentration appears to approximate

$$k_3 = \frac{k_3'}{[OH^-]}$$

The above equations become on substitution

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_3' [MnO_4^-]^3}{[OH^-]} = \frac{k_3' [MnO_4^-]^2 [CN^-]}{2[OH^-]}$$

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_3' [MnO_4^-]^3}{[OH^-]} = \frac{k_3' [MnO_4^-][CN^-]^2}{4[OH^-]}$$

The inverse dependence of rate on hydroxyl ion concentration does suggest the possibility that a proton is involved in the transition state of Reaction B.

Rearranging the previous equations and substituting for $[OH^-] = K_w/[H^+]$;

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_3'}{2K_w}[MnO_4^-]^2[H^+][CN^-] = \frac{k_3'}{2K_w}[MnO_4^-]^2[HCN] \qquad \text{(i)}$$

$$= \frac{k_3'}{4K_w}[MnO_4^-][H^+][CN^-]^2 = \frac{k_3'}{4K_w}[MnO_4^-][HCN][CN^-] \qquad \text{(ii)}$$

Equation (i) can be eliminated on the basis of the observed pH dependence of the permanganate-cyanide reaction. The rate in this case should decrease with increasing alkalinity as hydrocyanic acid is converted to cyanide ion. This result was not observed. Though these equations were derived in part by interpretation, the rate expression (ii) is in qualitative agreement with the observations concerning reaction B. Further, equation (ii) predicts a maximum rate when $[HCN]_o = [CN^-]_o$ i.e., where pH = pKa = 9.1. When a relative rate study was performed (Figure 29), a maximum in the rate was observed at pH = 9.1 indicating that hydrocyanic acid is involved.

The overall rate expression becomes

$$-\frac{d[MnO_4^-]}{dt} = k_2[MnO_4^-][CN^-] + \frac{k_3'}{4K_w}[MnO_4^-][CN^-][HCN]$$

A possible mode of oxidation which might be considered for Reaction B is the following:

$$MnO_4^- + HCN + CN^- \xrightarrow{slow} MnO_4^= + (CN)_2^- + H^+$$

$$(CN)_2^- + MnO_4^- \xrightarrow{fast} (CN)_2 + MnO_4^=$$

$$(CN)_2 + 2OH^- \xrightarrow{fast} CN^- + NCO^- + H_2O$$

This mode of oxidation is actually an oversimplication since more complex processes are indicated. Adamson (64) suggested that $(CN)_2^-$ was present as an intermediate in the ferricyanide oxidation of cyanide and that this species undergoes a fast reaction with water to produce the species $O{=}\dot{C}{-}NH_2$.

An initial reaction step worth considering for Reaction B

$$MnO_4^- + CN^- \rightleftharpoons CN\cdot + MnO_4^=$$

involves electron abstraction from the substrate by permanganate. A calculation of the heat of reaction $\Delta H_{rx.}$ can be made for this process. Using the known dissociation energy and the heat of formation (73) of cyanogen one can calculate the heat of formation of the cyanide radical;

Thus $(CN_2) \longrightarrow 2CN\cdot$

$$2\Delta Hf^\circ(CN\cdot) - D(CN)_2 = \Delta Hf^\circ(CN)_2$$

$$2\Delta Hf^\circ(CN\cdot) - 112 = 73.6$$

$$\Delta Hf^\circ(CN\cdot) = \frac{73.6 + 112}{2}$$

$$\therefore \quad \Delta Hf^\circ(CN\cdot) = 92.8 \text{ kcals/mole}$$

The heats of formation of permanganate, manganate and cyanide ions are known (74) and

$$\text{since } \Delta H_{rx} = \Delta Hf^\circ(\text{Products}) - \Delta Hf^\circ(\text{reactants})$$

$$= \left[\Delta Hf^\circ(MnO_4^-) + \Delta Hf^\circ(CN\cdot)\right] - \left[\Delta Hf^\circ(CN^-) + \Delta Hf^\circ(MnO_4^-)\right]$$

$$= -160.5 + 92.8 - 36.1 + 129.7$$

$$\Delta H_{rx} = 25.9 = 26 \text{ kcals/mole}$$

A process of this type does not appear energetically feasible if the calculated heat of reaction is compared to the heat of activation values estimated from the Arrhenius plots. The calculated heat of reaction is endothermic to the extent of 26 kcals/mole, a value which is a few times larger than the experimental heats of activation that range from 3.4 to 8.7 kcals/mole. One method which has been utilized to indicate whether a radical process was occurring, has been to attempt radical initiated polymerization reactions of monomers such as acrylonitrile or styrene. To solutions, consisting of a ten fold excess of acrylonitrile over cyanide concentration at pHs 8 and 12, permanganate was added dropwise to the stirred mixtures. Only reduction of the permanganate was observed to take place. Since the result was not positive, any conclusion would be tentative.

APPENDIX I

Permanganate Oxidation of 3,3,2,2-Tetrafluoro-1-propanol.

A preliminary kinetic study of the oxidation of the fluorinated primary alcohol 3,3,2,2-tetrafluoro-1-propanol has been obtained and will be reported briefly herein.

It has been reported (75) that the alcohol has been oxidized by permanganate to the corresponding fluorocarboxylic acid, the omega hydrogen being inert to permanganate. Presumably, the oxidation takes place in the following stages:

$$HCF_2CF_2CH_2OH \xrightarrow{slow} HCF_2CF_2\overset{O}{\overset{\|}{C}}H \longrightarrow HCF_2CF_2\overset{O}{\overset{\|}{C}}OH$$

Impure tetrafluoro-1-propanol was redistilled and a fraction boiling at 108-109° collected (Literature 109 - 110° (76)) from which 0.1 M aqueous solutions were prepared for the kinetic studies. The pKa of the primary alcohol was determined by a titration method using 0.1 M sodium hydroxide. The pH at half ionization, which is equal to the pKa was determined to be 12.10. An iodometric method was found suitable for following the rate of reduction of permanganate. Since manganate was found to be reduced in the oxidation mixture presumably by the intermediate aldehyde stage, barium nitrate was added initially in order to stop the reduction at the Mn VI stage. Thus the molar ratios of permanganate to substrate and integrated second-order rate expressions used were

For a molar ratio 4:1 , $$k_2 = \frac{1}{[\text{Alcohol}]_o \cdot t} \times \frac{V_o - V_t}{V_t - 4/_5 V_o} \quad \text{(i)}$$

For a molar ratio 8:1 , $$k_2 = \frac{-2.30}{[\text{Alcohol}]_o \cdot t} \times \log \frac{V_t - 9/_{10} V_o}{8V_t - 6.4V_o} \quad \text{(ii)}$$

For a molar ratio 2:1 , $$k_2 = \frac{4.61}{[\text{Alcohol}]_o \cdot t} \times \log \frac{V_t - 3/_5 V_o}{2V_t - 8/_5 V_o} \quad \text{(iii)}$$

Generally, linear second-order rate plots were obtained up to 60% completion of the reaction indicating that the reaction was second-order overall and first-order in permanganate and first in primary alcohol.

TABLE XX

Table of second-order rate constants for the oxidation of 3,3,2,2-tetrafluoro-1-propanol by permanganate under various conditions.

$[NaOH]$ - M	$[HCF_2CF_2CH_2OH]_o \cdot 10^4$ M[a]	k_2, l. mole^{-1}sec.$^{-1}$
pH = 10.2	28.4 [b]	0.0026
pH = 10.8	28.4 [b]	0.0102
0.01	3.98	0.459
0.02	3.98	0.828
0.05	3.98	1.53
0.075	3.98	1.76
0.075	1.99	1.79 [c]
0.075	7.96	1.61 [d]
0.10	3.98	1.95
0.14	3.98	2.12
0.18	3.98	2.18

(a) $[MnO_4^-]_o = 15.92 \times 10^{-4}$ M; $\mu = 0.2$, KNO_3 and $Ba(NO_3)_2$; Temperature 25.2 ± 0.05°.

(b) Rate expression, $k_2 = \dfrac{1}{[\text{Alcohol}]_o \cdot t} \times \dfrac{V_o - V_t}{V_t - 2/5 V_o}$;

$[MnO_4^-]_o = 37.8 \times 10^{-4}$ M; $\mu = 0.2$, K_2HPO_4 and KNO_3

(c) Equation (ii) used here.

(d) Equation (iii) used here.

TABLE XX (continued)

Temperature	k_2, l. mole^{-1}sec.$^{-1}$ (a)	k_2, l. mole^{-1}sec.$^{-1}$ (b)
34.95°	4.17	0.0501 pH = 11.1
34.5°	3.90	
25.2°	2.26	0.0278 pH = 11.1
16.6°	1.28	
16.6°	1.27	

(a) $[HCF_2CF_2CH_2OH]_o = 1/4[MnO_4^-]_o = 3.98 \times 10^{-4}$ M; $[NaOH] = 0.12$ M; $\mu = 0.2$; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from a linear Arrhenius plot. $\Delta H^{\ddagger} = 10.2$ kcals./mole, $\Delta S^{\ddagger} = -22$ e.u.

(b) $[HCF_2CF_2CH_2OH]_o = 3/4[MnO_4^-]_o = 1.20 \times 10^{-3}$ M; $\mu = 0.2$ K_2HPO_4; $\Delta H^{\ddagger} = 10.7$ kcals./mole, $\Delta S^{\ddagger} = -28.3$ e.u.

APPENDIX II

Summary of a Preprint of a Paper on Reduction of Permanganate by Cyanide

A preprint of a paper by Freund (77) on the kinetics of the reduction of permanganate by cyanide in basic solution was obtained near the completion of this thesis. A short review of the results are presented herein.

The rate of reduction of permanganate was followed spectrophotometrically. No deviation from linear second-order kinetics was reported when the permanganate concentration was varied from 0.4×10^{-4} M to 9.5×10^{-4} M and when the cyanide concentration was varied from 0.13×10^{-4} M to 3.8×10^{-4} M at 0.075 M hydroxyl ion concentration at 26°. The second-order rate constant given, k_2 = 2.6 l. $mole^{-1} sec.^{-1}$. No marked change in rate occurred when the alkalinity was varied to 0.18 M and 0.035 M hydroxide ion concentration. The latter experiment was performed under dilute reaction conditions, i.e., 1×10^{-4} M in cyanide.

The rate law reported

$$-\frac{d[MnO_4^-]}{dt} = k_2[CN^-][MnO_4^-]$$

$$\text{where } k_2 = 6.4 \times 10^7 \exp. (9.000/RT)$$

These kinetic results agree for the most part with that obtained for the second-order process, Reaction A. In none of these experiments did this worker exceed the concentration limits set out for Reaction A (see results). Though a salt effect was not indicated for the reaction, an increase in rate was observed in one kinetic experiment performed at 0.46 M sodium hydroxide. This result was interpreted in terms of an hydroxyl ion dependent process. Since a duplicate kinetic experiment at the same ionic strength was not performed or mentioned this conclusion is questionable.

Freund has pointed out that the oxygen transfer process as reported previously (65) could proceed via either of two mechanisms.

$$\text{(a)} \quad MnO_4^- + CN^- \longrightarrow OCN^- + MnO_3^-$$

$$\text{(b)} \quad MnO_4^- + CN^- \longrightarrow MnO_3 + OCN^=$$

$$MnO_4^- + OCN^= \longrightarrow MnO_4^= + OCN^-$$

In other words, transfer as an oxygen atom or as an oxygen radical ion. It is rather difficult to envisage the activated complex for both cases, i.e.,

$$(O_3Mn\text{----}O\text{----}CN)^=$$

breaking down as in case (b) to give the highly reactive species $OCN^=$ rather than the stable cyanate ion.

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FIGURE 1

Typical kinetic plots for the alkaline permanganate oxidation of 2,2,2-trifluoro-1-phenylethanols.

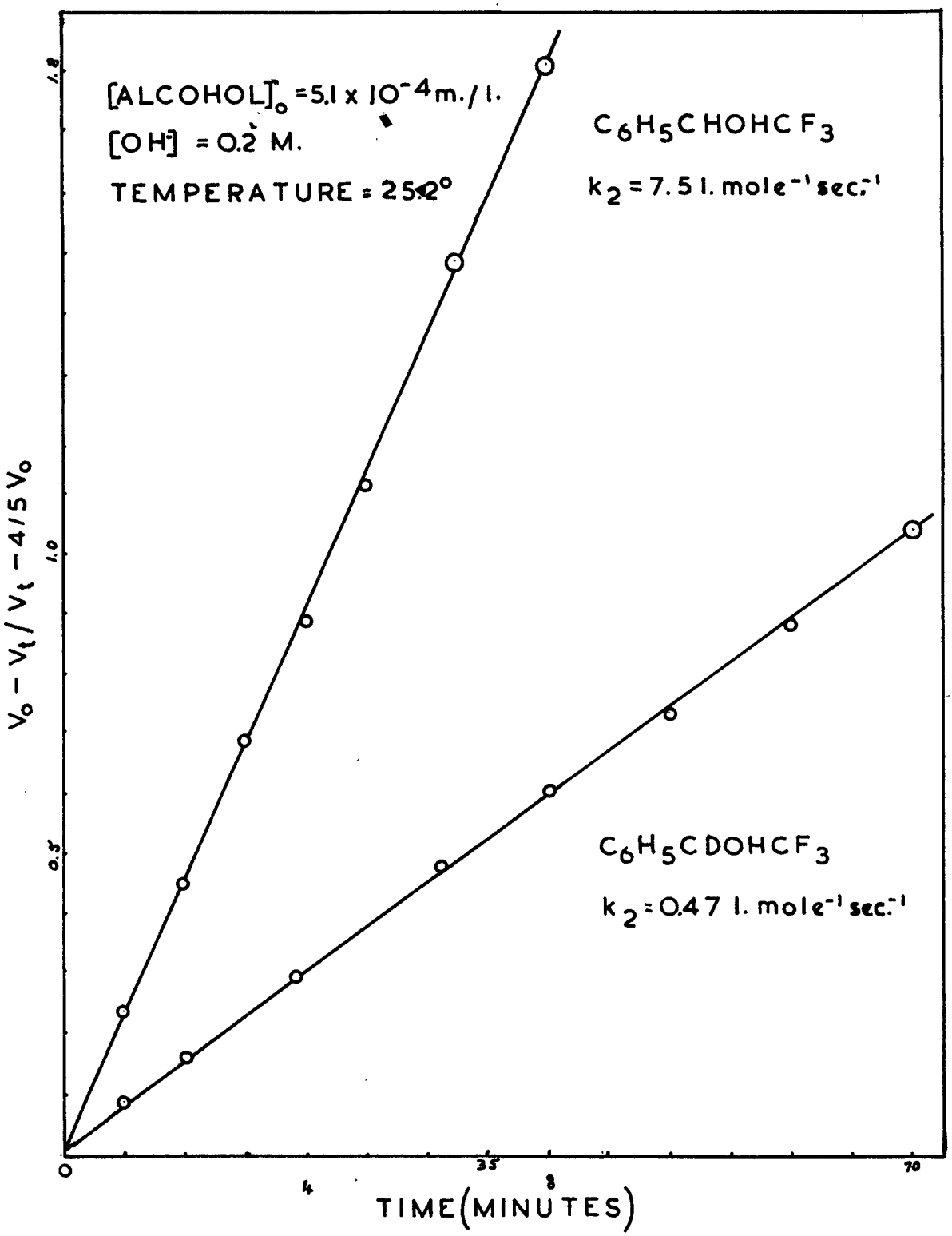


FIGURE 2

Plots of k_2 versus hydroxyl ion concentration for the permanganate oxidation of various 2,2,2-trifluoro-1-phenylethanols.

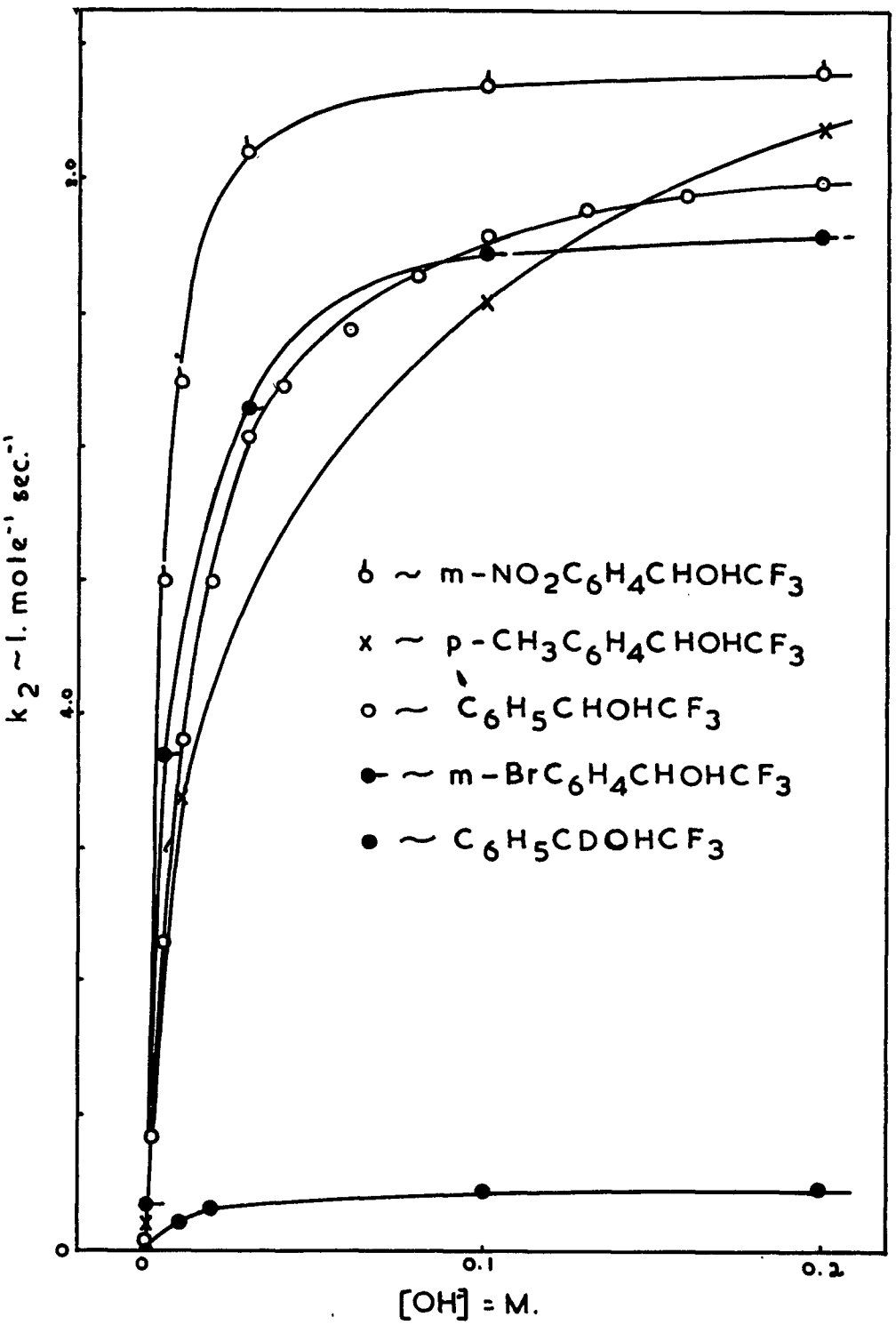


FIGURE 3

Plot of $\log k_2$ versus $\sqrt{\mu}$ for the permanganate: 2,2,2-trifluoro-1-(m-nitrophenyl)-ethanol reaction.

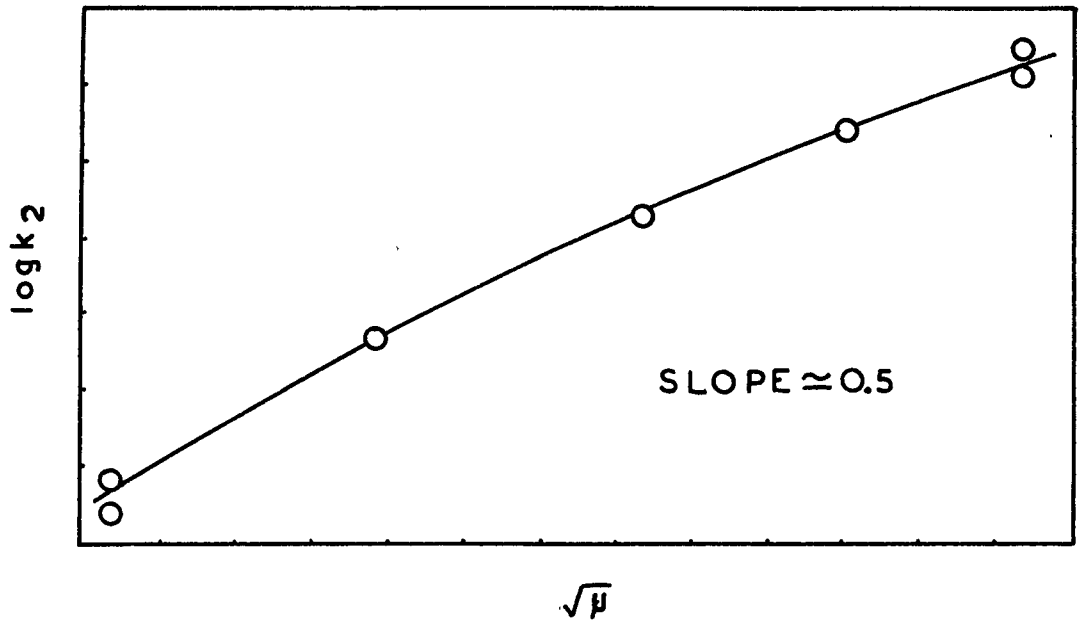


FIGURE 4

Plot of $\log k_2$ versus $\frac{1}{3.26 + 1/\sqrt{\mu}}$

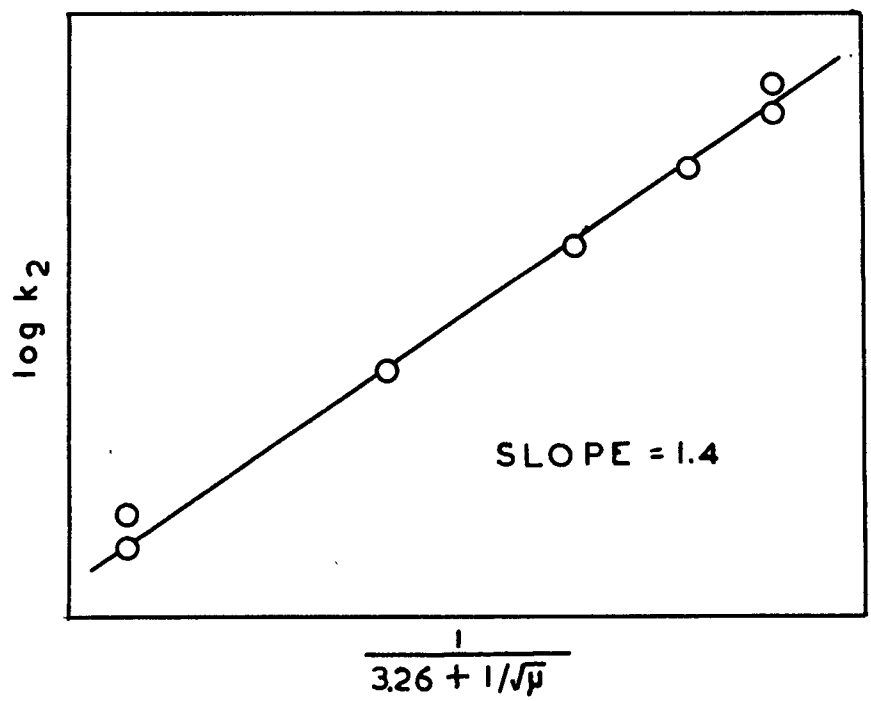


FIGURE 5

Plot of $\log k_2 / T^oK$ versus $1000/T^oK$ for the permanganate : 2,2,2 - trifluoro-1-phenylethanol reaction.

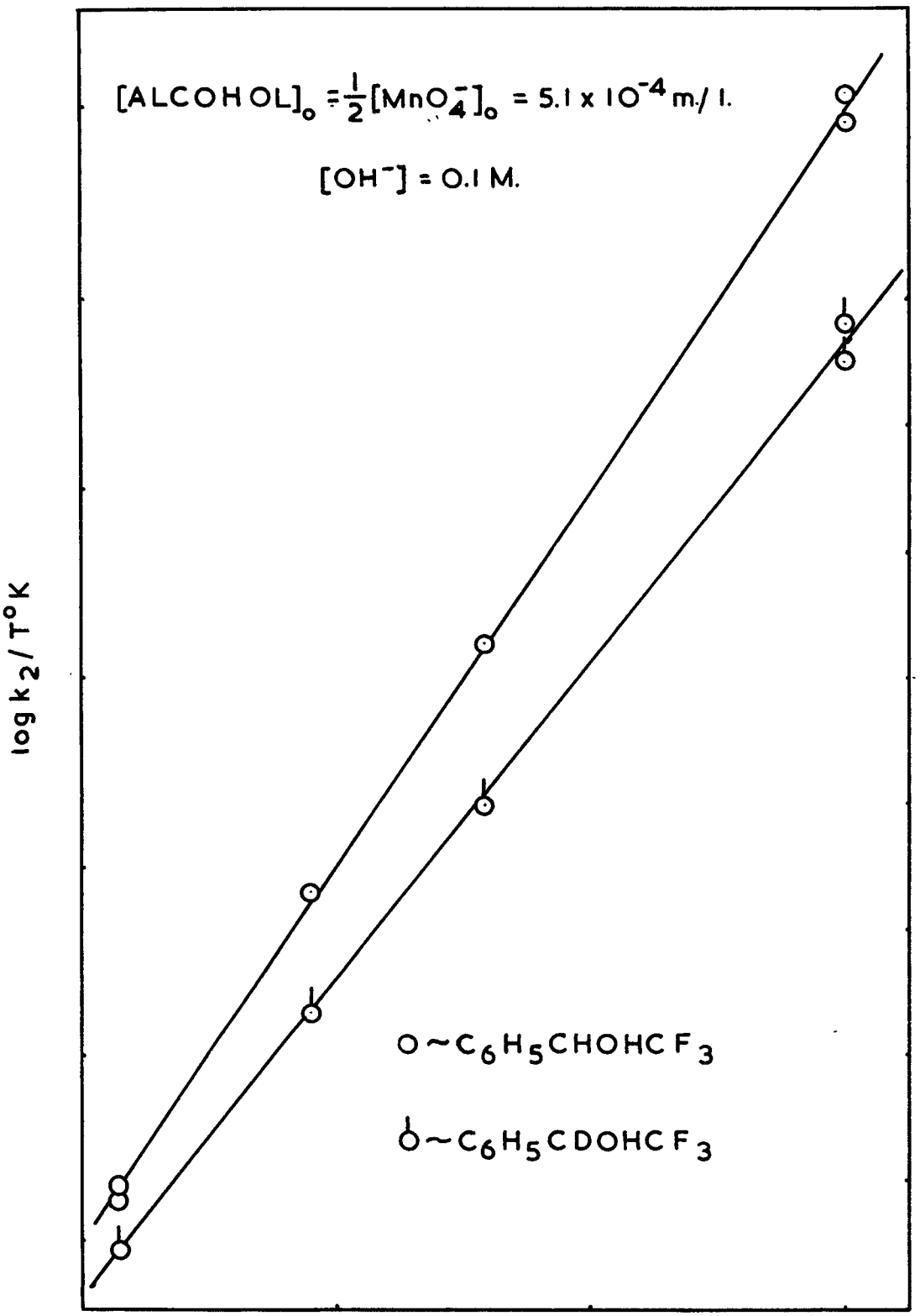


FIGURE 7

HAMMETT PLOT FOR THE

IONIZATION OF 2,2,2-TRIFLUORO-1-PHENYLETHANOLS.

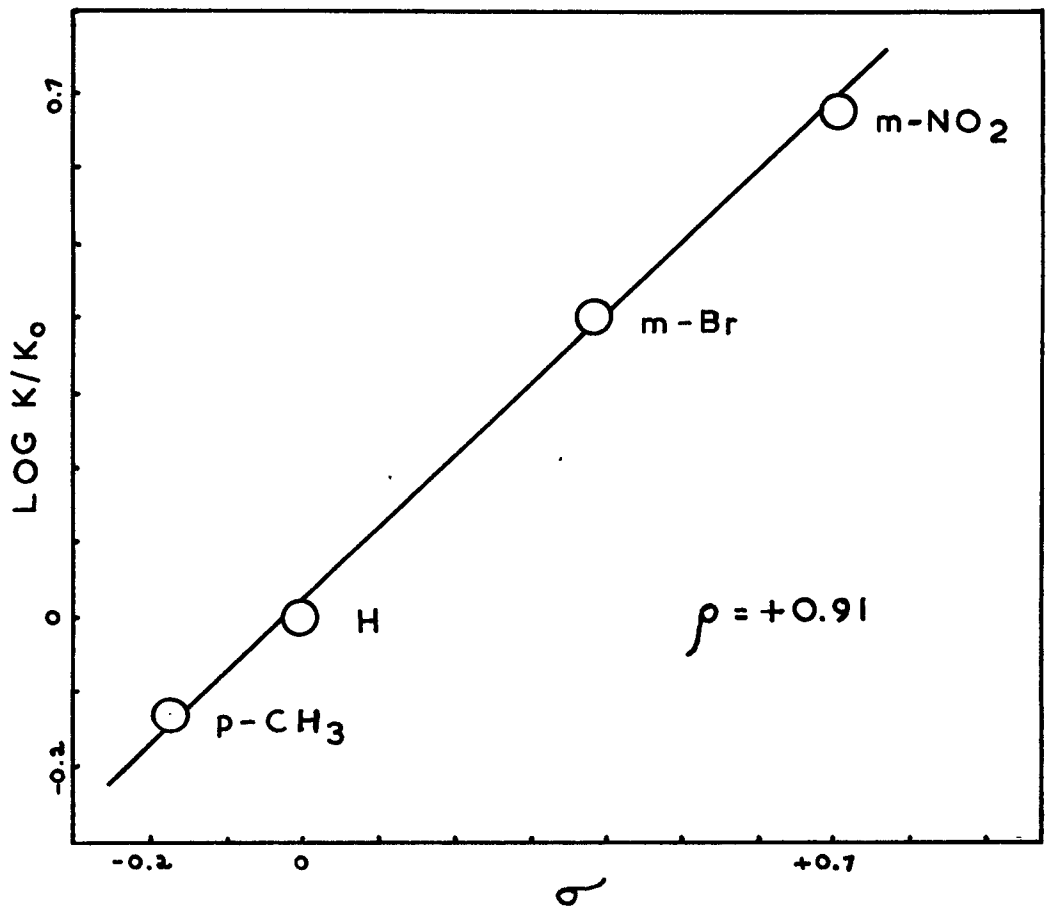
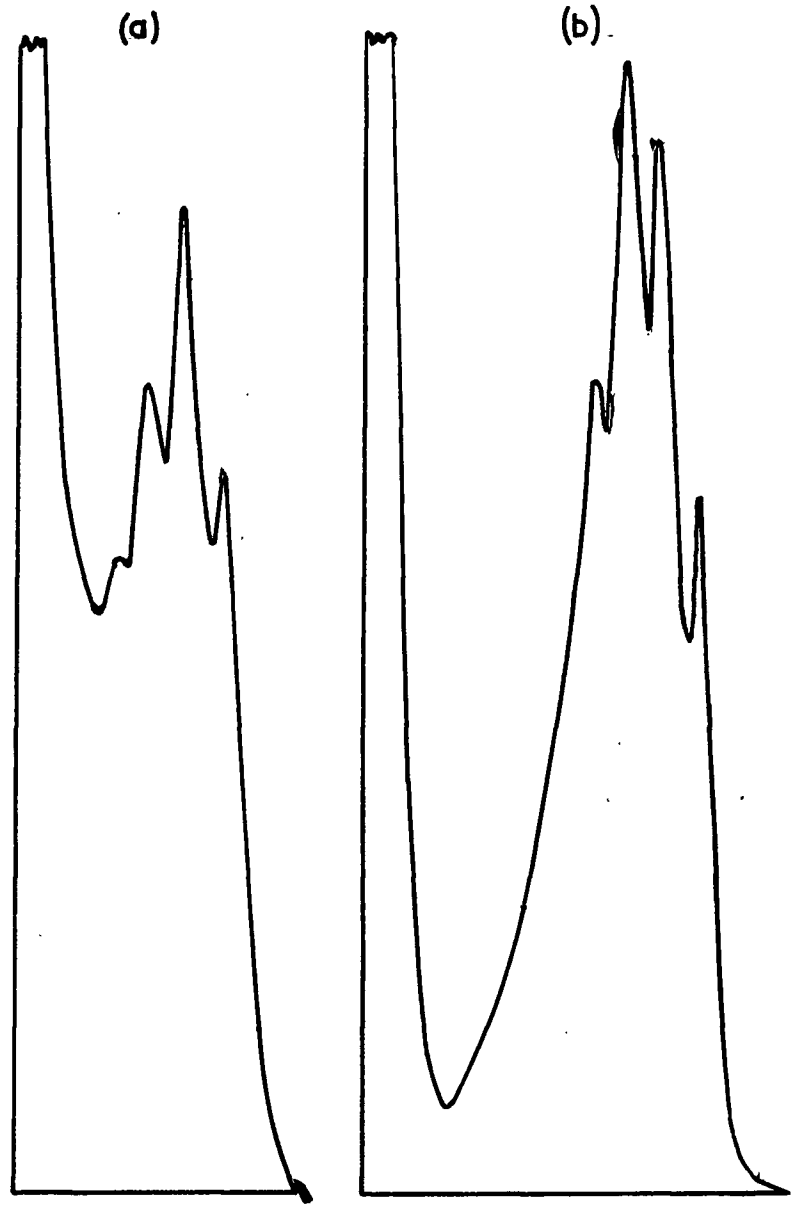


FIGURE 8

Ultraviolet spectra of 2,2,2-trifluoro-1-phenyl-ethanol-1-d using a Cary Model 14 Recording Spectrophotometer. [Alcohol] = 0.002,68 M.



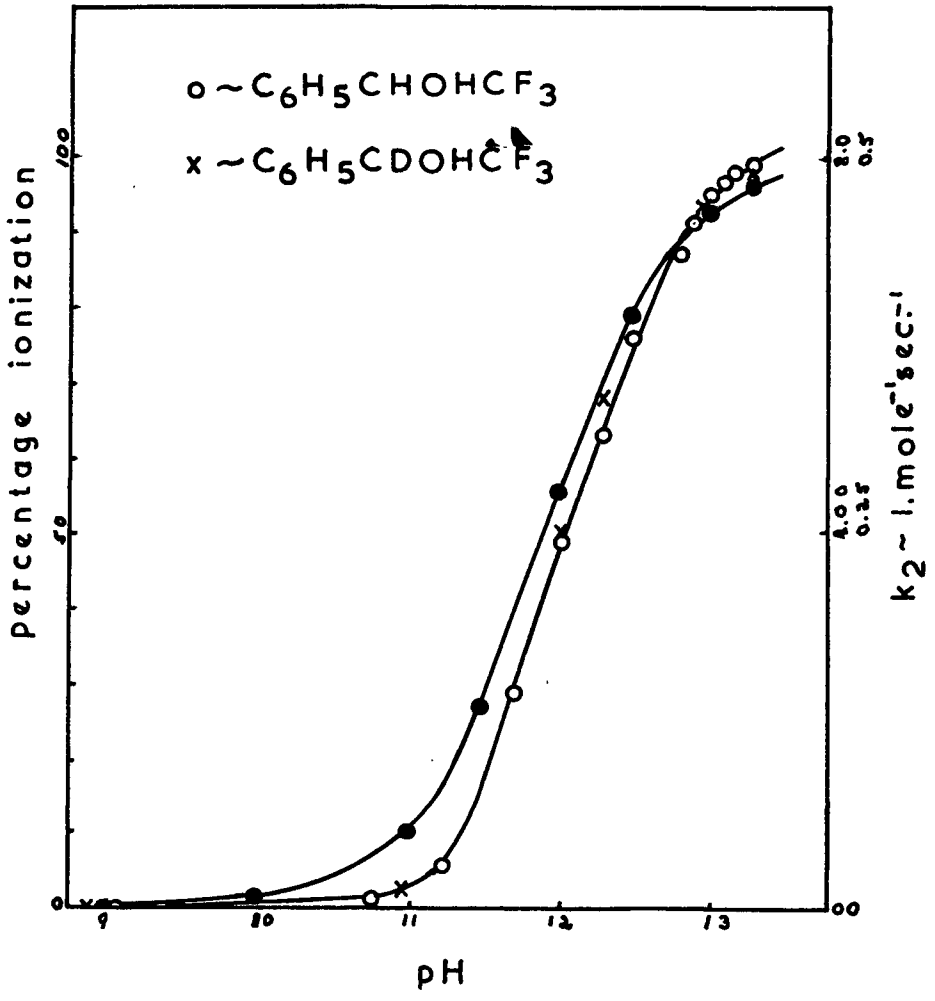
(a) Spectrum of $C_6H_5CDO^-CF_3$ at pH 13.6.

(b) Spectrum of $C_6H_5CDOHCF_3$ at pH 4.

FIGURE 9(a)

Plot of percentage ionization and k_2

for permanganate oxidation versus pH.

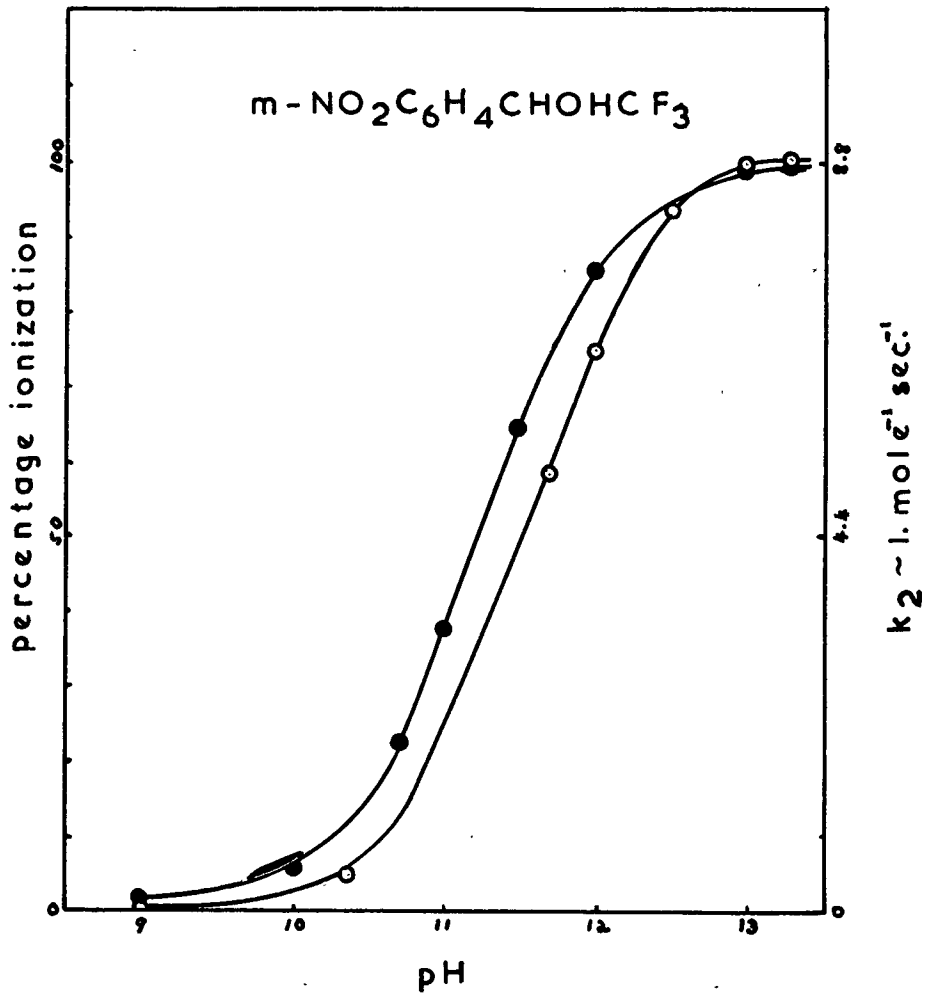


● ~ Theoretical ionization curve.

o, x ~ Experimental rate plots.

FIGURE 9(b)

Plot of percentage ionization and k_2 for permanganate oxidation versus pH.



● ~ Theoretical ionization curve.

o ~ Experimental rate plot.

FIGURE 10.

WIRING DIAGRAM FOR TIMER CIRCUIT

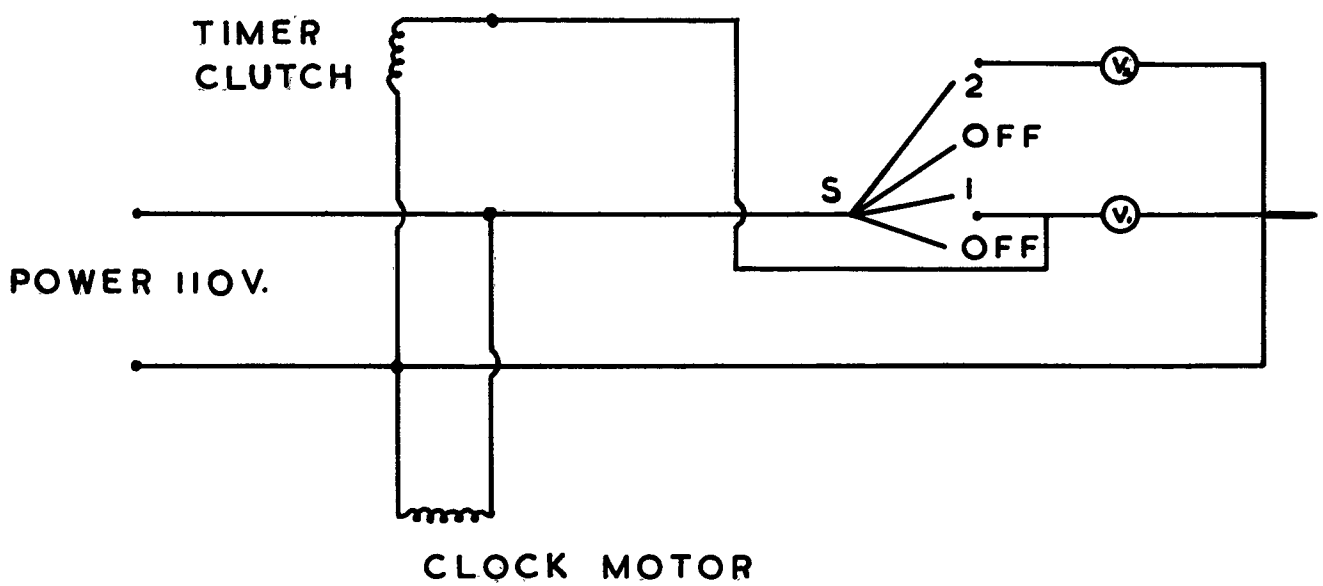


FIGURE 11.

APPARATUS USED TO STUDY RAPID REACTION KINETICS.

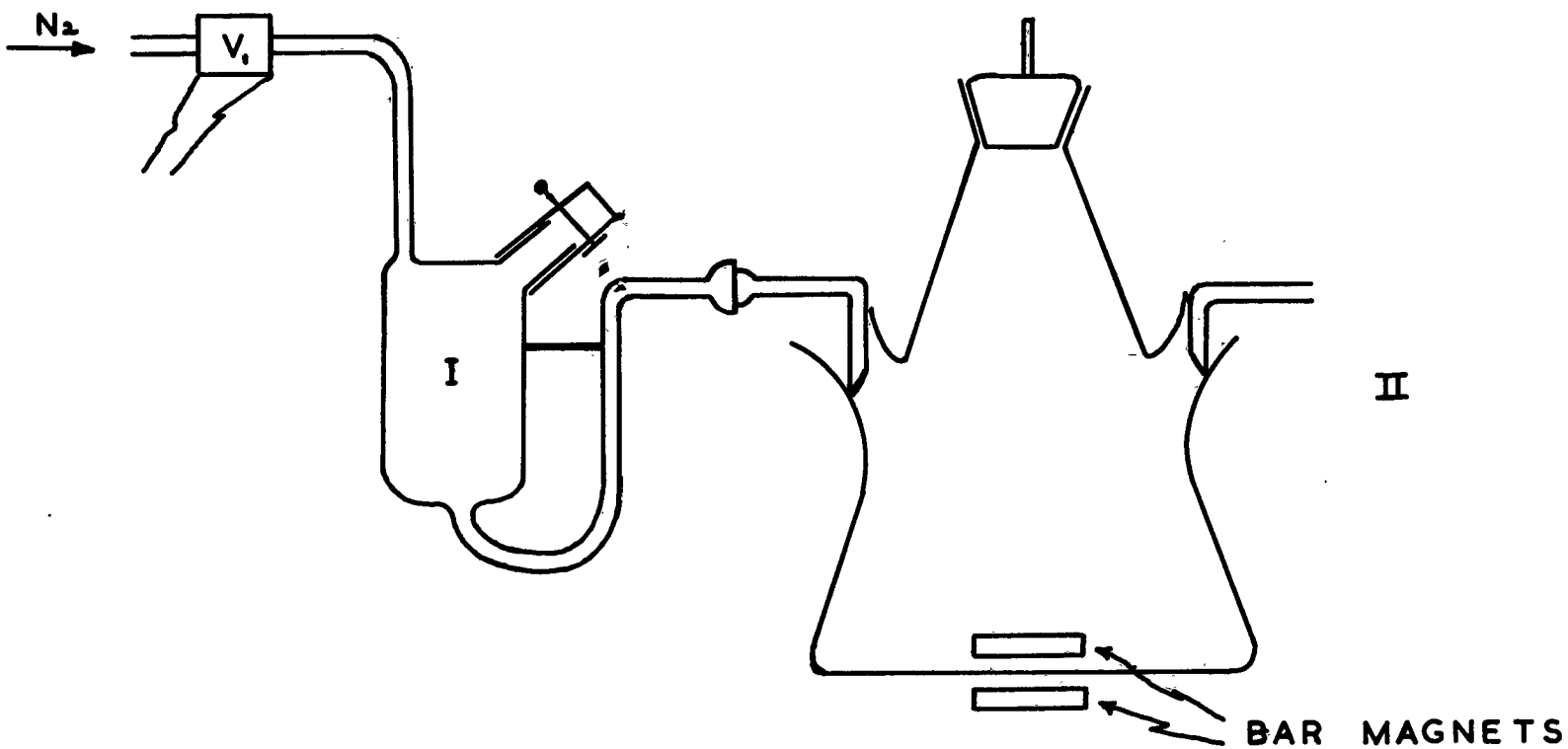


FIGURE 12

APPARATUS USED TO COLLECT CARBON DIOXIDE

FROM SILVER CYANATE SAMPLES.

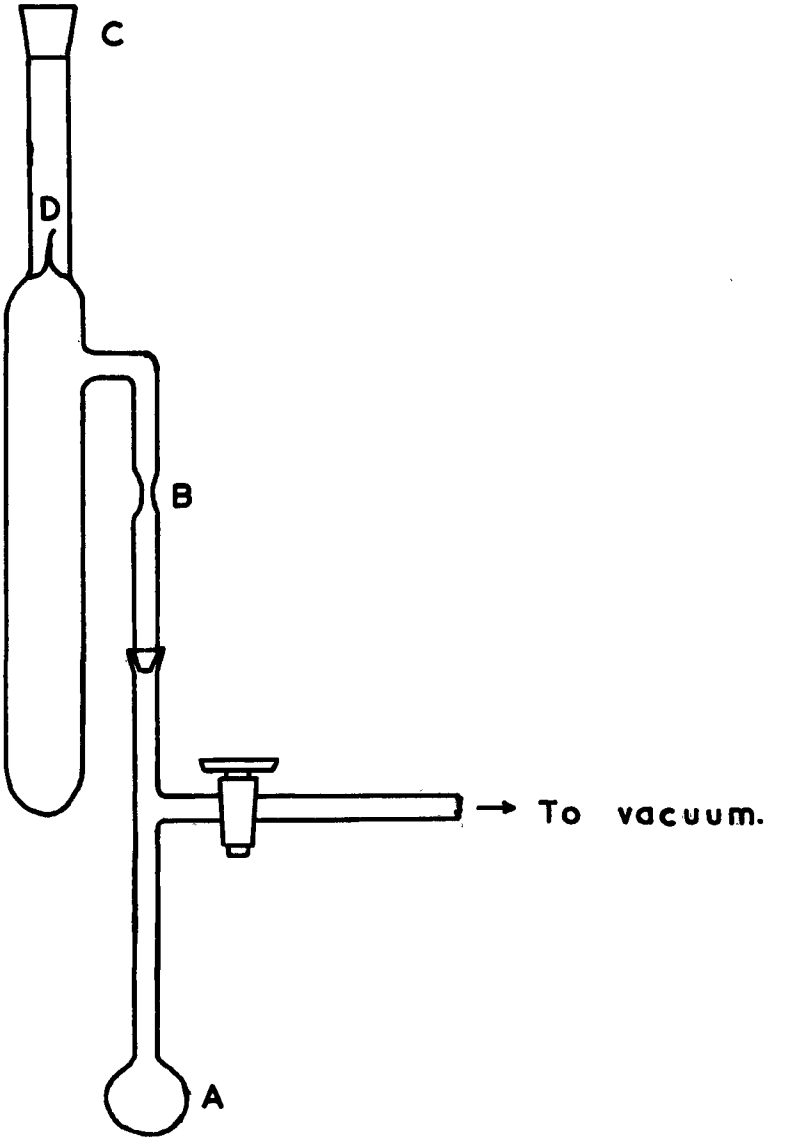


FIGURE 13

SPECTROPHOTOMETRIC METHOD; SECOND ORDER RATE PLOTS FOR THE PERMANGANATE:CYANIDE REACTION.

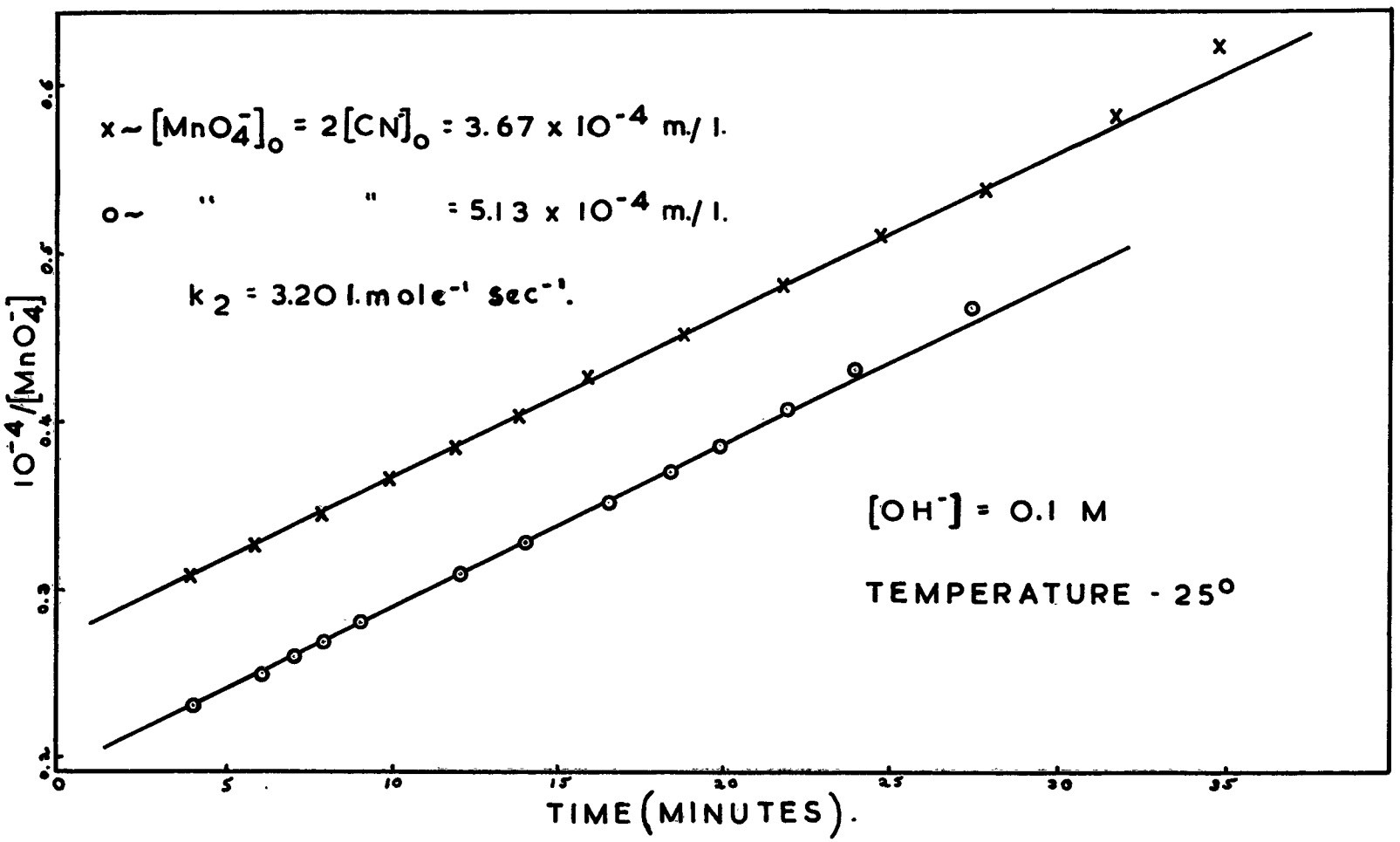


FIGURE 14

VARIATION OF THE SECOND ORDER RATE PLOT WITH REACTANT CONCENTRATION.

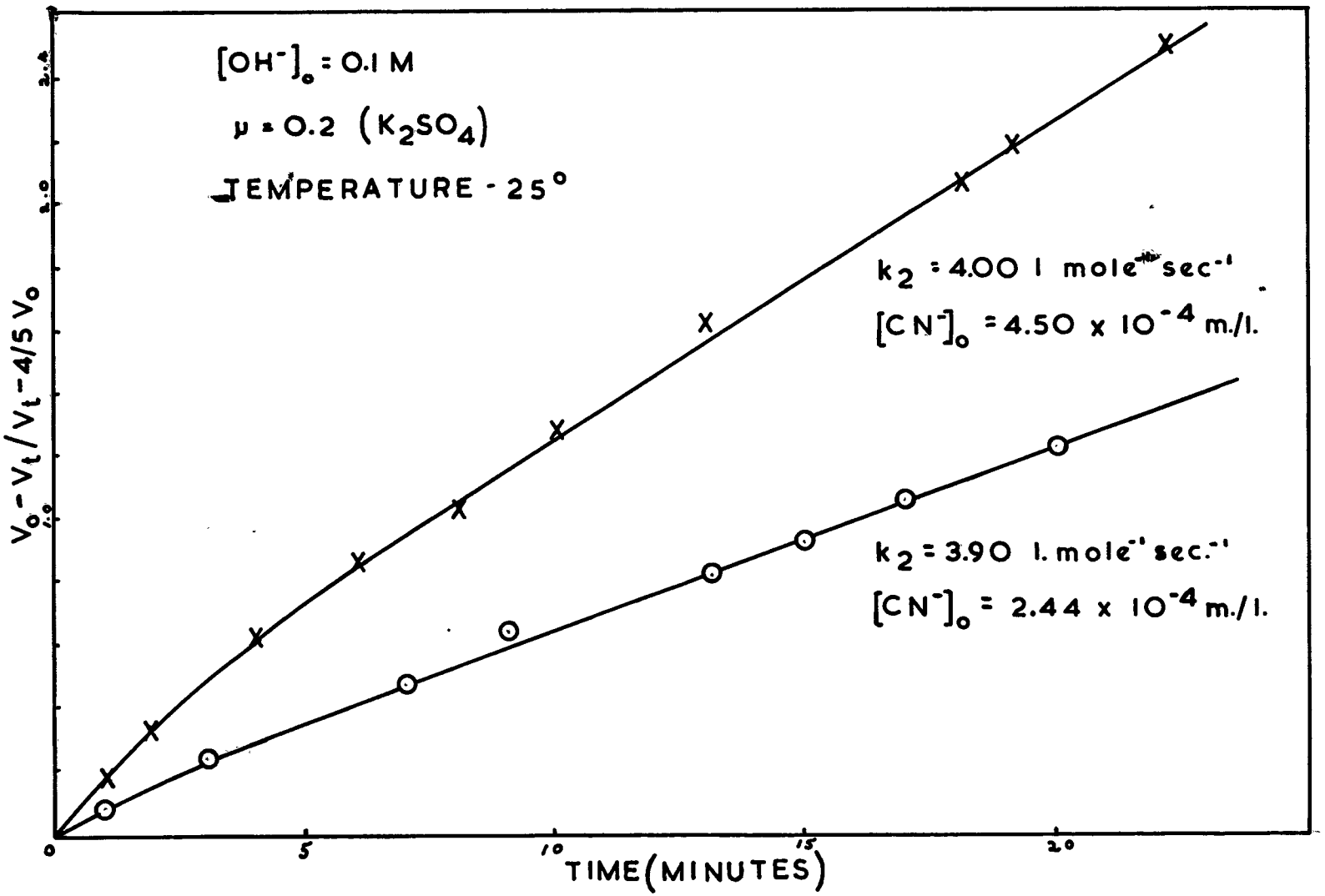


FIGURE 15

EFFECT OF ADDING INITIAL AMOUNTS OF MANGANATE ON THE SECOND ORDER REACTION.

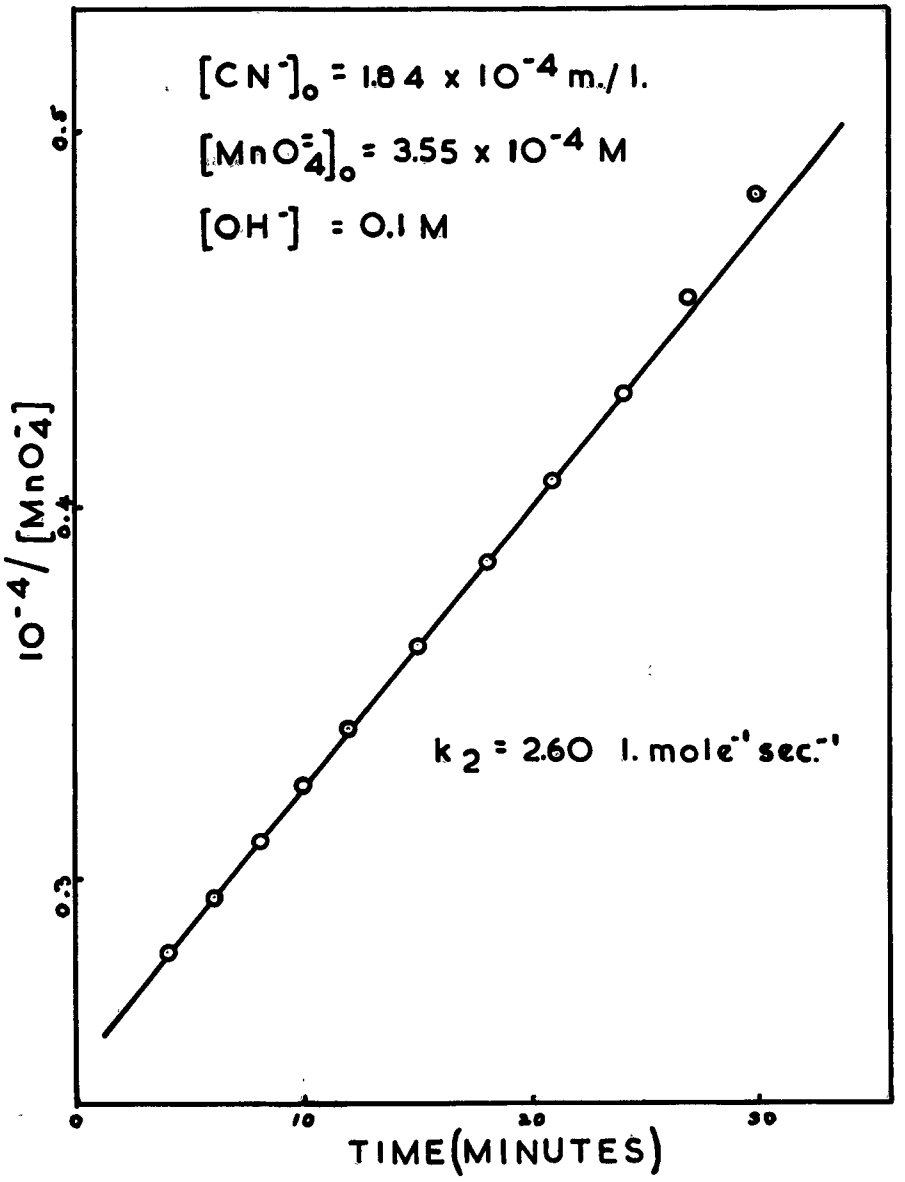


FIGURE 16.

EFFECT OF ADDING INITIAL AMOUNTS OF

BARIUM IONS ON THE SECOND ORDER REACTION.

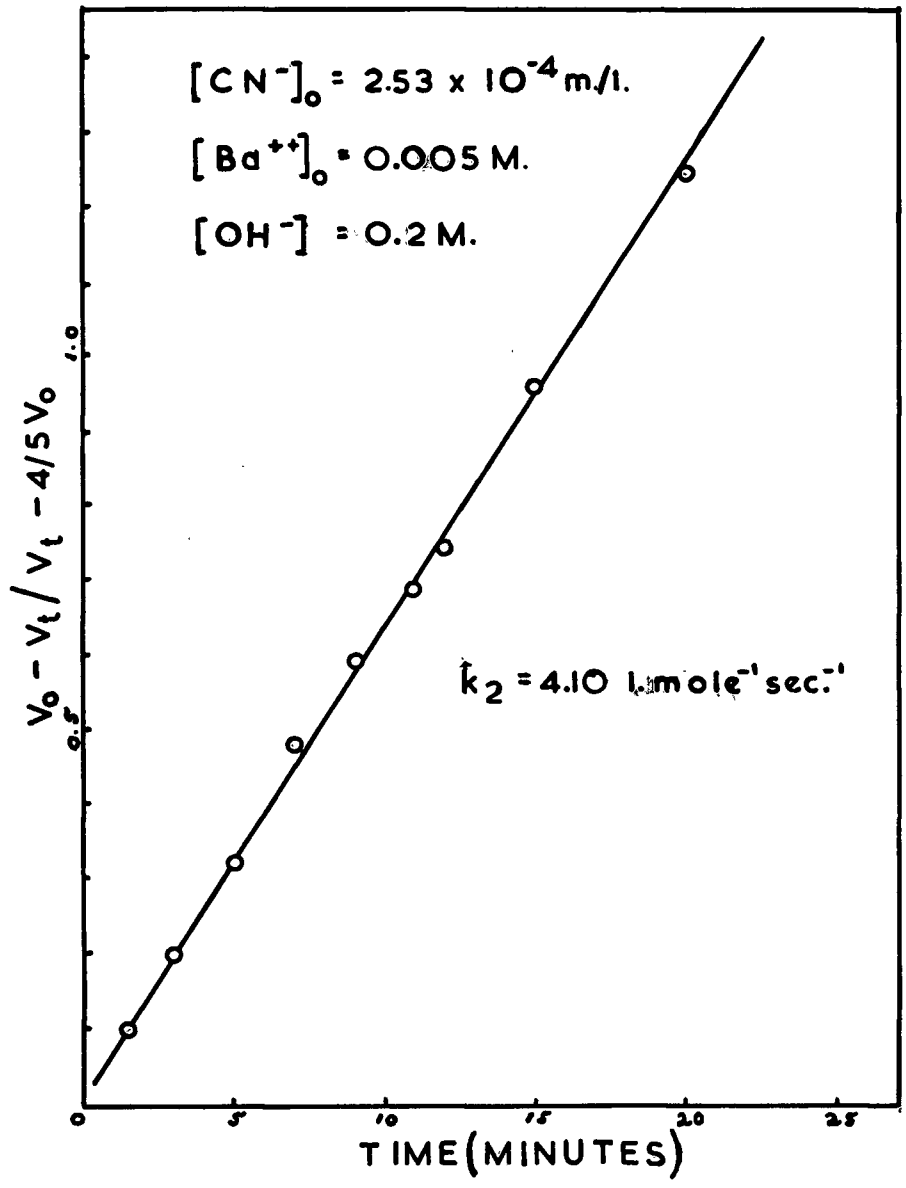


FIGURE 17

SECOND ORDER RATE PLOT FOR THE ALKALINE MANGANATE OXIDATION OF CYANIDE.

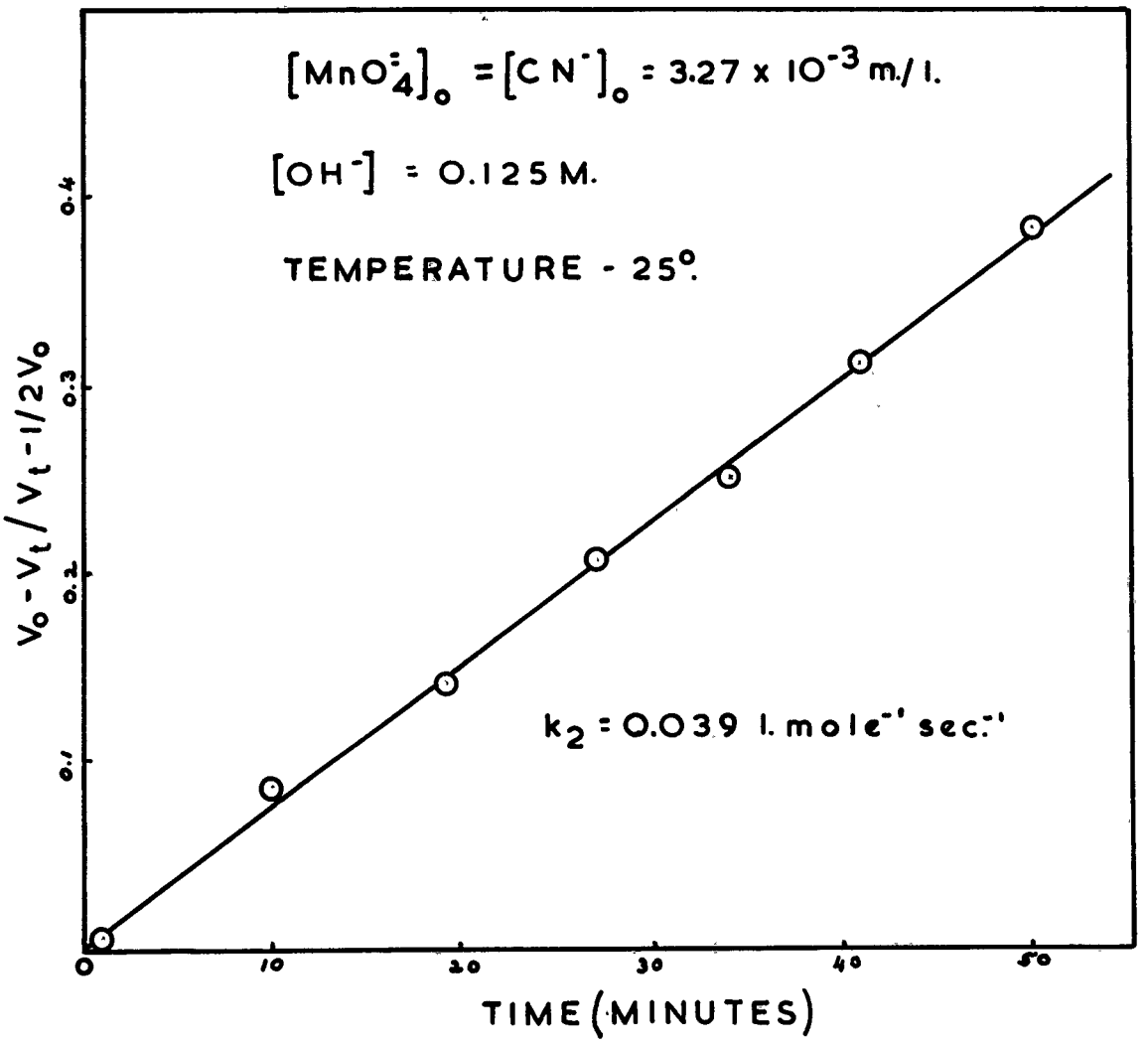


FIGURE 18

PLOT OF LOG k_2 VERSUS $\sqrt{\mu}$ FOR THE ALKALINE PERMANGANATE OXIDATION OF CYANIDE.

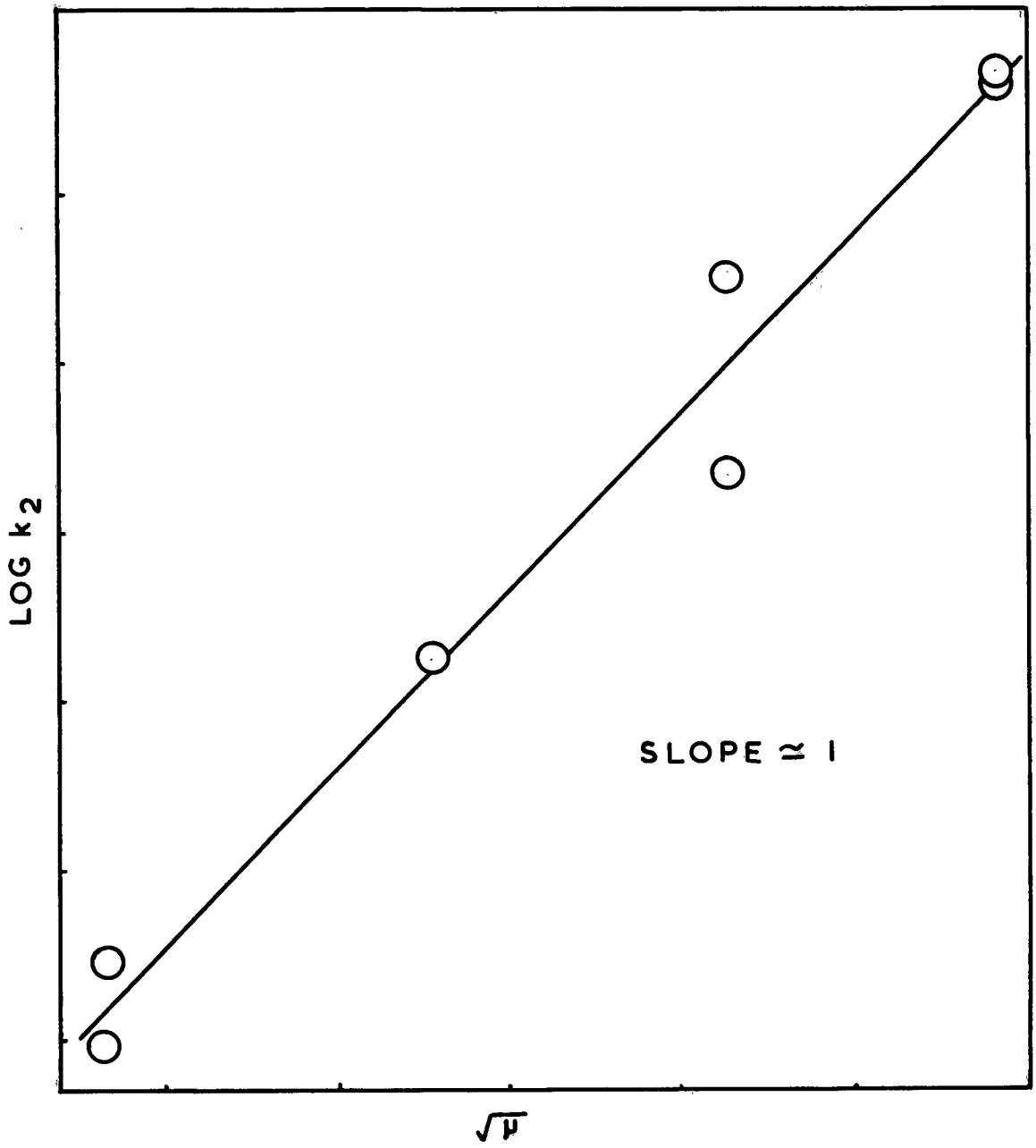


FIGURE 19

PLOT OF LOG k_2 / T°K VERSUS 1000/T°K FOR THE PERMANGANATE : CYANIDE REACTION AT 0.1M KOH.

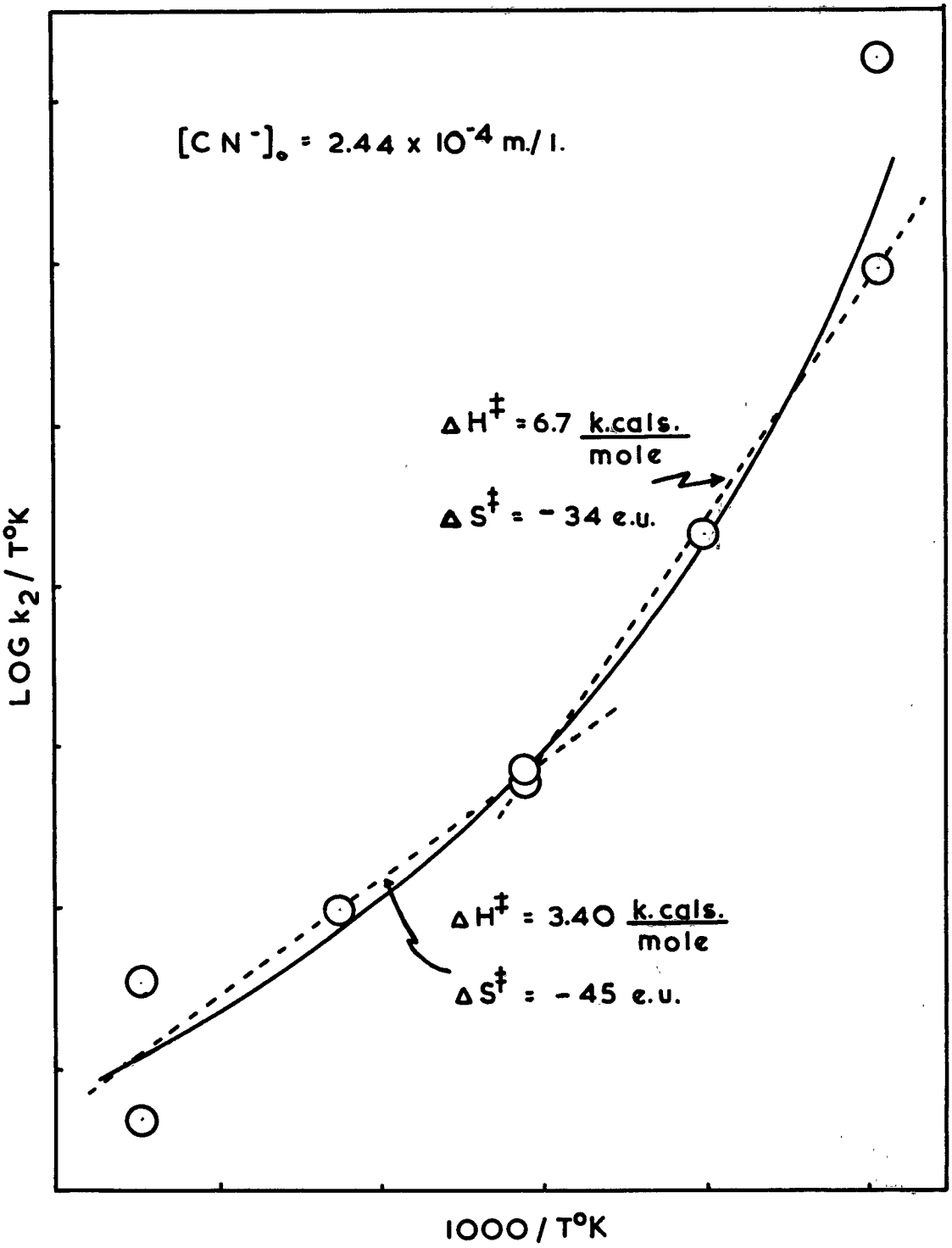


FIGURE 20

PLOT OF LOG k_2 / T°K VERSUS 1000/T°K AT 0.2M KOH

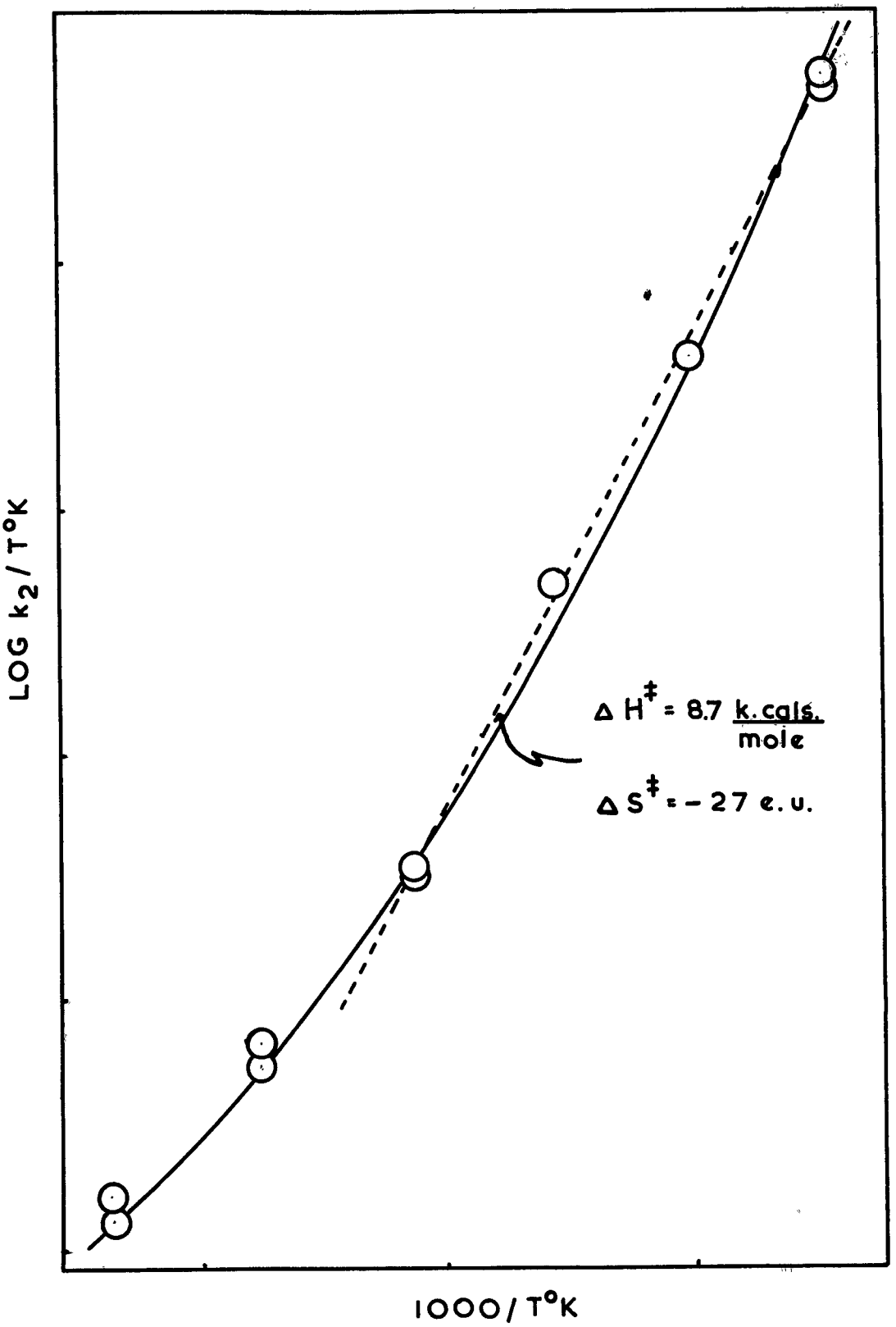


FIGURE 21

VARIATION OF THE SECOND ORDER RATE PLOTS WITH REACTANT CONCENTRATION AT 0.1M NaOH. $[MnO_4^-]_o = 2[CN^-]_o$.

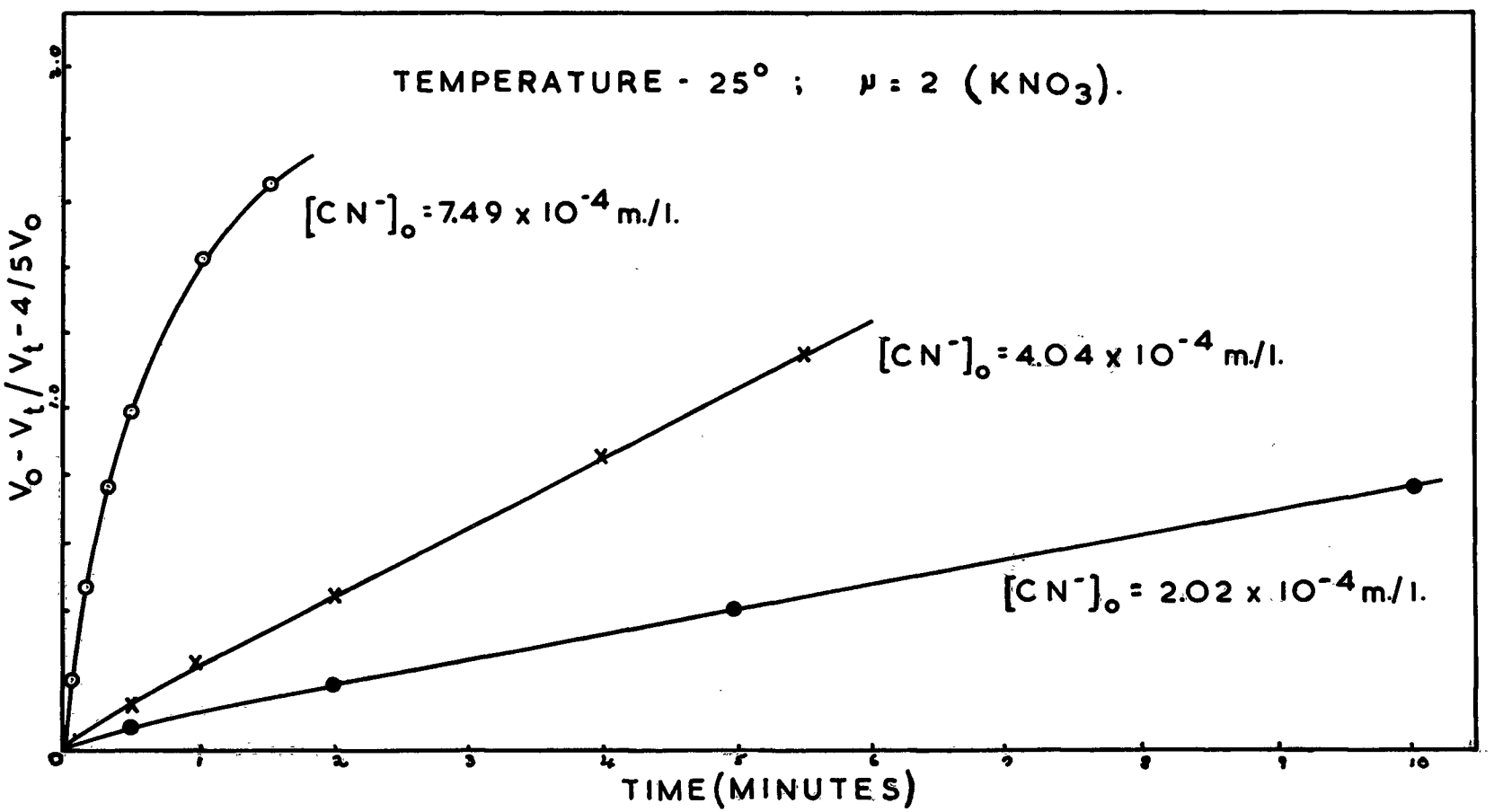


FIGURE 22

VARIATION OF THE SECOND ORDER RATE PLOTS WITH HYDROXYL ION CONCENTRATION. $[MnO_4^-]_o = 2[CN^-]_o$

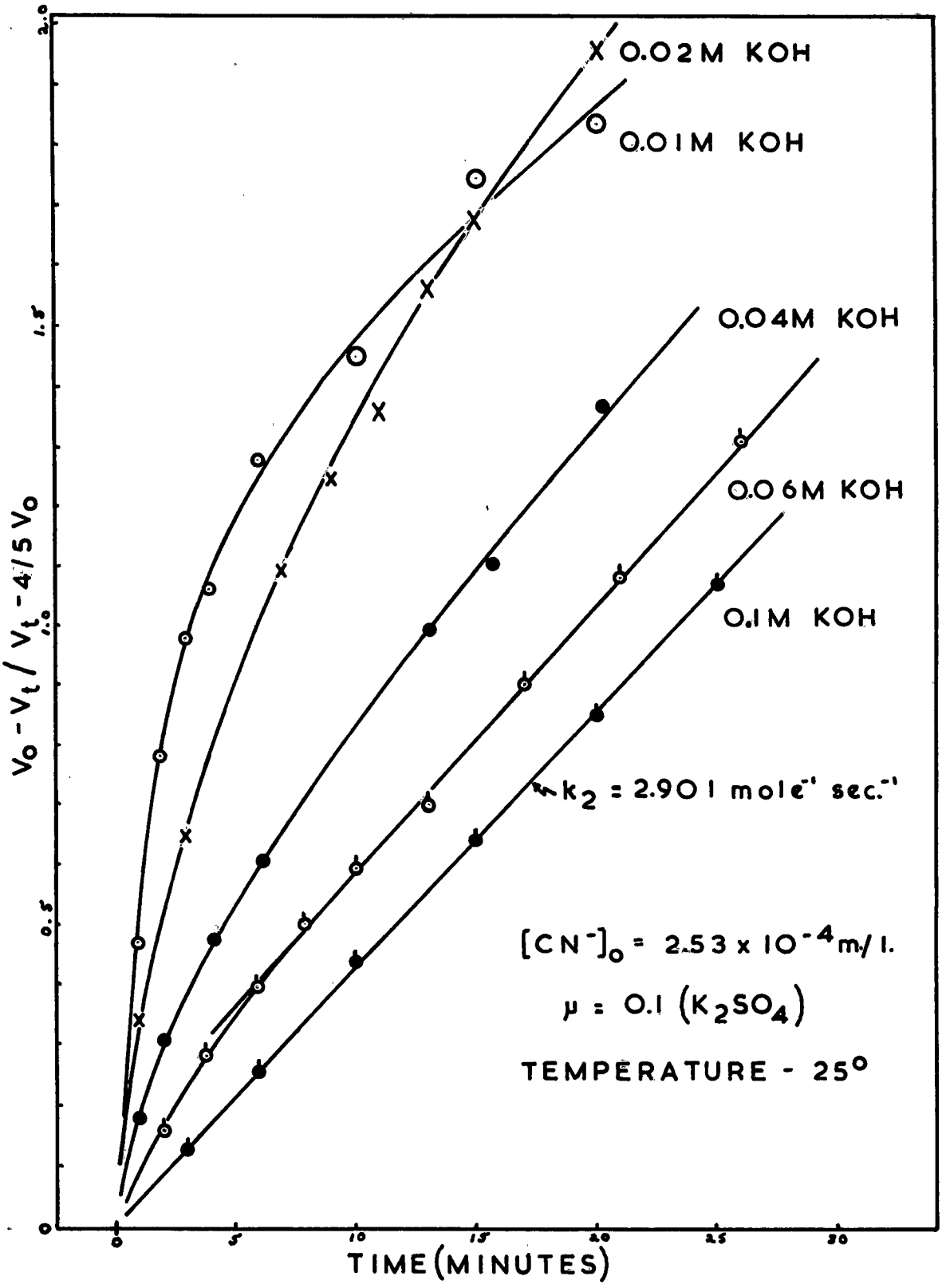


FIGURE 23

CONCENTRATION - TIME and THIRD ORDER RATE PLOTS

FOR THE PERMANGANATE - CYANIDE REACTION

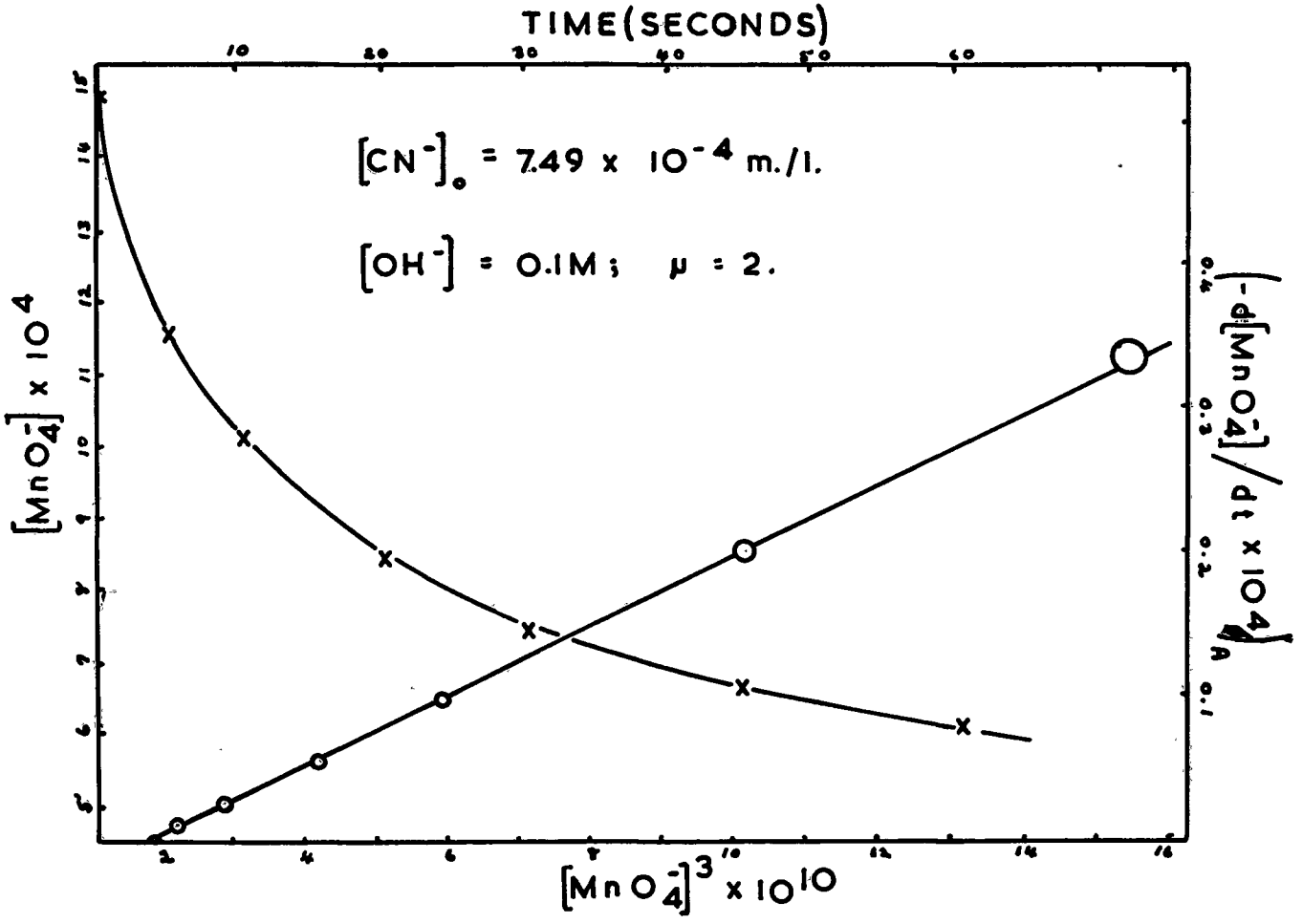


FIGURE 24

THIRD ORDER RATE PLOTS FOR THE PERMANGANATE - CYANIDE REACTION.

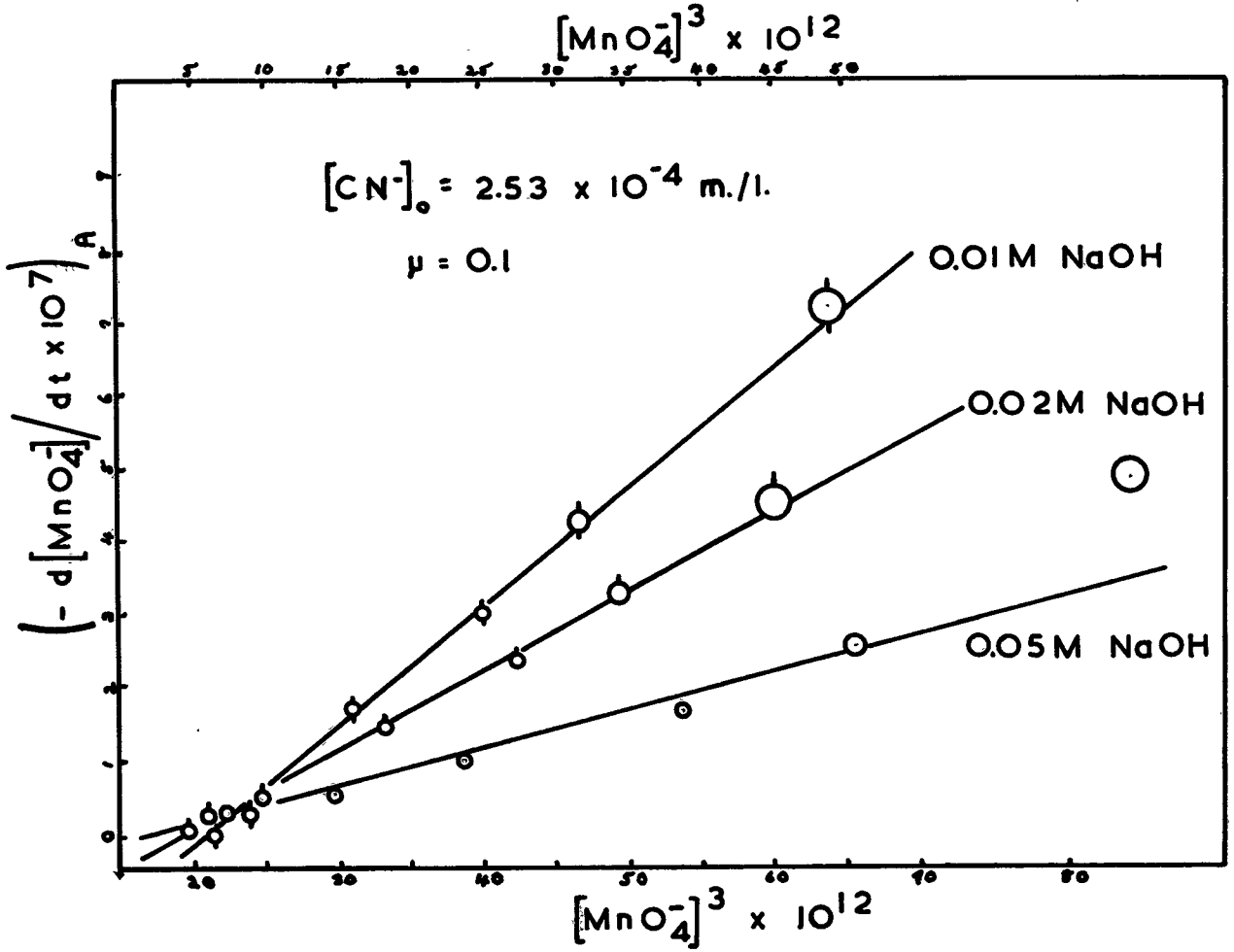


FIGURE 25

PLOT OF INITIAL RATE FOR THE PERMANGANATE -CYANIDE REACTION VERSUS $1/[OH^-]$; pH 12 TO 13.

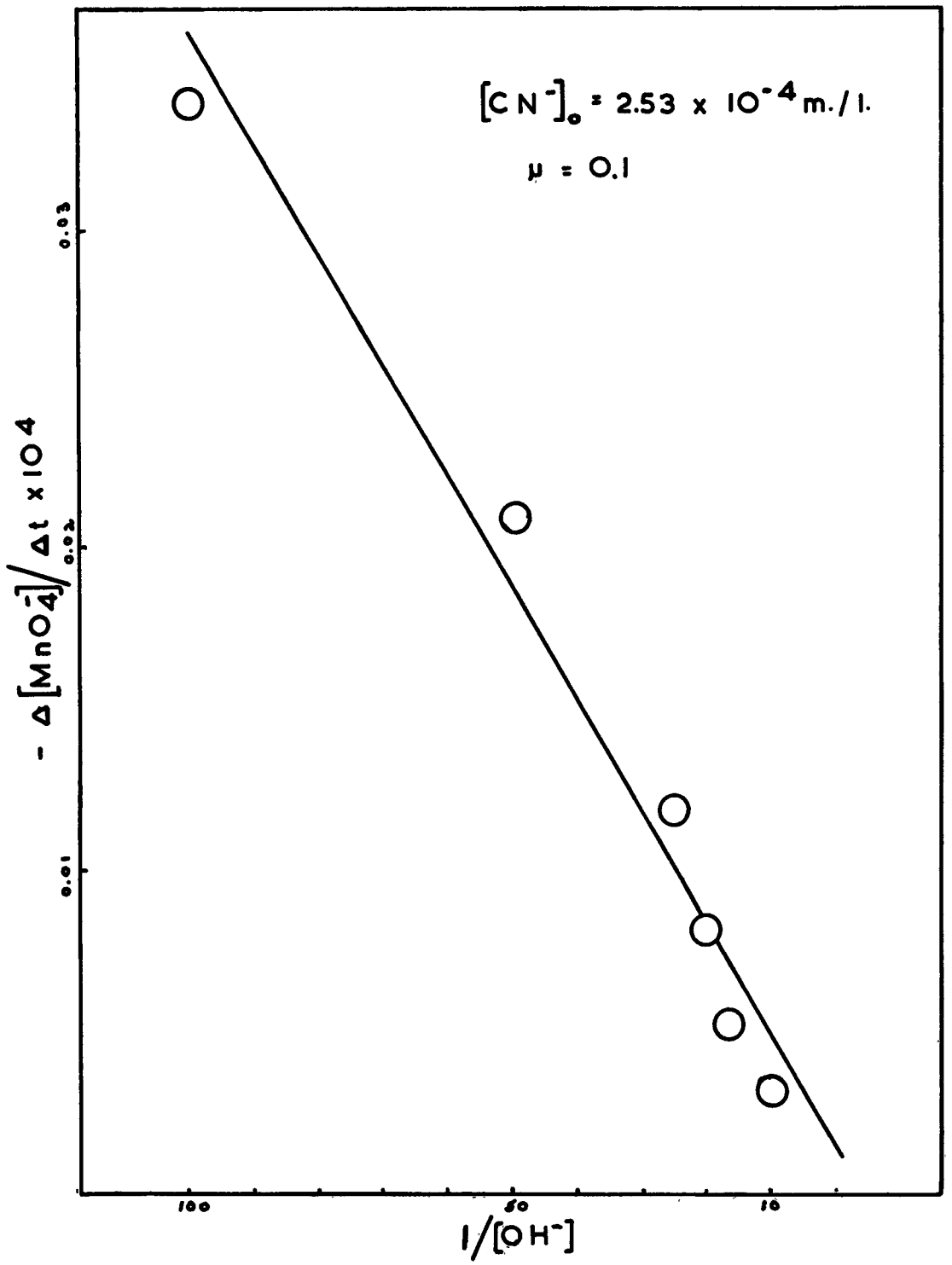


FIGURE 26

PLOT OF LOG $[MnO_4^-]$ VERSUS TIME FOR THE PERMANGANATE-CYANIDE REACTION.

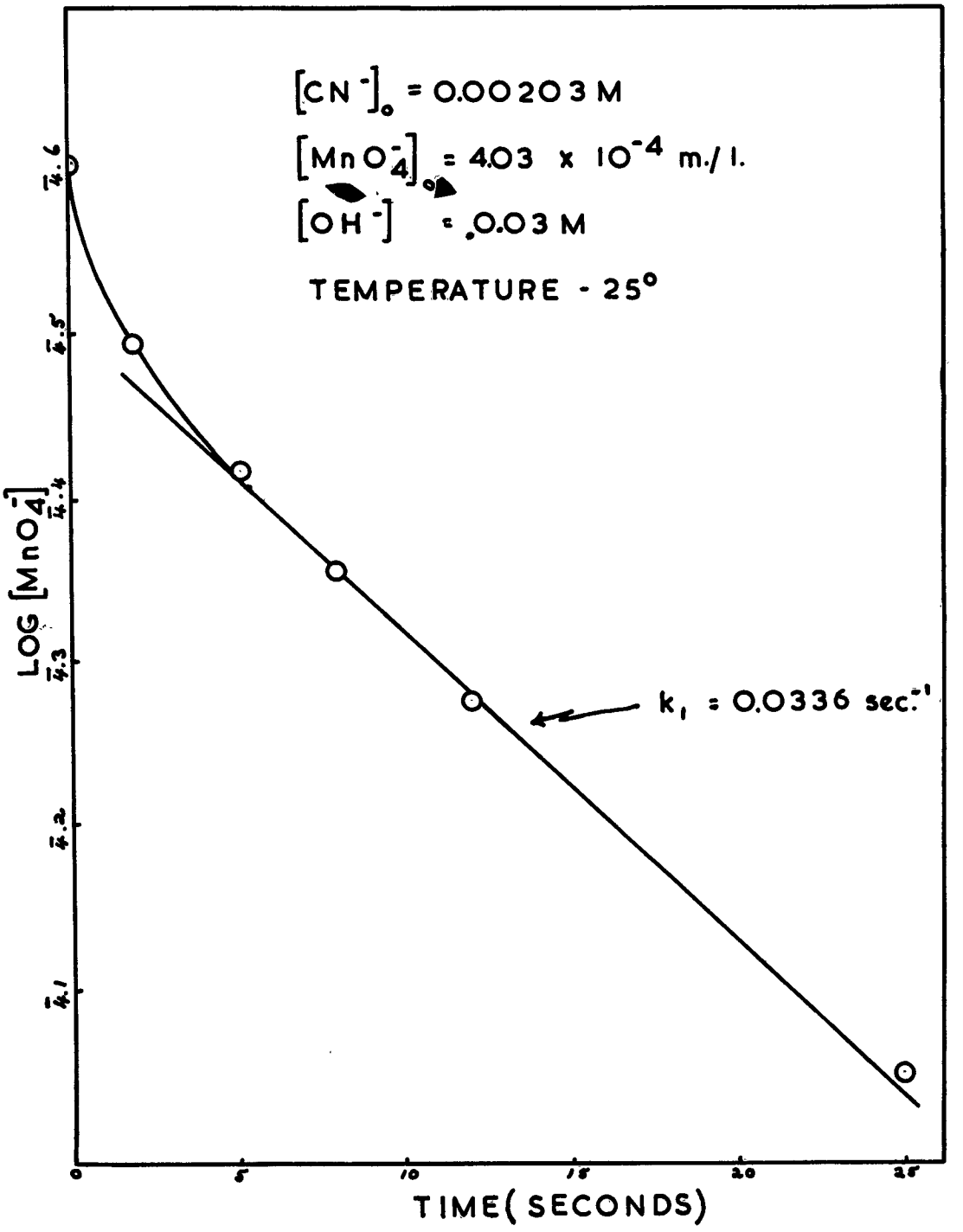


FIGURE 27

CONCENTRATION-TIME PLOTS FOR THE ALKALINE PERMANGANATE OXIDATION OF CYANIDE AS OBTAINED BY THE VARIOUS KINETIC METHODS.

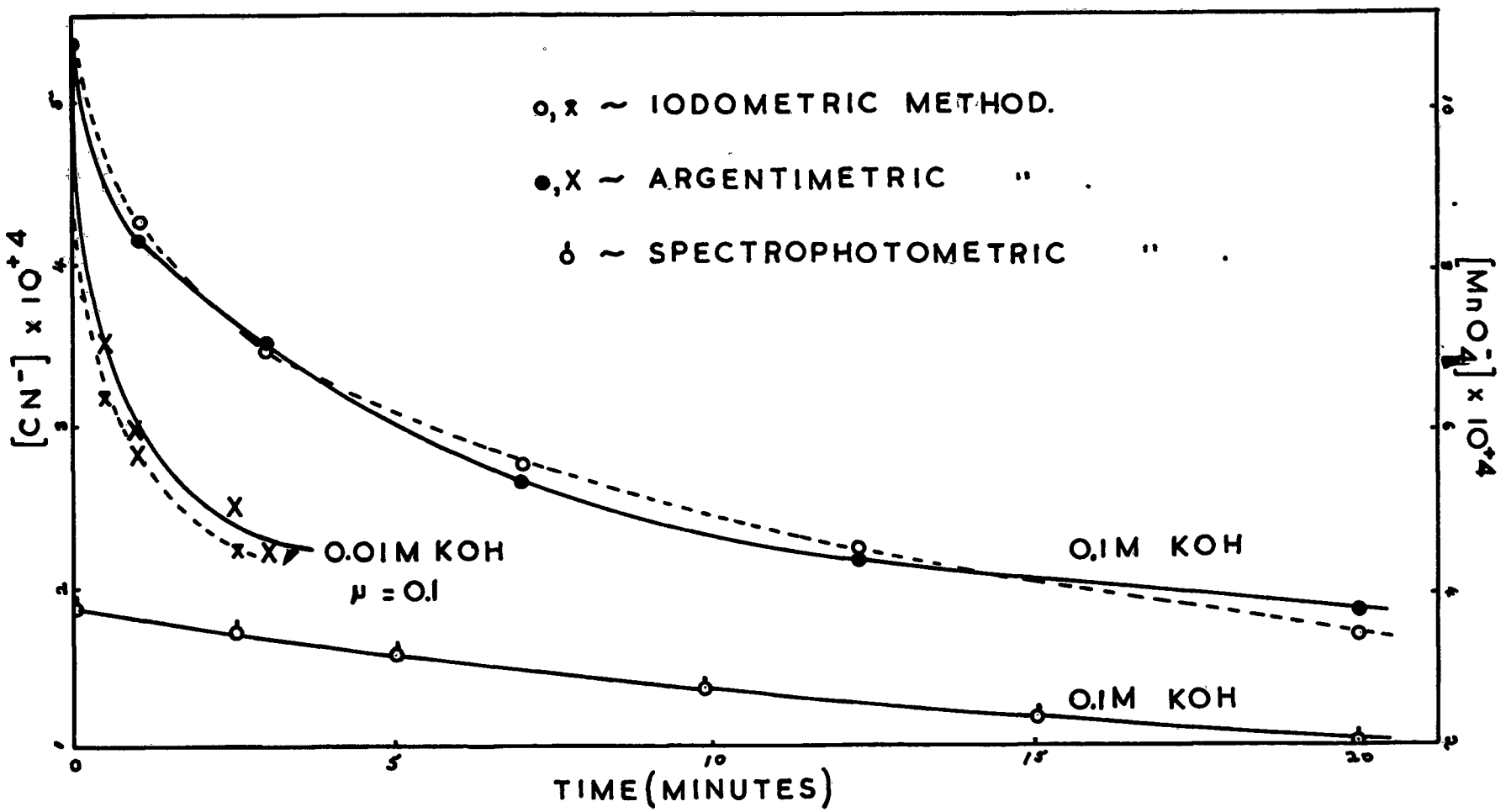


FIGURE 28

TYPICAL SECOND ORDER RATE PLOTS FOR

THE PERMANGANATE - CYANIDE REACTION AT LOW pH.

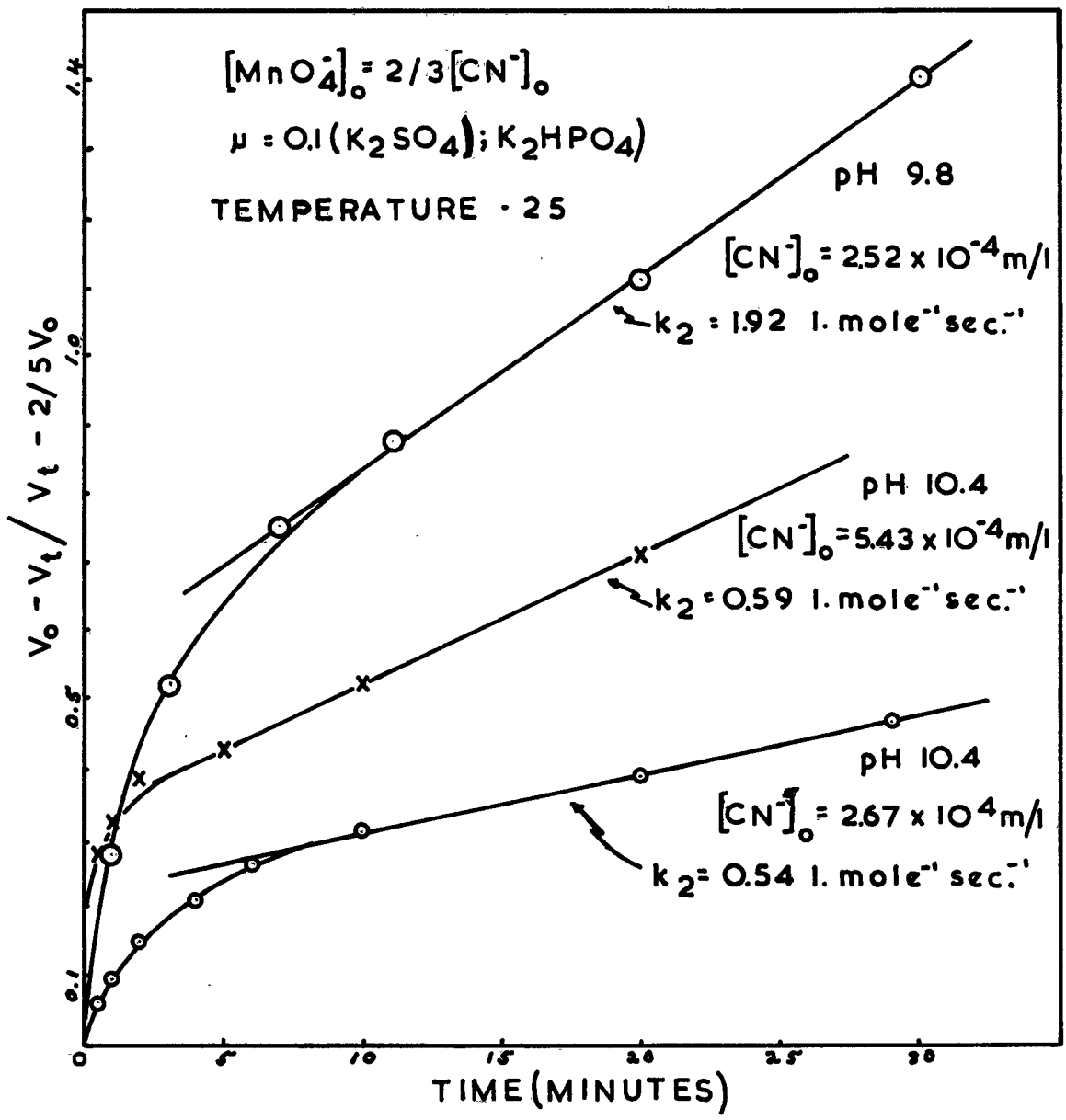


FIGURE 29

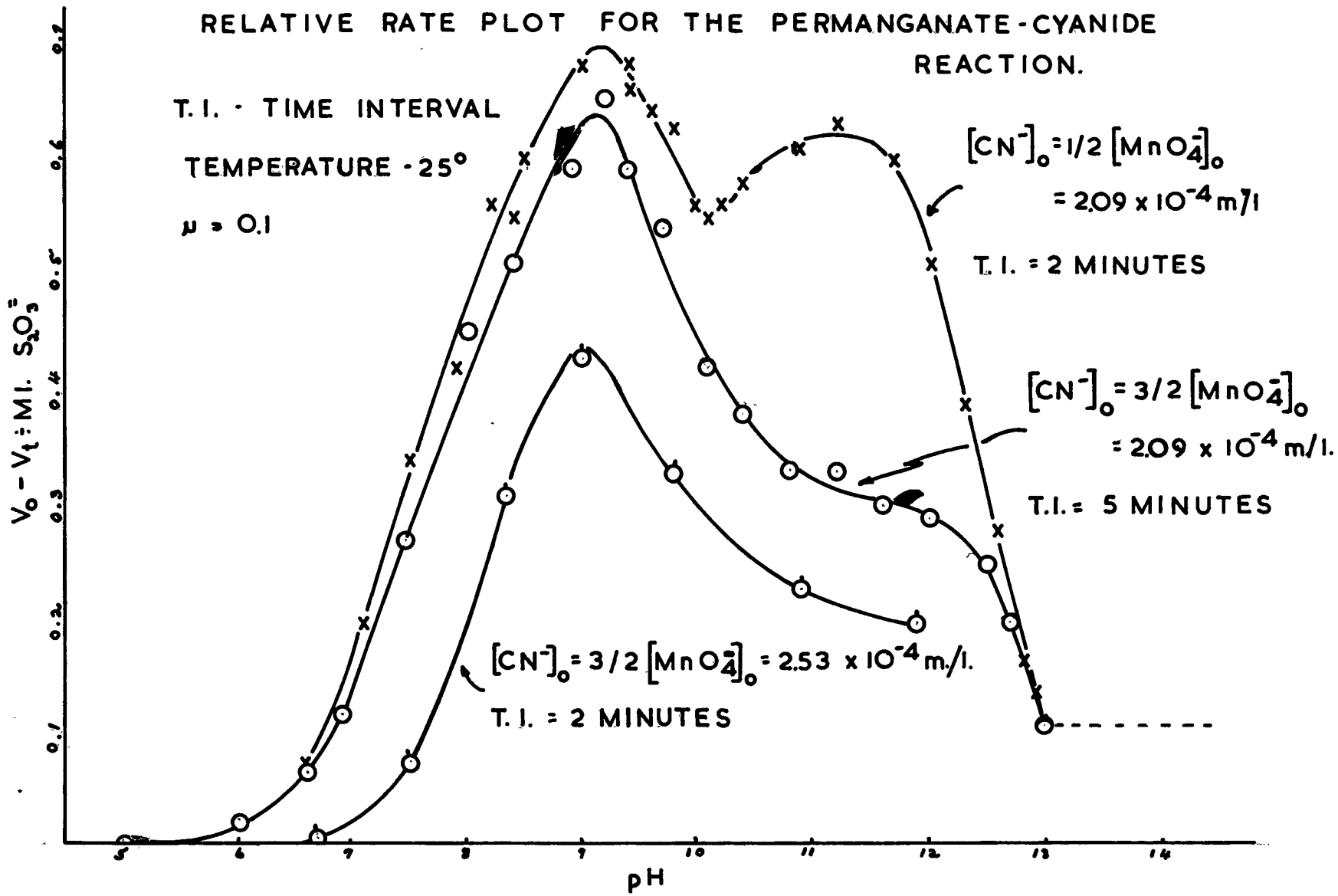

RELATIVE RATE PLOT FOR THE PERMANGANATE-CYANIDE REACTION.
T. I. - TIME INTERVAL
TEMPERATURE - 25°
μ = 0.1
$[CN^-]_o = 1/2\,[MnO_4^-]_o = 2.09 \times 10^{-4}$ m/l
T. I. = 2 MINUTES
$[CN^-]_o = 3/2\,[MnO_4^-]_o = 2.09 \times 10^{-4}$ m/l.
T.I. = 5 MINUTES
$[CN^-]_o = 3/2\,[MnO_4^-]_o = 2.53 \times 10^{-4}$ m./l.
T. I. = 2 MINUTES
$V_o - V_t$ = Ml. $S_2O_3^=$
0.1
0.2
0.3
0.4
0.5
0.6
0.7
5
6
7
8
9
10
11
12
13
14
pH

FIGURE 30

PERCENTAGE O^{18} TRANSFERED FROM PERMANGANATE TO CYANIDE VERSUS HYDROXYL ION CONCENTRATION