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THE MECHANISM OF PERMANGANATE OXIDATION OF
ALKANES, ARENES AND RELATED COMPOUNDS

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ABSTRACT

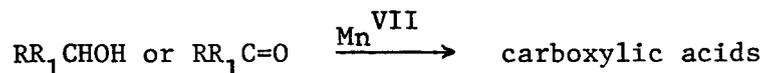
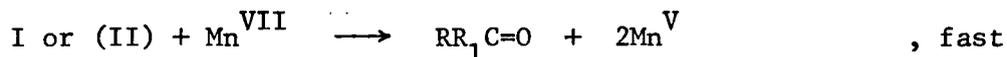
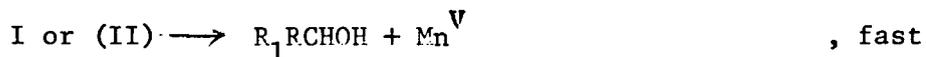
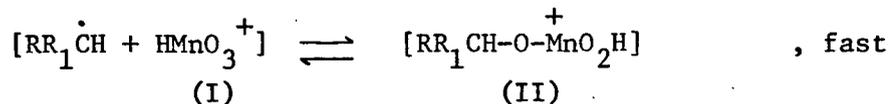
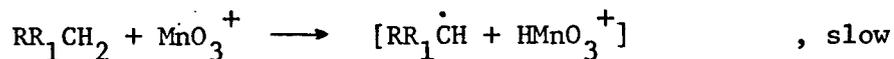
Supervisor: Professor Ross Stewart

The permanganate oxidation of alkanes and arenes has been studied in trifluoroacetic acid (TFA)-water. This solvent system has the unique advantage of being virtually inert to oxidative degradation and yet providing adequate solubilities for the reactants.

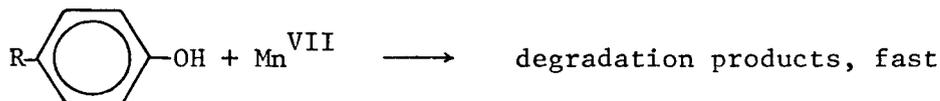
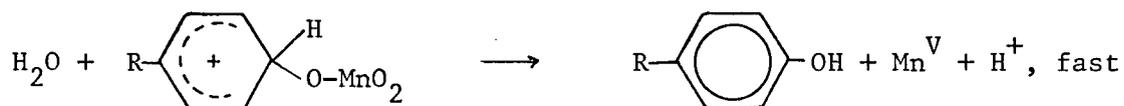
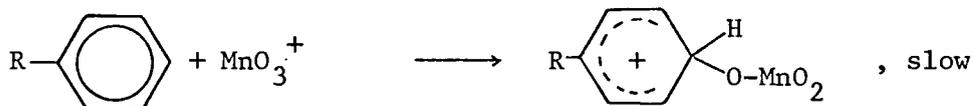
The mechanistic investigation involved kinetic studies to determine the orders with respect to oxidant, substrate, and acid. Complementary techniques such as product studies, substituent effects, activation parameters, and isotope effects completed the mechanistic investigation. The oxidation of several alcohols, aldehydes, and ketones was also investigated to aid in the interpretation of the results.

Because of the poor fit of the kinetic data with the previously determined H_o function for TFA-water the H_R function was determined using the Hammett approach of overlapping indicators. The identity of the oxidants in the acidic medium was established by cryoscopic and spectrophotometric means. It was found that the most vigorous oxidant was permanganyl ion (MnO_3^+), with some contributing oxidation by both permanganic acid ($HMnO_4$) and permanganate ion (MnO_4^-) in the case of easily oxidized compounds such as alcohols, aldehydes, or enols.

The mechanism of the acidic permanganate oxidation of alkanes (ethane to n-tridecane) was found to proceed via rate-determining homolytic carbon-hydrogen bond scission as depicted below.



The mechanism of arene oxidation was shown to proceed via rate-determining electrophilic attack by permanganyl ion on the aromatic ring to yield ring degradation products. Phenols are believed to be intermediates in this process as depicted below.



The mechanisms of the oxidation of alcohols, ketones, aldehydes, and formic acid were determined and shown to be consistent with mechanisms previously established under other conditions.

The behaviour of two electrophiles, nitrosonium ion (NO^+) and nitronium ion (NO_2^+), generated respectively from sodium nitrite and sodium nitrate, was examined in the TFA-water medium. It was found that the nitronium ions thus generated could be successfully used to carry out electrophilic aromatic nitrations in excellent yields but that the nitrosonium ions were inert.

It was also determined that the tetra(n-hexyl)ammonium permanganate salt could be prepared in good yield and used as an oxidant for a variety of substrates in benzene solution.

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Finally I wish to thank my wife, Leila, for encouragement and patience.

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ABBREVIATIONS AND SYMBOLS

USED IN TEXT

a_i	activity of ith component
c	constant of integration
ΔG	change in free energy
ΔH	change in enthalpy
ΔS	change in entropy
DPC	diphenylcarbinol
f_i	activity coefficient of ith component
F_i	mole fraction of ith component
g	grams
h	Planck's constant
hr	hour
H_o	acidity function defined by protonation of primary anilines
H_R	acidity function defined by ionization of carbinols
k	Boltzmann constant
k_n	rate constant, $n = 0,1,2,3$
k, k'	proportionality constants
kg	kilogram
$^{\circ}K$	degrees Kelvin
ln	natural logarithm
log	base 10 logarithm
m	molality, moles per 1000 g of solvent
M	molarity, moles per 1000 ml of solution
$\mu\ell$	microliter
ml	milliliter
min	minutes

n	number of particles generated
n_0	number of particles predicted by theory
N	normality, number of equivalent weights per liter of solution
NMR	nuclear magnetic resonance
p_i	pressure of ith component
s	seconds
TFA	trifluoroacetic acid
TPC	triphenylcarbinol
TPMCl	Triphenylmethyl chloride
vpc	vapour-liquid phase chromatography
r	reaction velocity
†	denotes transition state or activated complex
[]	denotes concentration in moles per litre

1. INTRODUCTION

1.1 Purposes of the Investigation

In the past decade considerable attention has been focused on environmental abuse by industrial pollutants. The pollutant considered as one of the most serious is oil not only because of the large quantities usually involved but also because of the immediate and long term toxicity to the environment. As a result of the economic loss and public pressure considerable effort is being expended to understand how the ecosystem attempts to cope with sudden additions of large quantities of hydrocarbons.

Researchers have found that certain micro-organisms can degrade hydrocarbons by utilizing them as a food source.¹⁻³ The initial approach of reseachers in this area was to utilize yeasts to profitably up-grade crude oils by the removal of waxy alkanes to yield some marketable proteins for animal feed.² Recently such micro-organisms have been recognized as potential oil-spill combatants which act by degrading the oil instead of dispersing it.³ Pilot batches have shown promise, with the added advantage of not being toxic to shellfish, which is a serious drawback of dispersants.

Presently, considerable interest is being focused on establishing the mechanism of this degradation process in order to maximize the

efficiency of these organisms. The precise route of the degradation is at present only speculative but some aspects of the process are now understood. It is known that some micro-organisms utilize only a specific series of hydrocarbons¹ and that the attack occurs at the terminal carbon, sometimes involving incorporation of oxygen from the atmosphere, as ¹⁸O studies have shown.^{1,4}

Although the main purpose of this investigation was to establish the mechanism of the acidic permanganate oxidation of arenes and alkanes, we were aware of the possibility that this study might provide some fundamental information about the ways in which carbon-hydrogen bonds are cleaved in saturated hydrocarbons. This information might help elucidate the mechanism of microbiological oxidation of hydrocarbons.

Permanganate has been recognized as a versatile oxidant that is active in both acidic and basic media and is capable of oxidizing a wide variety of substrates.⁵⁻⁷ The mechanisms by which these oxidations are performed are quite well understood with the exception of the oxidation of alkanes and arenes. Very little research has been directed towards this problem, probably because of low solubilities of these substrates in media capable of dissolving permanganate. This study attempts to establish the mechanism of the oxidation of alkanes and arenes by acidic permanganate in a homogeneous medium.

1.2 Properties of the Trifluoroacetic Acid-Water Medium

Alkanes are known to have some solubility in water but the alkane content even in saturated solutions is very low, in the order of 10^{-4} to 10^{-5} molar.⁸ These concentrations are insufficient for kinetic

investigation by conventional means. A co-solvent was required which could dissolve both permanganate and the alkanes and yet be resistant to oxidation. Trifluoroacetic acid (TFA) was found to be satisfactory for this purpose. TFA had the further advantage of allowing variation of the acidity of the medium, since it is a moderately strong acid with $pK_a = -0.26$.⁹

Trifluoroacetic acid has been successfully used for a variety of reactions ranging from oxidations¹⁰ to electrophilic aromatic substitutions.¹¹ Some of the properties of this solvent system are briefly outlined below.

Trifluoroacetic acid-water mixtures are not very strong protonating media as shown by the work of Randles and Tedder.¹² A maximum value of $H_o = -3.03$ is reached in neat TFA¹³ (46% wt. sulfuric acid has $H_o = -3.03$ ¹⁴). The dielectric constant of neat TFA is $\epsilon_{25} = 8.3 \pm 0.1$,¹⁵ which indicates that TFA is not a very strongly ionizing solvent. Conductivity studies confirm this but also show that salts containing ammonium cations are more dissociated than expected in this solvent, an effect which is thought to be due to hydrogen bonding.¹⁵ Brown and Wirkkala¹¹ found TFA to be an exceptionally good medium for aromatic electrophilic substitutions such as nitrations and brominations. The bromination kinetics were investigated and found to be simple second order without any of the complications which were encountered when acetic acid was used.

Several groups have observed that TFA can have strong solvent interactions with compounds^{16,17} and intermediates.^{18,19} It has been reported that neat TFA can solubilize salts by hydrogen bonding

$$K_{BH^+} = [B] f_B^{a_{H^+}} / [BH^+] f_{BH^+}, \quad f = \text{activity coefficient}$$

The definition is then made that $h_o = f_B^{a_{H^+}} / f_{BH^+}$. This then separates those terms hard to determine from those easily accessible by experimental measurements.

$$pK_{BH^+} = -\log K_{BH^+} = -\log[B]/[BH^+] - \log h_o$$

$$pK_{BH^+} = H_o - \log [B]/[BH^+]$$

or $H_o = pK_{BH^+} + \log [B]/[BH^+]$

Another function often used is H_R which measures the tendency of the medium to ionize carbinols.²¹ The function is derived in the following manner.



$$K_{R^+} = a_{ROH}^{a_{H^+}} / a_{H_2O}^{a_{R^+}} = [ROH] f_{ROH}^{a_{H^+}} / [R^+] f_{R^+}^{a_{H_2O}}$$

$$h_R = f_{ROH}^{a_{H^+}} / f_{R^+}^{a_{H_2O}} \quad \text{and} \quad H_R = -\log h_R$$

$$pK_{R^+} = -\log [ROH]/[R^+] - \log h_R$$

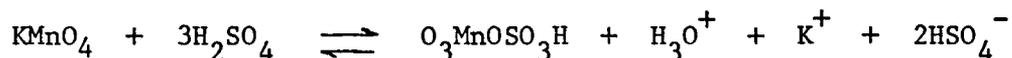
$$H_R = pK_{R^+} + \log [ROH]/[R^+]$$

Usually these functions are determined by using a technique referred to as "the method of overlapping indicators". The method consists of taking an indicator which has measurable ionization in a medium which has a measurable pH. Then the assumption is made that $H_x = \text{pH}$ in this very dilute region. The pK for this indicator can then be calculated. This pK value is used to then determine H_x for stronger mixtures by measuring the new ionization ratio ($[B]/[BH^+]$). Eventually this indicator will no longer be useful, which is arbitrarily defined to be when $0.1 < [B]/[BH^+] < 10$. To then extend H_x a weaker indicator has to be used which has measurable ionization in some solution of known H_x , i.e. it overlaps with the previous indicator. The pK can then be calculated since H_x is known and the new indicator ratio can be measured. This overlapping process is continued until H_x is established for the entire medium range, or until no more suitable indicators are available to extend H_x .

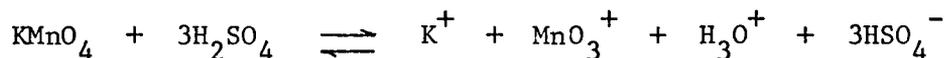
It is important that only those indicators are used where the overlap is good and, most important, that the indicators have parallel responses to the medium changes, i.e. $\log f_{B_1}/f_{BH_2} = \log c(f_{B_2}/f_{BH_2})$, $c = \text{a constant}$. This condition must be fulfilled otherwise H_x has no meaning because the overlap method uses H_x from the previous indicator to determine pK of the next indicator. This essentially forces H_x (indicator 1) to be equal to H_x (indicator 2), i.e. $-\log f_{B_1} a_{H^+}/f_{BH_1} = -\log f_{B_2} a_{H^+}/f_{BH_2}$. This condition can be tested by checking to see that $\log [B]/[BH^+]$ vs. H_x plots give lines that are parallel for overlapping indicators. If deviations are severe the deviant indicator should not be used.

1.4 Behavior of Permanganate in Acidic Medium

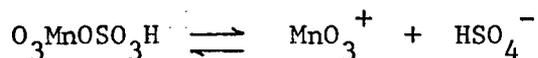
The distinctive absorbance by permanganate ion has been shown to be insensitive to solvent changes and cation variation,^{22,23} but if the medium is made very acidic a distinct spectral change is observed from purple to light green²⁴ (λ_{\max} of green species is 458 nm^{28,29}). The cause of this spectral change has not yet been resolved. Symons et al.²⁵ have suggested from conductivity measurements that the spectral change is due to the following process,



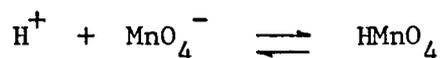
but Royer²⁶ interpreted similar conductivity measurements and cryoscopic data to be consistent with the reaction,



Stewart²⁷ has suggested that these interpretations may be reconciled by considering the following equilibrium.



This spectral change has been observed in partially aqueous media where the process is taken to be a protonation.^{28,29}



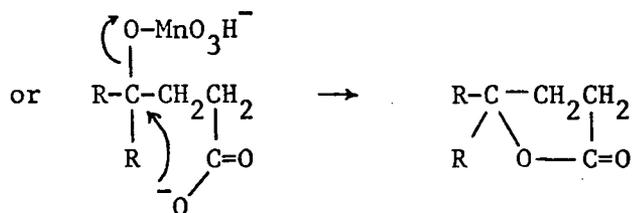
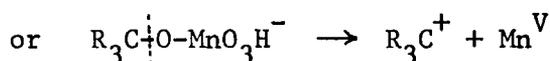
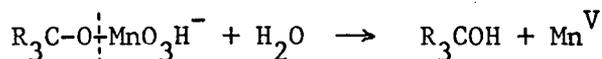
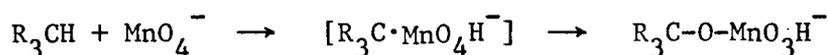
Symons et al.²⁸ has established this pK_a value to be -2.25 in perchloric acid using H_2O but Stewart and Mocek²⁹ found a value of -4.6 in sulfuric acid also using H_2O . The difference in pK_a values has been attributed to the changes in the medium but there is considerable inconsistency in the interpretation of the spectral changes. In strongly acidic media the green color is attributed to MnO_3^+ ²⁶ or to O_3MnOSO_3H ²⁵ but in the more aqueous region permanganic acid is thought to cause the green color.

In this study it will be demonstrated that only three manganese species are present in TFA-water mixtures, namely permanganate ion (MnO_4^-), permanganyl ion (MnO_3^+) and permanganic acid ($HMnO_4$), and that their proportions depend upon the amount of TFA in the medium.

1.5 Permanganate Oxidation of Organic Substrates

1.5.1 Oxidation of Hydrocarbons

Very little is known about the permanganate oxidation of alkanes probably because of difficulties encountered as a result of their low solubility in aqueous media. Some researchers have avoided this problem by introducing inert solubilizing groups such as carboxyl.^{30,31} It was found that oxidations of such substrates as 4-methylhexanoic acid could be carried out in neutral or basic media. However the carboxyl group was shown to participate in the oxidations.^{30,31} These oxidations were believed to proceed via hydrogen atom abstraction to give a radical pair trapped in a solvent cage. The radicals quickly recombine to give an ester which can decompose in several ways, as outlined below.^{31,32}



The major pathway is thought to be through attack by water since ^{18}O studies show that labelled oxygen from permanganate is found present in the hydroxy group. The amount of ^{18}O incorporation was a minimum of 25%.³¹

Although there are no further reports on the permanganate oxidation of alkanes the chromic acid oxidation of alkanes has been well established.³³⁻³⁶ Some of the mechanistic features are:

(a) The rate law was found to be $r = k[\text{alkane}][\text{CrO}_3]h_o$.³⁵

(b) A kinetic isotope effect of $k_H/k_D = 2.5$ was found for the oxidation of 3-methylheptane.³⁶

(c) Hydrogen atom abstraction appears to occur in the rate determining step since the ratios of $1^\circ:2^\circ:3^\circ$ were 1:110:7000,³⁴ similar values to those found for free-radical bromination.

(d) The methylenes in n-alkanes appear to be equivalent since the rates increase only by a statistical factor for the series of C_4H_{10} , C_7H_{16} , C_9H_{20} , $C_{11}H_{24}$, $C_{16}H_{34}$, and $C_{22}H_{46}$.³⁵

(e) In cycloalkanes the transition state is thought to involve a tri-covalent carbon rather than a penta-covalent carbon since the logarithm of the oxidation rates parallel the logarithm of the solvolysis rates of corresponding tosylates.³³

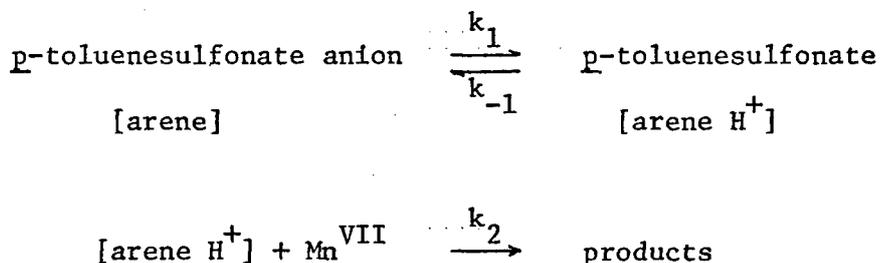
Although Rocek and Mares found that the methylenes in n-alkanes were identical in their reactivity to chromic acid,³⁵ other researchers have reported that in processes such as nitration the terminal methylenes react faster than the internal methylenes.^{37,38}

Alkanes appear to be oxidized via a radical mechanism, not only in the case of chromic acid oxidation but also in the photochemical reaction with oxygen.³⁹

1.5.2. Oxidation of Arenes

From a variety of reports on the use of permanganate to oxidize arenes⁴⁰⁻⁴³ only Cullis and Ladbury⁴⁴ and Lee and Singer⁴⁵ attempted to study the mechanism of this oxidation in acidic media. Cullis and Ladbury⁴⁴ were the first to attempt a thorough study of the oxidation of toluenes in a medium of 54.2% w/v acetic acid-water. Unfortunately second order kinetics were not maintained and initial rates had to be used. The complicated kinetics were thought to be due to the participation of intermediate oxidation states of manganese. They reported that some ring degradation occurred but that the major products, benzoic acid and benzaldehyde, resulted from side chain oxidation. Electron-donating substituents were observed to accelerate the rate and also to increase the degree of ring decomposition. Salt effects were only observed if salts were added that interacted with higher oxidation states of manganese.

Recently Lee and Singer⁴⁵ attempted to clarify the mechanism of arene oxidation. They used *p*-toluenesulfonic acid to avoid the solubility problems and perchloric acid to avoid the kinetic problems thought to be caused by the acetic acid. Although the kinetics were no longer complicated the sulfonate group caused important mechanistic changes. They found that the order with respect to permanganate changed from first-order to zero-order at higher acidities. The mechanism proposed is the following.



Using the steady state approximation on $[\text{arene H}^+]$ the following rate law results.

$$r = \frac{k_1 k_2 [\text{arene}] [\text{Mn}^{\text{VII}}]}{k_{-1} + k_2 [\text{Mn}^{\text{VII}}]}$$

It was stated that the observed order shift could be explained as follows.

$$\text{If, } k_{-1} \gg k_2 [\text{Mn}^{\text{VII}}], \quad r = k k_2 [\text{arene}] [\text{Mn}^{\text{VII}}]$$

$$\text{If, } k_{-1} \ll k_2 [\text{Mn}^{\text{VII}}], \quad r = k_1 [\text{arene}]$$

At higher acidities the protonation of the *p*-toluenesulfonate ion became the rate-determining step.

In general the oxidation of arenes seems to have a rate law of the form, $r = k[\text{arene}][\text{MnO}_4^-]$ in the acidic region but the exact mechanism is not completely clear.

The alkaline permanganate oxidation of benzylic tertiary carbon-hydrogen bonds to alcohols is quite well established.^{40,42,43} The process is known to have a rate law of $r = k[\text{arene}][\text{MnO}_4^-]$ in the dilute alkaline region ($[\text{OH}^-] < 0.01$) but has the form of $r = k[\text{arene}][\text{MnO}_4^-][\text{OH}^-]$ in more concentrated alkali.⁴² There is still some dispute as to how the hydrogen is abstracted in the rate-determining step. Heckner et al.⁴² have interpreted their data and their observed isotope effect of $k_{\text{H}}/k_{\text{D}} = 7.8$ to indicate hydride abstraction but Brauman and Pandell,⁴³ who observed an isotope effect of $k_{\text{H}}/k_{\text{D}} = 11.5$ and some retention of configuration, interpret their data in terms of hydrogen atom abstraction.

1.5.3. Oxidation of Alcohols

Since this investigation is primarily concerned with the permanganate oxidation of arenes and alkanes all subsequent compounds considered will only have the pertinent features of their oxidation mechanisms outlined.

Alcohols have been subjected to extensive mechanistic investigation in acid, neutral, and basic media. Some of the features of the oxidation mechanism are outlined below.

(a) Basic media

(i) In basic media the catalysis observed is due to the generation

of an alkoxide ion from the alcohol.^{46,47} The rate law has the form $r = k[\text{alcohol}][\text{MnO}_4^-][\text{OH}^-]$.

(ii) The observed salt effects are consistent with a bimolecular transition state resulting from the alkoxide ion and permanganate ion.⁴⁷

(iii) Carbon-hydrogen bond cleavage is involved in the rate-determining step since substantial deuterium isotope effects are observed. These can become exceptionally large in fluorinated alcohols, e.g. $k_H/k_D = 16$ for the oxidation of 1-phenyl-2,2,2-trifluoroethanol.⁴⁶

(b) Acidic media

(i) In acidic medium the rate accelerations observed with increased acidity are believed to be due to the generation of permanganic acid.⁴⁸⁻⁵⁰

(ii) The rate-determining step involves carbon-hydrogen bond scission. Isotope effects of $k_H/k_D = 2.4-3.2$ are observed for the oxidation of cyclohexanols.⁵⁰ In the case of 2-carboxycyclohexanols effects of $k_H/k_D = 7-8$ were reported.⁵¹

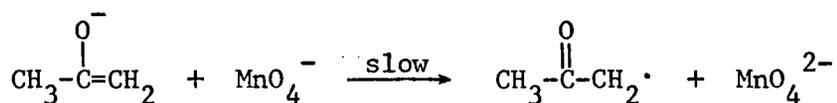
(iii) There was no evidence found for the participation of intermediate oxidation states of manganese in the rate-determining step for the oxidation of benzyl alcohol to benzaldehyde in perchloric acid-water mixtures.⁵²

(iv) In most cases the rate law follows H_o .^{48-50,52} Tri(p-tolyl)-carbinol was exceptional in that it followed H_R .⁴⁸ Similar dependence upon H_R was found for the chromic acid oxidation of triphenyl carbinol.⁵³

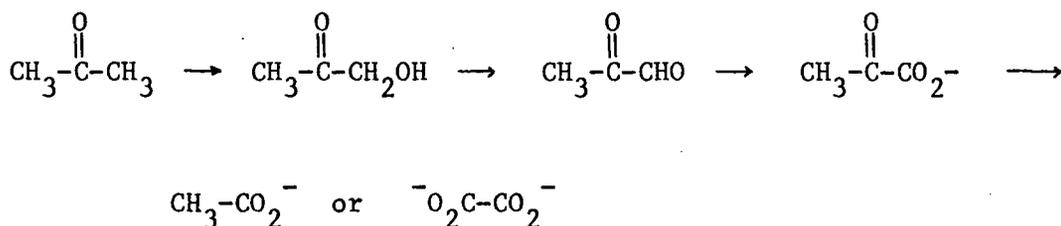
(v) Stewart and Banoo⁴⁸ found that the permanganate oxidation of di- and tri-phenyl carbinols involved the ionization of the carbinol to the carbonium ion which then formed a permanganate ester. This ester then decomposed to products possibly via a cyclic process similar to that accepted for chromic acid oxidations of alcohols.^{54,55}

1.5.4. Oxidation of Ketones and Aldehydes

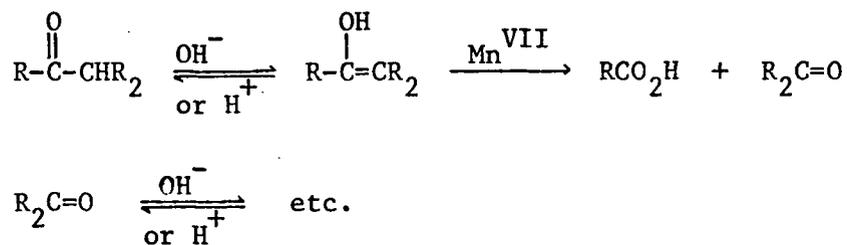
Ketones are subject to facile oxidation only in their enol form. As such they are rapidly oxidized in alkaline and acidic media.⁵⁶ Under most conditions permanganate oxidizes double bonds by cis addition to yield cis diols,^{57,58} but when the medium is glacial acetic acid the major products are α -diketones (yields up to 80%).⁵⁹ Enolic double bonds are not always degraded by cis addition since Wiberg and Geer⁶⁰ have presented evidence to show that the enolate ion generated from acetone reacts by electron transfer in the following manner.



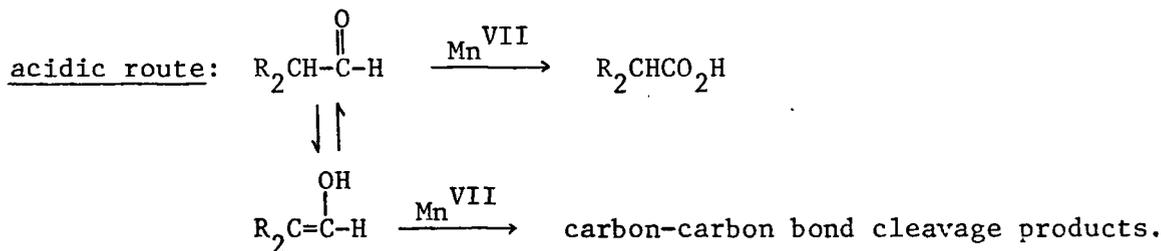
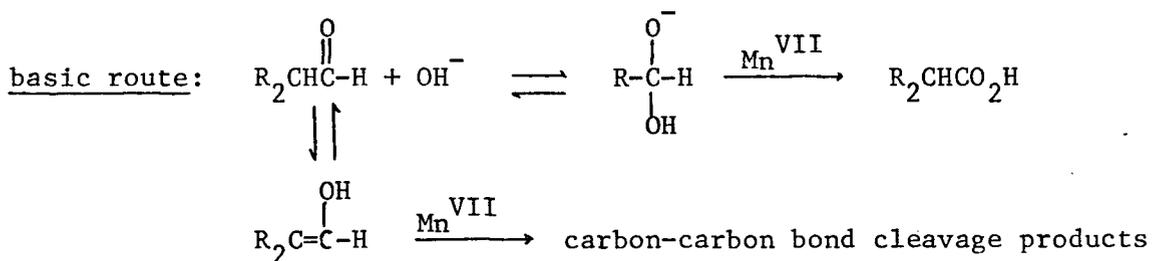
The oxidation pathway for acetone can be shown as α attack, with subsequent carbon-carbon bond cleavage,⁶⁰



or in a more general form for all enolizable ketones as;



Aldehydes are readily oxidized in any medium, yielding chiefly the respective acid although some carbon-carbon bond cleavage may also occur, presumably via the enol.⁵⁶ In basic media the reaction is believed to go via the aldehyde hydrate anion.^{61,62} Wiberg and Geer have shown that only such an intermediate can explain the incorporation of ¹⁸O from the medium in the oxidation of furfurals.⁶² In basic and acidic media the oxidative schemes have been found to be the following;



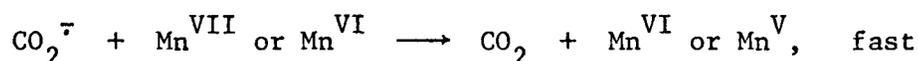
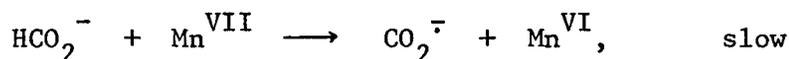
1.5.5 Oxidation of Formic Acid

The permanganate oxidation of formic acid to carbon dioxide has been thoroughly studied and the mechanism in both acidic and basic

solutions is well established.^{63,64} In aqueous solution more basic than pH 5 the reaction clearly involves the formate ion and the permanganate ion.⁶⁵⁻⁶⁷ Carbon-hydrogen bond cleavage is taking place in the transition state since isotope effects near 7 were observed.⁶⁴⁻⁶⁷ A substantial solvent isotope effect of $k_{D_2O}/k_{H_2O} = 2.7$ (pH not specified) was reported by Taylor and Halpern,⁶⁶ in contrast to the value of $k_{D_2O}/k_{H_2O} = 0.92$ (again pH not specified) observed by Bell and Onwood.⁶⁴ There is some oxygen transfer from the permanganate to the formic acid during the oxidation, since ^{18}O from permanganate was found in the product, carbon dioxide.⁶⁵

As the medium becomes more acidic the rate decreases due to the decrease in the concentration of formate ion⁶³ but when the acidity is increased beyond 20% sulfuric acid the rate increases, which is believed to be due to formation of permanganic acid.⁶⁸ Further rate increases are observed at acidities beyond 50% sulfuric acid and these are believed to be due to formation of permanganyl ion (MnO_3^+).

The oxidation is visualized as successive one-electron transfers according to the following scheme.^{63,64}



1.6 Permanganate Oxidations in Organic Solvents

Recently two methods have been described which extend the use of permanganate as an oxidant into organic solvents. Sam and Simmons⁶⁹

were able to prepare crown polyether complexes of permanganate which are soluble in organic solvents. These complexes can be used in situ or can be isolated and then used in some other solvent to achieve a wide variety of oxidations. Starks⁷⁰ was able to use the method of phase-transfer catalysis to readily oxidize 1-octene to heptanoic acid (author states hexanoic acid, possibly a printing error). This process involves the use of quaternary alkyl ammonium salts to extract the permanganate anion into the benzene layer. In this investigation Starks' method⁷⁰ will be extended by examining the oxidation of alcohols, aldehydes, and stilbenes by permanganate in benzene.

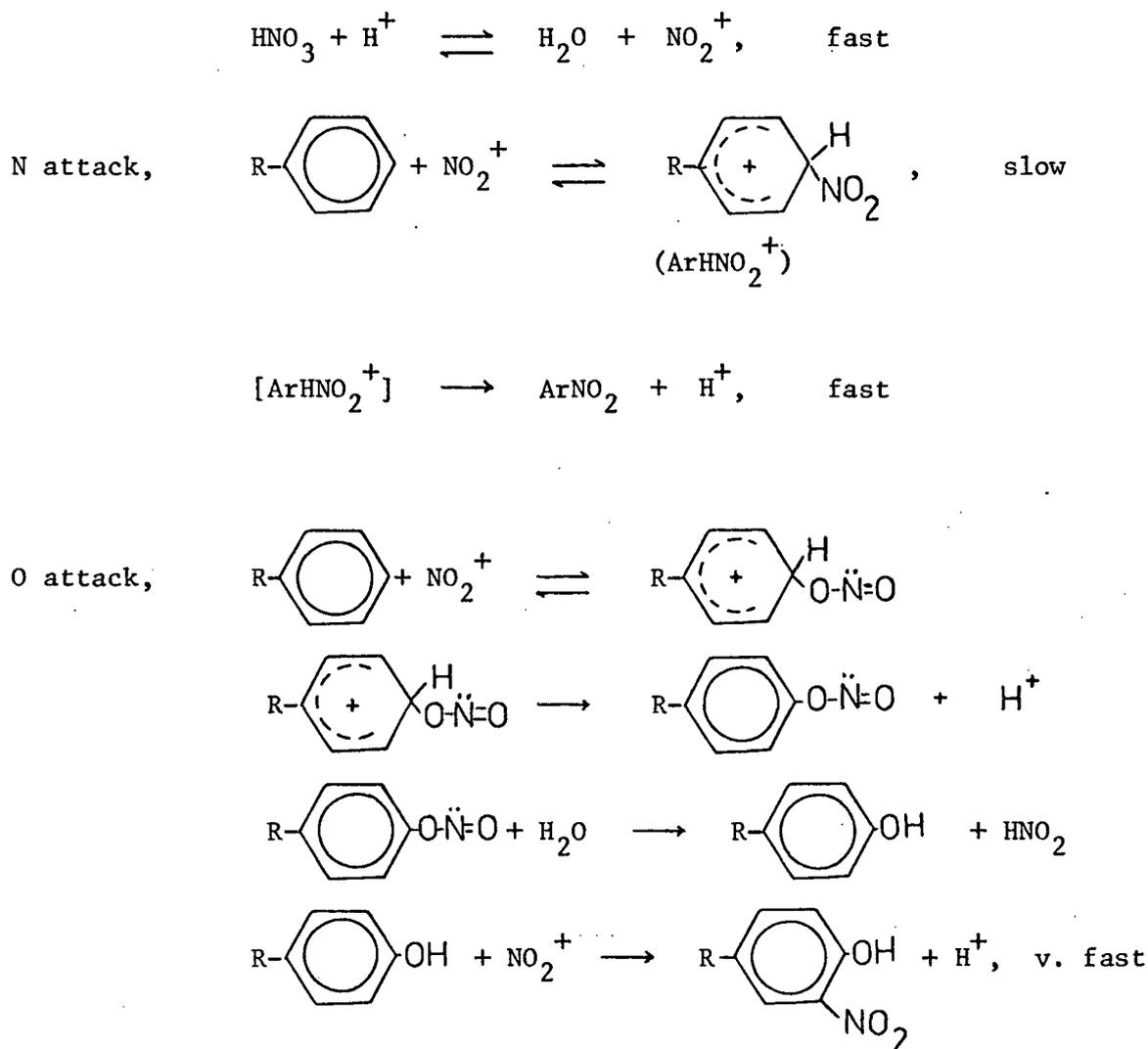
1.7 Electrophilic Aromatic Nitration

One of the oxidants that might be generated in acidic media is permanganyl ion (MnO_3^+). This species could attack the aromatic rings of arenes in a manner similar to that of the electrophile, nitronium ion (NO_2^+). Because of this possibility some of the features of electrophilic aromatic nitrations will be presented.

Electrophilic aromatic nitrations are known to follow the H_R function,^{72,73,21} more precisely $H_R + \log a_{\text{H}_2\text{O}}$,⁷³ carbon-hydrogen bond cleavage does not occur in the rate-determining step since only very small (secondary) isotope effects are observed.⁷⁴⁻⁷⁶ The nitration rates show some solvent dependence.⁷⁷ The rate-determining process is generally agreed to be electrophilic attack,⁷⁴⁻⁷⁸ which is followed by fast proton-loss to the solvent.⁷⁸

Small amounts of phenolic products have been isolated from the

nitration products of toluene.⁷⁹ The mechanism of the process yielding phenols is at present unknown. It could be possible that the complex resulting from O attack by nitronium ion can be hydrolyzed to yield phenols. The following scheme accounts for the known facts and proposes a route to the observed phenols.

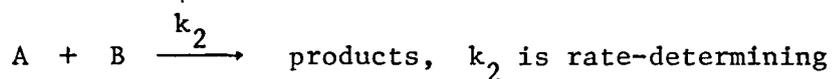


1.8 Applications of the Zucker-Hammett Hypothesis

An empirical test was proposed by Hammett and Zucker by which one could determine whether an acid-catalyzed reaction proceeds via an A-1

or A-2 mechanism.^{80a} They proposed that if $\log k_1$ vs $-H_o$ gives linear plots with close to unit slope that an A-1 mechanism is indicated but if $\log k_1$ vs $\log [H^+]$ gives linear plots with close to unit slope that an A-2 mechanism is operative. Although some known A-1 and A-2 reactions were found to be consistent with this criteria exceptions were reported^{80b} thus limiting the utility of the hypothesis.

One feature of their hypothesis remains potentially very useful. This is the conclusion that when $\log k_1$ vs $-H_o$ gives linear plots with unit slope the ratio of the activity terms in the rate expression changes in the same way as does the ratio of the activity terms of the indicators used to establish the acidity scale, (k_1 is the experimentally determined rate constant, corrected only for substrate concentration). This postulate can be generalized in the following manner: For a general case of a bimolecular reaction



the measured rate law is $r = k_1 [B][A]$

where

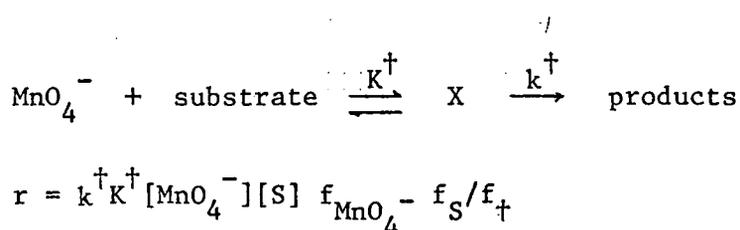
$$k_1 = k_2 f_A f_B / f_+$$

If $\log k_1$ vs $-H_x$ gives a linear plot this means that $h_x = f_A f_B / f_+$ and if h_x is defined as $h_x = a_{H^+} f_{B_x} / f_{B_x} H^+$ then $f_A f_B / f_+ = a_{H^+} f_{B_x} / f_{B_x} H^+$. This reasoning in itself does not clarify any mechanistic features but if some of the activity coefficients are known practical use can be

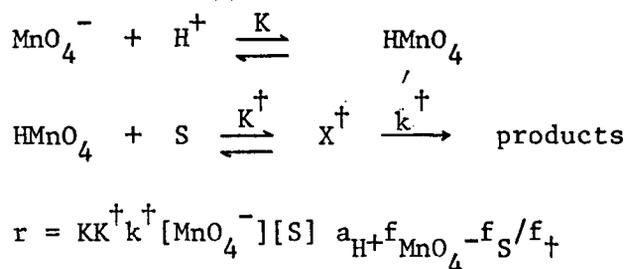
made of this relationship. This relationship can be used to evaluate a proposed mechanism by seeing if the activity terms predicted do in fact show parallel solvent changes to those of the indicators used in setting up the acidity scale.

In this investigation three different oxidants could be generated, which leads to at least three different mechanisms. The choice made between the three mechanisms listed below was based on how $\log k_1$ correlated with either H_0 or H_R . The three mechanisms are:

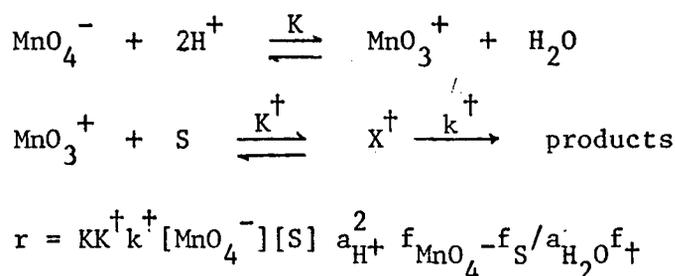
(a) Permanganate ion as oxidant.



(b) Permanganic acid as oxidant.



(c) Permanganyl ion as oxidant



2. SCOPE OF THE INVESTIGATION

The purpose of this investigation is to determine the mechanism of the oxidation of alkanes and arenes by permanganate. The medium used to achieve the necessary solubilities was trifluoroacetic acid-water. A pseudo first-order approach was used to determine the order of the oxidant. Concentration variations of substrate and acidity established their respective orders. Complementary techniques such as product studies, substituent effects, activation parameters and isotope effects completed the mechanistic investigation. The oxidation mechanism of several alcohols, aldehydes, and ketones was also investigated to aid in interpreting the results obtained with alkanes and arenes.

As a result of the poor fit of the kinetic data with the previously determined H_O function the H_R function was determined for the medium of TFA-water. The identity of the oxidants in this acidic medium was established by spectrophotometric and cryoscopic means.

Since the arene oxidation showed similarities to electrophilic aromatic substitution reactions the behavior of several electrophiles such as nitronium and nitrosonium ions was examined in the TFA-water medium.

3. EXPERIMENTAL

3.1 Reagents and Indicators

Most of the compounds used for this investigation were available commercially. The reagents, their source, method of purification and purity are presented in Table 1. The indicators used to establish the H_R acidity function along with pertinent physical data are presented in Table 2.

The trifluoroacetic acid (TFA) used throughout this investigation required special care in purification to minimize the decomposition of the oxidant, which was found to be due to minute impurities present in the acid. This procedure, and the synthetic routes followed for the preparation of the remaining compounds, are outlined below.

Trifluoroacetic acid: The commercial product supplied by Eastman could not be sufficiently purified by distillation through a 12" Vigreux column. It was found that if the acid was distilled from small amounts of potassium permanganate, approximately 0.5 g per kg of acid, that the fraction collected between 71.0-71.5° had no significant permanganate decomposition for aqueous solutions less than 5 M and gave only small blank corrections, ranging from 1-10% of the observed rate, for solutions 5-12 M. This method of using small amounts of potassium

Table 1. Specifications of Compounds.

Compound	Source	Purification method	Purity ^a	Literature
n-Pentane	E	v.p.c. column 1	>99.8%	
iso-Pentane	E	used as received	>99.8%	
n-Hexane	M	spectral grade	>99.8%	
n-Heptane	E	dist. 97.5-98.0°	>99.8%	
n-Octane	A	used as received	99.5%	
n-Nonane	F	dist. 149.5-150.0°	99.5%	
n-Decane	A	used as received	99.6%	
n-Undecane	A	v.p.c. column 1	99.7%	
n-Dodecane	E	dist. 215-216°	>99.8%	
n-Tridecane	A	used as received	>99.5%	
Cyclopentane	A	spectral grade U.A.R.	>99.8%	
Cyclohexane	E	spectral grade U.A.R.	>99.8%	
Cycloheptane	A	U.A.R.	>99.7%	
Cyclooctane	A	U.A.R.	>99.7%	
Methanol	B	spectral grade U.A.R.	>99.9%	
Ethanol	F	distilled	>99.8%	
2-Pentanol	A	v.p.c. column 1	>99.8%	
3-Pentanol	A	" " "	>99.8%	
Formaldehyde	F	37.4% standard soln.	-	
2-Pentanone	E	v.p.c. column 1	>99.8%	
3-Pentanone	E	" " "	>99.8%	
Cyclohexanol	E	dist. 158.0-158.5°	99.5%	
Cyclohexanone	E	dist. 151.0-151.5°	99.8%	
Acetone	E	spectral grade U.A.R.	>99.8%	
Formic acid	E	dist. 101.0-101.5°	>99.8%	
Propionic acid	F	U.A.R.	>99.8%	
2,4-Pentanedione	E	dist. 137.0-138.0°	99.5%	
Propionitrile	E	v.p.c. column 1	>99.8%	
Nitroethane	M	" " "	>99.8%	
1,1,1-Trichloroethane	F	" " "	>99.8%	

Table 1 (Continued)

Compound	Source	Purification method	Purity	Literature
Toluene	E	dist. 109.0-109.5°	>99.8%	
Ethylbenzene	E	v.p.c. column 1	>99.8%	
Cumene	E	" " "	>99.8%	
t-Butylbenzene	E	" " "	>99.8%	
Benzyl alcohol	E	dist. 203.0-204.0°	>99.8%	--
Benzaldehyde	E	dist. 173.5-174.0°	>99.8%	--
Acetophenone	E	v.p.c. column 1	>99.8%	--
Trifluoroaceto- phenone	K & K	" " "	99.5%	--
Benzene	F	spectral grade U.A.R.	>99.8%	--
Chlorobenzene	E	dist. 129.0-130.0°	>99.8%	132° ^{81a}
Fluorobenzene	E	dist. 82.5-83.0°	>99.8%	85.2° ^{81b}
Nitrobenzene	E	dist. 207.0-208.0°	>99.8%	210.85° ^{81c}
Anisole	E	dist. 150.0-150.5°	>99.8%	155° ^{81d}
2-Phenyl-2-propanol	A	U.A.R.	99.5%	--
2-Phenylethanol	A	U.A.R.	99.0%	--
1-Phenylethanol	A	U.A.R.	99.5%	--
p-Bromotoluene	E	recrystallized	>99.8%	--
m-Bromotoluene	F	dist. 180.0-180.5°	>99.8%	184° ^{81e}
m-Chlorotoluene	K & K	dist. 158.0-158.5°	>99.8%	162° ^{81f}
KMnO ₄	B	Baker analyzed	99.5%	--
Ethane	M	U.A.R.	99.99%	--
Propane	M	U.A.R.	99.5%	--
Butane	M	U.A.R.	99.5%	--
neo-Pentane	FLUKA	U.A.R.	99.92%	--
Cyclohexane-d ₁₂	MSD	U.A.R.	99% D	--
Methanol-d ₄	MSD	U.A.R.	99% D	--
Deuterium oxide	MSD	U.A.R.	99.8% D	--
Toluene-α-d ₃	MSD	U.A.R.	98% D	--
Toluene-d ₈	MSD	U.A.R.	98% D	--
H ₂ SO ₄	B	U.A.R.	97.4%	--

Table 1 (Continued)

Compound	Source	Purification Method	Purity	Literature
Benzoic acid	E	sublimed	mp 122.0-123.0°	122° ^{81g}
p-Nitrotoluene	E	recrystallized	mp 50.0-51.0°	52° ^{81h}
m-Nitrotoluene	E	dist. 230.0-231.0°	--	227° ^{81h}
p-Methylbenzoic acid	E	recrystallized	mp 178-180°	181° ⁸¹ⁱ
m-Methylbenzoic acid	E	"	mp 11.0-112.0°	111-113° ⁸¹ⁱ
Tetra-n-hexyl- ammonium iodide	E	U.A.R.	--	--
m-Nitrobenzyl alcohol	E	dist. 210.0-212.0° 10 mm	--	175-180° at 3 mm ^{81j}
m-Methoxybenzyl alcohol	A	dist. 254.0-256.0°	--	252° ^{81k}
p-Chlorobenz- aldehyde	E	recrystallized	mp 47.0-48.0°	47° ⁹¹
m-Methylbenz- aldehyde	K & K	dist. 201.0-202.0°	--	201° ^{81m}
p-Nitrobenz- aldehyde	K & K	recrystallized	mp 104.0-105.0°	106° ⁸¹ⁿ
Benzophenone	E	"	mp 48.0-49.0°	49° ^{81o}
cis-Stilbene	K & K	U.A.R.	fp 4-5°	5-6° ^{81p}
trans-Stilbene	F	U.A.R.	mp 121.0-123.0°	124° ^{81p}
Tolan	A	recrystallized	mp 60.0-62.0°	62.5° ^{81q}
p-Nitro-trans- stilbene	A	"	mp 155.0-158.0°	155° ^{81r}
p,p'-Dinitro-trans- stilbene	A	"	mp 296-299°	288° ^{81a}
p,m'-Dinitro-trans- stilbene	A	"	mp 220-221°	217° ^{81s}
Sodium nitrate	B	U.A.R.	analar grade	--
Sodium nitrite	F	U.A.R.	96.6%	--

Table 1 (Continued)

^a All compounds except the last 31 were checked by v.p.c. using column 1.

Column 1 - 20% Carbowax 20 M on firebrick - 20' x 3/8"

Column 2 - 20% Dionylphthalate on Chromosorb - 20' x 3/8"

U.A.R. - used as received
E - Eastman Chemical Co.
F - Fisher Scientific Co.
K & K - K & K Laboratories Ltd.
A - Aldrich
MSD - Merck, Sharp and Dohme
B - J.T. Baker Co.
M - Matheson of Canada Ltd.

Table 2. H_R Function Indicators for TFA- H_2O

No.	Compound ^c	Experimental			Literature ^a			Source
		mp	λ_{max}^b	$\log \epsilon^b$	mp	λ_{max}^b	$\log \epsilon^b$	
1	4,4',4''-Trimethoxy TPC	81.0-82.0°	480	5.04	81.0-82.0° ²¹	485 ²¹ 478 ⁸²	5.02 ²¹ 4.94 ⁸²	synthesized
2	4,4'-Dimethoxy-4''-methyl TPC	74.0-76.0°	487 427	4.93 4.67	-	-	-	synthesized
3	4,4'-Dimethoxy TPMCL	111.0-113.0°	495 410	4.88 4.56	-	500 ²¹	5.47 ²¹	Aldrich
4	4,4',4''-Trimethyl-TPC	91.0-92.5°	446	4.97	94.0° ⁸³	452 ²¹	5.03 ²¹	lab stock
5	4-Methoxy TPC	72.0-74.0°	469 394	4.82 4.38	60.0° ^{82,84} 82.0° ⁸⁵	476 ²¹	4.75 ²¹	lab stock
6	4,4'-Dimethyl TPC	78.0-78.5°	451	4.81	75.0° ⁸⁶ 75.5-76.5° ⁸⁷ 80.0° ⁸⁸	456 ⁸⁷	-4.44 ⁸⁷	lab stock
7	4,4'-Diethoxy DPC	56.0-57.0°	506	5.22	-	505 ⁸⁷	5.10 ⁸⁹	lab stock
8	Triphenylcarbinol	163.0-164.0°	425 403	4.60 4.60	164-165° ^{81t}	431 ²¹ , 425 ⁸² 404 ²¹ , 410 ⁸²	4.60 ²¹ , 4.64 ⁸² 4.60 ²¹ , 4.63 ⁸²	lab stock
9	4,4',4''-Trichloro TPC	91.0-93.0°	460	502	93.5-94.0° ⁹⁰	465 ²¹	5.01 ²¹	lab stock
10	4-Nitro TPC	96.5-98.0°	436 388	4.51 4.47	95.5-97.0° ⁹¹	454 ²¹	-	lab stock

Table 2. (Continued)

- a References 21, 87, 89 used a medium of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$.
Reference 82 used a medium of $\text{CF}_3\text{CO}_2\text{H-(CF}_3\text{CO)}_2\text{O}$.
- b Values for the respective carbonium ion generated
- c All compounds were checked by NMR for substituent identity.

TPC = triphenylcarbinol

TPMCL = triphenylmethyl chloride

DPC = diphenylcarbinol

permanganate avoided a problem also noted by Lee and Johnson.¹⁰ It was observed that a green species contaminated all of the distillate when large quantities of potassium permanganate were used.

Water: The water used for the determination of the pK of permanganic acid and the H_R function was redistilled from basic permanganate through a 14" Vigreux column. For the kinetic analysis distilled water was found to be satisfactory, causing no further permanganate decomposition.

Benzyl alcohol- α - d_2 : This compound was prepared by the lithium aluminum deuteride reduction of benzoic acid according to the following procedure. A 100 ml solution of dry ether containing 0.01 moles of benzoic acid was carefully added over a period of one hour to 0.008 moles of lithium aluminum deuteride suspended in 100 ml dry ether. The resulting mixture was allowed to reflux for a period of 14 hours. The solution was then quenched by the careful addition of 5 ml 95% ethanol followed by 10 ml water. The complex was destroyed by the addition of 50 ml 10% sulfuric acid. The ether layer was recovered, washed once with 50 ml 1 N sodium hydroxide, twice with 50 ml water and then dried over anhydrous magnesium sulfate. The ether layer was recovered and flash evaporated. The residue was purified by v.p.c. using a 20% carbowax 20 M on firebrick column 20' x 3/8". The yield was 20% of the desired alcohol with an isotopic purity of 95% as determined by NMR. The initial deuterium content of the lithium aluminum deuteride was 96.8%.

4,4',4''-Trimethoxytriphenylcarbinol: The method outlined by Baeyer and Villiger⁹² was used with minor modifications from Vogel.⁹³ To a Grignard solution prepared from 0.10 moles of magnesium turnings and 0.10 moles of 4-bromoanisole in 300 ml dry ether was added 0.10 moles of 4,4'-dimethoxybenzophenone dissolved in 100 ml dry ether at a rate to keep the ether refluxing. The mixture was refluxed a further two hours and then poured over a slurry of 750 g ice and 25 ml concentrated sulfuric acid. Twenty-five grams of ammonium chloride was then added to further decompose the magnesium complex. The ether layer was recovered, washed successively with 100 ml water, 100 ml 2% sodium bicarbonate, and 100 ml water. The ether was removed by flash evaporation yielding a viscous red oil. This oil was steam distilled and then dissolved in hot n-heptane. Recovery of the desired product was extremely difficult and the following somewhat primitive method was found successful. The hot solution of n-heptane was slowly cooled, whereupon a red substance oiled out. Upon standing for a day crystals were observed growing from the red oil. Several seed crystals were chosen to impregnate a string, the solution was reheated to dissolve all substances, and then the seeded string was suspended in the solution which was allowed to cool slowly. Considerable crystal growth occurred on the string and beaker walls. These pale orange crystals were further readily recrystallized from n-heptane yielding 30% of the white product mp 81.0-82.0°, literature mp 81.0-82.0°. ²¹

4,4'-Dimethoxy-4''-methyltriphenylcarbinol: This compound was prepared in a similar manner to that described for 4,4',4''-trimethoxytriphenylcarbinol with the exception that 4-bromotoluene was used to prepare the Grignard reagent. Similar purification problems were also encountered. The final white crystalline product, obtained in 10% yield, had mp = 74.0-76.0°.

Elemental analysis: theoretical, C - 79.02%, H - 6.63%.

experimental, C - 78.96%, H - 6.51%.

3.2 Kinetic Procedure in Acid-Water Medium

In all of the kinetic experiments except numbers 180-184, 219-223, 240-249, 252-266 and 275-284, a pseudo first-order approach was used, the initial substrate concentration being in a 20-fold excess or more. All of the rate constants were obtained by observing the disappearance of the 526 nm permanganate absorbance. These spectrophotometric measurements were made using a Bausch and Lomb 505 spectrophotometer except for some very slow reactions in which a Cary 16 was used. Both machines were equipped with thermostated cell compartments. All kinetic experiments except where noted were performed at $25.0 \pm 0.2^\circ$.

A typical kinetic run was initiated by placing nine parts (2.70 ml) of substrate stock solution into a cuvette, adding one part (0.30 ml) of potassium permanganate stock solution, stoppering, mixing thoroughly and then placing the cuvette into the cell compartment and observing the 526 nm absorbance with respect to time. The permanganate stock solution had previously been thermostated at 25.0° and was composed of a precisely weighed amount of potassium permanganate in 100 ml of

water to give a concentration close to 4.0×10^{-3} M. The kinetic concentration was then 4.0×10^{-4} M which gave an initial absorbance of 0.9. The substrate stock solution was also thermostated prior to use at such a temperature that the mixture reached a temperature of 25° upon mixing. Usually the heat of mixing was no more than 2° . After the kinetic run the 3.00 ml sample was titrated with 2.00 N sodium hydroxide to obtain the acid molarity.

Because a wide variety of compounds were examined several methods had to be used for the preparation of substrate stock solutions. The TFA-water solutions of the desired acid strength were prepared by making up to volume a measured quantity of water with TFA. Stock solutions of substrates which were neither excessively volatile nor underwent reaction with the solvent (such as alcohols which esterified) were simply prepared by adding a known weight or volume of substrate to a known volume (usually 10.0 ml) of TFA-water solution and mixing thoroughly. Stock solutions of alcohols were sometimes prepared in this manner but had to be used within one minute because of esterification. Some of the kinetic experiments involving larger quantities of alcohol were initiated by adding several $\mu\ell$ of alcohol to a 9:1 mixture of acid-water and permanganate-water solutions.

Stock solutions of the gaseous compounds investigated, namely neopentane, n-butane, propane and ethane, were prepared in the following ways. Neopentane at 0° was syringed into a 25 ml volumetric containing a known quantity of TFA-water solution. The solution was shaken vigorously, opened to the atmosphere and then reweighed. The increase in weight was taken as the amount of neopentane per known

volume of TFA-water solution. Stock solutions of the other three gases were prepared by subjecting 10.0 ml of TFA-water solution in a 25 ml volumetric flask containing a small magnetic stirring bar to 2 lbs pressure of the desired gas by means of a rubber tube connecting the gage and the flask. The tubing, but not the flask had been flushed with the desired gas to exclude air. The solution was then stirred at a moderate rate by means of the magnetic stirrer for a time not exceeding two minutes. The stirring time depended upon the amount of dissolved gas desired. The connecting hose was removed and the volumetric flask was restoppered and reweighed. The weight gain was taken as the amount of gas uptake. These solutions were usable up to one hour after preparation after which time gas losses became serious. The rate constants obtained from these experiments were of fair reproducibility, ranging from the poorest, $\pm 10\%$ per duplicate and $\pm 20\%$ for k_2 ($k_2 = k_{\text{observed}} / [\text{substrate}]$) over a 2.5-fold concentration range for ethane, to the best, n-butane, which gave $\pm 10\%$ for duplicates and $\pm 11\%$ for k_2 over a twenty-fold concentration range. It was concluded that these results were not biased by air displacement to an extent beyond their reproducibility.

Some experiments were performed using a medium of sulfuric acid-water. These experiments were carried out in the same manner as described for those in which a medium of TFA-water was used. Unfortunately the results were unsatisfactory, as will be demonstrated in Section 4.3.

3.3 Kinetic Analysis

The time-absorbance data were analyzed by the method of least squares by arranging the data in a linear form of $y = mx + b$. The least squares analysis was performed by a set of programs previously developed by the author.⁹⁴

The basic kinetic equations used were derived from the general rate equation (1) in the following manner.

$$[O_x] = [MnO_4^-]$$

k = Boltzmann's constant

$$[S] = [\text{substrate}]$$

h = Planck's constant

h = applicable acidity function

c = constant of integration

T = temperature °K

$n, m,$ and l are powers

$$(1) \quad -d[O_x]/dt = k_3 [O_x]^n [S]^m h^l$$

In the pseudo-order approach h , S and T are kept constant which reduces equation 1 to equation 2.

$$(2) \quad -d[O_x]/dt = k_1 [O_x]^n$$

where $k_1 = k_3 [S]^m h^l$

Only two values of n were encountered in this study, namely $n = 1$, a pseudo first-order case, and $n = 0$, a zero-order case. These are solved below.

when n = 0:

$$-d[O_x]/dt = k_o$$

$$(3) \quad -d[O_x] = k_o dt$$

Integration of equation 3 yields equation 4.

$$(4) \quad [O_x] = k_o t + c$$

When $[O_x]$ is plotted against time the slope is the desired rate constant, k_o .

when n = 1:

$$-d[O_x]/dt = k_1[O_x]$$

$$(5) \quad -d[O_x]/[O_x] = k_1 dt$$

Integration of equation 5 yields equation 6.

$$(6) \quad -\ln[O_x] = k_1 t + c$$

When $-\ln[O_x]$ is plotted against time the slope gives the desired rate constant k_1 .

In practise the actual analysis is performed by using absorbance values in equations 4 and 6 since by Beer's law $[O_x] \cdot \epsilon = \text{Absorbance}$ ($\epsilon = \text{molar extinction coefficient}$). In the case where $n = 0$ the

slope is then equal to $\epsilon \cdot k_0$ but in the case where $n = 1$ the slope is still k_1 since $\ln[O_x] = \ln \text{Abs.} - \ln \epsilon$ and $\ln \epsilon$ is a constant which then only affects the intercept.

Once k_1 or k_0 had been determined for a set of different conditions the influence of the other parameters could be evaluated as follows. For a set of k_1 values (a parallel situation exists for k_0) where only $[S]$ varies,

$$k_1 = k_3[S]^m h^1 = k_2[S]^m, \quad k_2 = k_3 h^1$$

and it follows that $\log k_1 = m \log[S] + \log k_2$. When $\log k_1$ is plotted against $\log [S]$ the slope is the order of the substrate. By varying the acidity one can in an analogous manner, establish which acidity function best fits the experimental data.

$$k_2 = k_3 h^1 = k_1/[S]^m$$

$$\log k_2 = 1 \log h + \log k_3$$

or in the more familiar form

$$-\log k_2 = 1 H_x + c$$

where the slope of the $-\log k_2$ vs H_x plot gives the order of the reaction with respect to h_x .

The activation parameters were obtained in the usual manner by

converting the Wynne-Jones Eyring equation⁹⁵ into a linear form.

$$k_2 = \left(\frac{k}{h}\right) \cdot e^{-\Delta G^\ddagger/RT}$$

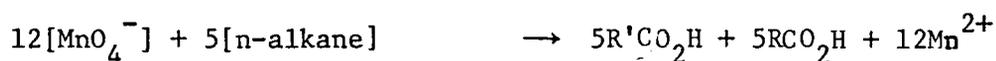
$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

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

$$\ln(k_2/T) = -(\Delta H^\ddagger/RT) + \Delta S^\ddagger/R + \ln(k/h)$$

When $\ln(k_2/T)$ was plotted against $1/T$ the slope gave $-\Delta H^\ddagger/R$ and the intercept was equal to $\Delta S^\ddagger/R - \ln(k/h)$, from which ΔS^\ddagger and ΔH^\ddagger were easily obtained.

The previously mentioned 45 trials which were not analyzed by a pseudo first-order approach were analyzed by equation 8 which is derived below. This equation is valid for all similar kinetics where the substrate is not in sufficient excess. All that is required is the stoichiometry of the reaction.



the stoichiometry for this example is $12/5 = 2.4$.

The subscripts t and o denote time = t and time = 0, respectively

$$-d[\text{O}_x]/dt = k_2[\text{O}_x]_t[\text{S}]_t$$

$$[S]_t = [S]_o - \frac{1}{2.4} ([O_x]_o - [O_x]_t)$$

$$\frac{-d[O_x]_t}{dt} = k_2 [O_x]_t ([S]_o - \frac{1}{2.4} [O_x]_o + \frac{1}{2.4} [O_x]_t)$$

$$(7) \quad \frac{-d[O_x]_t}{[O_x]_t ([S]_o - \frac{1}{2.4} [O_x]_o + \frac{1}{2.4} [O_x]_t)} = k_2 dt$$

Equation 7 can be readily integrated since it is of type $\int \frac{dx}{x(a+bx)} = -\frac{1}{a} \ln \frac{a+bx}{x}$ ⁹⁶ to give equation 8.

$$(8) \quad \frac{1}{([S]_o - \frac{1}{2.4} [O_x]_o)} \ln \left(\frac{[S]_o}{[O_x]_t} - \frac{1}{2.4} \frac{[O_x]_o}{[O_x]_t} + \frac{1}{2.4} \right) = k_2 t + c$$

In actual practice absorbance was used instead of $[O_x]_t$. This conversion was readily made by Beer's law, $[O_x]_t = A/\epsilon$.

3.4 Inorganic Product Study

The inorganic products were determined by iodometric titration. A 4×10^{-3} M solution of permanganate was made up in a TFA-water medium in which the substrate had a fast oxidation rate. Then to 10.0 ml of this solution was added enough neat substrate to ensure at least a ten-fold excess. The solution was thoroughly mixed by means of a magnetic stirrer until no further reaction was observed but in no case were any reactions allowed to go past two hours. After this time no permanganate ion could be detected but in most cases manganese dioxide

precipitate could be observed. The total solution was titrated for remaining manganese oxidizing power (essentially the amount of manganese dioxide present) by adding 10 ml of 4×10^{-2} M potassium iodide in aqueous 2% sodium bicarbonate and then titrating with a standardized solution of sodium thiosulfate to a starch end-point. The Thyodene indicator was added near the end of the titration. Blank corrections for particular TFA-water solutions were made, if necessary.

3.5 Organic Product Studies

3.5.1 Permanganate Oxidations in TFA-Water

Organic products were determined for selected compounds which are listed in Table 3 along with reaction medium and product detection methods. Typically the procedure was to prepare 20-25 ml of the desired TFA-water solution in which was dissolved 0.5 g of potassium permanganate. When all of the potassium permanganate had dissolved 4.00 ml of the substrate was added quickly with constant stirring by means of a magnetic stirrer. The reaction was allowed to proceed for one hour or until all the permanganate was consumed. The amount of substrate added was enough to ensure at least a five-fold excess except for three substrates. n-Pentane, cyclohexane and toluene were not completely soluble so a two phase system existed in these cases. The reaction after completion or one hour duration was quenched by the addition of 40 ml water, saturated with sodium chloride and then extracted three times with 50 ml ether. The ether extracts were combined, dried over anhydrous magnesium sulfate and flash-evaporated to reduce the volume to 30 ml or less depending upon the volatility

Table 3. Products of KMnO_4 Oxidations in TFA-Water Medium

Substrate	wt. ^a	$-\text{H}_R^b$	% Recovered ^c	Products	wt.	% ^d	Method
n-Pentane	2.5	7.5	40%	2-Pentanone	-	66%	1
				3-Pentanone	-	34%	1
				Propionic acid	-	-	2
2-Pentanol	3.2	7.5	89%	2-Pentanone	-	-	3
				Propionic acid	-	-	2
3-Pentanol	3.3	7.5	90%	3-Pentanone	-	-	3
				Propionic acid	-	-	2
2-Pentanone	3.3	7.5	94%	Propionic acid	-	-	2
3-Pentanone	3.3	7.5	90%	Propionic acid	-	-	2
Cyclohexane	3.1	7.5	83%	Cyclohexanol	~0.01	5%	4
				Cyclohexanone	~0.01	5%	4
				Adipic acid	0.2	90%	5
Cyclohexanol	3.9	7.5	95%	Cyclohexanone	~0.03	4%	4
				Adipic acid	0.35	91%	5
				Tar	0.03	5%	
Cyclohexanone	4.0	7.5	89%	Adipic acid	0.5	90%	5
				Tar	0.05	10%	
Toluene	3.5	4.5	95%	Benzoic acid	.25	-	6
Toluene	3.5	7.5	82%	Benzoic acid	.05	-	6

Table 3 (Continued)

Substrate	wt. ^a	-H _R ^b	% Recovered ^c	Products	wt.	% ^d	Method
Benzyl alcohol	4.2	4.5	91%	Benzoic acid	.3	-	6
Benzaldehyde	4.2	4.5	93%	Benzoic acid	.4	-	6
Acetophenone	4.1	7.5	92%	Benzoic acid	.2	-	6
1-Phenylethanol	4.1	5.0	95%	Acetophenone	.4	100%	7
2-Phenylethanol	4.1	5.0	93%	Phenylacetaldehyde Phenylacetic acid	(trace) .1	 99%	 8 9

^a initial amount of substrate added in grams; ^b acidity of reaction medium; ^c based on total materials (products and reactants) recovered; ^d based only on products recovered.

1. Collected from chromosorb 102 1/4" x 10' column, repurified on the 20% carbowax 20 M on firebrick 60/80 column 3/8" x 20' as a mixture. Identified as the ketones by retention times and NMR. Ratio determined from NMR integral.
2. Collected from underneath the CF₃CO₂H peak from the chromosorb 102 column. Identified by NMR.
3. Identified by retention times on chromosorb 101 and 102 columns against known compounds.
4. Identified by retention times on chromosorb 101 and Carbowax 20 M columns against known samples. Cyclohexanol existed as the trifluoroacetate ester.
5. Isolated, then purified by recrystallization, mp = 145-148°, literature mp = 149-150°. ^{81u}
6. Isolated, the purified by sublimation, mp = 121-122°, literature mp = 122°. ^{81q}
7. Identified by retention times against known compound on the Carbowax 20 M and the 10% Silicon GE SF-96 firebrick 60/80, 1/4" x 10' columns.
8. Collected from the Silicon GE SF-96 column. Identified by NMR.
9. Isolated, then purified, mp = 70-73°, literature mp = 76°. ^{81v} Verified by NMR.

of the compounds. It was observed that reaction would continue after dilution with 40 ml water for the phenylethanols, which was probably due to the hydrolysis of esters formed with TFA (see Section 4.5). For n-pentane a sample of the original ether extracts was retained before flash-evaporation to determine the amount remaining after oxidation. The concentrated ether extracts were then analyzed by v.p.c. for volatile components on a Varian Aerograph 90-P coupled with a Varian A-25 recorder using the series of columns mentioned in Tables 3 and 4. Non-volatile compounds, namely phenylacetic acid, benzoic acid, and adipic acid were recovered by evaporating the extracts to dryness and then purifying the crude products. Benzoic acid was readily sublimed and adipic acid could be recrystallized from ether or water. Phenylacetic acid, which was recovered from the oxidation of 2-phenylethanol, was identified by NMR since after several recrystallizations from petroleum ether the melting point was still low.

Several problems were encountered in the product analysis, the severest of which was that large quantities of TFA were extracted along with products. This masked the acidic products from the C-5 series, preventing yield calculations from being made. Only propionic acid could be collected. Although one would expect some acetic acid none of the columns, even the Chromosorb 101 column which is specifically designed for low molecular-weight acids, were capable of separating it from the larger amounts of TFA. It was also found that 2-pentanone and 3-pentanone could not be separated from each other. This problem was finally avoided by collecting the trace amounts present of this

ketone mixture and verifying their identities by NMR. The 2-pentanone to 3-pentanone ratio could be calculated from the peak integrals of the NMR spectrum of the mixture.

3.5.2 Nitration and Nitrosation Products in TFA-Water

It was found from the freezing-point depression experiments that the TFA medium could be used to generate nitronium ions from sodium nitrate and nitrosonium ions from sodium nitrite. It was considered worthwhile to see how effectively nitration and nitrosation could be carried out in this medium.

The general procedure was to dissolve 0.01 moles of the salt in neat TFA and then to add 0.01 moles of substrate while constantly stirring the mixture with a magnetic stirrer. The reaction was allowed to continue for four hours after which time it was quenched by the addition of 20 ml water. The resulting solution was made basic by the addition of either 6 N sodium hydroxide or sodium hydroxide pellets, then saturated with sodium chloride and extracted with three successive 50 ml portions of ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, and reduced to 50 ml by flash-evaporation. The resulting concentrates were analyzed by v.p.c. The results are listed in Table 4.

It was noted that the basic aqueous layers were highly colored. This color could be removed by acidification and restored by the addition of base. Subsequent investigation of the u.v. characteristics of the basic and acidic solutions indicated phenolic compounds. The recorded spectra strongly resembled those of ortho and para nitrophenol. See Section 4.1.3 for further discussion and also reference 79.

Table 4. Nitration and Nitrosation Products.

Reactants	% Recovered	% Converted	Products	% of Product	Detection Method
Phenol and NaNO ₃	-	-	black tar ^a	-	-
Toluene and NaNO ₃	97	95	<u>p</u> -nitrotoluene <u>o</u> -nitrotoluene <u>m</u> -nitrotoluene phenols	31.7 67.0 1.3 <.05	1 1 1 2
Benzene and NaNO ₃	100	100	nitrobenzene phenols	100.0 <.05	1 2
Toluene and NaNO ₂	98	1-2	nitrotoluenes	~1-2	1
Benzene and NaNO ₂	97	2-3	nitrobenzene	~2-3	1

^a rapid reaction could possibly be hazardous.

1. V.p.c. using 10% Silicon GS SF-96 on firebrick 60/80 1/4"x10' column at 162°, 40 cc helium per minute flow rate. Matched against known samples. Retention times were; o-nitrotoluene 8.5 min, p-nitrotoluene 11.1 min, m-nitrotoluene 10.5 min, toluene 1.5 min, benzene ~ 0.5 min.
2. U.V. indicated the presence of phenols. See Section 4.1.3 and also reference 79 where similar phenols were isolated from the nitration of toluene.

3.6 Determination of Stoichiometries

The stoichiometry could only be determined for those compounds where the competitive decomposition of permanganate was small. As a result the stoichiometry for weak reductants such as ketones and some alkanes could not be determined.

The general procedure was to make up substrate solutions in TFA-water of such strength that when 20-30 μl was added to 3.00 ml of a solution 4×10^{-4} M in potassium permanganate made from the same TFA-water solution as the substrate the oxidant was always in excess. The absorbance of the permanganate ion was determined before addition of substrate and then again when no further decrease in absorbance was noted. This was done for both the reacting cuvette and the control cuvette. Then 2.00 ml from each was added to 10.0 ml of an aqueous solution which was 4×10^{-3} M in potassium iodide and 2% in sodium bicarbonate. The liberated iodine was titrated with a 2×10^{-4} M standardized sodium thiosulfate solution to a starch end point. These experimental values are tabulated in Table 5.

3.7 Freezing-Point Depression Procedure

It was observed that when potassium permanganate was dissolved in neat TFA that a green species was generated similar to that previously reported for sulfuric acid solutions of this compound.²⁴ It was considered important to determine the identity of this species since it could very well be involved in the oxidations. Previous attempts to identify the species in sulfuric acid²⁶ had not been conclusive.^{25,27} It was felt that since TFA is a mono-protic acid the

Table 5. Experimental Data for Stoichiometric Determinations for
KMnO₄ Oxidations in TFA-H₂O.

Compound	H _R ^a	Moles substrate applied = X x 10 ⁷	Moles MnO ₄ ⁻ x 10 ⁷ in Blank Trial	Difference ^b x 10 ⁷ = Y	Y/X
Isopentane	-8.42	5.15	9.49 3.95	5.54	1.08
n-Pentane	"	2.60	9.37 8.36	1.01	0.39
n-Hexane	"	2.30	9.67 8.09	1.58	0.68
n-Heptane	"	1.36	9.43 8.15	1.28	0.94
n-Heptane	"	2.72	9.37 6.45	2.92	1.08
n-Octane	"	2.46	9.49 6.08	3.41	1.39
n-Nonane	"	1.67	9.49 6.42	3.07	1.85
n-Decane	"	1.54	9.25 6.05	3.20	2.08
n-Undecane	"	1.40	9.31 5.99	3.32	2.33
n-Dodecane	"	0.88	9.31 6.57	2.74	3.13
n-Tridecane	"	0.82	9.37 6.51	2.86	3.45
Cyclopentane	-7.82	4.82	9.67 6.69	2.98	0.62
Cyclohexane	"	4.17	9.40 6.72	2.68	0.64
Cycloheptane	"	3.72	9.12 6.69	2.43	0.65
Cyclooctane	"	2.23	9.25 6.99	2.26	1.01
Methanol	"	5.56	10.10 5.90	4.20	0.76
Methanol	-6.70	5.56	11.07 9.91	1.16	0.21
Ethanol	-7.90	5.13	9.37 6.99	2.38	0.46
2-Pentanol	"	2.76	9.12 8.09	1.03	0.37
3-Pentanol	"	5.55	9.37 6.69	2.68	0.48
Cyclohexanol	-7.82	1.92	10.46 9.61	0.85	0.44
Cyclohexanol	"	5.77	9.37 7.24	1.95	0.34
Formaldehyde	"	5.27	10.28 5.23	5.05	0.96
Cyclohexanone	"	3.05	9.82 8.18	1.64	0.54
Benzene	-6.70	3.37	11.07 3.89	7.18	2.13
Benzene	-7.50	1.13	7.53 4.52	3.00	2.67
Phenol	"	0.611	6.86 5.47	1.40	2.28
Toluene	"	0.941	6.86 4.98	1.88	2.00
Toluene	-6.70	2.82	11.01 2.92	8.09	2.86
Toluene	-3.65	8.47	10.89 2.07	8.82	1.04
Ethylbenzene	-7.50	0.817	7.47 5.89	1.58	2.35
Ethylbenzene	-6.70	1.63	11.56 6.08	5.48	3.33
Cumene	"	1.44	11.19 6.45	4.74	3.33
Cumene	-7.50	0.719	7.95 6.13	1.82	2.53
t-Butylbenzene	-7.50	0.646	7.59 6.07	1.52	2.35
t-Butylbenzene	-6.70	1.29	11.37 7.06	4.31	3.33
Benzyl alcohol	-2.30	14.5	9.79 2.25	7.54	0.52
Benzyl alcohol	-3.65	8.67	10.97 2.92	8.05	0.96
Benzyl alcohol	-6.70	2.89	11.19 4.32	6.87	2.38
Benzaldehyde	-2.30	14.7	9.73 2.37	7.36	0.50

Table 5. (Continued)

Compound	H_R^a	Moles substrate applied = $X \times 10^7$	Moles MnO_4^- in Blank Trial	Difference ^b $Y/X \times 10^7 = Y$	Y/X
Benzaldehyde	-2.30	7.36	10.73 4.22	6.51	0.88
Benzaldehyde	-3.65	8.83	11.86 4.44	7.42	0.84
Benzaldehyde	-6.70	2.94	11.13 5.96	5.17	1.75
1-Phenylethanol	-3.65	4.97	11.31 9.85	1.46	0.29
1-Phenylethanol	-7.50	0.834	7.77 6.98	0.79	0.95
2-Phenylethanol	-7.50	0.837	7.71 5.22	2.49	2.97
2-Phenylethanol	-3.65	7.54	11.50 3.95	7.55	1.0
Acetophenone	-8.42	5.13	9.12 4.44	4.68	0.91
C-H \rightarrow C-OH					0.40
C-H \rightarrow C=O					0.80
C-H \rightarrow CO ₂ H					1.20
C-OH \rightarrow C=O					0.40
C-OH \rightarrow CO ₂ H					0.80
C=O \rightarrow CO ₂ H					0.40
R ₂ CH ₂ \rightarrow 2RCO ₂ H					2.40

^a acidity of the TFA-H₂O medium in which the reaction took place.

^b the moles of MnO_4^- used up according to the data.

data analysis would be simpler than in the case of sulfuric acid. We attempted to substantiate our conclusions by investigating analogous reactions in which known species are generated, such as nitronium and nitrosonium ions.

A typical freezing-point depression experiment was carried out in the following manner. Using the apparatus illustrated in Figure 1 a 20.0 ml sample of pure TFA was supercooled to 10° below its freezing point by means of a dry ice-acetone bath. Crystallization was induced by touching the wall with a small piece of dry ice. The solution was completely frozen to degas it and then remelted. Next it was cooled to one degree below the freezing point and crystallization was again induced with a piece of dry ice. The resulting warming curve was recorded until the temperature reached the equilibrium plateau indicative of the liquid-solid equilibrium temperatures. When the solution was supercooled by no more than 2° this plateau extended over a time interval of 2 to 4 minutes, allowing precise determination of the freezing point. Once the freezing point had been verified for the pure compound the sample of interest was added and completely dissolved. Then using the same supercooling technique the new freezing point was determined and verified at least twice. Sometimes when larger amounts of compounds were added the solutions tended to supercool too much, giving no warming plateau. Whenever this occurred the acetone-bath temperature was slowly lowered until crystallization could be maintained. In this manner freezing points could be determined to $\pm 0.01^\circ$. For pure TFA the reproducibility was $\pm 0.005^\circ$. Fresh TFA was used for each sample investigated and all determinations were performed under a

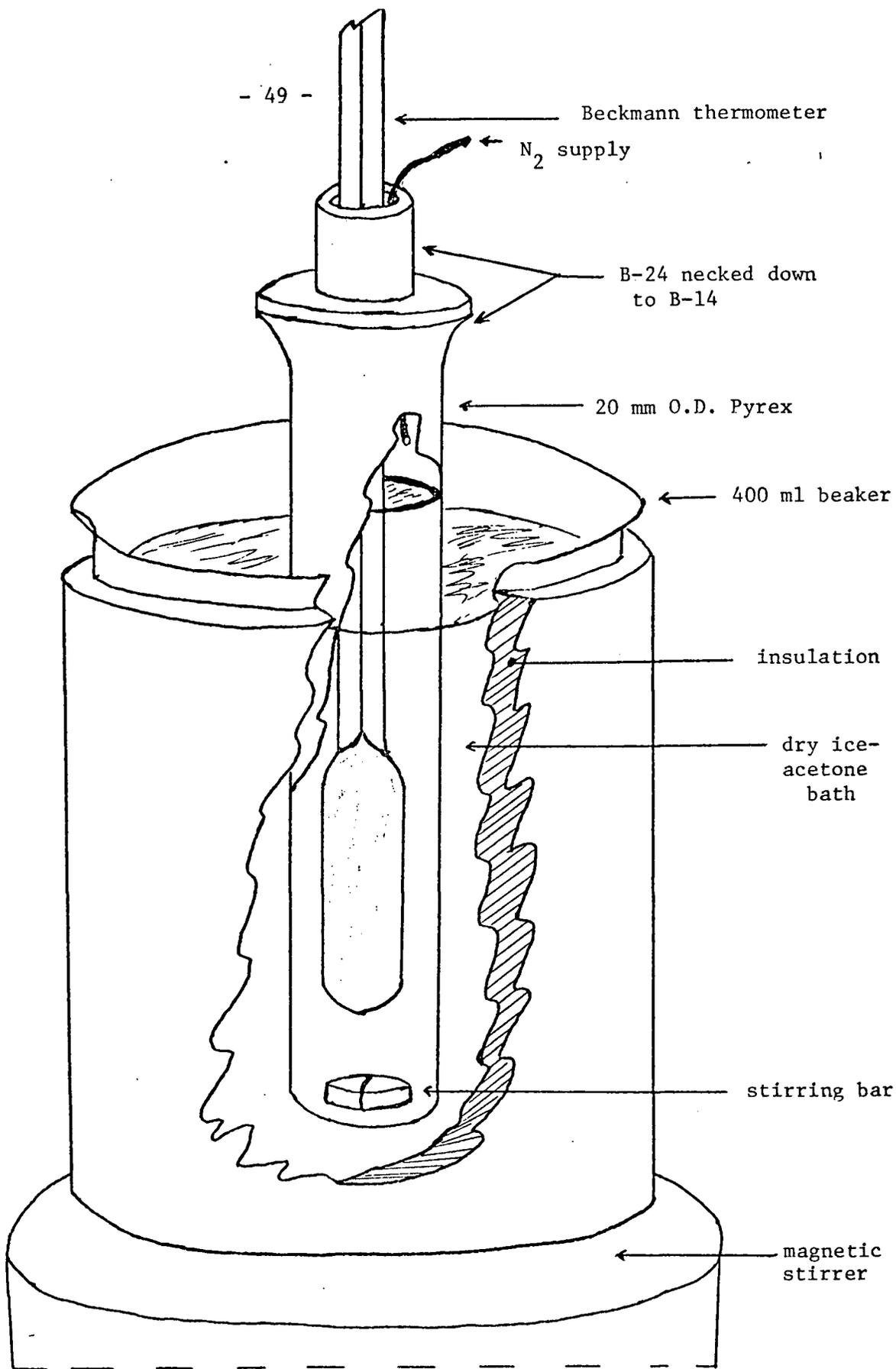


Figure 1. Freezing-point apparatus.

nitrogen atmosphere. The results obtained are presented in Table 6 and 7.

3.8 Determination of the H_R Function for TFA-Water

When the initial kinetic oxidation data were analyzed it was found that the order with respect to h_o was extremely high, in excess of five. It became apparent that this was not the proper function. The H_R function was then considered as a possible alternative.

The H_R function for TFA-water solutions was determined in the following manner. Stock solutions of the indicators were made up in neat TFA of such concentration that when 0.50 ml was made up to 5.00 ml the fully ionized absorbance value would be near 0.8. Stock solutions in neat TFA were stable for up to several weeks with no indicator decomposition. The absorbance of the cations in the series of solutions used was measured on a Cary 16 spectrophotometer at 25°. The uncertainty of the absorbance measurement was $\pm 0.1\%$. The acidity of each solution used was then determined by titrating with 2.00 N sodium hydroxide.

The Hammett approach of overlapping indicators was used. The series had good overlap, as Figure 2 illustrates, with quite parallel slopes necessary for the approach.⁹⁷ Two indicators were used to tie the function into the standard pH function. For this purpose indicators 1 and 2 (see Table 2) were used. Both were appreciably ionized in solutions which had measurable pH values. A Radiometer model No. 26 pH meter was used, equipped with a set of glass and calomel electrodes. This machine was standardized with Fisher pH = 2.00 standard solution.

Table 6. Determination and Verification of K_f^a for Trifluoroacetic Acid.

Substrate	Moles of substrate	Molality = m	ΔT	$K_f = \Delta T/m$		
<u>Determination</u>						
Benzene	0.02250	0.7329	3.94	5.38		
"	"	"	4.00	5.46		
"	"	"	3.96	5.40		
"	"	"	3.99	5.44		
"	"	"	4.08	5.57		
"	"	"	4.00	5.46		
				$\bar{K}_f = 5.45 \pm 0.02$		
				$m_x = \Delta T/K_f$	$n = m_x/m$	n_o^b
<u>Verification</u>						
Toluene	0.01882	0.6130	3.46	0.6349	1.04	1.0
Sodium acetate	0.001533	0.04993	0.835	0.1532	3.07	3.0
"	0.001102	0.03589	0.580	0.1064	2.96	3.0
"	0.000625	0.02035	0.330	0.06052	2.98	3.0
"	0.000244	0.00794	0.140	0.02796	3.42	3.0
"	0.000244	0.00794	0.148	0.02569	3.23	3.0
"	0.000138	0.00450	0.085	0.01559	3.46	3.0
			0.080	0.01468	3.26	3.0
			0.075	0.01376	3.06	3.0

^a K_f is the molal freezing point depression constant.

^b n_o is the number of particles predicted theoretically.

Table 7. Cryoscopic Data for Substrates in Trifluoroacetic Acid.

Substrate	Moles added	Molality = m	ΔT	$m_x = \Delta T / K_f$	$n = m_x / m$
Water	0.01665	0.5423	3.41	0.6257	1.15
"	0.00555	0.1808	1.28	0.2349	1.30
"	0.01665	0.5423	3.65	0.6697	1.23
"	0.01110	0.3619	2.37	0.6349	1.20
KMnO ₄	0.001179	0.03840	0.63	0.1156	3.01
"	0.0009430	0.03072	0.60	0.1101	3.58
"	0.0008464	0.02757	0.56	0.1028	3.73
"	0.0006348	0.02068	0.39	0.0716	3.46
"	0.0004945	0.01611	0.33	0.0606	3.76
"	0.0002781	0.009059	0.22	0.0404	4.46
"	0.0003122	0.009912	0.16	0.0294	4.25
"	0.0006356	0.02070	0.37	0.0679	3.28
"	0.0001948	0.006345	0.17	0.0312	4.92
"	0.0001429	0.004650	0.13	0.0239	5.14
"	0.0001215	0.003958	0.11	0.0202	5.10
Triphenyl- carbinol	0.0007547	0.02458	0.46	0.08441	3.43
"	0.0004380	0.01427	0.26	0.04771	3.34
"	0.0001984	0.006463	0.135	0.02477	3.69
"	"	"	0.140	0.02569	3.83
Sodium nitrate	0.001271	0.04141	0.575	0.1053	2.55
"	0.000475	0.01548	0.28	0.05138	3.32
"	0.000377	0.01226	0.205	0.0376	3.14
"	0.000233	0.07604	0.142	0.0261	3.42
"	"	"	0.165	0.0303	3.98
"	0.000168	0.005461	0.105	0.0193	3.53
"	"	"	0.110	0.0202	3.69
"	0.000113	0.003675	0.090	0.0165	4.49
"	"	"	0.095	0.0174	4.74
Sodium nitrite	0.001401	0.04563	1.02	0.1872	4.10
"	"	"	1.03	0.1890	4.14
"	0.0009384	0.03057	0.73	0.1339	4.38
"	"	"	0.75	0.1376	4.50
"	0.0007304	0.02379	0.575	0.1055	4.43
"	"	"	0.60	0.1101	4.62
"	0.0003567	0.01167	0.270	0.04954	4.26
"	"	"	0.275	0.05046	4.34
"	0.0001471	0.004792	0.110	0.02018	4.21
"	"	"	0.120	0.02202	4.59

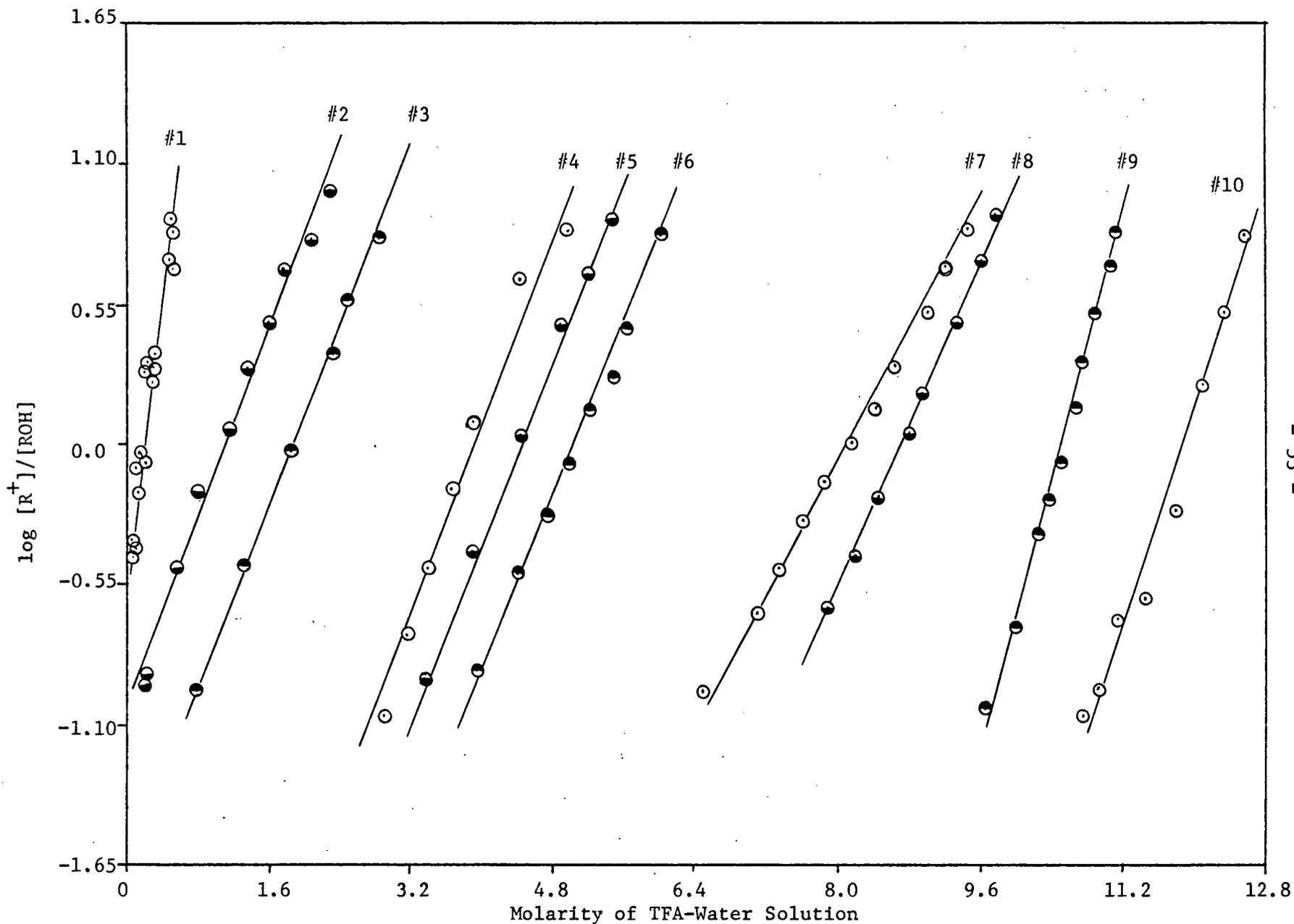
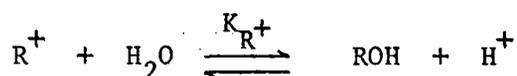


Figure 2. Indicator ratio plots for the H_R function (see Appendix A for data).

Since the H_o function established by Randles and Tedder¹² was in terms of weight percent we found it necessary to determine the molarity for these solutions so that the two functions could be compared. These data are presented in Table 8.

The equation used to establish H_R is derived in the following manner.



$$K_{R^+} = \frac{[ROH]a_{H^+}}{[R^+]a_{H_2O}} \cdot \frac{f_{ROH}}{f_{R^+}}$$

$$\log K_{R^+} = \log \frac{[ROH]}{[R^+]} + \log \frac{a_{H^+} \cdot f_{ROH}}{a_{H_2O} \cdot f_{R^+}}$$

let
$$h_R = \frac{a_{H^+} \cdot f_{ROH}}{a_{H_2O} \cdot f_{R^+}} \quad \text{then} \quad H_R = -\log h_R$$

$$H_R = -\log K_{R^+} + \log \frac{[ROH]}{[R^+]}$$

or
$$H_R = pK_{R^+} + \log \frac{[ROH]}{[R^+]}$$

Experimentally $[ROH]/[R^+]$ was determined as follows:

$[R^+] =$ Absorbance of cation observed

$[ROH] =$ Absorbance of fully ionized cation - absorbance observed.

Since none of the indicators used had detectable decompositions spectrophotometric measurements were readily made. Occasional

Table 8. Molarity of Weight % Solutions of TFA-Water.

Molarity	Weight % of TFA in TFA-H ₂ O
0.77	8.33
1.76	18.11
2.53	24.23
3.46	34.12
3.90	37.83
4.28	40.77
4.82	44.91
5.51	50.35
6.20	55.36
6.78	59.62
7.98	67.76
8.76	71.71
9.32	75.59
9.85	78.78
10.58	83.32
11.05	86.32
11.45	89.07
12.20	93.67
12.95	96.49
13.13	100

difficulty was encountered in determining the fully ionized absorbance, presumably because of solvent effects on the spectra of the carbonium ions. There were no λ_{\max} shifts, only a small increase of absorbance with increased acidity. Whenever this was the case the absorbance values close to the region where the sigmoid curve leveled off were used to determine the fully ionized absorbance value. Only one indicator, 4,4',4''-trimethoxytriphenylcarbinol, had absorbance increases of more than 0.01 over a range of three H_R units beyond the approximate fully ionized absorbance value.

3.9 Vapour-Liquid Phase Equilibrium Study

In the previous section the H_R relationship was derived. One of the factors that determine its magnitude is a_{H_2O} . The normal method to determine a_{H_2O} is to measure vapour pressure under isothermal conditions varying substrate and then applying the equation $a_i = kp_i$,⁹⁸ where a_i = activity of solvent in solution p_i = vapour pressure of solvent over solution and k = proportionality constant. But for pure solvent $a = 1 \therefore 1 = kp_0$ or $k = 1/p_0$ so the equation takes the familiar form $a_i = p_i/p_0$. We did not have the necessary equipment to measure the vapour pressure at 25° directly but the amount of water present when vapour-liquid boiling equilibrium is achieved should be proportional to activity. Boiling-point equilibrium studies were quite simple to perform on the TFA-water system in the following manner. One hundred ml of one of the components was brought to reflux and the equilibrium temperature recorded; then 10 ml portions of the other component were added until the added component was in excess. After each

10 ml addition the solution was brought to boiling-reflux equilibrium, the equilibrium temperature was recorded and a sample of the condensate was trapped by means of the apparatus illustrated in Figure 3. After cooling, a 2.00 ml portion of the condensate and residue was titrated to determine the amount of TFA present in each sample. In this manner by starting with each component in turn a complete vapour-liquid phase diagram could be constructed. The a_{H_2O} could be then approximated in the following manner; $a_{H_2O} \equiv$ mole fraction of water in the vapour which results from the following derivation. As previously mentioned $a_i = kp_i$. If one makes the assumption that the partial pressure of the *i*th component is proportional to the mole fraction of *i* present in the vapour then $p_i = k'F_i$ (*F* = mole fraction). Then $a_i = kk'F_i$. But for a system composed of pure component *i* the activity of *i* (a_o)_{*i*} = 1, and the mole fraction of component *i* in the vapour must be unity.

So, $a_o = 1 = kp_o$

but, $p_o = k'F_o = k'$

then, $kk' = 1$

therefore, $a_i = F_i$

It must be remembered that these values of a_{H_2O} are only approximate since isothermal conditions did not exist. The values obtained are presented in Table 9. Figure 4 presents the vapour-liquid equilibrium data.

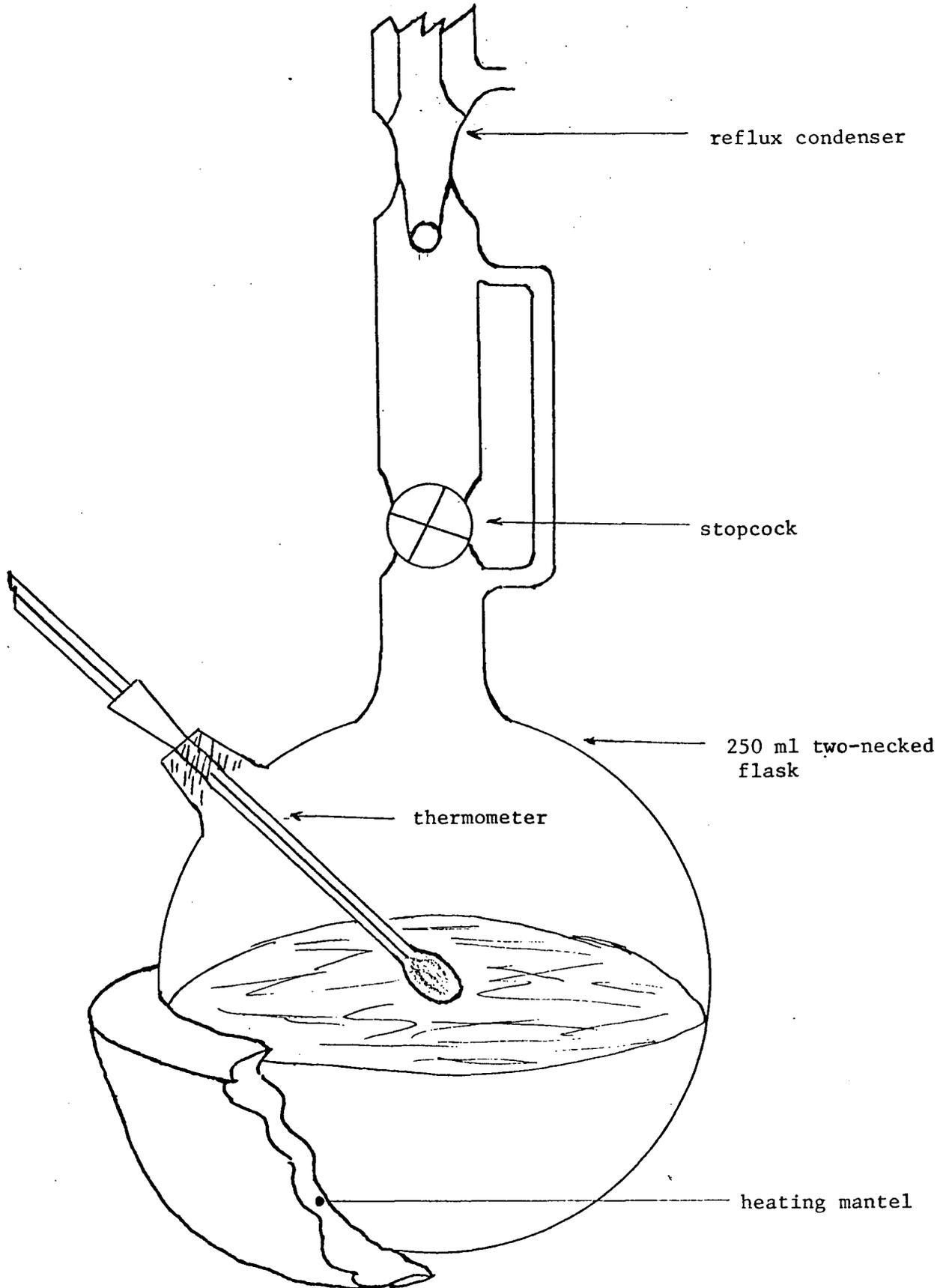


Figure 3. Vapour-liquid equilibrium study apparatus.

Table 9. Vapour-Liquid Equilibrium Data for the TFA-Water System.

Boiling point	N of liquid	N of vapour	$F_{H_2O}^a$ in liquid	$F_{H_2O}^a$ in vapour	Log F vapour
71.0	13.0	13.0	0	0	-
79.2	12.40	12.70	0.254	0.169	-.772
88.1	12.0	12.80	0.346	0.130	-.886
96.0	11.65	12.80	0.410	0.130	-.886
99.9	11.30	12.45	0.466	0.250	-.620
103.7	10.60	11.60	0.556	0.416	-.381
104.7	10.30	10.70	0.585	0.547	-.262
104.9	10.00	9.60	0.614	0.652	-.186
104.5	9.70	8.60	0.641	0.720	-.143
103.5	9.00	7.00	0.693	0.800	-.097
102.3	8.40	5.80	0.731	0.852	-.070
101.8	7.80	5.15	0.765	0.875	-.058
101.3	7.35	4.00	0.785	0.893	-.049
101.0	7.00	3.95	0.800	0.910	-.041
100.8	6.55	3.55	0.821	0.921	-.036
100.65	6.20	3.50	0.837	0.922	-.035
100.35	5.65	3.15	0.858	0.932	-.031
100.15	5.00	2.80	0.881	0.941	-.026
100.0	4.20	2.40	0.905	0.951	-.022
99.4	3.30	2.00	0.928	0.960	-.018
99.6	2.30	1.50	0.953	0.971	-.013
99.3	1.30	0.80	0.975	0.986	-.006
98.0	0	0	1.0	1.0	0.0

^a F designates mole fraction of water present in solution or vapour.

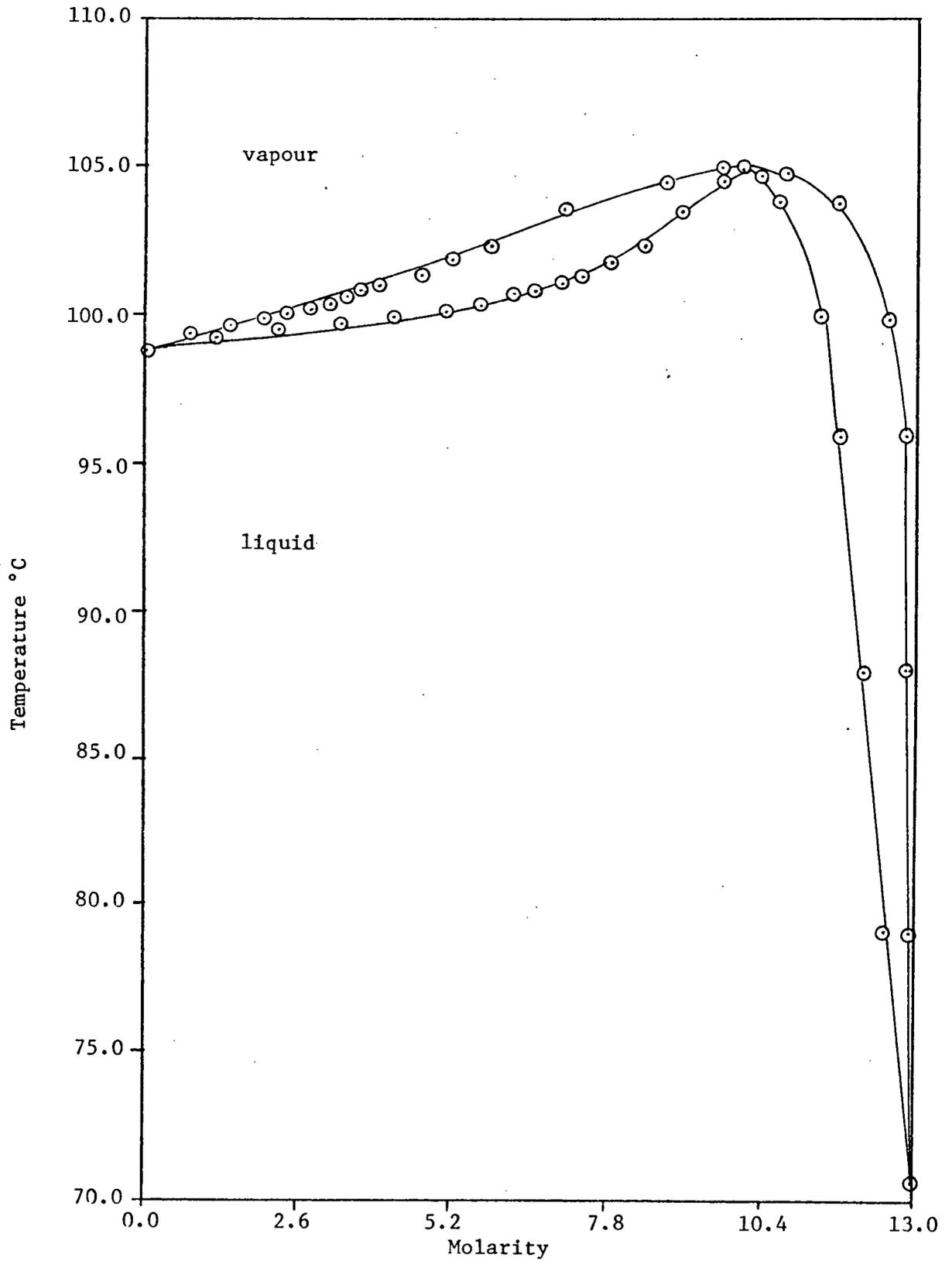


Figure 4. Phase diagram of TFA-water mixtures.

3.10 Determination of pK of Permanganic Acid in H₂O and D₂O

It has been previously mentioned that permanganate exists as a green species in neat TFA. It was further noted that addition of water regenerated the permanganate ion, MnO_4^- . It became apparent that an equilibrium existed between these two species which was determined in the following manner. Stock solutions of permanganate were prepared in either H₂O or D₂O of such strength that when 50 μl was added to 5.00 ml of the desired acid-water or acid-deuterium oxide solution that the maximum absorption for complete transformation into permanganate ion was approximately 0.8. The equilibrium between the green species ($\lambda_{\text{max}} = 458 \text{ nm}$, $\epsilon_{\text{max}} \approx 600$) and permanganate anion was monitored by noting the change in absorbance of the 546 nm absorption peak of permanganate ion by means of a Cary 16 spectrophotometer, thermostated at 25.0°. At this wavelength no absorption was detected for the green species or any decomposition products. For each experiment a timer was started at the time of mixing to allow extrapolation of the absorbance to zero time for those solutions where decomposition occurred. The pK value was calculated by least squares analysis of the log ($[\text{green species}]/[\text{MnO}_4^-]$) vs H_o or H_R data and was taken as that value of H_o or H_x where $\log([\text{green species}]/[\text{MnO}_4^-]) = 0$. The data obtained are presented in Table 10 and analyzed graphically in Figures 5 to 8.

The assumption was made that $[\text{green species}]_x = [\text{MnO}_4^-]_o - [\text{MnO}_4^-]_x$, where $[\text{MnO}_4^-]_x \equiv$ absorbance of permanganate in some solution x where some green species was formed and $[\text{MnO}_4^-]_o =$ absorbance of permanganate in a solution where no green species was generated. Then the $\text{pK} = \text{H}_x$ when $\log([\text{green species}]/[\text{MnO}_4^-]) = 0$.

Table 10. Protonation Data for MnO_4^- in Mediums of TFA- H_2O or D_2O .

$-\text{H}_R$	$-\text{H}_O$	x=Absorbance	Abs. F - Abs. = y	Q = y/x	log Q
H ₂ O - set #1					
10.92	3.06	0.0325	0.7696	23.680	1.374
10.80	3.01	0.0449	0.7572	16.864	1.227
10.58	2.90	0.0573	0.7448	12.998	1.114
10.49	2.85	0.0777	0.7244	9.323	0.970
10.24	2.76	0.1098	0.6923	6.305	0.800
10.02	2.57	0.1869	0.1652	3.292	0.517
9.90	2.50	0.2602	0.5419	2.083	0.319
9.60	2.26	0.3585	0.4436	1.237	0.093
9.36	2.06	0.4689	0.3332	0.711	-0.148
9.19	1.95	0.5459	0.2562	0.469	-0.329
8.80	1.80	0.6213	0.1808	0.291	-0.536
8.55	1.65	0.6631	0.1390	0.210	-0.679
8.23	1.46	0.7053	0.0968	0.137	-0.863
7.82	1.31	0.7281	0.0740	0.102	-0.993
7.62	1.22	0.7543	0.0478	0.063	-1.198
6.96	1.00	0.7701	0.0320	0.042	-1.381
6.22		0.8066	Abs. F = 0.8021		
5.88		0.7982			
H ₂ O - set #2					
10.26	2.78	0.1092	0.8018	7.343	0.866
10.14	2.66	0.1609	0.7501	4.662	0.669
9.94	2.52	0.2286	0.6824	2.985	0.475
9.71	2.35	0.3120	0.5990	1.920	0.283
9.42	2.09	0.4100	0.5010	1.222	0.081
9.30	2.02	0.5710	0.3400	0.595	-0.225
8.96	1.82	0.6370	0.2740	0.431	-0.366
8.58	1.67	0.6840	0.2270	0.332	-0.479
8.32	1.50	0.7410	0.1700	0.229	-0.639
7.56	1.21	0.8310	0.0800	0.096	-1.017
7.02	1.02	0.8900	0.0210	0.024	-1.627
6.18		0.9110	Abs. F = 0.9110		
D ₂ O-CF ₃ CO ₂ H					
10.92	3.06	0.0406	0.7818	19.26	1.285
10.51	2.88	0.0600	0.7624	12.71	1.104
10.09	2.63	0.1139	0.7063	6.096	0.785
9.72	2.36	0.2324	0.5900	2.539	0.405
9.50	2.18	0.3544	0.4680	1.321	0.121
9.34	2.03	0.4634	0.3590	0.7747	-0.111
9.12	1.92	0.5628	0.2596	0.461	-0.336

Table 10 (Continued)

$-H_R$	$-H_O$	x=Absorbance	Abs. F - Abs. = y	Q = y/x	log Q
D ₂ O (continued)					
8.76	1.74	0.6263	0.1961	0.3131	-0.504
8.07	1.44	0.7195	0.1029	0.1430	-0.845
7.44	1.18	0.7678	0.0546	0.071	-1.148
6.90	0.99	0.7949	0.0275	0.035	-1.461
6.12		0.8236	Abs. F = 0.8224		
5.78		0.8212			
H ₂ O 14.6°					
9.90	2.50	0.2682	0.5536	2.069	0.315
9.36	2.06	0.4850	0.3368	0.6944	-0.158
8.80	1.80	0.6409	0.1809	0.2818	-0.549
8.23	1.46	0.7133	0.1085	0.1521	-0.818
5.88		0.8218	Abs. F = 0.8218		
H ₂ O 20.0°					
9.90	2.50	0.2685	0.5363	1.997	0.301
9.36	2.06	0.4659	0.3389	0.7274	-0.138
8.80	1.80	0.6254	0.1794	0.2869	-0.542
8.23	1.46	0.6979	0.1069	0.1532	-0.815
5.88		0.8048	Abs. F = 0.8048		
H ₂ O 25.0°					
9.90	2.50	0.2557	0.5425	2.122	0.327
9.36	2.06	0.4612	0.3370	0.7307	-0.136
8.80	1.80	0.6151	0.1831	0.2977	-0.526
8.23	1.46	0.7025	0.0957	0.1362	-0.866
5.88		0.7982	Abs. F = 0.7982		
H ₂ O 30.5°					
9.90	2.50	0.2488	0.5521	2.219	0.346
9.36	2.06	0.4530	0.3479	0.768	-0.115
8.80	1.80	0.6144	0.1863	0.304	-0.518
8.23	1.46	0.7023	0.0986	0.140	-0.853
5.88		0.8009			

Table 10 (Continued)

$-H_R$	$-H_o$	x=Absorbance	Abs. F - Abs. = y	Q = y/x	log Q
H ₂ O 35.3°					
9.90	2.50	0.2226	0.5683	2.553	0.407
9.36	2.06	0.4168	0.3768	0.897	-0.047
8.80	1.80	0.6053	0.1856	0.307	-0.513
8.23	1.46	0.6629	0.1280	0.193	-0.714
5.88		0.7909			
D ₂ O-CF ₃ CO ₂ D					
10.06	2.61	0.0501	0.4749	9.479	0.977
9.45	2.11	0.1732	0.3518	2.031	0.308
9.34	2.04	0.1955	0.3295	1.685	0.227
8.96	1.84	0.2856	0.2394	0.838	-0.077
8.39	1.55	0.3572	0.1678	0.470	-0.328
8.06	1.38	0.3729	0.1521	0.408	-0.389
7.80	1.30	0.4174	0.1076	0.258	-0.589
7.44	1.15	0.4355	0.0895	0.206	-0.687
7.06	1.03	0.5292			
636		0.5048			
5.66		0.5338			
4.92		0.5559	Abs. F. = 0.5250		

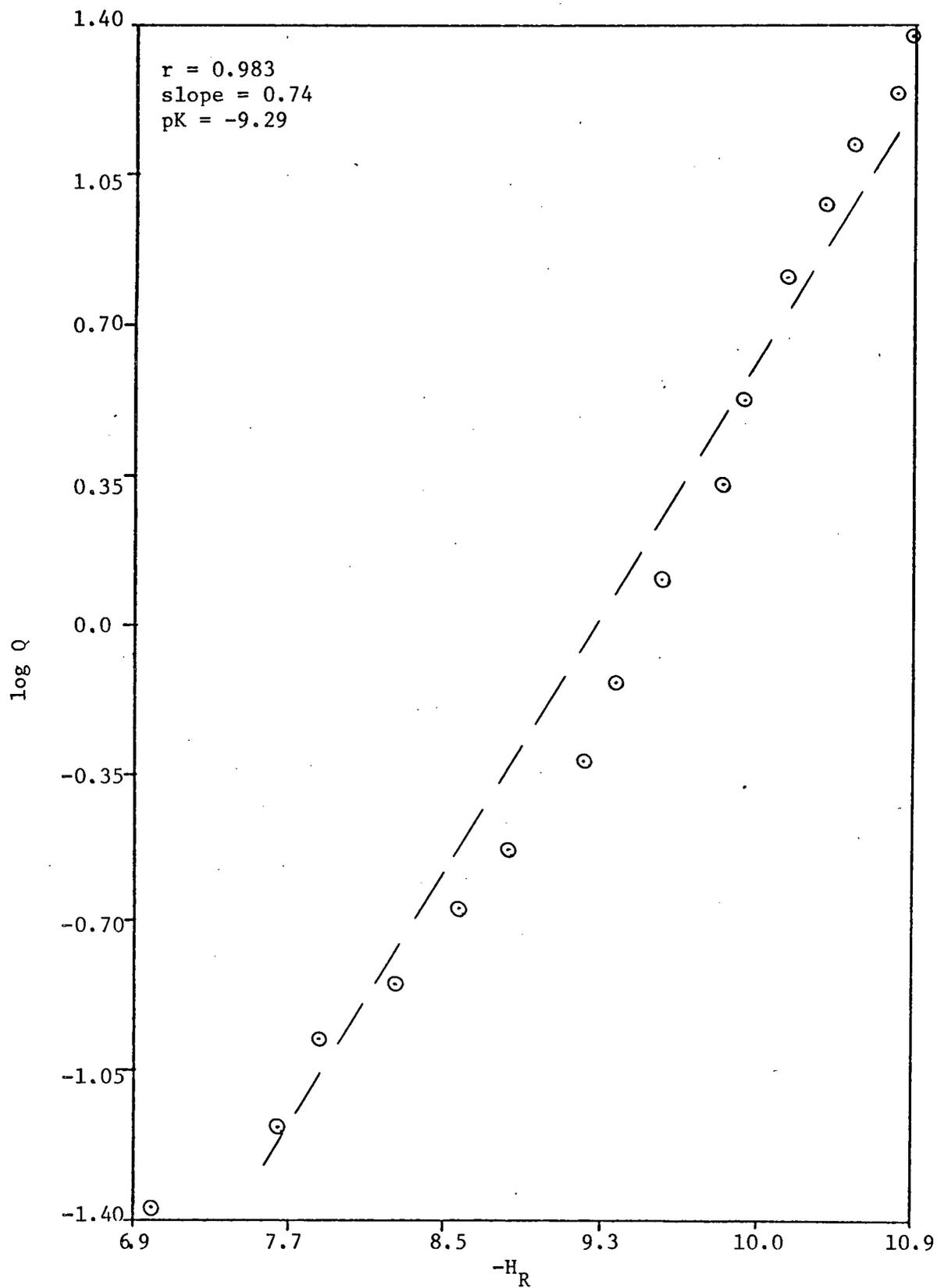


Figure 5. Log Q vs. H_R for the ionization of MnO₄⁻ in TFA-water. (Data set #1, Table 10).

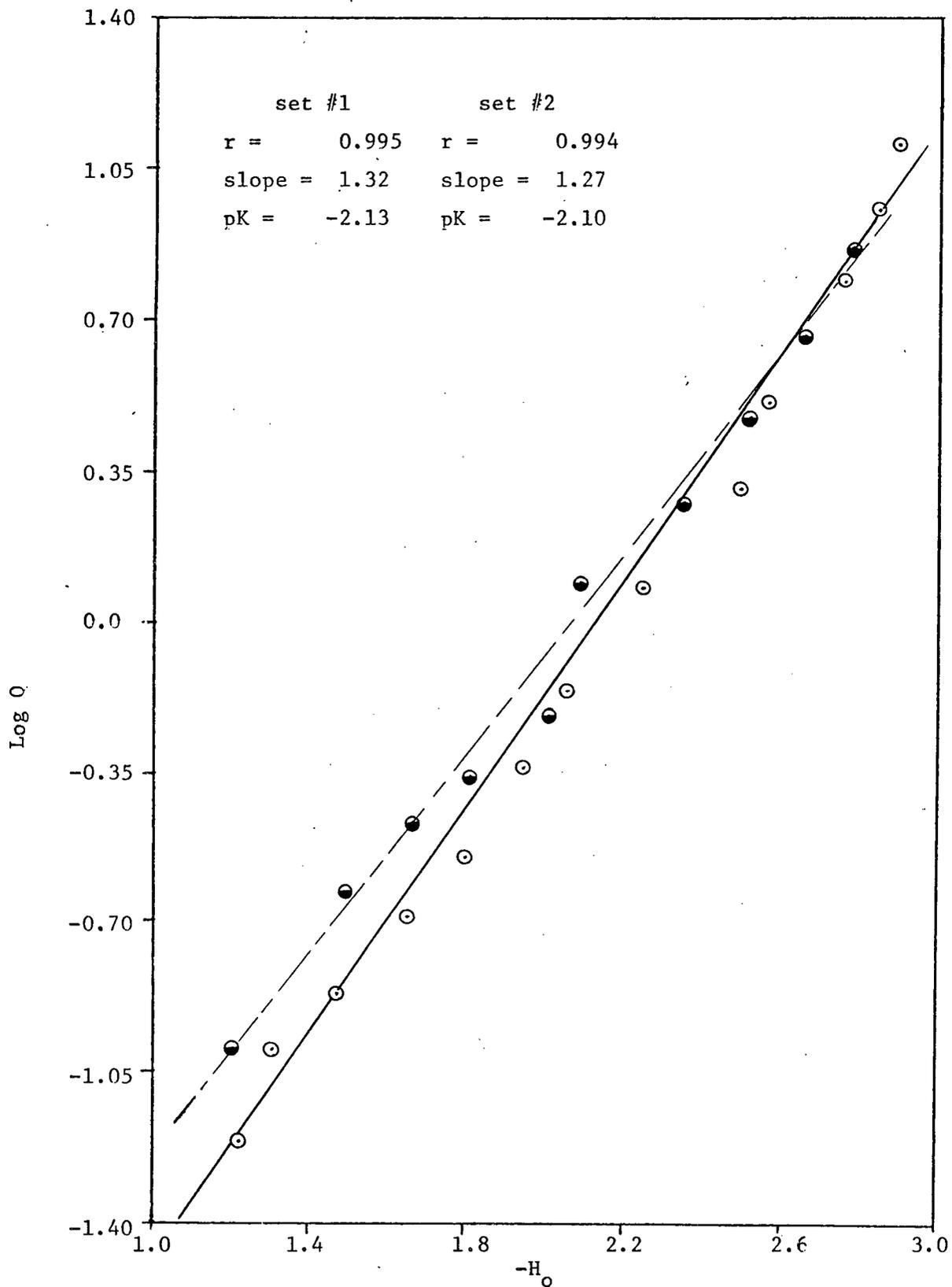


Figure 6. Log Q vs. H_0 for the ionization of MnO_4^- in TFA-water.
(\odot data set #1, \bullet data set #2, Table 10).

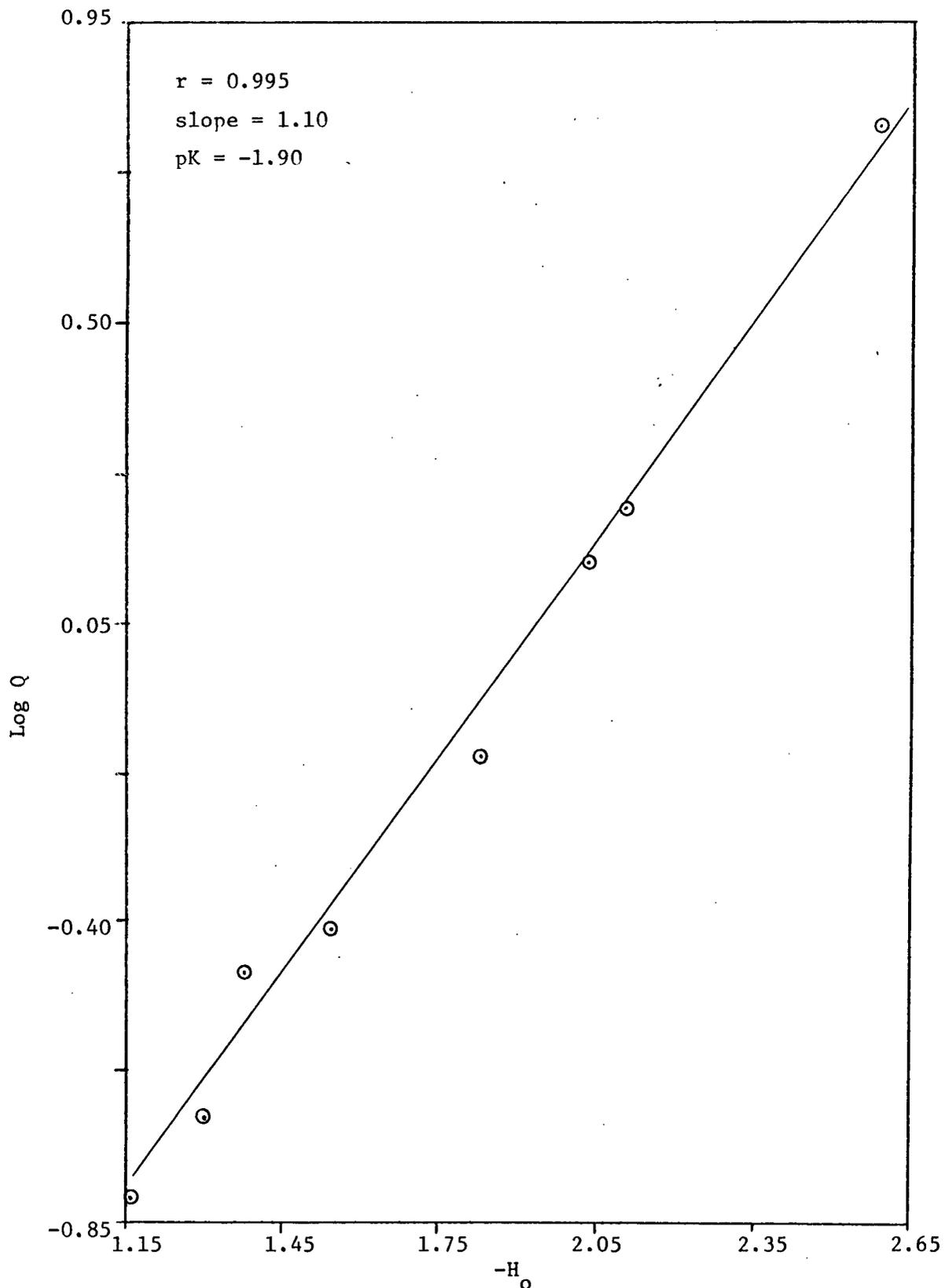


Figure 7. Log Q vs. H_o for the ionization of MnO_4^- in trifluoroacetic acid- d_1 -deuterium oxide.

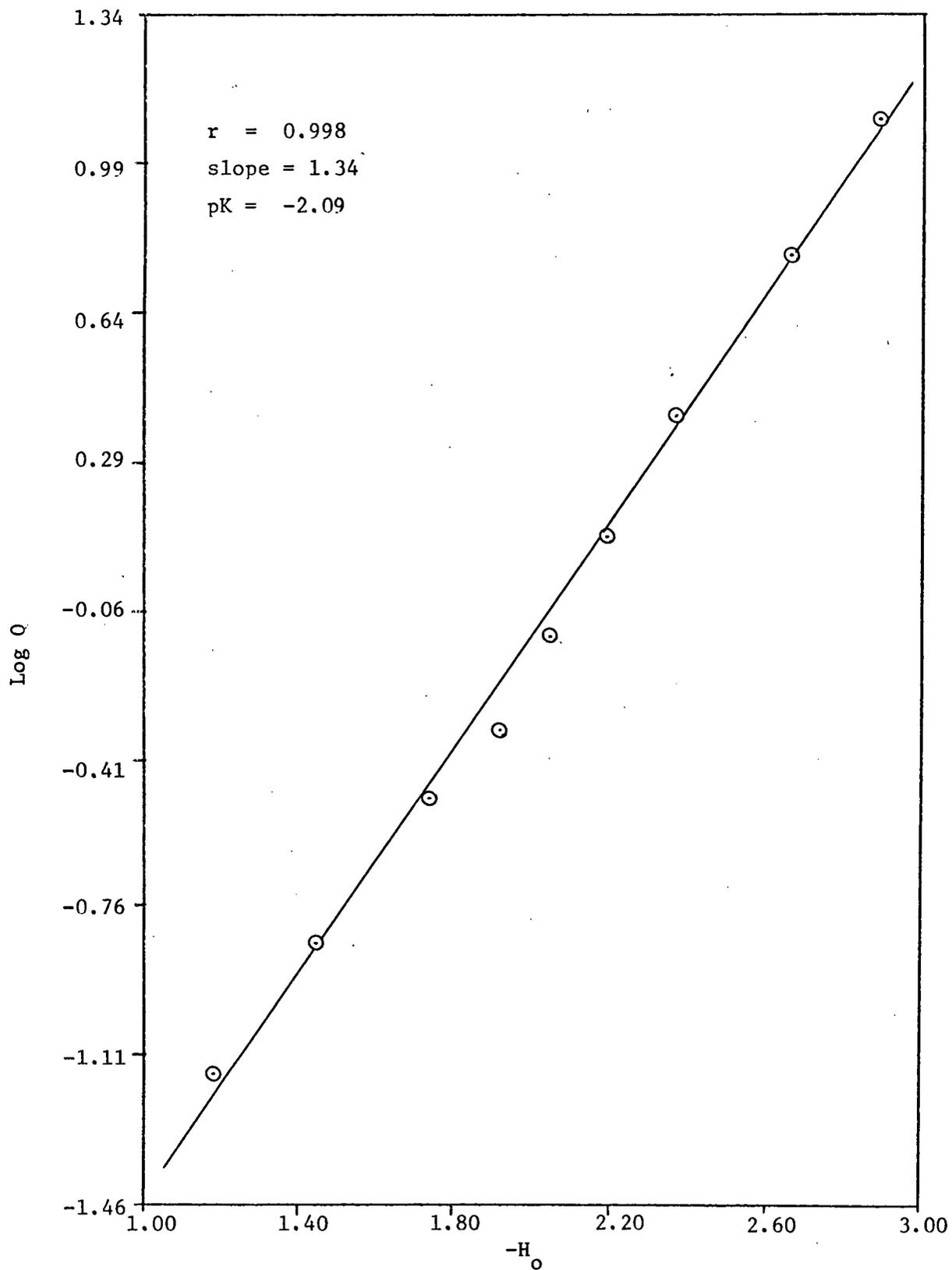


Figure 8. Log Q vs. H_o for the ionization of MnO_4^- in trifluoroacetic acid-deuterium oxide.

3.11 Permanganate in Benzene

It has been reported that permanganate anion can be extracted into benzene by using salts containing large alkylammonium cations.⁷⁰ We found that tetra(n-hexyl)ammonium cation could be used to achieve this transfer. This can be done by taking 50 ml of a benzene solution containing the tetra(n-hexyl)ammonium iodide salt (for spectral concentrations of MnO_4^- , 0.10 g per 250 ml of benzene) and mixing it vigorously with an aqueous solution of potassium permanganate. In short order the benzene layer has a deep colour of permanganate ion with the usual absorption, but better definition of the peaks as Figure 9 illustrates. Table 11 lists the spectral properties of this new salt along with comparative values.

It was possible to isolate the benzene-soluble salt by evaporating the benzene. The crude product could not be successfully recrystallized, even though a wide variety of solvents was used. However, it could be purified in the following manner. The benzene solution of the salt was carefully decanted leaving behind residues, then the benzene layer was flash-evaporated to recover the desired permanganate salt. The salt was redissolved in fresh benzene, the solution was again decanted to remove it from the residue, and then again flash evaporated. This process was repeated at least four times after which the purity of the salt was 94% as determined by elemental analysis. Table 12 lists some of the physical properties found.

Some kinetic experiments were performed using this benzene-soluble salt. A stock solution of permanganate in benzene was prepared by the before mentioned extraction technique. One part was then combined with nine parts of a benzene solution containing the substrate. The

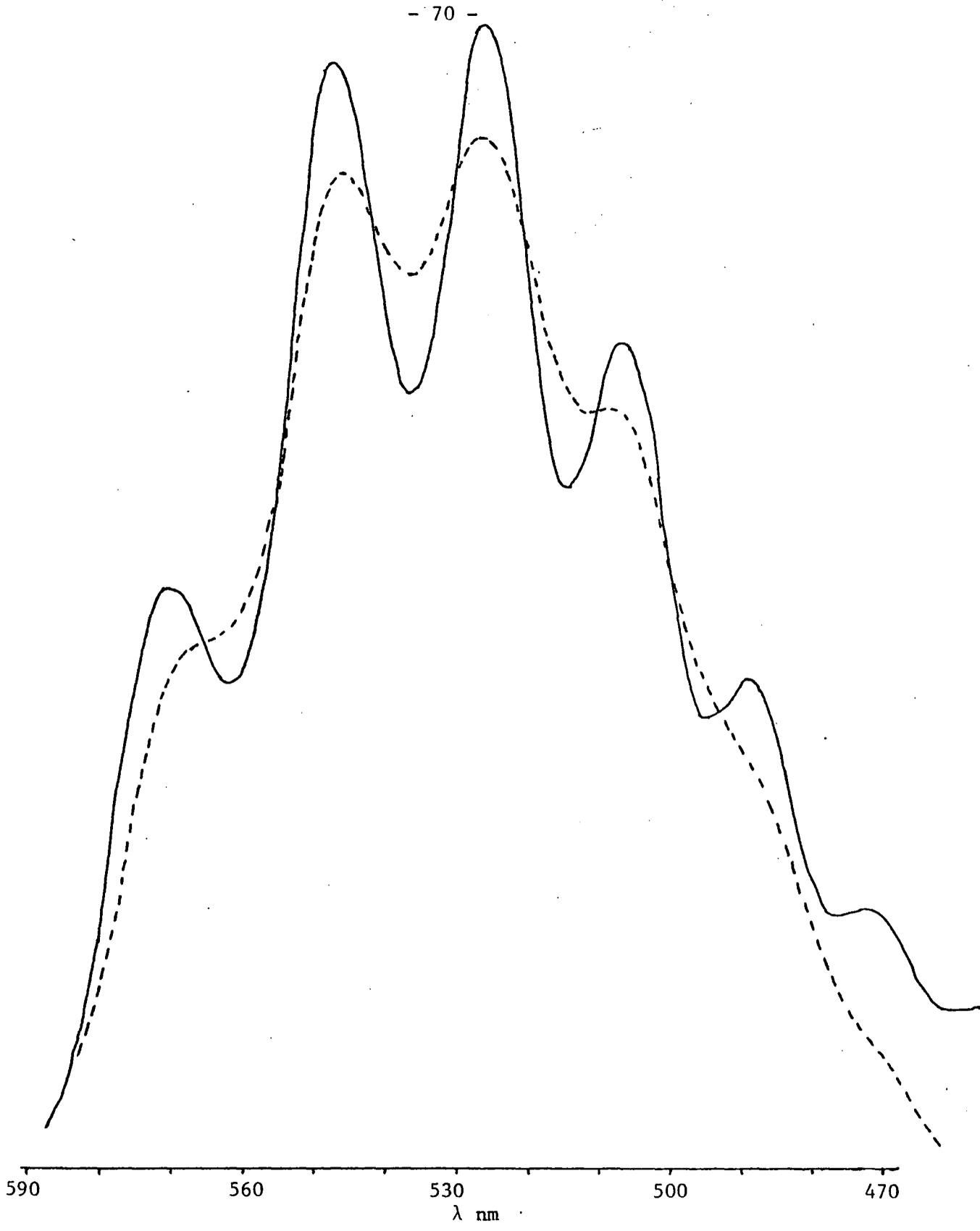


Figure 9. Spectra of MnO_4^- with different cations and solvent.
—, tetra(n-hexyl)ammonium cation, medium benzene
---, potassium cation, medium water

Table 11. Spectral Properties of Tetra(n-hexyl) ammonium Permanganate in Benzene.

Species	λ nm	ϵ
1a	571	1,322.
	548	2,286.
	527.5	2,340.
	507.5	1,771.
	490	1,150.
	473	831.
1b	571	1,306.
	548	2,289.
	527.5	2,337.
	507.5	1,737.
	490	1,121.
	473	722.
2	565	1,810.
	546	3,130.
	525	3,170.
	508	2,330.
3	546	2,380.
	526	2,400.

- 1 - Tetra(n-hexyl)ammonium permanganate at two different concentrations
a - 8.234×10^{-5} M; b - 5.0672×10^{-4} M.
- 2 - KMnO_4 complexed with dicyclohexyl-18-crown-6-ether as reported by Sam and Simmons.⁶⁹
- 3 - Aqueous permanganate.⁹⁹

Table 12. Properties of Tetra(n-hexyl) ammonium Permanganate.

mp = 86-88°.

Elemental analysis^a: calculated - C, 60.86%; H, 11.07%; N, 2.96%.

experimental - C, 57.42%; H, 10.63%; N, 2.73%.

Stability: several weeks if dry and stored in the dark.

Solubility:

Solvent	Solubility	Stability	Half life
Water	N	---	---
Cyclohexane	SS	d	~5 min
n-Hexane	N	---	---
n-Heptane	N	---	---
Diethyl ether	S	d	~5 min
Acetone	VS	d	~1 hr
Carbon tetrachloride	S	d	~2-3 hr
Dioxane	S	d	~1 min
Benzene	VS	d	~12 hr

^a Elemental analysis on the sample after four successive benzene recoveries. This is not intended as proof of composition but is to indicate the purity of the sample.

N - not soluble

SS - slightly soluble, pale purple color

VS - very soluble

S - soluble, purple in color but not opaque

d - decomposes.

disappearance of the 527 nm absorbance peak of permanganate was monitored by using a Cary 16 for slow runs and a Bausch and Lomb 505 for trials where the half-life was less than 10 minutes. All experiments were performed at 25.0° using thermostated cell compartments. In all cases blank decomposition corrections had to be made. The kinetic analyses were performed using the before mentioned pseudo first-order technique.

Product analysis was performed using a two phase system of 25 ml water containing 0.50 g potassium permanganate and 25 ml benzene containing 1.25 g of tetra(n-hexyl)ammonium iodide. To this mixture was then added approximately one gram of substrate with vigorous mixing by means of a magnetic stirrer. After the reaction had been allowed to proceed for several hours the manganese dioxide had to be destroyed by the addition of aqueous bisulfite, otherwise emulsion formation prevented ether extraction. The mixture was made basic to $\text{pH} > 10$ and extracted with three successive portions of ether to recover non-acidic products. The extracts were combined, dried over anhydrous magnesium sulfate, and evaporated to reduce the volume. The remaining aqueous solution was acidified to $\text{pH} < 3$ by the addition of sulfuric acid, saturated with sodium chloride and then extracted with three 50 ml portions of ether to recover acidic products. The basic extracts were analyzed by v.p.c. and acidic products were recovered by evaporating to dryness, after checking by v.p.c. for volatile acidic products. In all four cases the only product detected was benzoic acid, and in low yield as shown in Table 13.

Table 13. Permanganate in Benzene Oxidation Products.

Substrate	Initial wt.	Unchanged wt.	Products	Recovered wt.	% Yield ^a
Benzyl alcohol	1.0	0.65	Benzoic acid	0.15	(35%)78%
Phenylacetylene	1.0	0.60	Benzoic acid	0.10	(30%)69%
Tolan	0.30	0.12	Benzoic acid	0.15	(87%)87%
<u>trans</u> -Stilbene	1.0	0.80	Benzoic acid	0.12	(60%)87%

^a Based on total materials recovered, results in brackets based on material loss and products.

4. RESULTS AND DISCUSSION

4.1 Solvent System

4.1.1 H_R Function for the TFA-Water Solvent System

It has been previously observed that the rates of many acidic permanganate oxidations increase with increased acid content. It has been determined for some of these oxidations that plots of $\log k$ vs. H_O give unit slopes, i.e. a correlation exists between the oxidation rate and H_O .^{45,48} However, the permanganate oxidation of alkanes, arenes, alcohols, ketones, and formic acid in the medium TFA-water does not follow H_O . (A plot of $\log k_2$ vs. H_O gave slopes near five.)

Since it is established that H_R responds much faster to increased acid content than any other acidity function for a variety of acids,^{21,100,101} it was decided to determine H_R for the TFA-water solvent system to see if a possible correlation exists between H_R and $\log k_2$ (the oxidation rate).

The pK_{R+} values determined in this investigation for the indicators used to derive H_R are presented in Table 14 along with comparative values obtained in other solvent systems. It is immediately obvious that the pK_{R+} of indicator 1 differs by a small but significant amount from that reported for aqueous sulfuric and perchloric acids in a

Table 14. pK_{R+} Values for Aryl Carbinols.

Indicator ^a	CF_3CO_2H-	$HClO_4-$	H_2SO_4-	H_2SO_4-	
	H_2O	$H_2O,^{100}$	$CH_3CO_2H^{87}$	H_2O	H_2O
				Ref. 100,	Ref. 102
1. 4,4',4''-Tri-methoxy TPC	+0.92	+0.82	-	+0.82	+0.82
2. 4,4'-Dimethoxy-4''-methyl TPC	-0.28	-	-	-	-
3. 4,4'-Dimethoxy TPC	-0.97 ^b	-1.14	-	-1.24	-0.89
4. 4,4',4''-Tri-methyl TPC	-2.81	-	-	-3.56 ³	-
5. 4-Methoxy TPC	-3.18	-3.59	-3.23	-3.40	-3.20
6. 4,4'-Dimethyl TPC	-3.78	-	-4.39	-	-
7. 4,4'-Dimethoxy DPC ^c	-5.77	-	-	-5.71	-5.66
8. Triphenyl-carbinol (TPC)	-6.25	-6.89	-6.65	-6.63	-6.44
9. 4,4',4''-Tri-chloro TPC	-7.94	-8.01	-	-7.74	-7.43
10. 4-Nitro TPC	-9.58	-9.76	-	-9.15	-9.44
	CF_3CO_2H-	$HCl-$	H_2SO_4-		
	H_2O^{12}	H_2O^{103}	H_2O^{14}		
<u>p</u> -Nitroaniline	1.11	1.03	-		
<u>o</u> -Nitroaniline	-0.13	-0.29	-0.25		
4-Chloro-2-nitroaniline	-0.94	-1.03	-0.97		

^a TPC - triphenylcarbinol; DPC - diphenylcarbinol.

^b 4,4'-Dimethoxytriphenylmethyl chloride used.

^c Comparative values are for 4,4'-dimethoxy DPC.

region of very low acid concentration where one expects to find good agreement. (Examination of Table 14 indicates that pK of indicators show some variation when the solvent system is changed.) For this reason and because of the poor overlap of indicators 1 and 3, indicator 2 was synthesized and used in the determination of H_R . With two indicators having measurable ionizations in the accessible pH region (indicators 1 and 2) it was felt that the new function would satisfactorily tie into the pH scale. Although indicator 3 is an alkyl chloride, not a carbinol, such changes are known to have no effect on the H_R function.^{21,87}

Values of H_R for the TFA-water medium are listed in Table 15 and graphically depicted in Figure 10. This H_R function was calculated from the data listed in Appendix A by the method of overlapping indicators using the equations described in Sections 1.3 and 3.8, i.e. $H_R = pK_{R^+} - \log[R^+]/[ROH]$. Figure 10 also shows the H_O and J_O' functions for TFA-water. The H_O function originally derived by Randles and Tedder¹² is extrapolated to 100% TFA (dotted line) using the value of $H_O = -3.03$ reported by Hyman and Garber.¹³ Eaborn et al.¹⁸ reported slightly different values of H_O in this region. Their results (designated by ●) passed through a maximum value. The J_O' function, depicted in Figure 10, will be discussed shortly.

When it was attempted to extend H_R past 100% TFA by the addition of trifluoroacetic anhydride it was observed that very little change occurred in the ionization of 4-nitrotriphenylcarbinol until the medium was greater than 95% anhydride (the change in absorbance was from 0.690 to 0.680). When the medium was changed from 95% to 100%

Table 15. H_R Function for TFA- H_2O .

Molarity	$-H_R$	Molarity	$-H_R$	Molarity	$-H_R$
0.068	-1.29	3.34	2.26	8.53	6.10
0.069	-1.31	3.36	2.34	8.67	6.29
0.070	-1.37	3.60	2.65	8.81	6.46
0.072	-1.29	3.85	2.87	8.87	6.31
0.130	-0.96,-1.04	3.87	2.75	9.07	6.51
0.130	-1.01,-1.04	3.88	2.92,2.89	9.17	6.72
0.140	-0.96	4.44	3.27	9.33	6.67,6.63
0.144	-0.97	4.45	3.21	9.47	6.96
0.256	-0.59	4.46	3.42	9.53	6.93
0.260	-0.66	4.73	3.50	9.57	7.20,6.86
0.261	-0.63,-0.60	4.87	3.65	9.83	7.14
0.270	-0.62	4.92	3.63	9.87	7.24
0.515	-0.05,-0.31	4.96	3.70	10.10	7.60
0.525	-0.18	5.15	3.85	10.27	7.73
0.540	-0.16	5.23	3.91	10.40	7.89
0.544	-0.18	5.42	4.08,4.06	10.53	8.13
0.770	0.23,0.02	5.44	4.03	10.57	8.51
0.796	0.12	5.48	4.06	10.60	8.30
0.800	0.26	5.70	4.30	10.80	8.47
1.08	0.35	6.00	4.36,4.50	10.83	8.60
1.29	0.51	6.07	4.61	10.93	8.67
1.33	0.58	6.47	4.82	11.00	8.77
1.61	0.78	6.48	4.84	11.07	8.91
1.81	0.96	7.07	5.12	11.10	8.99
1.85	0.98	7.10	5.07	11.23	9.13
2.11	1.12	7.28	5.31	11.37	8.96
2.32	1.34	7.47	5.47	11.67	9.30
2.34	1.34	7.57	5.43	11.93	9.78
2.84	1.80	7.79	5.63	12.20	10.09
2.86	1.75,1.75	7.80	5.64	12.43	10.38
2.86	1.82	8.03	5.80	12.63	10.63
3.10	1.71	8.07	5.85		
3.16	2.05	8.30	5.91		
3.32	2.22	8.33	6.06		

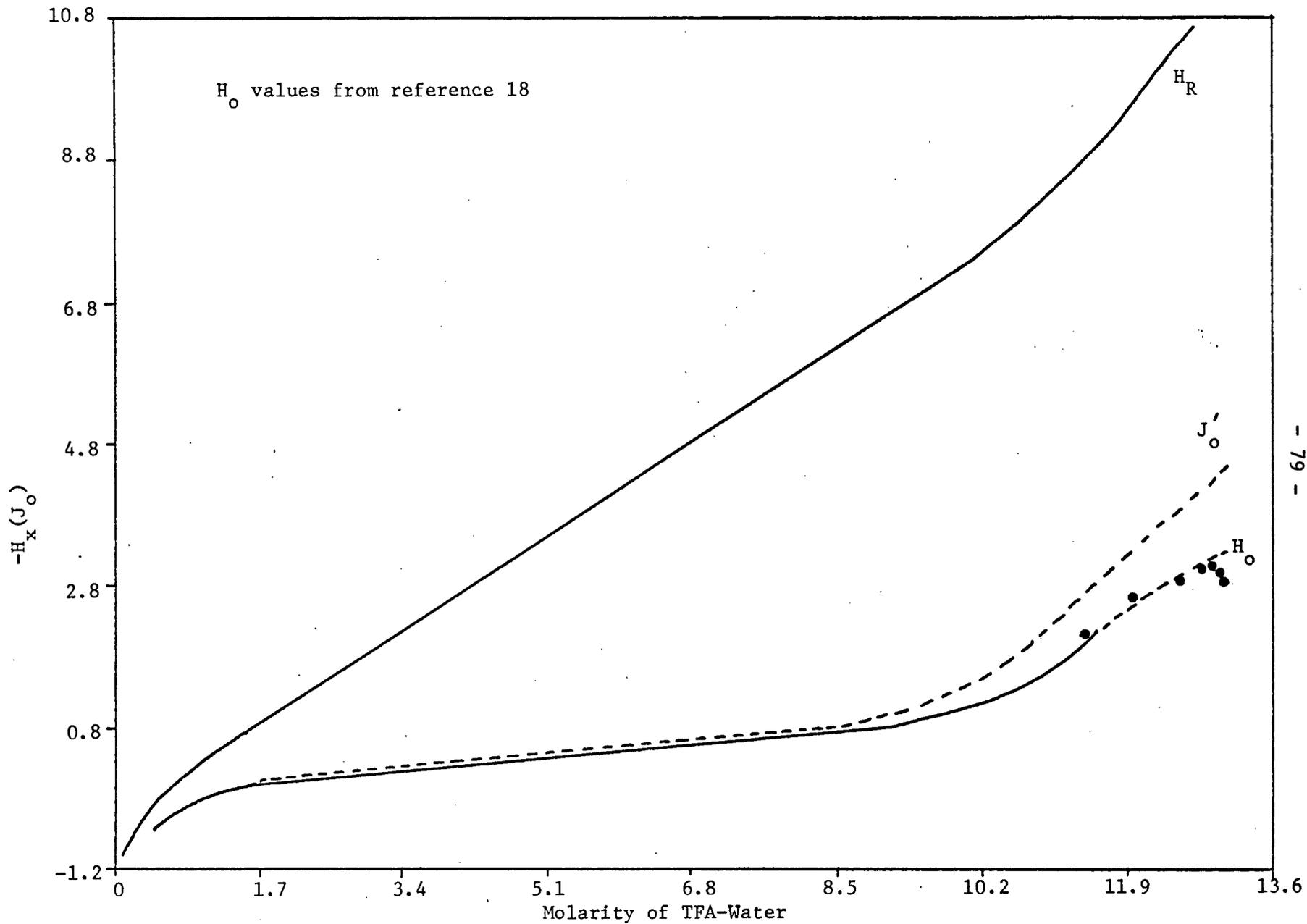


Figure 10. Acidity functions in TFA-water.

anhydride the absorbance suddenly dropped from 0.680 to 0.02. This sudden change was found to be due to reaction of the anhydride with the carbinol to give the trifluoroacetate ester. This ester was identified by N.M.R. and I.R. spectroscopy. Similar behaviour was observed when 4,4'-dimethyldiphenylcarbinol was used.

The H_R function does not appear to be very sensitive to temperature changes. The data contained in Tables 16 and 17 indicate that there is no general trend for the function but that the changes caused by temperature are indicator dependent. It seems that indicators which have substituents that interact strongly by resonance are more dissociated at higher temperatures. Similar results were reported by Arnett and Bushick.¹⁰²

When the pK_{R+} values from this study were correlated with Brown's σ^+ values¹⁰⁴ deviations were found for those indicators with resonance-interaction substituents, as is illustrated in Figure 11. When the σ^+ values derived by Deno and Evans¹⁰⁵ for tri- and diphenyl carbinols were used the deviant points fell on the extrapolated line.

These two observations on the behaviour of indicators which have resonance-interaction substituents can be explained by steric considerations. In order for these substituents to exert their full influence in stabilizing the carbonium ion the rings with the substituents must become co-planar. This results in a sterically crowded configuration. Such steric barriers are known to exist. The crystal structure of the salt depicted below has been determined and the phenyl rings were found to make angles of 26.7 to 38.0° with the planes defined by the central carbon atoms and their bonded neighbours.¹⁰⁶

Table 16. Temperature Dependence of pK_R^+ .

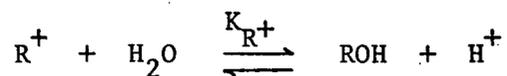
Indicator No.	14.8°	15.2°	19.6°	20.6°	25.0°	29.8°	30.7°	30.8°	35.70°	36.0°	36.8°
1	0.91			0.92	0.92	0.93					0.95
2		-0.33		-0.30	-0.28			-0.22	-0.23		
3	-1.05			-0.99	-0.97	-0.94					-0.86
4		-2.89		-2.82	-2.81			-2.75	-2.71		
5	-3.26		-3.22		-3.18		-3.15				-3.12
6	-3.83		-3.79		-3.78		-3.76				-3.74
7	-4.75		-5.76		-5.77		-5.76				-5.78
8		-6.19		-6.22	-6.25			-6.30			-6.33
9	-7.91		-7.92		-7.94		-8.00				-8.04
10		-9.58		-9.58	-9.58			-9.58	-9.62		

Table 17. Thermodynamic Parameters for the Ionization Equilibria of the Indicators Used to Determine H_R .

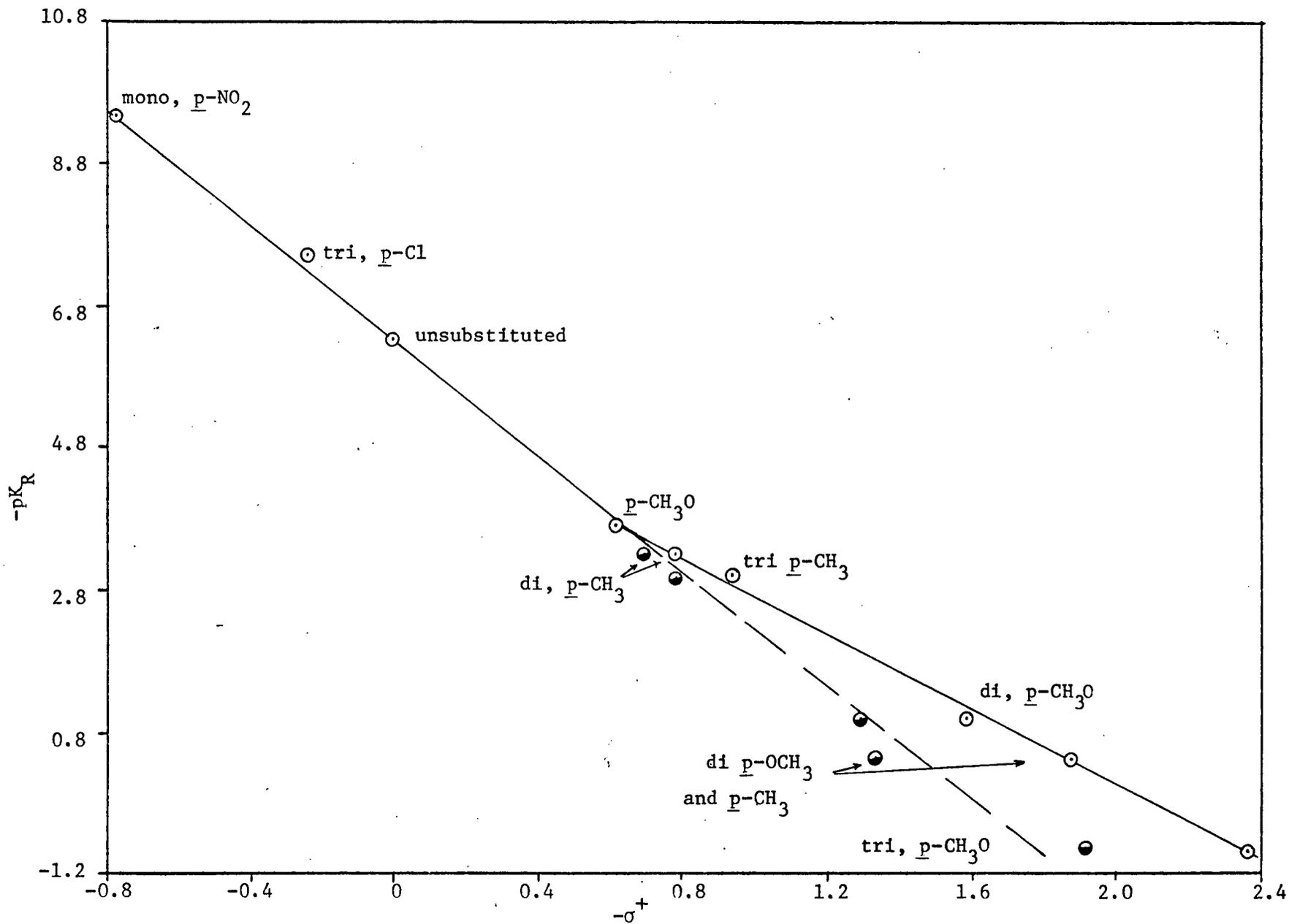
Indicator no.	ΔH°	kcal/mole	ΔS°	e.u.	r^a
	This study	Ref.102	This study	Ref.102	
1	-0.64	-2.49	-6.40	-12.10	0.850
2	-2.24	-	-6.27	-	0.960
3	-3.42	-5.68	-7.07	-14.95	0.980
4	-3.44	-	-1.28	-	0.980
5	-2.59	-6.48	5.91	-7.10	0.999
6	-1.56	-	12.1	-	0.999
7	+0.44	-	27.8	-	0.800
8	+2.24	-3.41	37.8	18.0	0.973
9	+2.53	-2.49	44.9	25.6	0.955
10	+0.61	+0.87	45.9	46.1	0.560

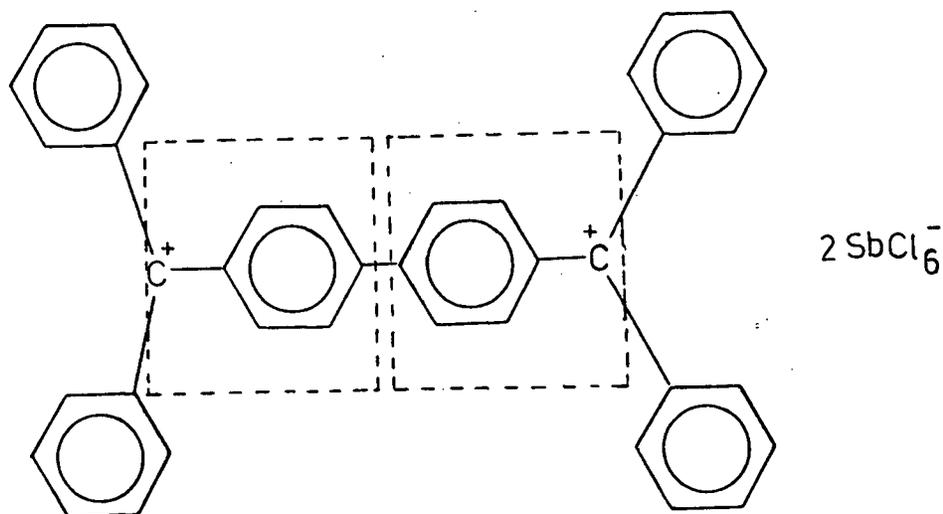
^a r, the correlation coefficient is for this study. ΔH and ΔS were calculated from the equation,

$$\log K_{R^+} = \frac{1}{T} \frac{\Delta H}{2.303R} - \frac{\Delta S}{2.303R}, \quad R = \text{gas constant}$$



$$K_{R^+} = \frac{[ROH][H^+]}{[R^+][H_2O]}$$





Furthermore, triphenylmethyl cations have been shown to exist in a propeller-like configuration in solutions.^{83,107} This steric barrier accounts for the necessity of using smaller σ^+ values to correlate with the pK_{R^+} values and for the observation that such carbinols are more ionized at higher temperatures.

The most important feature of Figure 10 is the large difference between H_o and H_R , larger in fact than that observed for any other acidic medium previously studied. Most inorganic acids have relatively small values of dH_R/dH_o (< 2) compared to that observed for TFA-water (> 5). Only one previous investigation, by Stewart and Mathews,¹⁰¹ showed a similar trend. The formic acid-water system was found to have $dH_R/dH_o > 3$.

Possibly two factors can account for the differences between H_o and H_R . It can be shown that $H_R = H_o + \log a_{H_2O} + \log f_{B^+R^+}/f_{BH^+ROH}$ (derived from $H_o = -\log a_{H^+B^+}/f_{BH^+}$ and $H_R = -\log a_{H^+f_{ROH}}/a_{H_2O f_{R^+}}$). One of the contributing factors can thus be the activity of water. The data presented in Table 18 shows that the change in water activity in TFA-water solutions is actually smaller than those observed for inorganic

Table 18. Activity of Water in Various Media.

Acid molarity	$-\log a_{\text{H}_2\text{O}}$		
	$\text{CF}_3\text{CO}_2\text{H}^{\text{a}}$	HCl ¹⁰⁹	H_2SO_4 ¹⁰⁹
0.5	-	0.008	0.008
1.0	0.005	0.017	0.018
1.5	0.007	0.027	0.030
2.0	0.012	0.039	0.043
2.5	0.015	0.053	0.063
3.0	0.017	0.070	0.085
3.5	0.019	0.087	0.111
4.0	0.020	0.107	0.142
4.5	0.023	0.130	0.176
5.0	0.026	0.155	0.219
5.5	0.031	0.181	0.267
6.0	0.036	0.211	0.320
6.5	0.039	0.244	0.377
7.0	0.042	0.279	0.439
7.5	0.053	0.318	0.510
8.0	0.061	0.358	0.587
8.5	0.074	0.399	0.670
9.0	0.095	0.444	0.761
9.5	0.125	0.490	0.859
10.0	0.191	0.539	0.968
10.5	0.320	0.591	1.082
11.0	0.500		
11.5	0.800		
12.0	0.886		
12.5	0.770		

^a These values were approximated by the method discussed in Section 3.9.

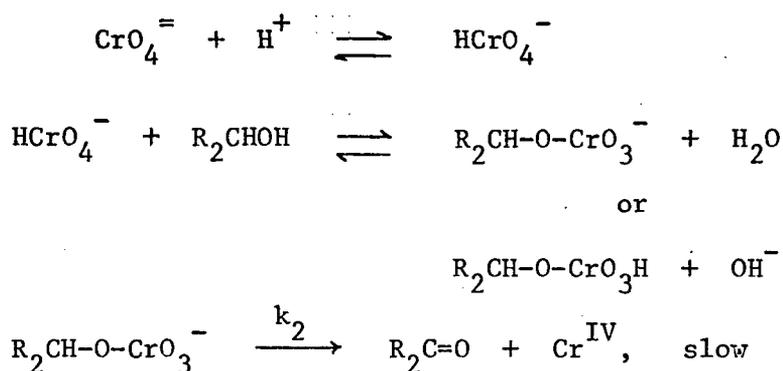
acids. Thus it is not surprising that J_o' , which is defined as $J_o' = H_o + \log a_{H_2O}$, does not approximate H_R (refer to Figure 10). The large value of dH_R/dH_o for TFA-water must then be chiefly due to changes in activity coefficients as the medium increases in acid content.

Some activity coefficients have been determined in sulfuric acid-water mixtures by Boyd¹⁰⁸ and these allow one to estimate the value of $\log f_{B^+}f_{R^+}/f_{BH^+}f_{ROH}$. The value of this term changes from -0.39 in 9.62% sulfuric acid to -3.71 in 50.5% sulfuric acid whereas $\log a_{H_2O}$ changes only from -0.03 to -0.3 over the same sulfuric acid range. Clearly, in sulfuric acid-water systems the differences between H_o and H_R are largely accounted for by the changes in the activity coefficients of the indicators.

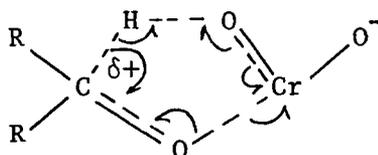
In TFA-water the changes in the activity terms must also account for the difference between H_o and H_R since the change in $\log a_{H_2O}$ that occurs is too small to account for differences that range from -0.08 to -8.0. Although no activity coefficient data for solutes other than water are available for TFA systems some of the solvent properties of TFA-water mixtures are consistent with the logarithms of the activity coefficient quotient $(f_{B^+}f_{R^+}/f_{BH^+}f_{ROH})$ becoming increasingly negative as the TFA content increases. It is known that TFA supports ionization yet is not nucleophilic^{6,110,111} and further, it has been reported that TFA can stabilize carbonium ion intermediates.^{18,19}

It has been demonstrated for sulfuric acid-water mixtures that reactions which involve a positively charged transition state as a result of formal hydroxide ion loss from a neutral molecule correlate well with H_R , giving close to unit slopes for $\log k$ vs. H_R plots.^{21,72,112,113}

One might expect similar correlations for such reactions in TFA-water. Only one data set is available in the literature to test this possibility. Lee and Johnson examined the chromic acid oxidation of 2-propanol in TFA-water mixtures.¹⁰ Figure 12 shows how their data correlate with H_0 and H_R . The plot of $\log k_2$ against H_R has almost unit slope up to the region where the reaction rates show irregularities because of changes in the identity of the oxidant.¹⁰ The oxidation is proposed to proceed by the following scheme,



A cyclic transition state as depicted below can be visualized where positive charge develops on the α -carbon atom.



4.1.2 Identification of the Manganese(VII) Species Generated in TFA-Water Mixtures

Before any mechanism can be established it is first necessary to identify the reactants. In this investigation only two substrate types

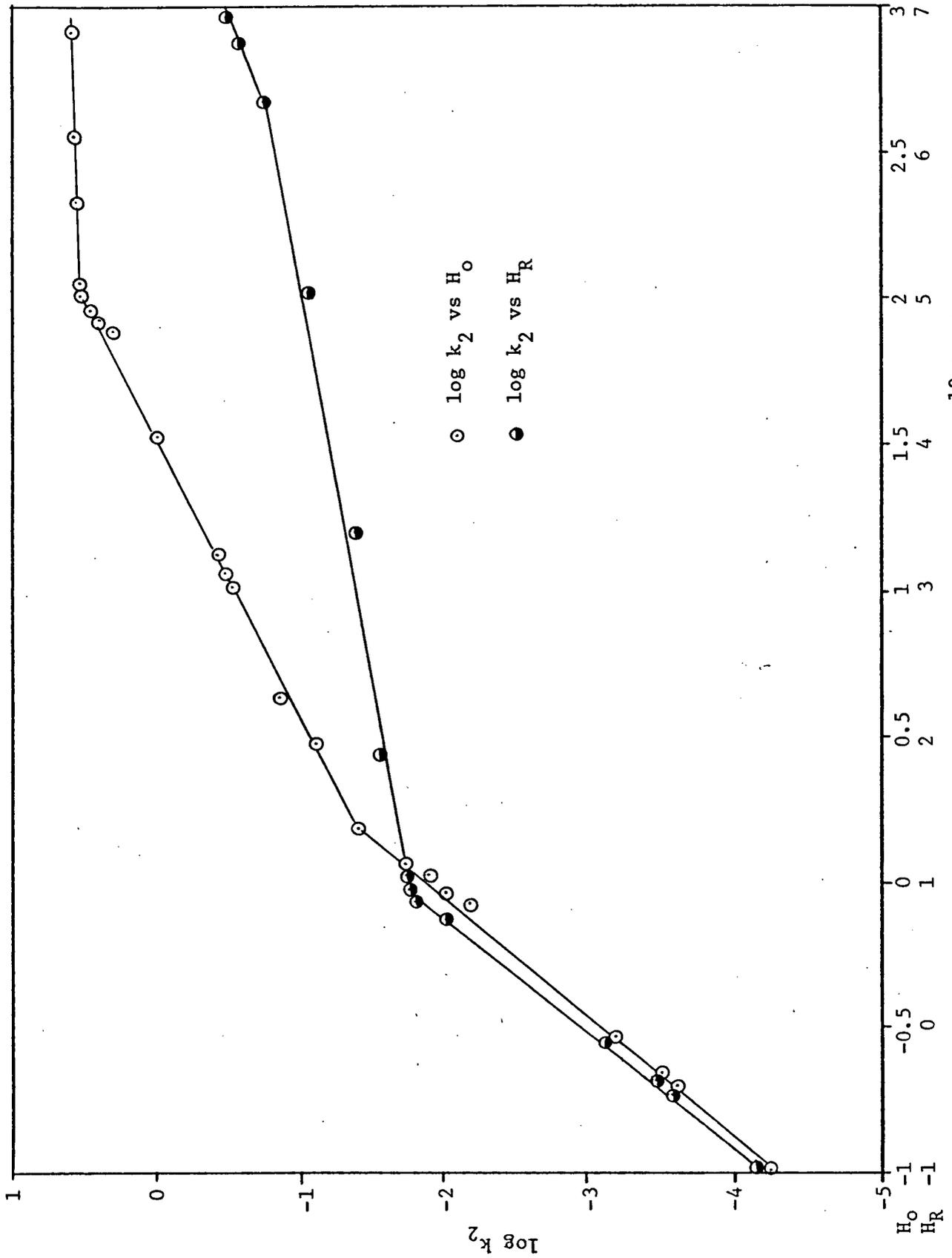


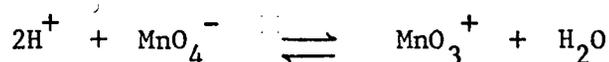
Figure 12. Chromic acid oxidation of 2-propanol in TFA-water¹⁰ $\log k_2$ vs H_0 and H_R .

appear to undergo pre-oxidative changes which affect their reactivity.

Ketones are subject to enolization and alcohols can be esterified.

It is very unlikely that any of the other substrates (alkanes, arenes, and acids) are subject to reactions with the TFA-water medium since the acidity, as determined by H_0 , is low even for neat TFA where the maximum value of H_0 is -3.03 .¹³ This is insufficient to protonate even alcohols or ketones since ethanol is only half protonated at $H_0 = -5.9$,¹¹⁴ 3-pentanone at -7.6 ,¹¹⁵ and acetophenone at -6.5 .¹¹⁶

The oxidant, permanganate ion, is known to undergo a color change from purple to light green when the medium becomes concentrated in acid.²⁷ The nature of this color change is not yet clearly understood. It has been attributed to the formation of permanganic acid in both aqueous perchloric acid²⁸ and aqueous sulfuric acid,²⁹ but at higher acidities the colored species has been assigned to permanganyl cation, MnO_3^+ by Royer,²⁶ and to O_3MnOSO_3H by Symons and Mishra.²⁵ There is at present no agreement about the identity of this green manganese(VII) species. One then has the choice of three species which could account for the reversible color change.

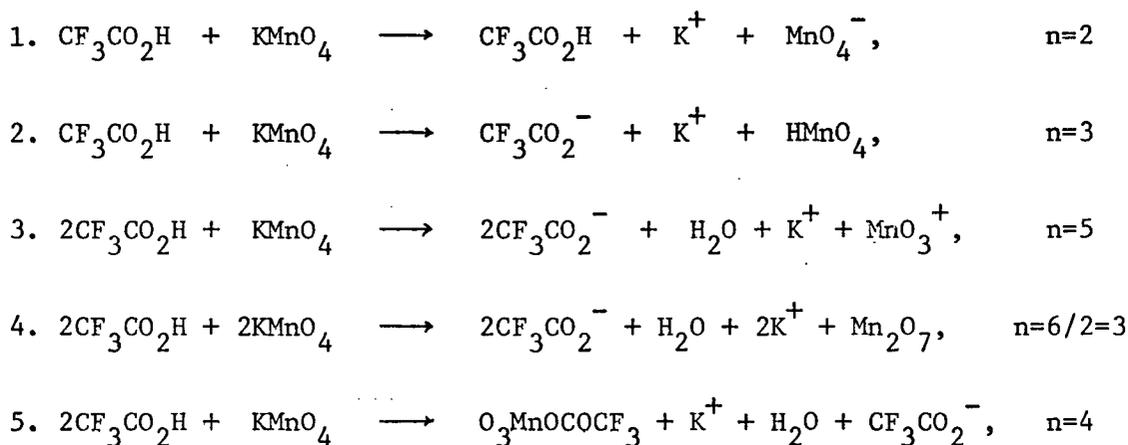


It was observed that the green species generated in neat TFA was

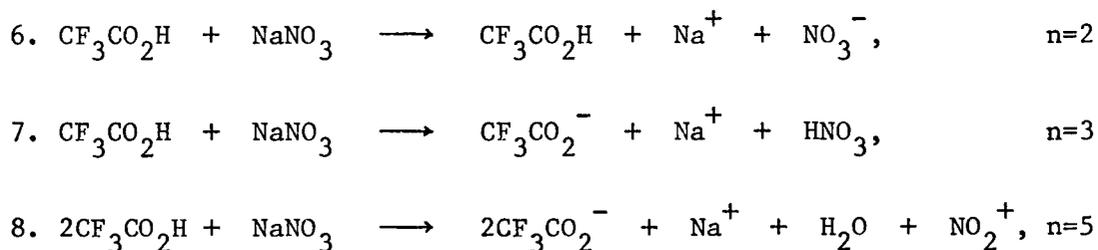
spectrally identical to that generated in sulfuric acid²⁵ and perchloric acid.²⁸ Since its identity has not been established and since it could be the active oxidant it was decided to apply cryoscopic measurements to attempt to resolve this problem. The cryoscopic data previously listed in Tables 6 and 7 are illustrated in Figures 13 and 14.

Since TFA is a mono-protic acid the selection of possible reaction schemes is simplified, and they are outlined below.

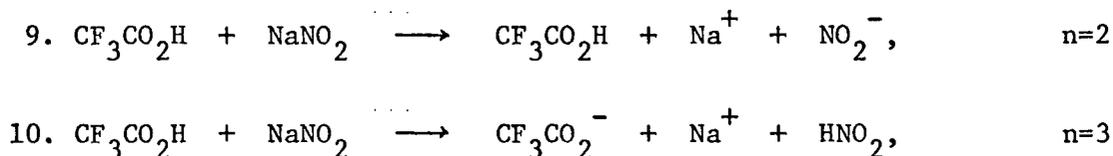
(a) Potassium Permanganate.



(b) Sodium Nitrate



(c) Sodium Nitrite



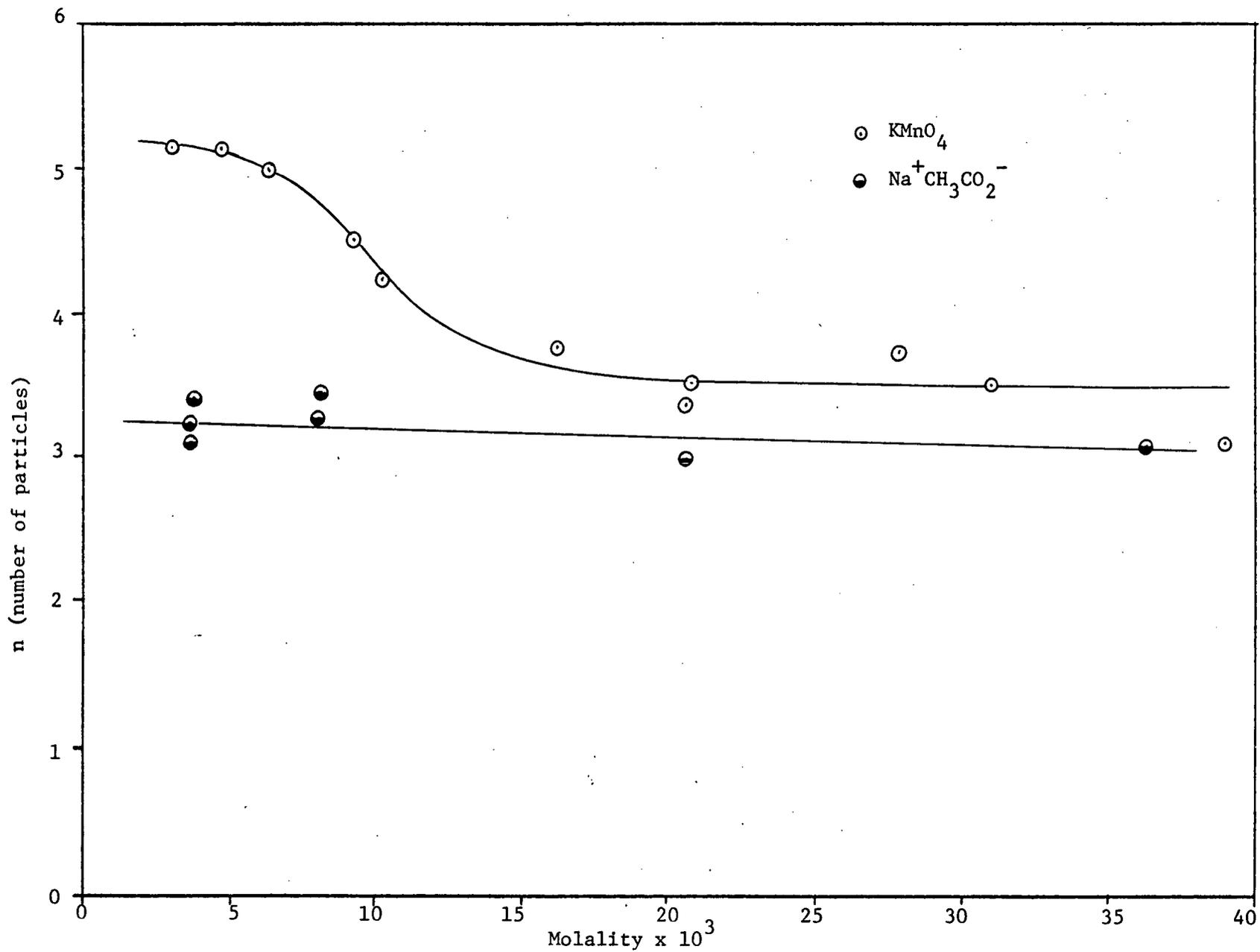


Figure 13. Particulation of potassium permanganate and sodium acetate in TFA.

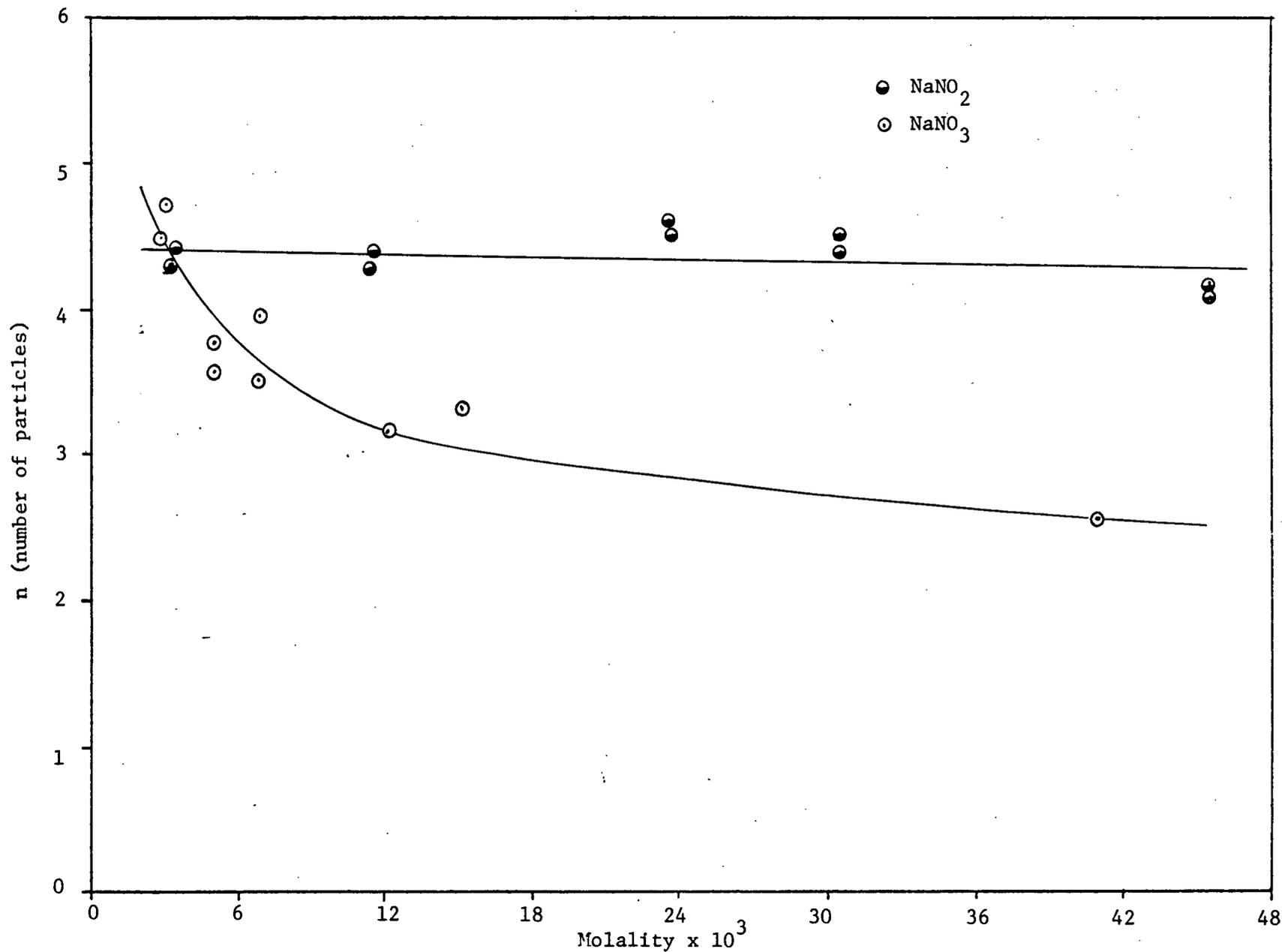
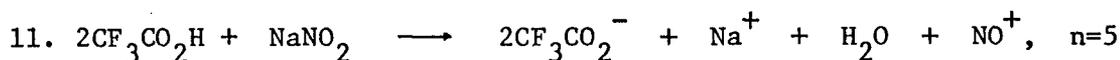
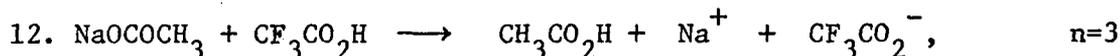


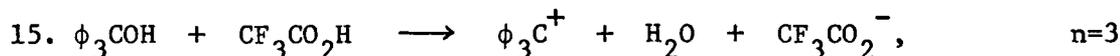
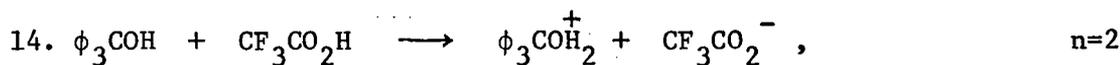
Figure 14. Particulation of sodium nitrate and sodium nitrite in TFA.



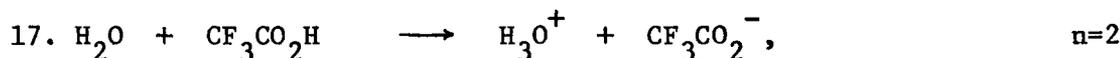
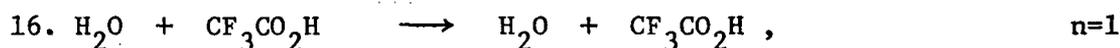
(d) Sodium Acetate



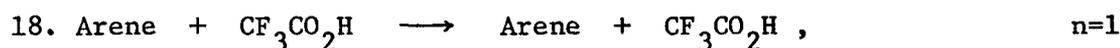
(e) Triphenylcarbinol



(f) Water



(g) Benzene or Toluene



(n refers to the number of particles formed when the above reactions proceed completely to the right. Experimentally n for water has a value close to 1.2 indicating partial protonation, see Table 7).

The various reaction possibilities for permanganate have different values of n. The experimental determination of n=5 suggests that MnO_3^+ is generated in TFA (reaction 3). However, it remains to be shown that known processes analogous to reaction 3 do indeed give experimental values of n close to five. The generation of nitronium ion and nitrosonium ion via schemes 8 and 11 are two such analogous reactions.

From the observation that benzene and toluene are readily nitrated by solutions of sodium nitrate in neat TFA (see Table 4) and from the results reported by Brown and Wirkkala¹¹ on aromatic nitration in TFA it seems certain that nitronium ions are, in fact, generated in TFA. The data contained in Table 7 and Figure 14 show that n varies from 2.5 to 4.7, indicating that nitronium ion becomes the major component of the equilibrium mixture at low concentrations of sodium nitrate. It is unlikely that any measurable amounts of nitric acid would be generated since it is a much stronger acid than TFA. (The H_0 value of 100% nitric acid is -6.3 ¹¹⁷ compared to -3.03 for TFA.) The decrease of n as the concentration of sodium nitrate increases is possible due to simple dissociation via scheme 6.

When sodium nitrite was dissolved in TFA nitrosonium ions were detected by an absorption at $\lambda_{\max} = 260$ nm, $\epsilon_{\max} = 2,200$. The reported spectrum of nitrosonium ion in perchloric acid has $\lambda_{\max} = 260$ nm, $\epsilon_{\max} = 4,200$.¹¹⁸ The extinction coefficient recorded in neat TFA suggested that the process for the generation of nitrosonium ion was 60% complete. This predicts that n should be 3.9 if the other process is simple ionization or that n should be 4.3 if the other process is generation of nitrous acid. The experimental values ranged from 4.1 to 4.6 (see Table 7 and Figure 14). These results suggest that the cryoscopic method can be used to test which ionization process is occurring since the agreement between the spectroscopic and cryoscopic results is excellent.

The experimental values of n for potassium permanganate varied from 3.0 to 5.1 depending upon the concentrations used. Royer²⁶ also

reported similar variations of n . The values of n near five at concentrations less than 6×10^{-3} molal (9×10^{-3} molar) are consistent only with scheme 3. The reaction shown by scheme 5, ester formation, is not consistent with the experimental data nor with evidence from analogous systems. At higher concentrations of permanganate the value of n can be consistent with either scheme 2 or 4, but at present it is not possible to distinguish between them.

The changes recorded in n with concentration changes are not due to variations in K_f . The value of K_f for TFA, which was determined by using benzene as a solute with an assumed value of $n = 1$, was verified over the entire concentration range used by using toluene and sodium acetate as solutes. The data in Table 6 show only small deviations from theoretical values.

It can be concluded that in TFA the green species generated from permanganate is permanganyl ion (MnO_3^+) when concentrations of permanganate are less than 9×10^{-3} molar. No other reaction scheme can accommodate the cryoscopic data.

It was found that permanganyl ion could be reversibly generated from permanganate by varying the acid content of TFA-water mixtures. The pK values for this process in a variety of solvents and at a variety of temperatures are listed in Table 19. As was shown in Section 3.10 the ionization correlated best with H_0 . The pK of -2.12 is very similar to that reported for perchloric acid-water solutions, where $pK = -2.25$.²⁸ It should also be noted that if a deuterated system is used that the ionization is half completed at lower acid concentrations.

It can be concluded that three manganese(VII) species are generated

Table 19. pK^a for the Ionization of Permanganate Ion to Permanganyl Ion.

Solvent System ^b	H_R units			H_O units		
	-pK	Slope ^c	r	-pK	Slope ^c	r
CF ₃ CO ₂ H-H ₂ O, set #1	9.35	0.77	0.985	2.13	1.31	0.995
CF ₃ CO ₂ H-H ₂ O, set #2	9.26	0.69	0.978	2.10	1.27	0.994
CF ₃ CO ₂ H-D ₂ O	9.24	0.75	0.974	2.09	1.35	0.997
CF ₃ CO ₂ D-D ₂ O	8.97	0.59	0.982	1.90	1.10	0.995
CF ₃ CO ₂ H-H ₂ O, 14.6°	9.52	0.68	0.991	2.23	1.12	0.995
" " , 20.0°	9.52	0.67	0.994	2.23	1.10	0.994
" " , 25.0°	9.49	0.71	0.997	2.21	1.17	0.997
" " , 30.5°	9.47	0.72	0.997	2.20	1.17	0.997
" " , 35.3°	9.39	0.69	0.985	2.14	1.13	0.986

^a pK is defined for the reaction, $MnO_4^- + 2H^+ \xrightleftharpoons{K} MnO_3^+ + H_2O$

and was experimentally determined by the following equation,

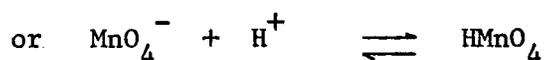
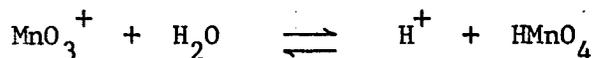
$$pK = H_O \text{ (or } H_R) - \log[MnO_4^-]/[MnO_3^+].$$

^b The compounds used to make up the solutions. The original data is listed in Table 10.

Note: The H_O or H_R values were assigned by determining the acid content by titration. It was assumed that $D_O = H_O$ and $D_R = H_R$ since it is known that H_O and D_O are identical for 0.6 to 12.0 molar sulfuric acid solutions¹¹⁹ and that H_R is identical to D_R in all sulfuric acid solutions.¹²⁰ The same molar acid solutions, however, are more ionizing when deuterium is substituted for hydrogen.^{119,120}

^c Slope of $\log Q$ vs. H_O or H_X . See Table 10 and Figures 5 to 8.

in TFA-water solutions and that their proportions depend upon the amount of TFA. They are; permanganate ion (MnO_4^-), confirmed by its characteristic spectrum, permanganyl ion (MnO_3^+), confirmed by the cryoscopic data, and permanganic acid (HMnO_4), possibly present in small amounts as a result of the following equilibria.



4.1.3 Nitration and Nitrosation in TFA

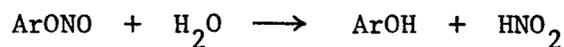
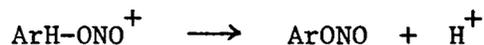
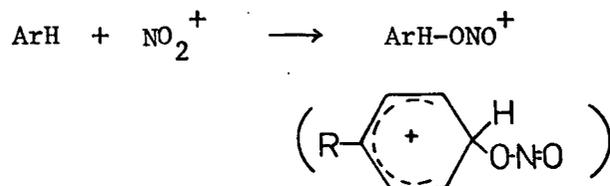
It was found that neat TFA could be used to generate nitrosonium and nitronium ions respectively from sodium nitrite and sodium nitrate. The nitronium ions thus generated were used to achieve aromatic nitrations in excellent yields as the data in Table 4 illustrate. The distribution of products from the nitration of toluene was found to be 31.7% para, 67.0% ortho and 1.3% meta, quite similar to the results of Brown and Wirkkala¹¹ who found 35.8% para, 61.6% ortho and 2.6% meta.

Nitrosations were not successful. Evidently the nitrosonium ion is too weak an electrophile to attack benzene or toluene. It was observed that when the organic substrate was added to TFA solutions of sodium nitrite a very dark solution resulted which could be decomposed by the addition of water to regenerate the substrates. It has been previously reported that such complex formation readily occurs between nitrosonium ions and aromatic rings without further reaction occurring.¹²¹

It was suspected that some phenolic products were formed during

the nitration of toluene and benzene (see Table 4). Figures 15 and 16 show the spectral similarities of the suspected phenols with that of known phenols. Unfortunately the yield of the phenolic products was too minute to allow positive identification. There is one report in the literature of phenols being isolated in trace amounts as byproducts from the nitration of toluene⁷⁹ and it is known that nitrophenols can be obtained in up to 85% yield from the oxynitration of benzene, a process which makes use of mercuric nitrate dissolved in concentrated nitric acid.¹²²

It is proposed that the phenols formed in small amounts in this investigation result from attack by the oxygen end of the nitronium ion via the following scheme.



4.2 Products and Stoichiometries

The organic products from the permanganate oxidation of a variety of substrates in TFA-water are in most cases carboxylic acids.

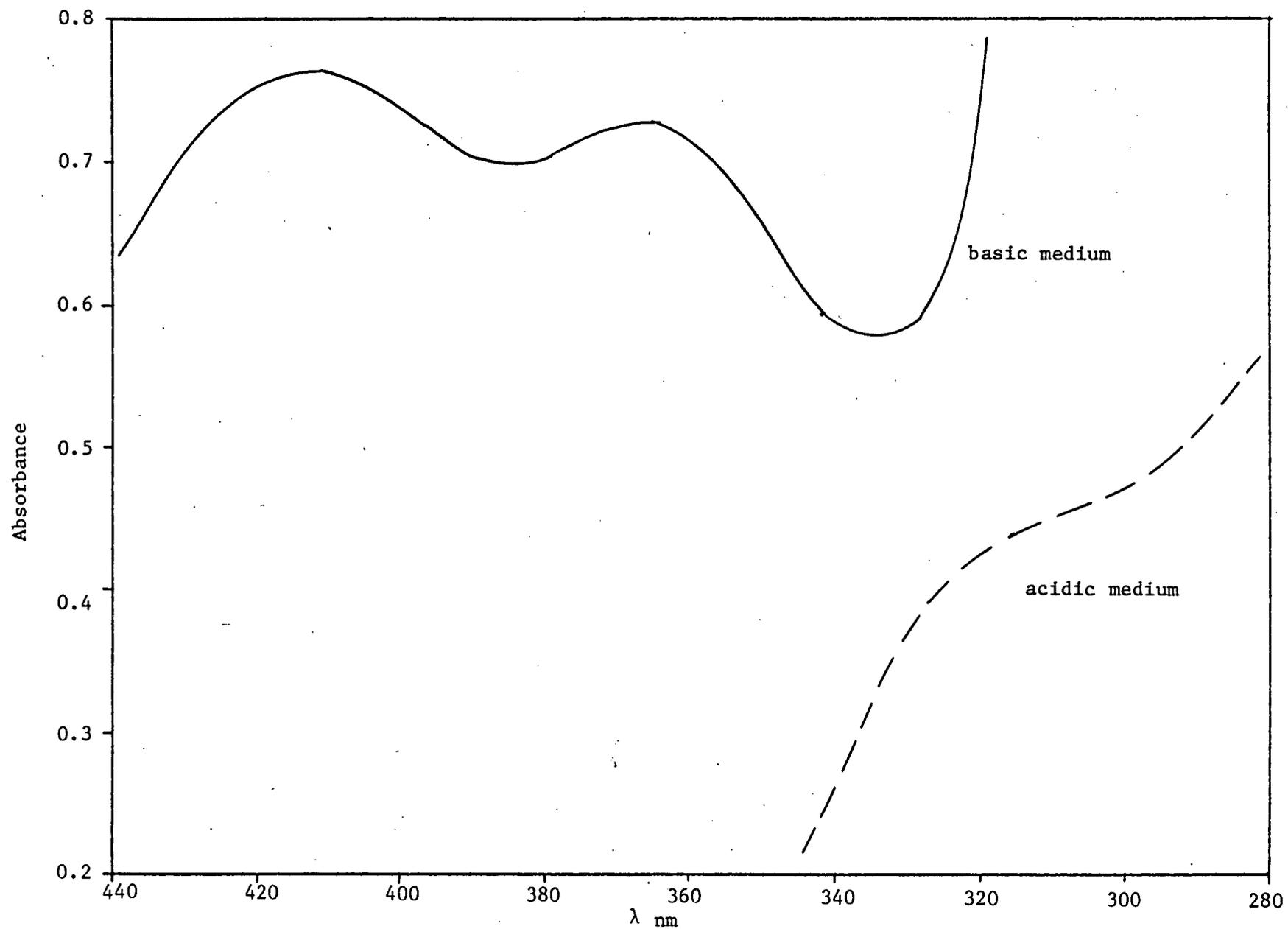


Figure 15. Spectra of side products (from the nitration of benzene) in acidic and basic media.

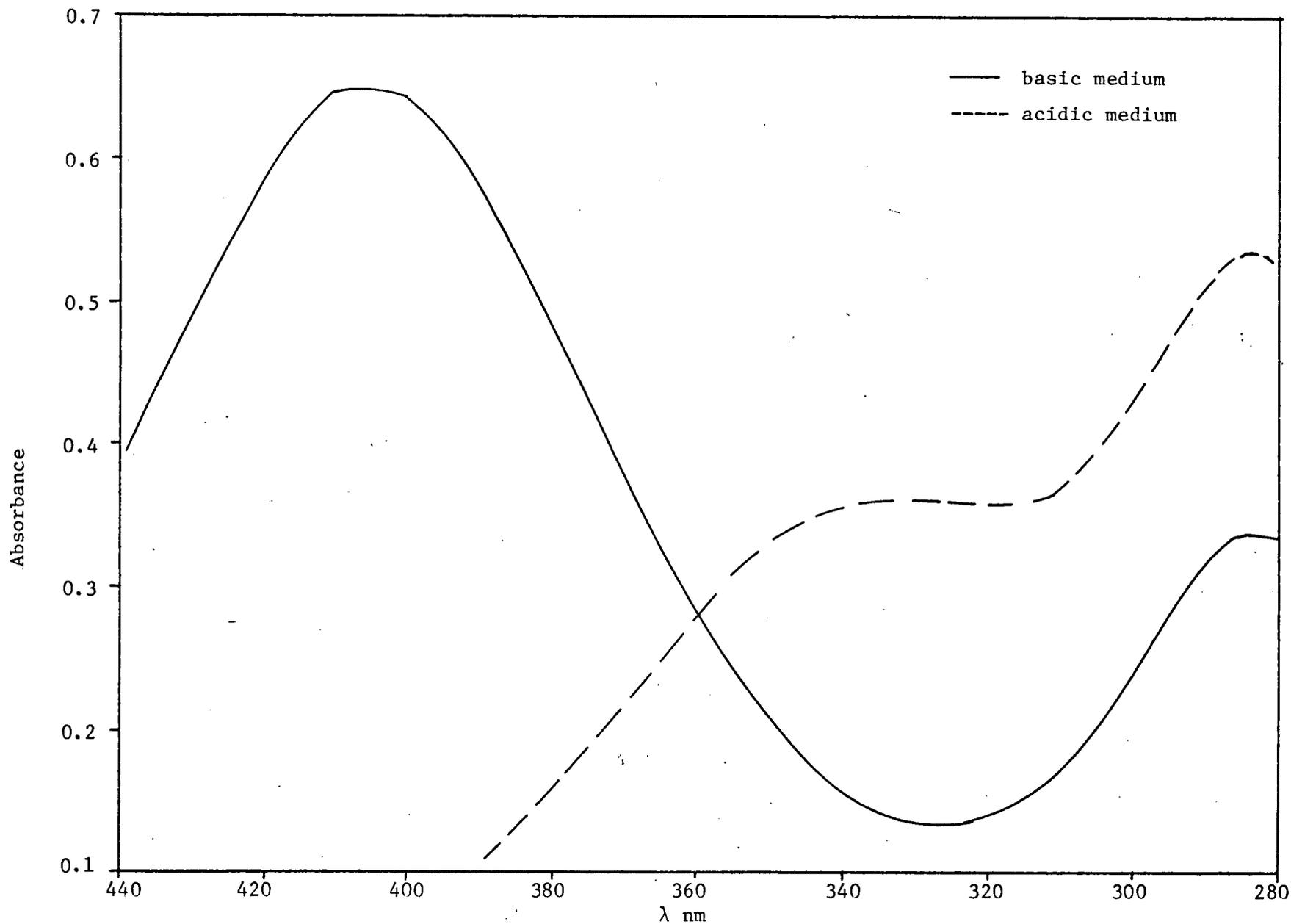


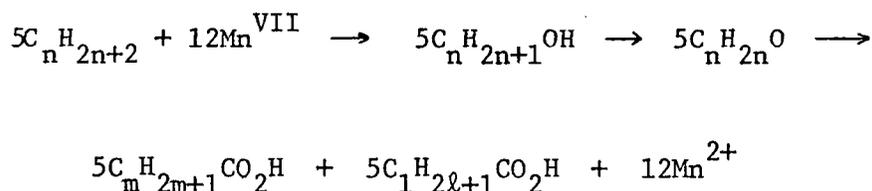
Figure 16. Spectra of 1:1 mixture of ortho and para-nitrophenol in basic and acidic media.

If an aromatic ring is present extensive degradation can occur yielding, usually, no identifiable products (see Table 3). The inorganic reduction products appear to be manganese dioxide, which could be observed as a fine precipitate, and manganese(II). The respective amounts of these two products are listed in Table 20.

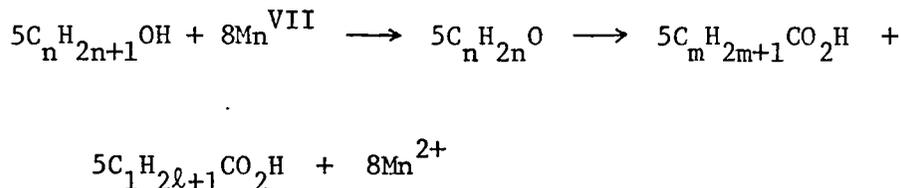
From these results the following reaction sequences can be outlined and these will be further elaborated in subsequent discussions. The sequences are outlined for a five-valent change ($Mn^{VII} \rightarrow Mn^{II}$). Another parallel series could be listed for a three-valent change ($Mn^{VII} \rightarrow Mn^{IV}$).

note: $n = m + \ell + 2$

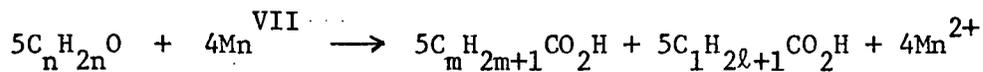
(a) Alkanes



(b) Alcohols



(c) Ketones



(d) Aldehydes



Table 20. Manganese Reduction Products from KMnO_4 Oxidations.

Reductant	% Mn^{2+}	% MnO_2	Reductant	% Mn^{2+}	% MnO_2
$H_R = -6.00$					
Toluene	98	2	Cyclopentane	57	43
Benzene	64	36	Cyclohexane	57	43
Ethylbenzene	98	2	Cycloheptane	56	44
Cumene	98	2	Cyclooctane	62	38
<i>t</i> -Butylbenzene	95	5	Cyclohexanol	57	43
Methanol	47	53	Cyclohexanone	56	44
2-Pentanol	38	62	Acetophenone	56	44
3-Pentanol	42	58	2-Pentanone	30	70
Benzyl alcohol	76	24	3-Pentanone	30	70
Benzaldehyde	73	27	Formaldehyde	49	51
1-Phenylethanol	79	21	Acetone	DNR	DNR
2-Phenylethanol	79	21			
2-Phenyl-2-propanol	80	20	$H_R = -3.5$		
			Benzyl alcohol	67	33
			Benzaldehyde	71	29
			1-Phenylethanol	63	37
			2-Phenylethanol	87	13
			2-Phenyl-2-propanol	80	20
$H_R = -8.00$					
<i>n</i> -Pentane	50	50			
<i>n</i> -Hexane	50	50			
<i>n</i> -Heptane	50	50			
<i>n</i> -Octane	49	51			
<i>n</i> -Nonane	49	51			
<i>n</i> -Decane	49	51			
<i>n</i> -Undecane	44	56			
<i>n</i> -Dodecane	42	58			
<i>n</i> -Tridecane	38	62			
Benzene	96	4			
Isopentane	74	26			

DNR - did not react sufficiently.

(e) Arenes



These outlines are all consistent with the experimentally determined stoichiometries listed in Table 5.

4.3 Oxidation of Alkanes

Initially a sulfuric acid-water medium was considered as a possible solvent system to investigate the homogeneous oxidation of alkanes by permanganate. Appendix B lists the data obtained using this solvent system. Although extreme care was taken to ensure homogeneous solutions reproducibility was poor and, worst of all, the order with respect to alkane varied from 0.7 to 2.0 with no apparent pattern. The kinetics were consistently first order with respect to permanganate but the discrepancies with respect to substrate order could not be resolved. Perhaps micelle formation is responsible for the random rate increases with increased substrate content, since micelles are known to give rise to anomalously fast rates in some cases.¹²³

The TFA-water system, on the other hand, was found to be extremely satisfactory, being capable of solubilizing all substrates examined and yet causing very little decomposition of the oxidant. All of the alkane oxidation data are listed in Appendix C, trials 129-489, 1209-1216, and 1306-1307.

The excellent correlation of the absorbance-time data for up to two half-lives of permanganate with the pseudo first-order rate

equation (see Section 3.3 for the equation) confirms a first order dependence upon permanganate (refer to correlation coefficients of the alkane trials). The data presented in Table 21 and illustrated in Figures 17 and 18 indicate that the rate law contains terms which show first-order dependence both upon alkane concentration and h_R . The complete rate law can be written as,

$$-d[\text{MnO}_4^-]/dt = k_3[\text{MnO}_4^-][\text{alkane}]h_R$$

The data presented in Table 22 shows that a large primary kinetic isotope effect is observed over a wide range of acidity. (All of the oxidation rates for deuterated compounds were corrected for the presence of some protium using the equation of Lewis and Funderbuck;¹²⁴

$$k_D = (k_{\text{obs}} - f k_H) / (1 - f).$$

f = fraction of protium present in compound

k_{obs} = observed rate for deuterated compound

k_H = observed rate for protium analogue.

These results are consistent with a transition state involving one molecule each of oxidant and alkane. The rate-determining step clearly involves carbon-hydrogen bond scission, as indicated by the large primary isotope effects. The cleavage of the carbon-hydrogen bond could involve either hydride transfer or hydrogen abstraction. The statistically corrected $1^\circ:2^\circ:3^\circ$ ratios obtained from the oxidation rates of neopentane, n-pentane, and isopentane were found to be 1:180:3,300. These ratios are comparable to results obtained for reactions which are believed to occur by hydrogen-atom abstraction.

Table 21. Order of Reactants Involved in the Permanganate^a Oxidation of Alkanes in TFA-Water.

Substrate	Order in substrate	Trials	r	Order in h _R	Trials	r
Ethane	1.1	129-134	.960	N		-
Propane	0.6	141-148	.973	N		-
<u>n</u> -Butane	1.1	149-155	.998	N		-
<u>n</u> -Pentane	1.0	163-169	.999	1.0	170-177	.995
<u>I</u> sopentane	1.0	298-304	.993	1.1	285-311	.999
	1.0	305-311	.985			-
	1.0	285-290	.994			-
Neopentane	1.1	330-336	.991	0.8	322-336 ^b	.991
Cyclopentane	1.0	341-347	.994	1.0	337-359 ^b	.999
<u>n</u> -Hexane	1.1	192-198	.994	1.0	185-223 ^b	.997
	0.9	185-191	.991			-
Cyclohexane	1.0	373-379	.997	1.1	360-435 ^b	.994
	1.0	408-423	.999			-
Cyclohexane-d ₁₂	N		-	1.1	384-405 ^c	.990
<u>n</u> -Heptane	1.1	228-233	.999	1.1	224-244 ^b	.997
Cycloheptane	1.0	438-444	.998	0.9	436-459 ^b	.999
Cyclooctane	1.1	469-475	.998	0.8	466-489 ^b	.996

Note: error in orders are \pm 5%.

^a Order with respect to permanganate was in all cases 1.00, r = 0.999.

^b Only those trials where the solvent was TFA-H₂O and T = 25.0° were used.

^c Only those trials where C₆D₁₂ was used.

N Designates order not determined.

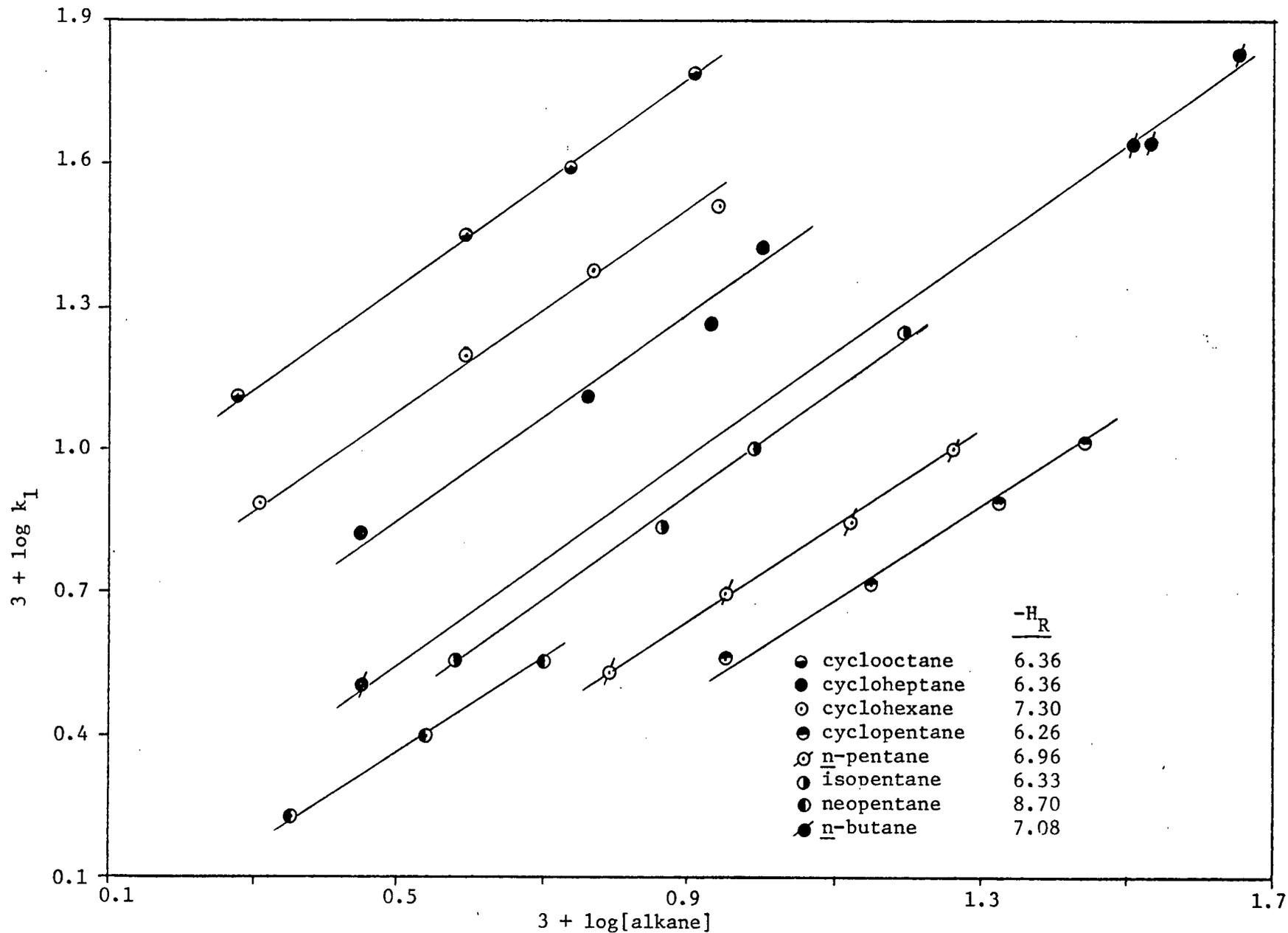


Figure 17. $\log k_1$ vs. $\log[\text{alkane}]$ for the oxidation of variety of alkanes.

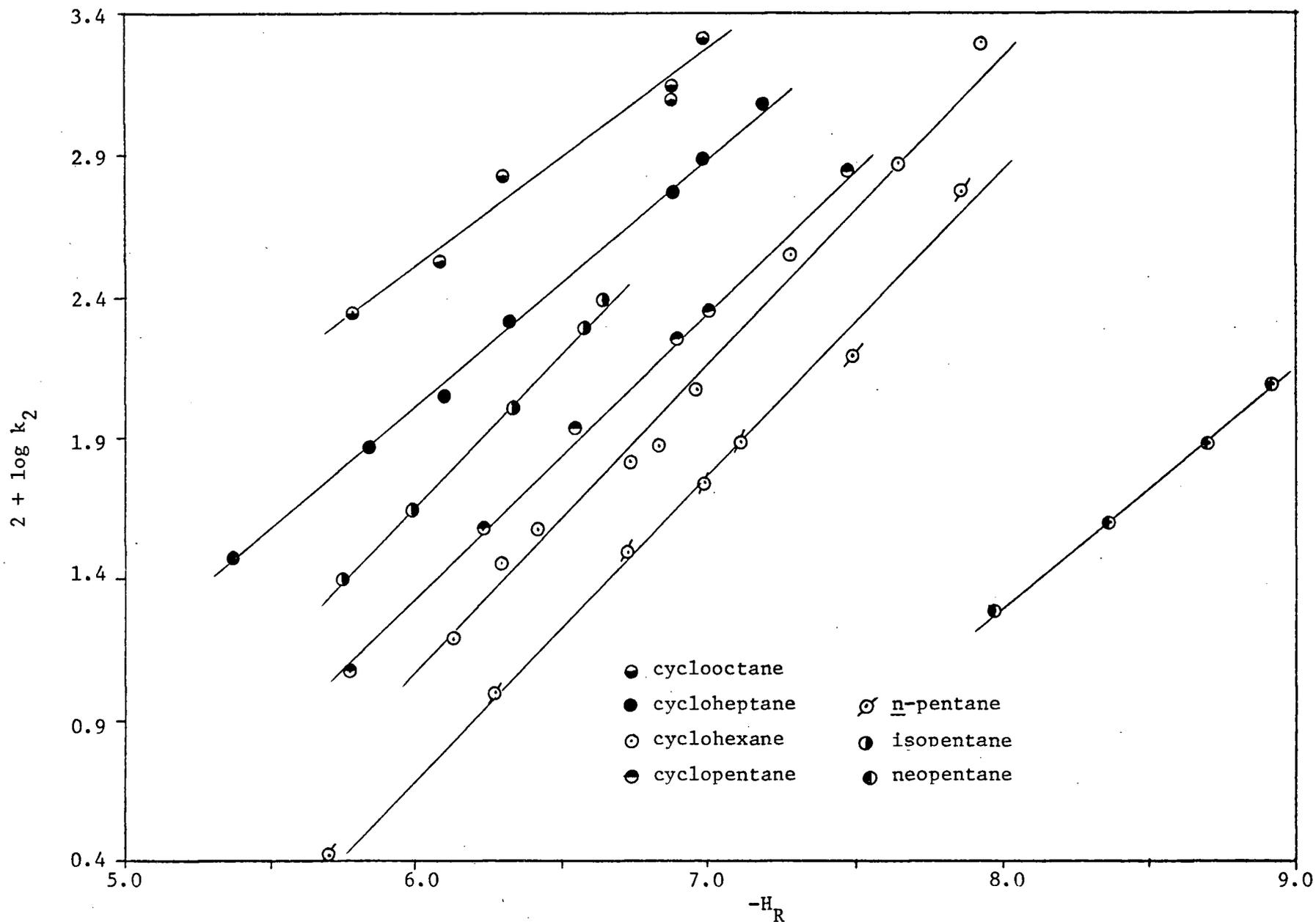


Figure 18. $\log k_2$ vs. H_R for the oxidation of a variety of alkanes.

Table 22. Kinetic Isotope Effects in the Permanganate Oxidation of Cyclohexane.

$-H_R$	$k_{C_6H_{12}}/k_{C_6D_{12}}$	$k_{C_6H_{12}}/k_{C_6D_{12}}$ (corrected) ^a
6.12	5.3	5.5
6.38	4.7	4.8
6.66	4.3	4.5
6.74	4.3	4.5
6.96	4.2	4.4
7.40	4.7	4.9
7.70	5.7	6.0
7.91	4.0	4.1

$-H_R$	k_{D_2O}/k_{H_2O} ^b
6.26 ^c	1.2
6.93 ^c	1.0
6.96 ^c	1.0
6.10 ^d	2.6
7.48 ^d	2.3

^a Corrected using the equation $k_D = (k_{obs} - f k_H)/(1-f)$, as discussed in the text.

^b For isopentane, $k_{D_2O}/k_{H_2O} = 1.2$ ($H_R = -5.95$, 76% D) and for n-hexane, $k_{D_2O}/k_{H_2O} = 1.0$ ($H_R = -6.93$, 72% D). In both cases the solvent was made up from TFA and D_2O .

^c Solvent system made from CF_3CO_2H and D_2O (74% D at $H_R = -6.26$, 72% D at $H_R = -6.93$, 71% D at $H_R = -6.96$).

^d Solvent system made from CF_3CO_2D and D_2O .

The free-radical bromination ratios for butanes are 1:82:1,600¹²⁵ and the chromic acid oxidation ratios for alkanes are 1:110:7,200,³⁴ both processes taking place by hydrogen-atom abstraction. On the other hand, the ratios for benzyl chloride solvolysis are 1:100:100,000, and this reaction is known to proceed via carbonium ions¹²⁶ (equivalent to hydride transfer in the present case). Further, the data obtained for the oxidation of cycloalkanes in this study are consistent only with processes known to involve hydrogen-atom abstraction (see Tables 23 and 24).

The effect of substituents is illustrated in Figure 19. The ρ^* of -2.4 indicates that considerable positive charge develops in the transition state. The magnitude of ρ^* is comparable to that for solvolysis reactions where carbonium ions are involved ($\rho^* \approx -3.0$ ¹²⁹), and is considerably larger than that observed for the chromic acid oxidation of aliphatic alcohols ($\rho^* = -1.06$ ¹³⁰).

The values of σ^* used for Figure 19 are those reported by Taft,¹³¹ some of which were refined by Cohen et al.¹³² The σ^* for R = $-\text{CH}_2\text{NO}_2$ was not available in the literature. It was estimated using $\sigma^* = -0.50$ for R = $-\text{CH}_2\text{CH}_2\text{NO}_2$ and a factor of 2.5 approximated from Taft's data for the attenuation effect of one methylene. This gives a $\sigma^* = -1.25$ for R = $-\text{CH}_2\text{NO}_2$.

There was no observable salt effect upon the oxidation rate, as shown by the results depicted in Figure 20.

Before proposing a mechanism which accounts for all of the before mentioned observations it remains to be determined which of the three possible oxidants are involved in the reaction; namely permanganate ion

Table 23. Comparative Reactivities of Methylene Groups in Cycloalkanes Relative to Those in the Corresponding *n*-Alkane.

Reaction ^a	Ratios ^b			
	C ₅	C ₆	C ₇	C ₈
1. (CH ₃) ₃ CO·, CCl ₄ , T = 0°	1.45	1.47	2.18	2.49
T = 49.5°	1.38	1.47	2.02	2.17
2. Br·, CH ₃ CN, T = 74.5°	1.47	0.47	3.24	8.43
T = 125°	1.31	0.75	2.79	5.56
3. CCl ₃ ·, CH ₃ CN, T = 74.5°	1.43	0.95	-	3.53
CCl ₃ · CCl ₄ , T = 74.5°	1.75	0.43	-	5.10
4. C ₆ H ₅ ·, CH ₃ CN, T = 74.5°	1.52	0.54	2.39	3.83
5. Mn ^{VII} , TFA-H ₂ O, T = 25.0°	2.61	0.75	2.8	6.4

^a Reactions 1 to 4 are hydrogen abstraction by the radical shown in the particular solvent. All the data for processes 1 to 4 are courtesy of Dr. N Bunce.¹²⁷ Reaction 5 is from this study.

^b All the ratios were calculated in the following manner;
Ratio = k(cyclic)/k(open chain)

k(cyclic) = k experimental/number of CH₂ groups in ring

k(open chain) = k experimental/number of CH₂ groups in chain.

Table 24. Comparative Reactivities of Cycloalkanes.

Reactions	Ratios ^a			
	C ₅	C ₆	C ₇	C ₈
1. CrO ₃ , 99% CH ₃ CO ₂ H, T = 60° ³³	1.98	1	6.6	22.4
2. Mn ^{VII} , TFA-H ₂ O, T = 25°	1.4	1	5.2	14.5
3. Acetolysis of tosylates, T = 70° ¹²⁸	14.0	1	25.3	191

^a Ratios are k(cycloalkane)/k(cyclohexane).

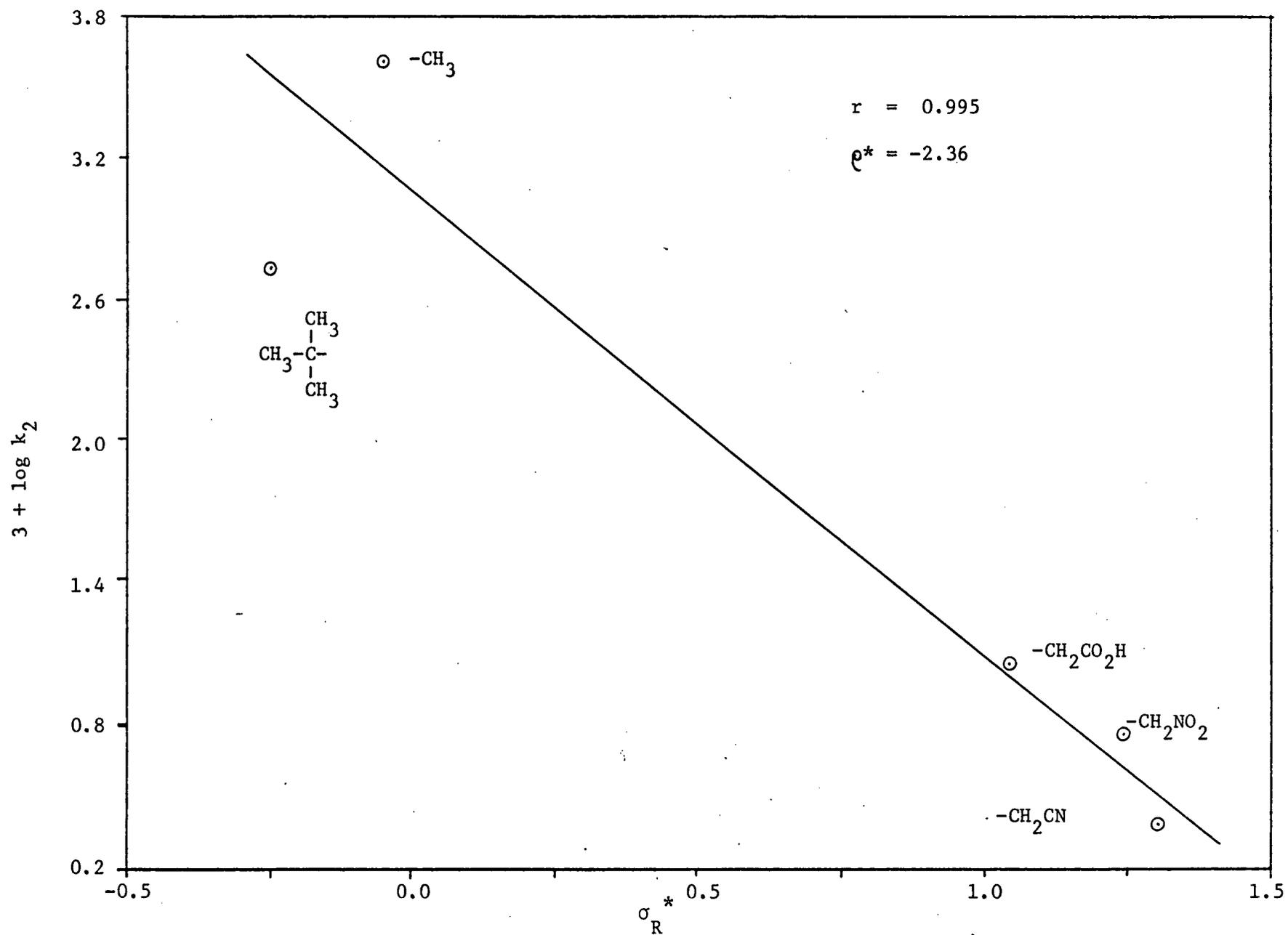


Figure 19. Substituent effects in the permanganate oxidation of ethanes $(\text{R}-\text{CH}_3) \cdot \sigma_{\text{R}}^*$ vs. $\log k_2$. [trials 129-140, 324-326].

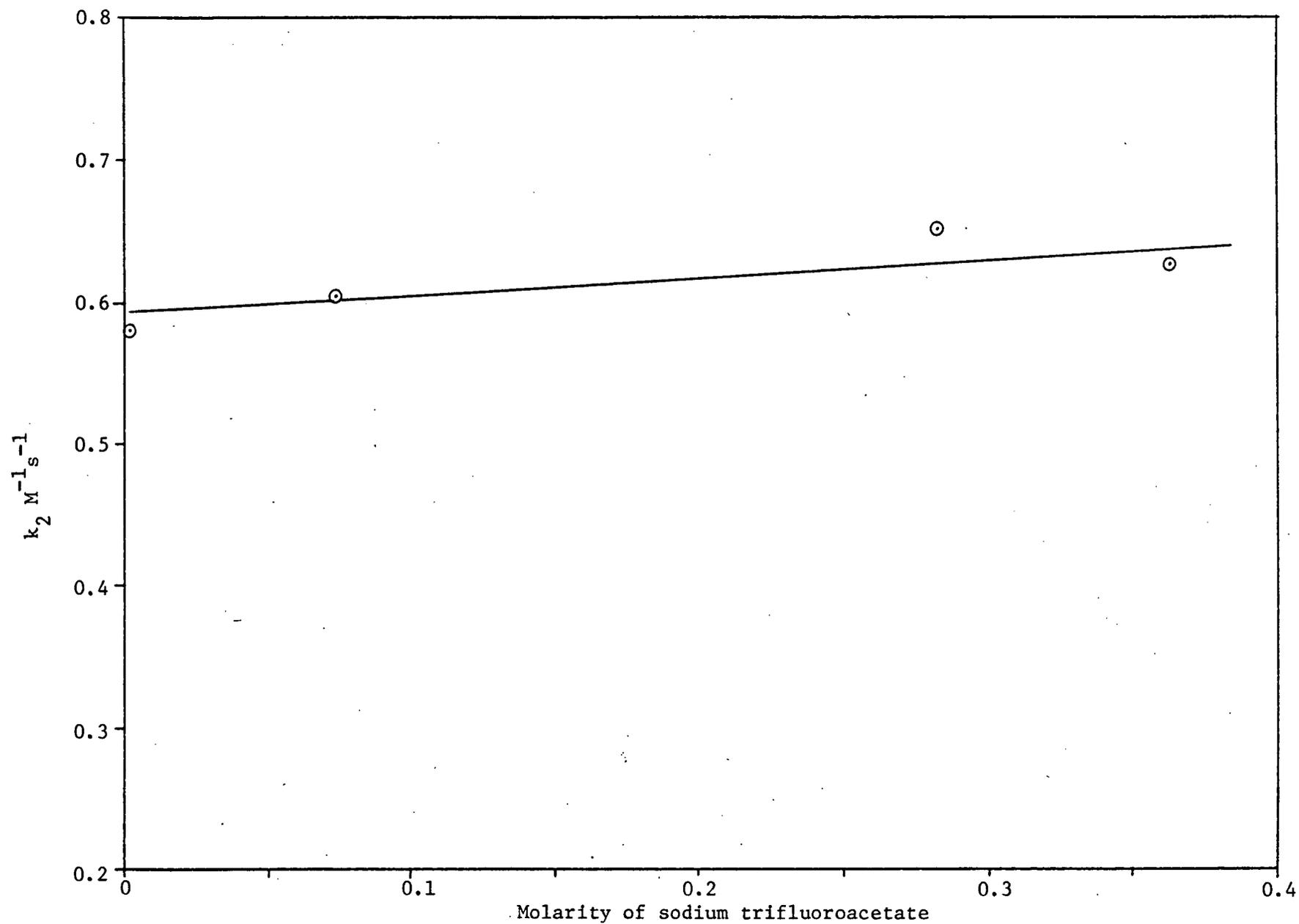


Figure 20. Salt effects on the permanganate oxidation of cycloheptane ($H_R = -5.6$, trials 460-465).

(MnO_4^-), permanganyl ion (MnO_3^+), and permanganic acid (HMnO_4).

Permanganate ion can be excluded as one of the major oxidants since in the highly aqueous region, where it is the dominant species, very little oxidation is observed. Further, if permanganate were one of the major oxidants one would not expect such large rate increases with increased acid content since the concentration of permanganate ion actually decreases as the acid content rises.

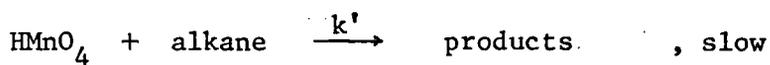
It has been demonstrated in Section 4.1.2 that the green species generated from permanganate ion at low concentrations of water in the TFA-water system is permanganyl ion (MnO_3^+). The equilibrium constant for this process showed a small isotope effect if the medium was made up from $\text{CF}_3\text{CO}_2\text{H}$ and D_2O (i.e. less than 100% D) but a large isotope effect if the medium was made up from $\text{CF}_3\text{CO}_2\text{D}$ and D_2O ($\text{pK}(\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{O}) = -2.13$, $\text{pK}(\text{CF}_3\text{CO}_2\text{H}-\text{D}_2\text{O}) = -2.09$, and $\text{pK}(\text{CF}_3\text{CO}_2\text{D}-\text{D}_2\text{O}) = -1.90$). If permanganyl ion is one of the major oxidants these solvent effects predict that if the oxidation is carried out in $\text{CF}_3\text{CO}_2\text{H}-\text{D}_2\text{O}$ that $k(\text{H}-\text{D}_2\text{O})/k(\text{H}-\text{H}_2\text{O})$ (H or D designates $\text{CF}_3\text{CO}_2\text{H}$ or $\text{CF}_3\text{CO}_2\text{D}$) should be greater than one and should increase as the D_2O content increases. Further, if $\text{CF}_3\text{CO}_2\text{D}-\text{D}_2\text{O}$ is used $k(\text{D}-\text{D}_2\text{O})/k(\text{H}-\text{H}_2\text{O})$ should be appreciably greater than one with a possible maximum value of 1.7 (analog of 0.23, the difference in pK's). Table 22 lists the solvent isotope effect observed and this trend is indeed observed. This strongly suggests that permanganyl ion is the major oxidant, which is consistent with the large negative value of ρ^* .

It is not possible to directly show the amount of oxidation due to permanganic acid. However, from the results of aldehyde and alcohol

oxidation, which are discussed in Sections 4.5 and 4.6, it appears that permanganic acid is not an effective oxidant of alkanes compared to permanganyl ion.

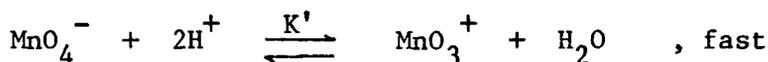
By applying the arguments presented in Section 1.8 to the observation that the alkane oxidation rate shows near unit-order dependence upon h_R it is possible to decide which of the two possible mechanisms best fits the experimental data. The two possible mechanisms, those involving permanganic acid and permanganyl cation, are:

(a) HMnO_4 as the oxidant,



$$r = Kk'[\text{MnO}_4^-][\text{alkane}]f_{\text{MnO}_4^-}f_{\text{alkane}}^{-f}a_{\text{H}^+}^{f/f_+}$$

(b) MnO_3^+ as the oxidant,



$$r = K'k''[\text{MnO}_4^-][\text{alkane}]f_{\text{MnO}_4^-}f_{\text{alkane}}^{-f}a_{\text{H}^+}^2/a_{\text{H}_2\text{O}}^{f_+}$$

The experimental rate law is $r = k_3[\text{MnO}_4^-][\text{alkane}]h_R$.

The evaluation consists of seeing which of the two sets of activity coefficients shows medium responses parallel to that shown

by h_R , i.e. the experimental fact that $\log h_R$ vs. $\log k_3$ has unit slope is tested. Normally such evaluations are not possible since the necessary activity coefficients are not known, but if four assumptions are made the evaluation can be made in this case. These assumptions are:

(i) The activity coefficients, which are only available for sulfuric acid-water systems, will be assumed to show similar changes in TFA-water solutions; (ii) The activity of the proton (a_{H^+}) will be approximated by f_{BH^+}/f_B since $a_{H^+} = h_o f_{BH^+}/f_B$ and h_o is almost constant over large concentration variations of TFA-water mixtures; (iii) A transition state containing permanganyl ion (MnO_3^+) and alkane is assumed to have solvation requirements similar to a carbonium ion whereas a transition state containing permanganic acid ($HMnO_4$) and alkane is assumed to have solvation requirements similar to a neutral molecule; (iv) It will be assumed that $f_{MnO_4^-} = f_{ClO_4^-}$ and $f_{alkane} = f_{benzene}$.

For mechanism (a) to be correct the activity quotient which should correlate with H_R is $\log f_{MnO_4^-} f_{alkane} a_{H^+}/f_{\ddagger}$ which becomes $\log f_{ClO_4^-} f_{\ddagger} f_{BH^+}/f_{\ddagger} f_B$. For mechanism (b) to be correct the activity quotient which should correlate with H_R is $\log f_{MnO_4^-} f_{alkane} a_{H^+}^2/a_{H_2O} f_{\ddagger}$ which becomes $\log f_{ClO_4^-} f_{\ddagger} f_{BH^+}^2/a_{H_2O} f_{R^+} f_B^2$. Table 25 contains all the values of the activity coefficients used and also list the values for the quotients predicted by the two mechanisms along with H_o and H_R for comparative purposes.

It can be seen that only the changes in the quotient from mechanism (b) parallel the changes in H_R , the changes of the quotient from mechanism (a) being closer to changes in H_o . (The changes observed from

Table 25. Activity Coefficients in Sulfuric Acid-Water Mixtures.

Salt or Compound		% H ₂ SO ₄ in H ₂ SO ₄ -water solution				
		9.6%	19%	29%	40%	50.5%
Triphenylcarbinol ¹⁰⁸	log f _{ROH}	0.34	0.37	0.73	0.83	0.73
Benzene ¹³³	log f _φ	0.14	0.24	0.31	0.36	0.36
2,6-Dichloro-4-nitro-aniline ¹⁰⁸	log f _B	0.03	0.07	0.03	-0.14	-0.40
Tri(p-methoxyphenyl)-carbonium ⁺ PCP ⁻ ¹⁰⁸	log f _{R⁺} ^a	0.02	0.04	-0.13	0.20	-0.32
p-Chloroanilium ⁺ PCP ⁻ ¹⁰⁸	log f _{BH⁺} ^a	0.10	0.44	0.86	1.64	2.26
Tetrabutylammonium ⁺ ClO ₄ ⁻ ¹³³	log f _{ClO₄⁻} ^b	-0.30	-0.39	-0.52	-0.80	-1.18
Functions						
log a _{H₂O} ¹⁰⁹		-0.03	-0.06	-0.12	-0.25	-0.44
-H _R ¹³⁴		0.72	1.90	3.18	4.80	6.60
log f _{ClO₄⁻} - f _φ f _{BH⁺} ² / a _{H₂O} f _{R⁺} + f _B ²		-0.01	0.61	1.77	3.17	5.26
log f _{ClO₄⁻} - f _{BH⁺} / f _B		-0.23	-0.02	0.31	0.98	1.48
-H _O ¹³⁴		0.31	1.01	1.70	2.41	3.38

PCP⁻, pentacyanopropenide.

^a The activity coefficient of the cations are relative to a standard cation, $f_+ = f'_+ / f_{S^+}^S$, S⁺ is the standard cation, tetraethylammonium ion.

^b The activity coefficients of the anion is relative to the standard cation, $f_- = f_- \cdot f_{S^+}$.

high to low acid content are, $\Delta H_R = 5.88$, $\Delta H_O = 3.07$, Δ mechanism (a) = 1.71, and Δ mechanism (b) = 5.27.)

This evaluation, although made with some assumptions, shows that only the mechanism involving permanganyl ion is consistent with the experimentally observed acid catalysis.

The activation parameters listed in Table 26 are comparable to those reported for a wide variety of permanganate oxidations ($\Delta H^\ddagger = 5$ to 16 kcal/mole, $\Delta S^\ddagger = -15$ to -38 e.u.¹³⁵). There appears to be a general trend in this data. As the TFA content increases (larger negative H_R values) the enthalpy decreases and the entropy becomes more negative. This may be caused by increased solvation of the transition state by TFA. The ability of TFA to solvate carbonium ion-like species has been previously noted.^{18,19}

The evidence presented in this section, along with the product studies and stoichiometries, are consistent with the following mechanism.

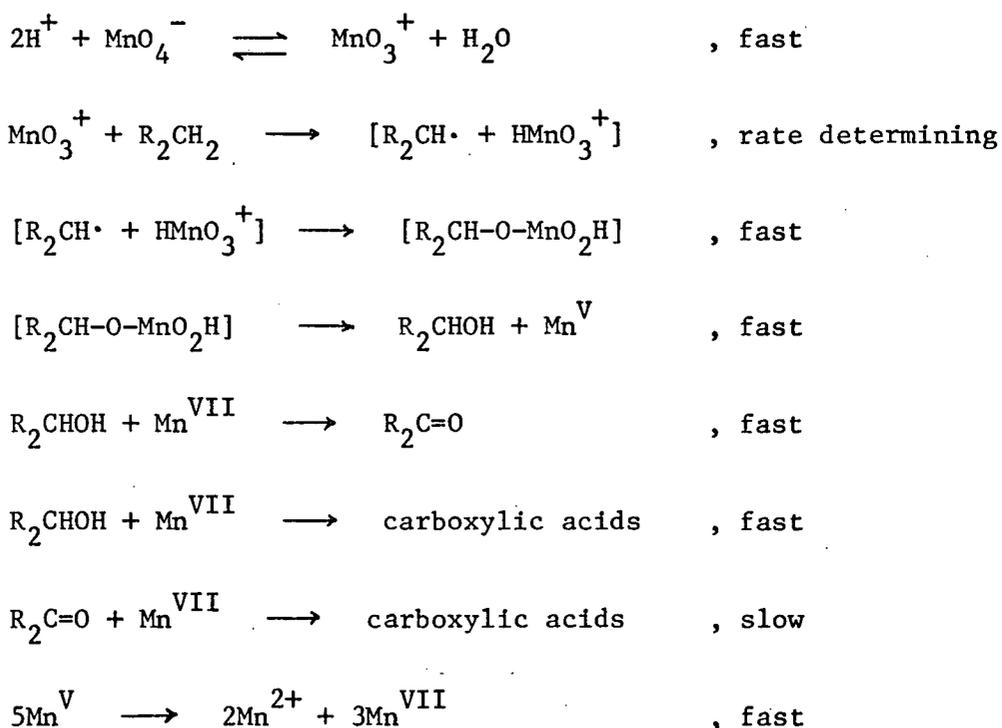


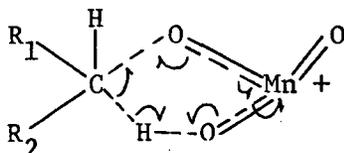
Table 26. Activation Parameters^a for Permanganate Oxidations in TFA-Water.

Substrate	Trials	$-H_R$	ΔH^\ddagger	kcal/mole	$-\Delta S^\ddagger$	e.u.	r
<u>n</u> -Pentane	170-177	7.52	7.87	± 0.08	31.2	± 0.5	.987
<u>n</u> -Hexane	211-218	7.77	5.74	± 0.02	35.5	± 0.2	.999
<u>n</u> -Dodecane	269-274	7.41	8.37	± 0.08	25.0	± 0.3	.989
Cyclopentane	350-357	7.02	7.15	± 0.05	33.1	± 0.5	.992
Cyclohexane	428-433	7.70	5.24	± 0.07	36.8	± 0.7	.974
Cycloheptane	450-457	7.20	6.07	± 0.02	32.9	± 0.1	.999
Cyclooctane	480-487	6.80	7.21	± 0.08	29.0	± 0.5	.983
Benzene	518-525	5.70	5.57	± 0.09	40.7	± 0.9	.969
Toluene	749-753	2.52	11.37	± 0.1	25.2	± 0.3	.986
	705-714	4.13	10.59	± 0.1	22.1	± 0.3	.955
	695-704	4.26	9.43	± 0.08	25.9	± 0.3	.979
	741-748	5.17	5.58	± 0.08	35.5	± 0.7	.973
Methanol	791-795	3.18	12.29	± 0.08	25.0	± 0.3	.995
3-Pentanol	850-857	5.84	7.75	± 0.1	33.1	± 0.6	.977
Cyclohexanol	869-879	5.40	7.03	± 0.1	36.1	± 0.6	.951
Benzyl alcohol	923-930	3.58	8.21	± 0.04	32.3	± 0.2	.997
	931-937	6.72	6.86	± 0.2	27.6	± 1.5	.840
2-Pentanone	1024-1031	8.86	9.79	± 0.2	25.3	± 0.8	.953
Cyclohexanone	1065-1072	6.34	11.45	± 0.06	21.3	± 0.2	.997
3-Pentanone	1187-1196	7.90	5.64	± 0.03	40.0	± 0.03	.999
Acetophenone ^b	1246-1255	6.41	8.31	± 0.03	52.0	± 0.03	.999

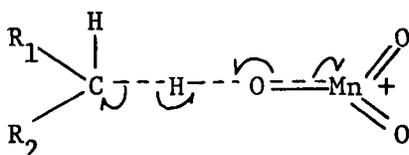
^a Calculated from k_2 where, rate = $k_2[\text{MnO}_4^-][\text{substrate}]$.

^b Zero-order data was used. k was from rate = $k[\text{acetophenone}]$.

The transition state can be cyclic,



or acyclic



In the first case the initial product will be the Mn(V) ester and in the second case a radical and Mn(VI), which would probably quickly recombine to give the Mn(V) ester. It is not possible at present to distinguish between these two possibilities.

The product studies revealed only minor amounts of alcohols and ketones. The alcohols can be intermediates in the oxidative sequence since in all cases the alcohol is much more reactive than the alkane. Ketones, however, cannot be free intermediates since they were found to be less reactive than the alkane (see Appendix C). It is possible that ketones are formed but that they react with some manganese species of intermediate valency with which they are trapped in a solvent cage.

Some previous reports on the reactions of n-alkanes indicated that not all methylenes are equivalent in reactivity.^{37,38,136} This also appears to be the case in this investigation. When the products of the oxidation of n-pentane were analyzed it was found that a small amount of ketone was formed. This was actually a mixture of 2-pentanone (66%)

and 3-pentanone (34%). The kinetic data for the oxidation of these two ketones indicate that 3-pentanone is six times more reactive to oxidation by permanganate than is 2-pentanone. This fact, along with the statistical correction of two (2-pentanone can be formed by attack at two positions in pentane but 3-pentanone at only one position), showed that initially the 3-position in n-pentane is favoured 6:1 over the 2-position. Consulting Table 27 it can be seen that Taft's σ^* values indicate that the internal methylenes should differ in reactivity from the methylenes adjacent to the methyl group. In the case of this oxidation process, where $\rho^* = -2.4$, the internal methylenes should be preferentially attacked. In general the number of most reactive methylenes can be calculated by $n-4$, where n is the total number of carbons in the chain.

Figure 21 shows that as the alkane chain length increases there is a regular increase in the rate of oxidation. These experimental rates, expressed as ratios relative to one of the alkanes, compare favourably only with the number of most reactive methylenes. Tables 28 and 29 contain these comparisons.

It appears that the chromic acid oxidation of n-alkanes in acetic acid does not exhibit such selectivity. The rate data reported by Rocek and Mares³⁵ clearly correlate with the total number of methylenes (see Table 30).

It can be concluded from this investigation that the oxidation of alkanes by permanganyl ion and micro-organisms are governed by quite different factors. The biological system is known to attack the terminal methyl group selectively, possibly because of steric control,

Table 27. Calculated $-\sigma^*$ Values of Individual Carbon Atoms in Some n-Alkanes.^a

Compound	Carbon number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	
propane	.100	0	.100											
<u>n</u> -butane	.115	.100	.100	.115										
<u>n</u> -pentane	.130	.115	.200	.115	.130									
<u>n</u> -hexane	.145	.130	.215	.215	.130	.145								
<u>n</u> -heptane	.160	.145	.230	.230	.230	.145	.160							
<u>n</u> -octane	.175	.160	.245	.245	.245	.245	.160	.175						
<u>n</u> -nonane	.190	.175	.260	.260	.260	.260	.260	.175	.190					
<u>n</u> -decane	.205	.190	.275	.275	.275	.275	.275	.275	.190	.205				
<u>n</u> -undecane	.220	.205	.290	.290	.290	.290	.290	.290	.290	.205	.220			
<u>n</u> -dodecane	.235	.220	.305	.305	.305	.305	.305	.305	.305	.305	.220	.235		
<u>n</u> -tridecane	.250	.235	.320	.320	.320	.320	.320	.320	.320	.320	.320	.235	.250	

^a σ^* was calculated by adding σ^* of the two alkyl segments using Taft's σ^* values¹³¹ and extrapolated values.

Note: σ^* values are available only up to alkyl segment length of C_4 (n-butyl), all other σ^* values of segments longer than C_4 were approximated by assuming a constant increase of 0.015 (i.e. $C_2 = -0.100$, $C_3 = -0.115$, $C_4 = -0.130$, and $C_5 = -0.145$ etc.) The important features of this table are that methylenes next to the methyl groups are always significantly different from the internal methylenes, which are identical to each other.

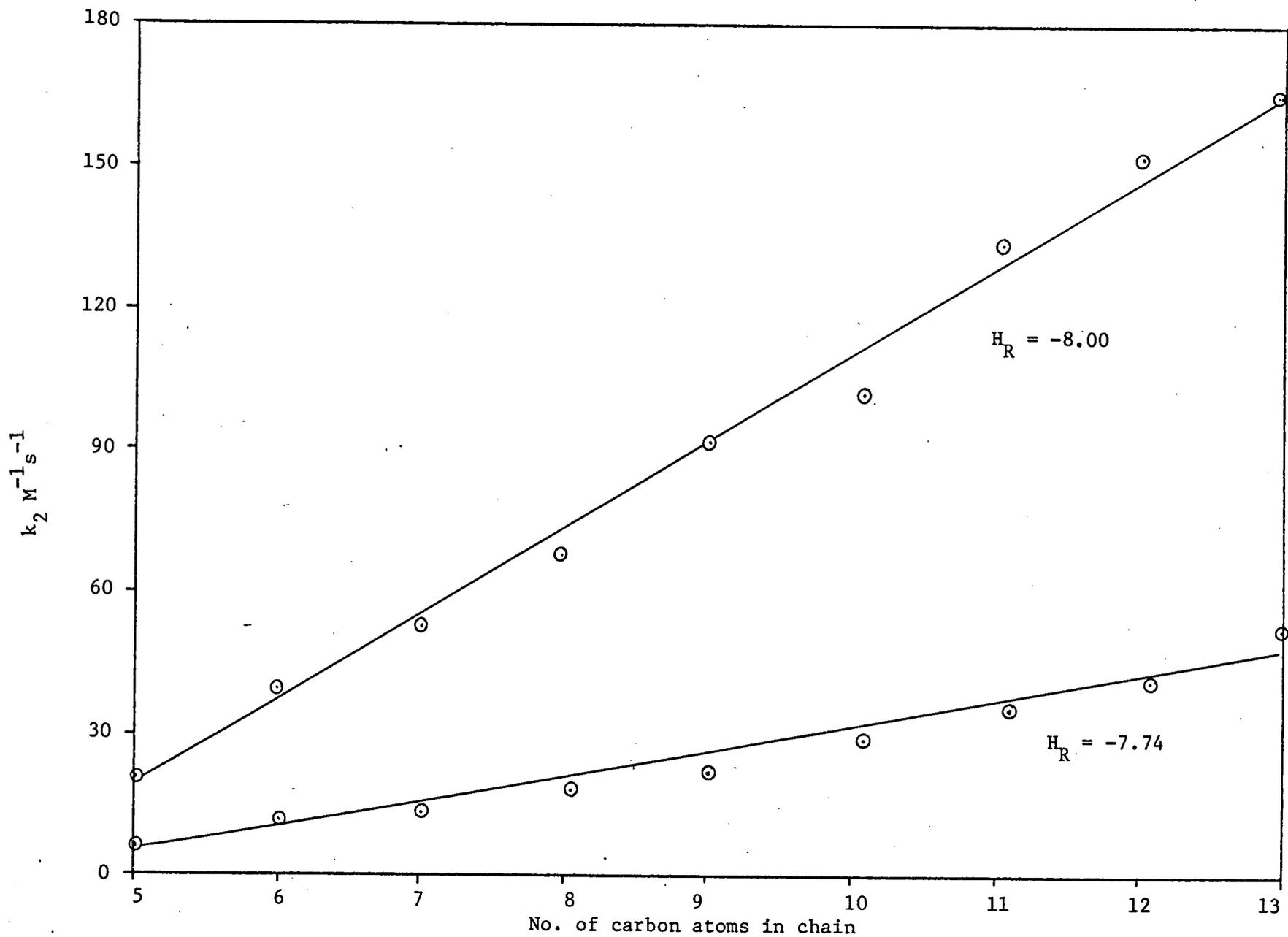


Figure 21. Oxidation rate vs. number of carbon atoms in n-alkanes.

Table 28. Relative Ratios of Numbers of Methylenes Present in n-Alkanes.

Compound	(a) Relative to			(b) Relative to		
	<u>n</u> -Pentane	<u>n</u> -Hexane	<u>n</u> -Heptane	<u>n</u> -Pentane	<u>n</u> -Hexane	<u>n</u> -Heptane
<u>n</u> -Pentane	1.00	0.75	0.60	1.0	0.5	0.33
<u>n</u> -Hexane	1.33	1.00	0.80	2.0	1.0	0.67
<u>n</u> -Heptane	1.67	1.25	1.00	3.0	1.5	1.00
<u>n</u> -Octane	2.00	1.50	1.20	4.0	2.0	1.33
<u>n</u> -Nonane	2.33	1.75	1.40	5.0	2.5	1.67
<u>n</u> -Decane	2.67	2.00	1.60	6.0	3.0	2.00
<u>n</u> -Undecane	3.00	2.25	1.80	7.0	3.5	2.33
<u>n</u> -Dodecane	3.33	2.50	2.00	8.0	4.0	2.67
<u>n</u> -Tridecane	3.67	2.75	2.20	9.0	4.5	3.00

(a) Ratios of the total number of methylenes present.

(b) Ratios of the most reactive methylenes present in the alkane. This number was determined by assuming that the trend shown in Table 27 continues, i.e. the methylenes next to the methyl group are less reactive. This number of methylenes is given by $n-4$ (n = total number of carbon atoms in n-alkane).

Table 29. Experimental Ratios for n-Alkane Oxidation Rates.

Compound	Relative to			Predicted Ratios	
	<u>n</u> -Pentane	<u>n</u> -Hexane	<u>n</u> -Heptane	Reactive -CH ₂ -	Total -CH ₂ -
(a) $H_R = -7.74$, $T = 25.0^\circ$, $[\text{MnO}_4^-] = 4.136 \times 10^{-4} \text{ M}$					
<u>n</u> -Pentane	1	0.4	0.4	1.0	1.0
<u>n</u> -Hexane	2.5	1	0.9	2.0	1.3
<u>n</u> -Heptane	2.7	1.1	1.0	3.0	1.7
<u>n</u> -Octane	3.9	1.6	1.5	4.0	2.0
<u>n</u> -Nonane	5.0	2.0	1.9	5.0	2.3
<u>n</u> -Decane	7.1	2.9	2.6	6.0	2.7
<u>n</u> -Undecane	8.6	3.5	3.2	7.0	3.0
<u>n</u> -Dodecane	10.2	4.2	3.8	8.0	3.3
<u>n</u> -Tridecane	14.5	5.9	5.4	9.0	3.7
(a) $H_R = -8.00$, $T = 25.0^\circ$, $[\text{MnO}_4^-] = 4.024 \times 10^{-4} \text{ M}$					
<u>n</u> -Pentane	1	0.5	0.4	1.0	1.0
<u>n</u> -Hexane	1.8	1.0	0.8	2.0	1.3
<u>n</u> -Heptane	2.5	1.3	1.0	3.0	1.7
<u>n</u> -Octane	3.2	1.7	1.3	4.0	2.0
<u>n</u> -Nonane	4.4	2.4	1.8	5.0	2.3
<u>n</u> -Decane	5.1	2.8	2.1	6.0	2.7
<u>n</u> -Undecane	6.3	3.4	2.5	7.0	3.0
<u>n</u> -Dodecane	7.4	4.0	3.0	8.0	3.3
<u>n</u> -Tridecane	8.0	4.3	3.3	9.0	3.7

Table 30. Theoretical and Experimental Data for the Chromic Acid Oxidation of n-Alkanes^a.

Compound	$k \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	Ratios ^b		Statistical ^c		Most Reactive CH ₂ ^d	
C ₄ H ₁₀	1.12	1.0	0.39	1.0	0.4	1.0	0.67
C ₇ H ₁₆	2.90	2.59	1.0	2.5	1.0	1.5	1.0
C ₉ H ₂₀	3.90	3.48	1.34	3.5	1.2	2.5	1.66
C ₁₁ H ₂₄	5.40	4.82	1.86	4.5	1.8	3.5	2.33
C ₁₆ H ₃₄	8.07	7.20	2.78	7.0	2.8	6.0	4.0
C ₂₂ H ₄₆	11.14	9.95	3.84	10.0	4.0	9.0	6.0

^a All kinetic data from reference 35.

^b Ratios from the experimental data obtained by dividing by either k for n-butane or n-heptane.

^c Ratios expected considering all methylenes as in Table 28.

^d Ratios expected from most reactive methylenes as in Table 28.

whereas permanganyl ion preferentially attacks the internal methylenes because of electronic effects.

Summary

The data presented for the Mn(VII) oxidation of alkanes is consistent with a mechanism which involves attack by permanganyl ion on the neutral substrate molecule. In the transition state considerable positive charge develops on the carbon atom subject to attack. The rate-determining step involves homolytic carbon-hydrogen bond scission. Not all methylenes appear to be equal in their reactivity towards oxidation by permanganyl ion. In general the number of reactive sites for n-alkanes longer than four carbon atoms is given by $n-4$ (n = number of carbon atoms in the chain).

4.4 Oxidation of Arenes

The kinetic data for the oxidation of arenes by permanganate in TFA-water solutions are tabulated in Appendix C, trials 490-769 and 1197-1208.

The excellent correlation of the time-absorbance data for up to two half-lives of permanganate with the pseudo first-order equation confirms the first-order dependence upon permanganate concentration. The data listed in Table 31 (some of which is depicted in Figures 22 and 23) indicate that the rate equation contains first-order terms both in substrate concentration and h_R . The general rate equation can be expressed as;

$$-d[\text{MnO}_4^-]/dt = k_3[\text{MnO}_4^-][\text{arene}]h_R$$

Table 31. Order of Reactants Involved in the Permanganate^a Oxidation of Arenes.

Substrate	Order in substrate	Trials	r	Order in h_R	Trials ^b	r
Benzene	1.0	496-502	0.999	1.0	490-536	0.996
Toluene	1.0	544-550	"	0.8 ^c	537-763	0.993
	1.0	661-668	0.998	0.7 ^c	537-571	0.999
	1.1	551-557	0.995	0.7 ^c	572-605	0.998
	0.9	537-543	0.961	0.8 ^c	606-694	0.992
	1.0	558-564	0.995	0.8 ^c	695-763	0.991
	0.8	565-571	0.989			
	1.2	572-578	0.998			
	1.1	579-585	0.989			
	1.1	586-592	0.984			
	1.0	593-599	0.998			
	0.9	600-605	0.980			
Toluene-d ₈	1.0	669-676	0.999	0.9 ^c	618-736	0.993

Note: Errors in orders are $\pm 5\%$.

- ^a In all cases the order of permanganate was 1.00, $r = 0.999$.
- ^b Only those trials where $T = 25.0^\circ$, H_2O was the co-solvent.
- ^c The order of h_R was consistently less than one but if h_o was used the order was near five with poorer correlation coefficients.

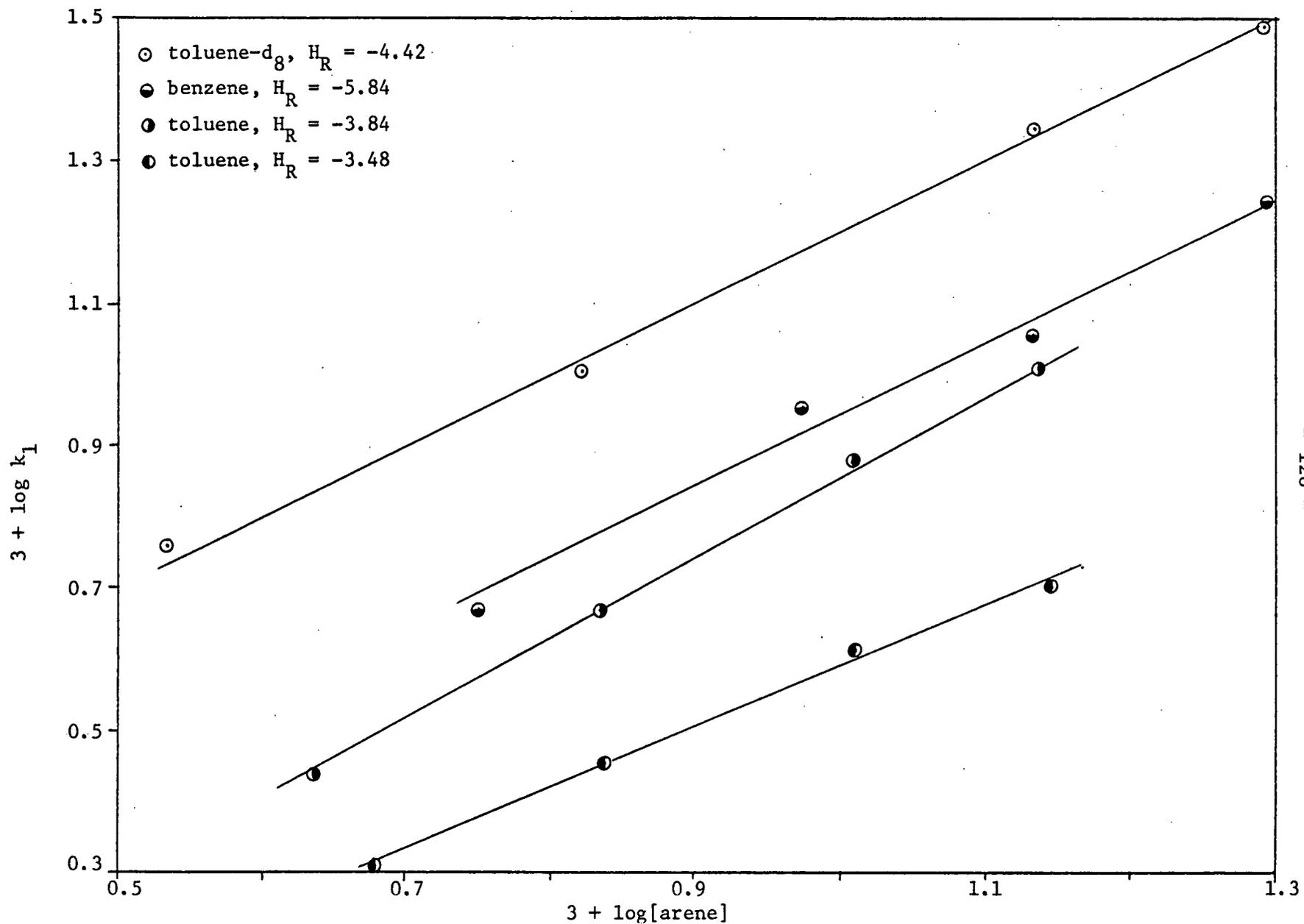


Figure 22. Log k_1 vs. log[arene] for the oxidation of toluene and benzene.

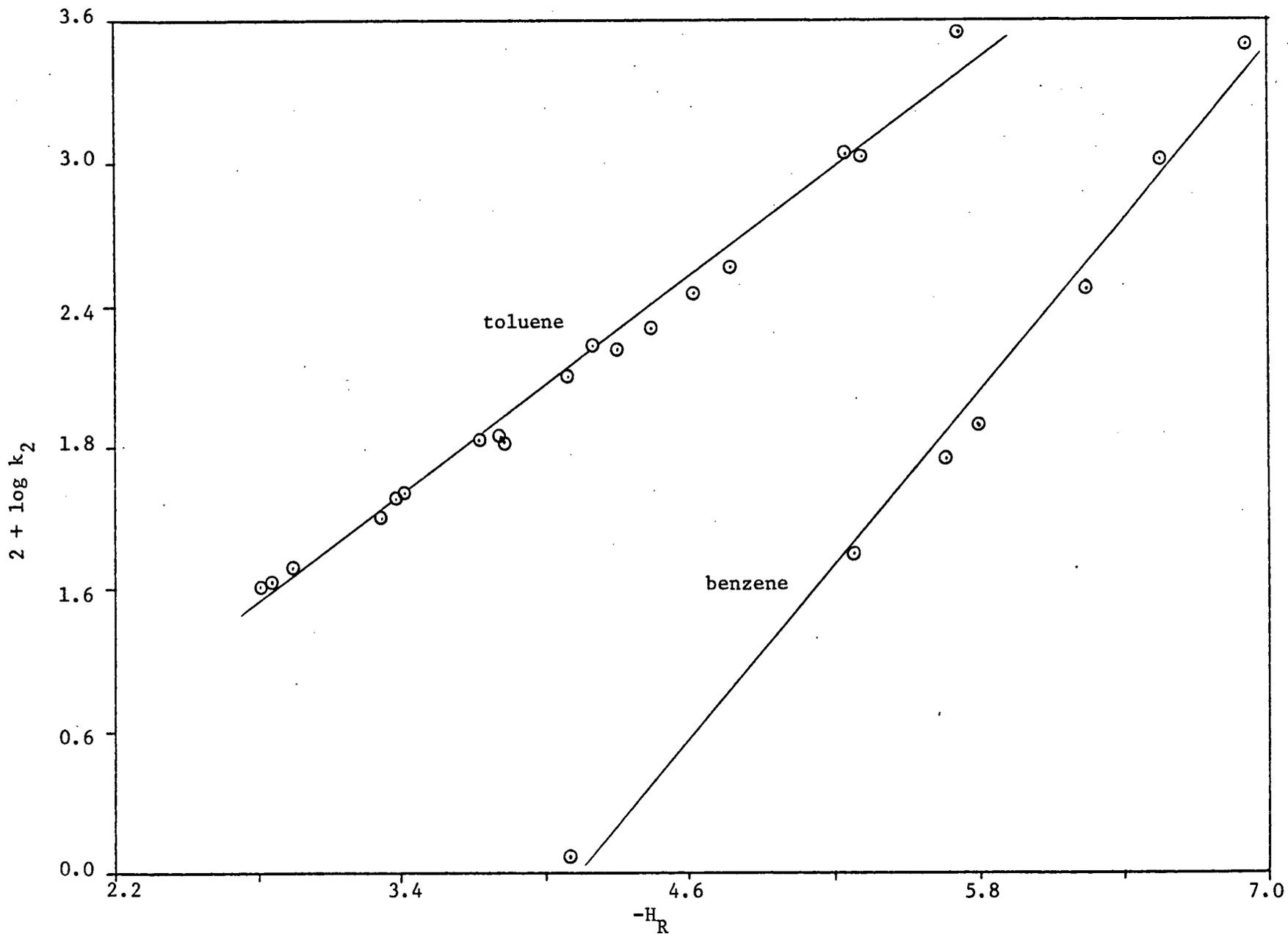


Figure 23. $\log k_2$ vs. H_R for the oxidation of toluene and benzene.

Figure 24 illustrates that the oxidation rate is not affected by added salts. The transition state appears to be achieved from one molecule of arene and one molecule of oxidant. The clear dependence upon H_R and the observed solvent isotope effects (see Table 32) indicate, as was the case with alkanes, that permanganyl ion is the active oxidant. (The observed rate increases with increased deuterium content parallel the changes in the pK for the generation of permanganyl ion.) Up to this point the arene oxidation appears to be similar to the alkane oxidation, but the data in Tables 32 and 33 indicate definite mechanistic differences. There is no primary kinetic isotope effect observed when either toluene- α - d_3 or toluene- d_8 are used in place of toluene. Further, there are only very little rate differences observed when the alpha carbon-hydrogen bond is varied from primary to tertiary. These data indicate that in the rate-determining step there is no carbon-hydrogen bond scission, either on the ring or on the alpha carbon.

Table 33. Comparative Rate Ratios for the Permanganate Oxidation of Toluene, Ethylbenzene, and Cumene.

$-H_R$ of Medium	Toluene:Ethylbenzene:Cumene
3.07	1:1.9:1.8
3.18	1:1.5:1.3
3.39	1:1.7:1.6
3.88	1:1.4:1.5
4.44	1:1.4:1.4
4.50	1:1.3
4.82	1:1.3:1.4
5.39	1:1.2:1.2

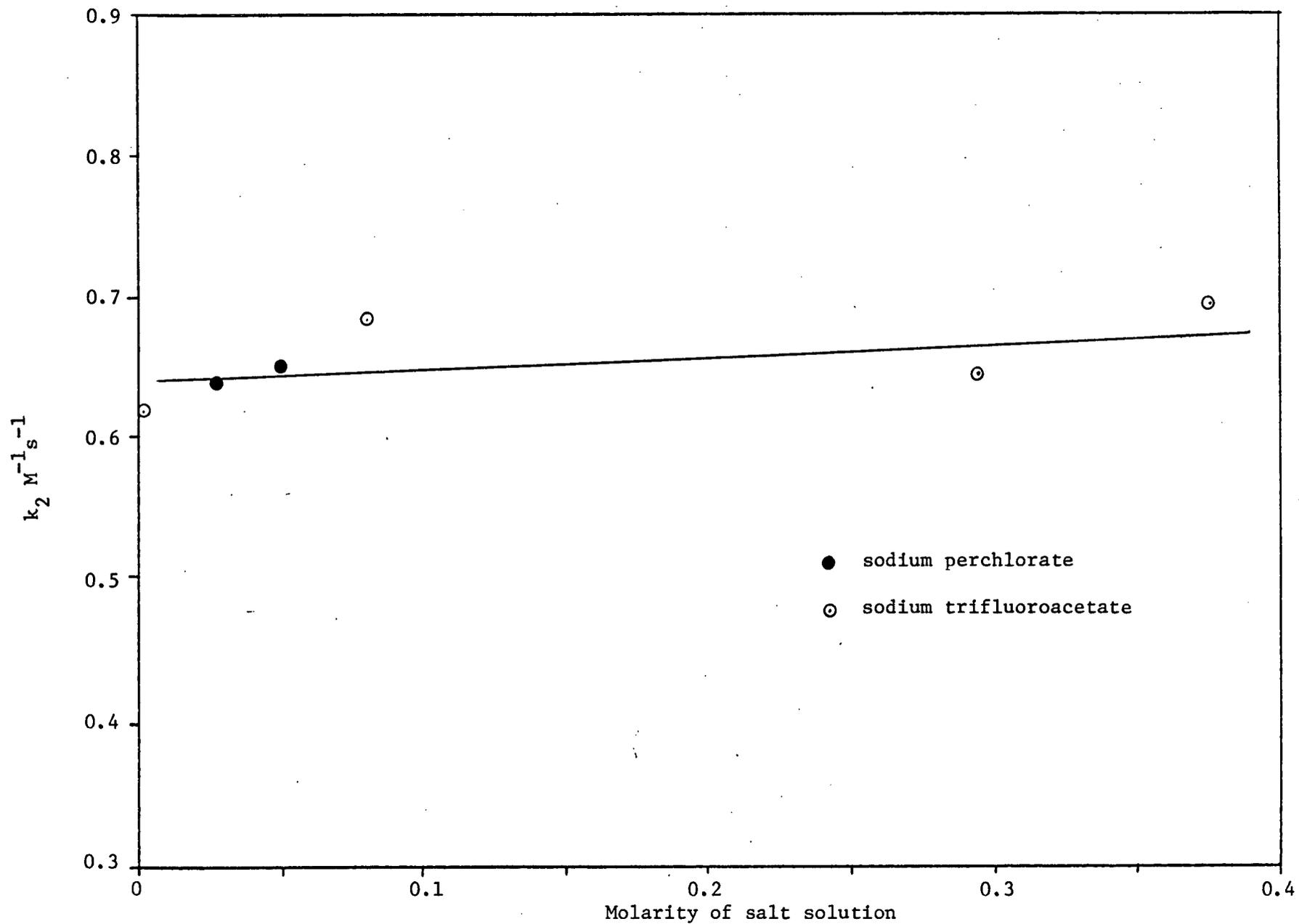


Figure 24. Salt effects on the permanganate oxidation of benzene. (Trials 526-533).

Table 32. Kinetic Isotope Effects for the Permanganate Oxidation of Arenes.

Substrate	k_H/k_D	$k(D_2O)/k(H_2O)^a$	$-H_R$
Toluene/toluene-d ₈	1.06		2.34
	1.11		3.07
	0.98		3.39
	0.95		3.52
	1.00		3.88
	1.00		4.42
	0.93		4.44
	1.01		4.44
	0.91		4.50
	1.01		4.82
	1.03		5.28
	0.99		5.29
	0.93		5.70
Toluene/toluene-α-d ₃	0.94		2.34
	1.01		3.52
	1.04		4.44
	1.10		5.28
Toluene		2.06	4.47
		2.23	4.83
Toluene-d ₈		2.22	4.83
Benzene		1.16	5.67
		1.48	5.78
		1.14	6.26
		1.04	6.96

^a CF₂CO₃H-D₂O solvent system.

The product studies and stoichiometries (see Tables 3 and 5) indicate that considerable ring degradation occurs. The stoichiometry of 2.5 is well above that of 1.2 predicted for the oxidation of toluene to benzoic acid (Mn^{VII} reduced to Mn^{2+}). Further, the rate of oxidation of *t*-butylbenzene is comparable to the rate of oxidation of toluene which is consistent with considerable ring attack.

The substituent effects on the oxidation of benzene correlate best with σ^+ values (see Figure 25). The large negative value of $\rho^+ = -5.2$ indicates considerable positive charge development on the ring in the transition state.

When the oxidation of toluene is considered as a sidechain oxidation the substituent effects, depicted in Figure 26, show random scatter, but if the substituted toluenes are considered as di-substituted benzenes undergoing ring attack the substituent effects are more orderly (see Figure 27). The correlation in the latter case is still poor, possibly owing to considerable side-chain oxidation when electron-withdrawing substituents such as carboxy or nitro are present.

The permanganate oxidation of arenes has several features in common with electrophilic aromatic nitration. Nitrations in sulfuric acid-water medium are known to correlate with H_R ,⁷¹ more precisely $H_R + \log a_{\text{H}_2\text{O}}$,⁷³ and they are known to exhibit no primary isotope effects.⁷⁴⁻⁷⁶ These features are believed to be due to a mechanism involving rate-limiting electrophilic attack⁷⁴⁻⁷⁸ followed by fast proton loss to the solvent⁷⁸ to yield the nitration product. It appears that all the kinetic and supplementary evidence from this investigation on the permanganate oxidation of arenes is consistent

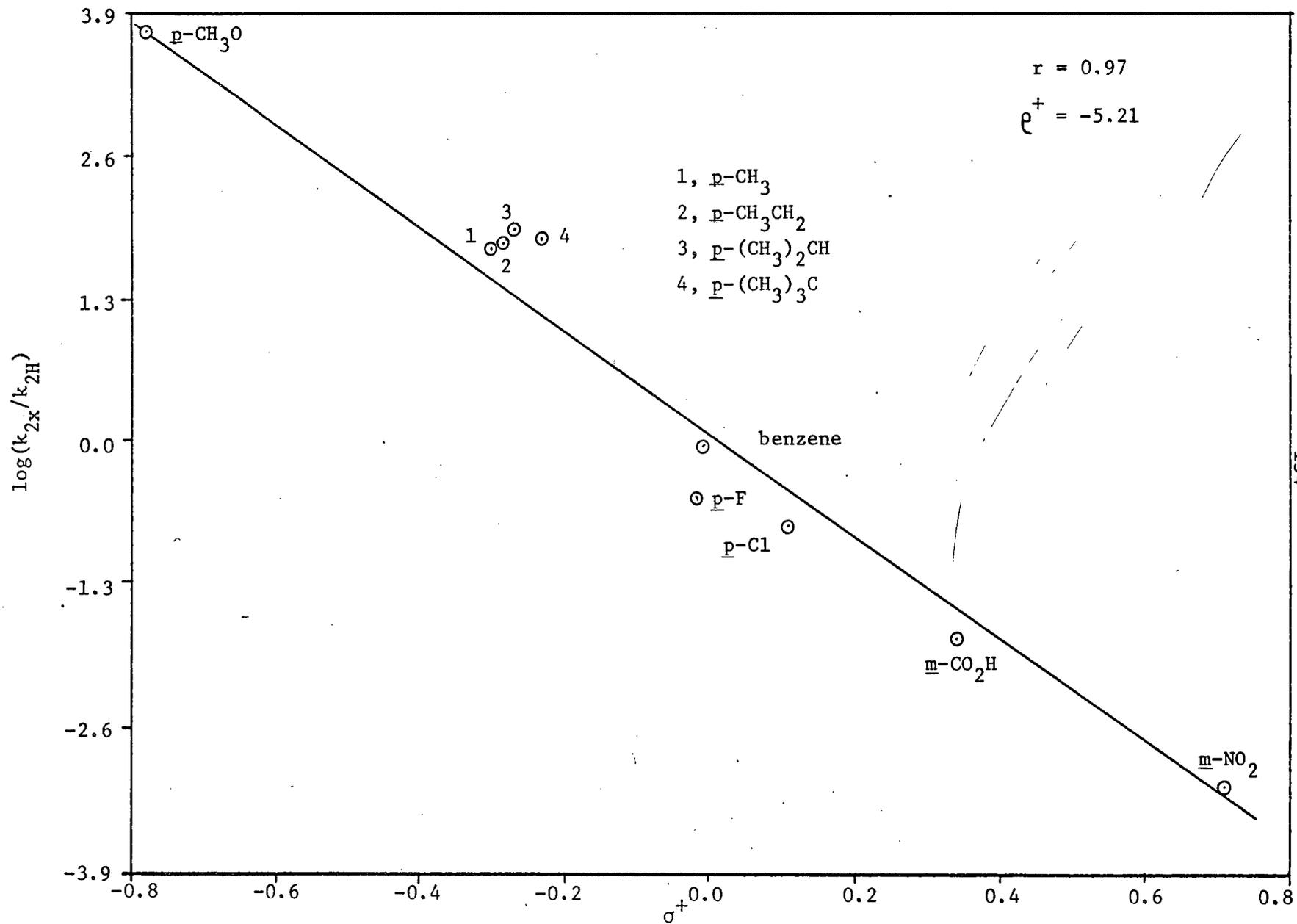


Figure 25. Substituent effects on the permanganate oxidation of benzene. $\log k_2$ vs. σ^+ (trials 505-517). \underline{m} or \underline{p} designates the particular σ^+ value used.

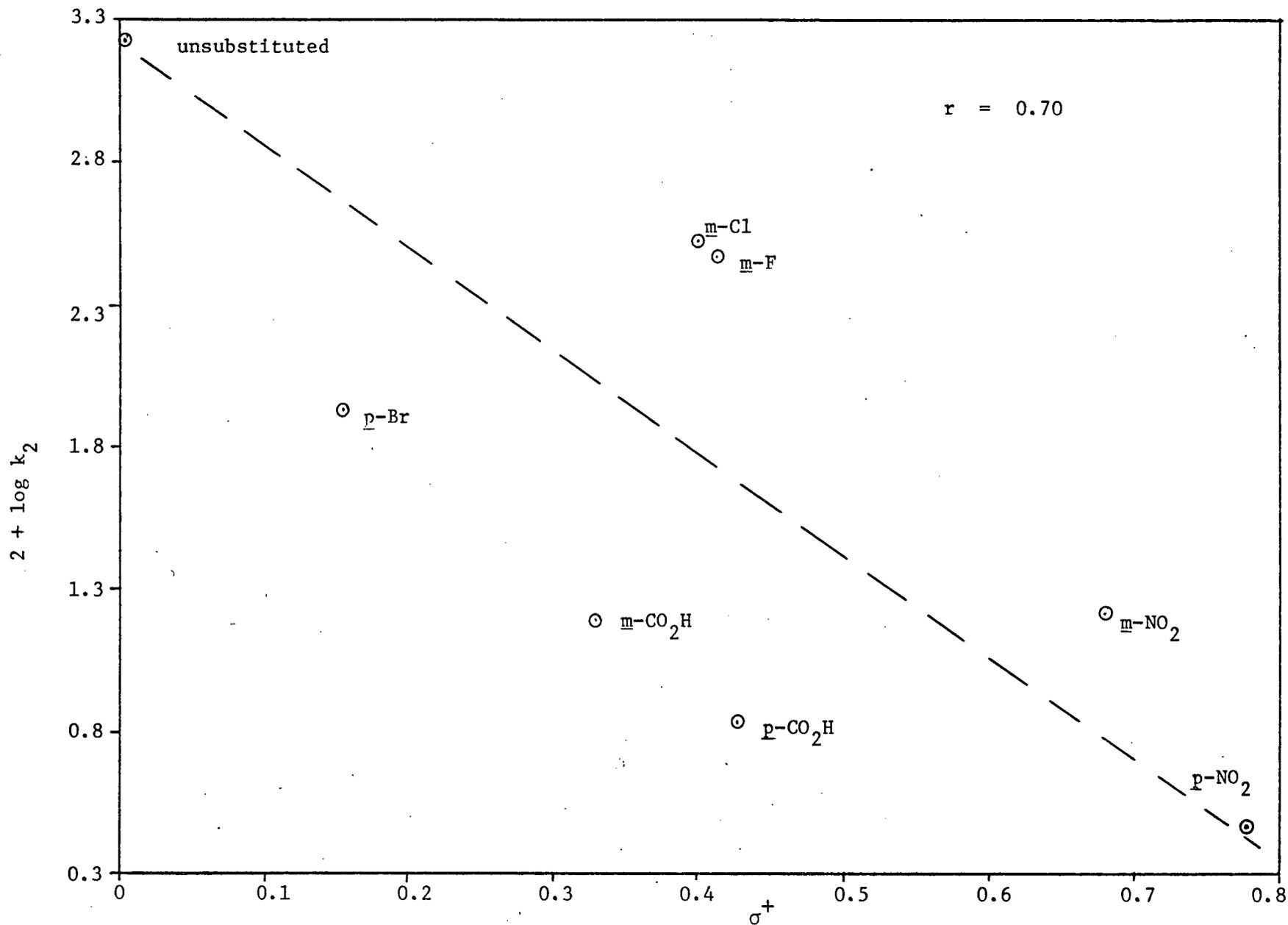


Figure 26. Substituent effects on the permanganate oxidation of toluene. $\log k_2$ vs. σ^+ . (Trials 681-694).

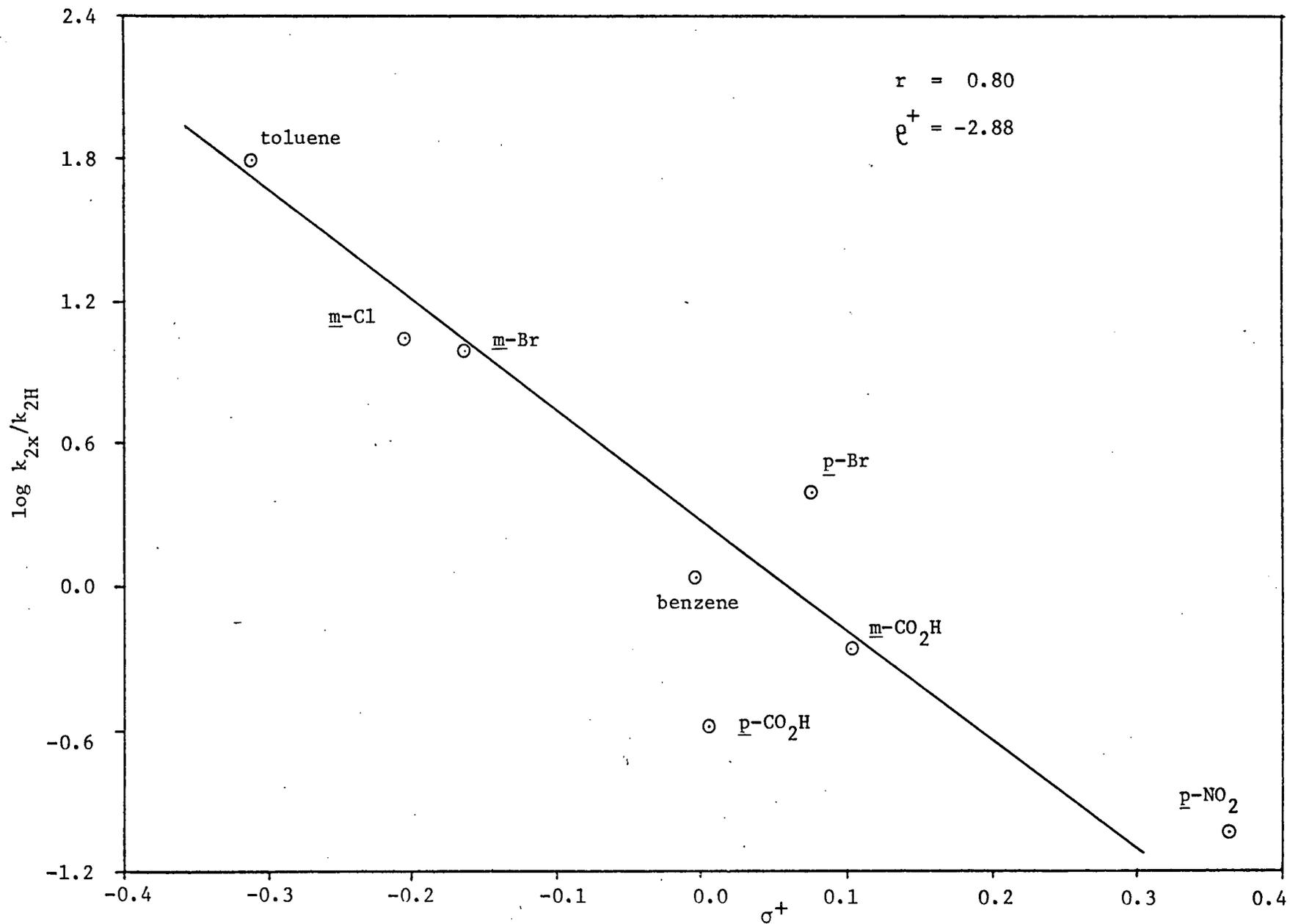
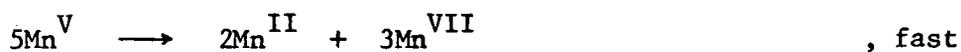
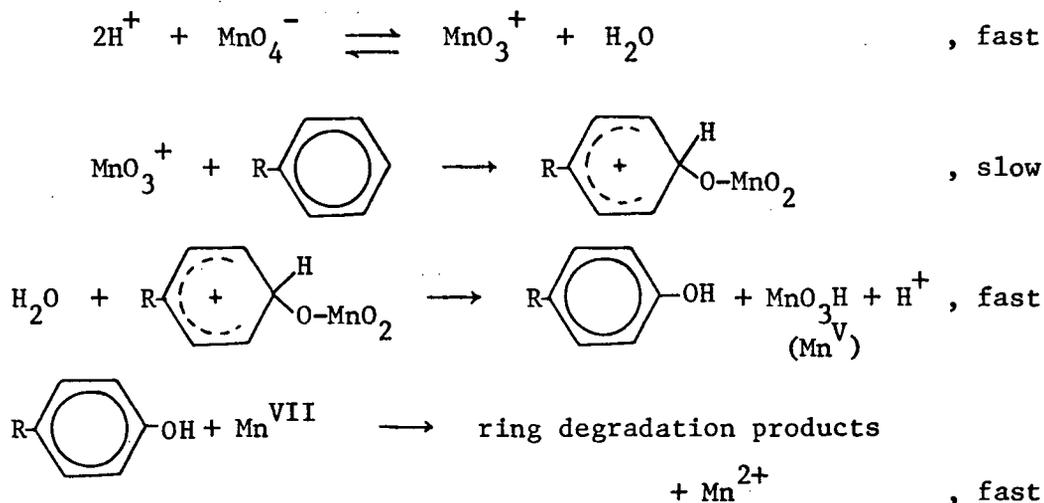


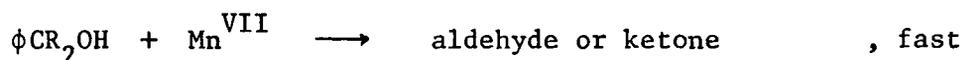
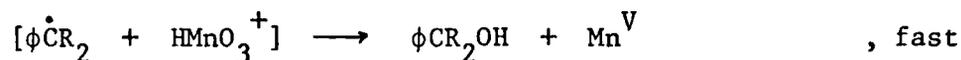
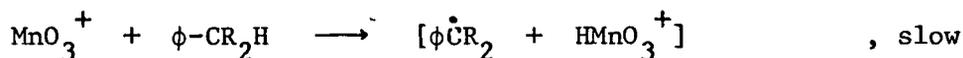
Figure 27. Revised σ^+ vs $\log k_{2x}/k_{2H}$ plot for toluenes. Toluenes considered as substituted benzenes. (Trials 681-694).

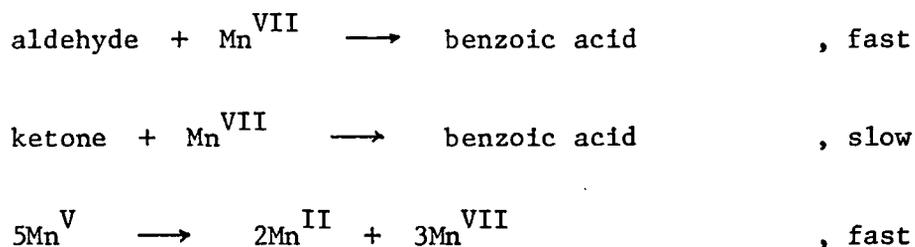
with a mechanism that involves rate-limiting electrophilic aromatic attack by permanganyl ion. A possible scheme which accounts for all the observations can be depicted as the following:

(a) Ring attack,



(b) Side chain attack, (ϕ = phenyl group)





It will be noted that phenol is proposed as a possible intermediate in the ring degradation. There is no direct evidence for the existence of phenols in the reaction mixture since phenols are subject to rapid oxidation even in aqueous medium but, as is shown in Table 5, the stoichiometry for the oxidation of phenol shows less permanganate consumed than in the case of toluene. This observation is consistent with phenol being an intermediate.

The two separate oxidative pathways proposed for arenes are consistent with the product studies. It appears that the side chain oxidation tends to increase as the medium becomes more aqueous. This can be seen by the increases in the yield of benzoic acid (see Table 3) and the increase of the 1°:2°:3° rate ratios listed in Table 33.

In the Introduction two studies on the permanganate oxidation of arenes in acidic medium were discussed. Although neither study clearly established the mechanism of the arene oxidation they have features in common with this investigation. Cullis and Ladbury⁴⁴ who were the first to attempt a thorough investigation of this reaction, were severely hindered by their choice of aqueous acetic acid as a reaction medium. Second order kinetics were not maintained throughout the reaction, forcing them to use the data from the first 10% of the reaction to approximate initial rates. (Acetic acid is also known to

complicate aromatic bromination kinetics, a problem which disappears when TFA is substituted for acetic acid.¹¹⁾ Cullis and Ladbury observed that there was no effect of added salts (if the salt did not react with some manganese species) and that there was appreciable ring degradation. The ring degradation and the oxidation rate were observed to increase when electron-donating substituents were present. All of these observations are consistent with the data from this study. They do report one fact which deviates from our observations. It was reported that benzaldehyde could be detected as a reaction product along with benzoic acid from the oxidation of toluene whereas in this study no evidence could be found for benzaldehyde as a product. However, consulting Figure 28 it can be seen that at higher acidities toluene is more reactive than benzaldehyde. In fact, Figure 28 shows that the usual order of reactivity towards oxidation (benzaldehyde > benzyl alcohol > toluene) becomes inverted. This appears to be due to ring attack becoming important and the side chain now acts as a substituent. The effect of these groups on ring attack would be expected to produce the order, toluene > benzyl alcohol > benzaldehyde which is, indeed, observed.

The second more recent study, by Lee and Singer,⁴⁵ concerned the acidic permanganate oxidation of *p*-toluenesulfonic acid in a medium of aqueous perchloric acid. Although they found that the sulfonate group caused drastic mechanistic changes (refer to Section 1.5.2) in the region where oxidation was the rate-determining process a rate law of $r = k_3[\text{arene}][\text{Mn}^{\text{VII}}]_0$ was obeyed. Clearly the rate dependence upon acid content in their system differs from that in this study. Since

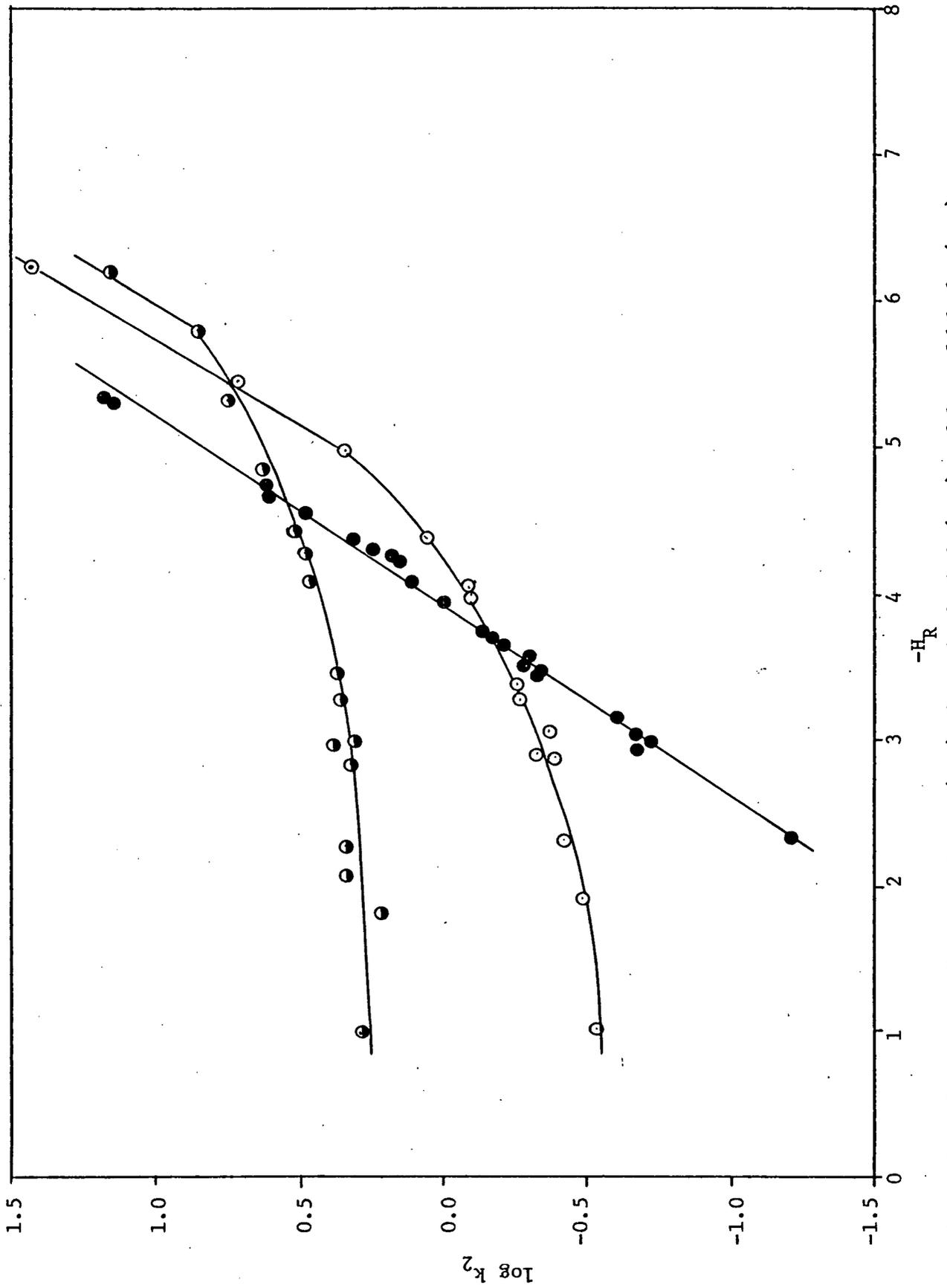


Figure 28. $\log k_2$ vs. H_R for toluene (●), benzyl alcohol (⊙) and benzaldehyde (⊙).

their mechanism involves substrate protonation and ours does not it is not surprising that different acid catalyses are observed.

Summary: The oxidation of arenes tends to proceed mainly via electrophilic aromatic ring attack by permanganyl ion. The transition state formed from the permanganyl ion and arene molecule develops considerable positive charge on the ring. No ring degradation products could be isolated although complete oxidation to carbon dioxide does not occur. The evidence presented in this study is consistent with a mechanism involving phenols as intermediates.

4.5 Oxidation of Alcohols

The kinetic data for the series of alcohols investigated are listed in Appendix C, trials 770-1003.

The kinetic experiments of all alcohol oxidations required special care to prevent inert trifluoroacetate esters being formed by reaction between alcohol and solvent. The data in Figure 29 indicate the magnitude of this interfering reaction. All of the data listed in the appendix were obtained by a technique which eliminated this effect (see Section 3.2 for the kinetic procedure).

The excellent fit of the time-absorbance data with the pseudo first-order rate equation for more than two half-lives of permanganate confirms a first-order dependence upon permanganate. The data contained in Table 34 and presented graphically in Figures 30 and 31 indicate a composite rate-law of the following type; $-d[\text{MnO}_4^-]/dt = k_3[\text{MnO}_4^-][\text{alcohol}]h_o + k_3^1[\text{MnO}_4^-][\text{alcohol}]h_R$. At acidities greater than seven molar TFA h_R

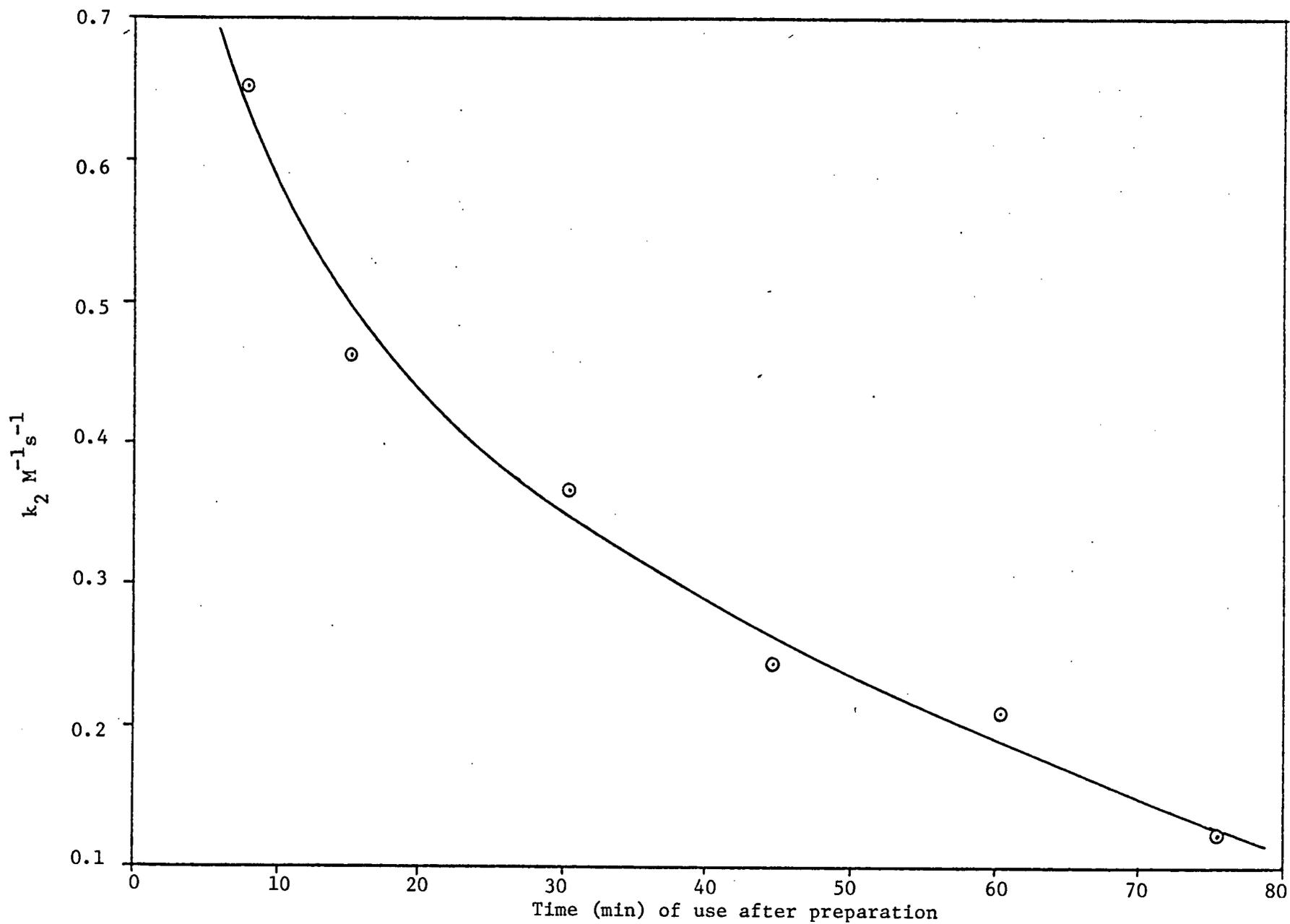


Figure 29. Decrease of oxidation rate with age of solution. Methanol in TFA-water.

Table 34. Order of Reactants in the Permanganate^a Oxidation of Alcohols in TFA-Water.

Substrate	Order in substrate	r	Trials	Order in h_R^b	r	Order in h_o^c	r
Methanol	0.8	0.999	770-773	0.9	0.994		
						4.0	0.94
2-Pentanol	0.9	0.999	827-830	0.8	0.999		
						2.1	0.999
3-Pentanol	1.0	0.999	839-842	0.9	0.998		
						3.9	0.999
Cyclohexanol	1.0	0.999	858-861	0.8	0.990		
						3.0	0.999
Benzyl alcohol	1.0	0.999	884-887	1.1	0.995		
						1.0	0.90
1-Phenylethanol	1.0	0.997	991-994	-		-	
2-Phenylethanol	1.1	0.999	995-997	-		-	

^a The order in permanganate was in all cases 1.00, r = 0.999.

^b Only those trials where $-H_R > 6.0$ are included.

^c Only those trials where $-H_R < 5.0$ are included.

Note: Error in orders are $\pm 5\%$.

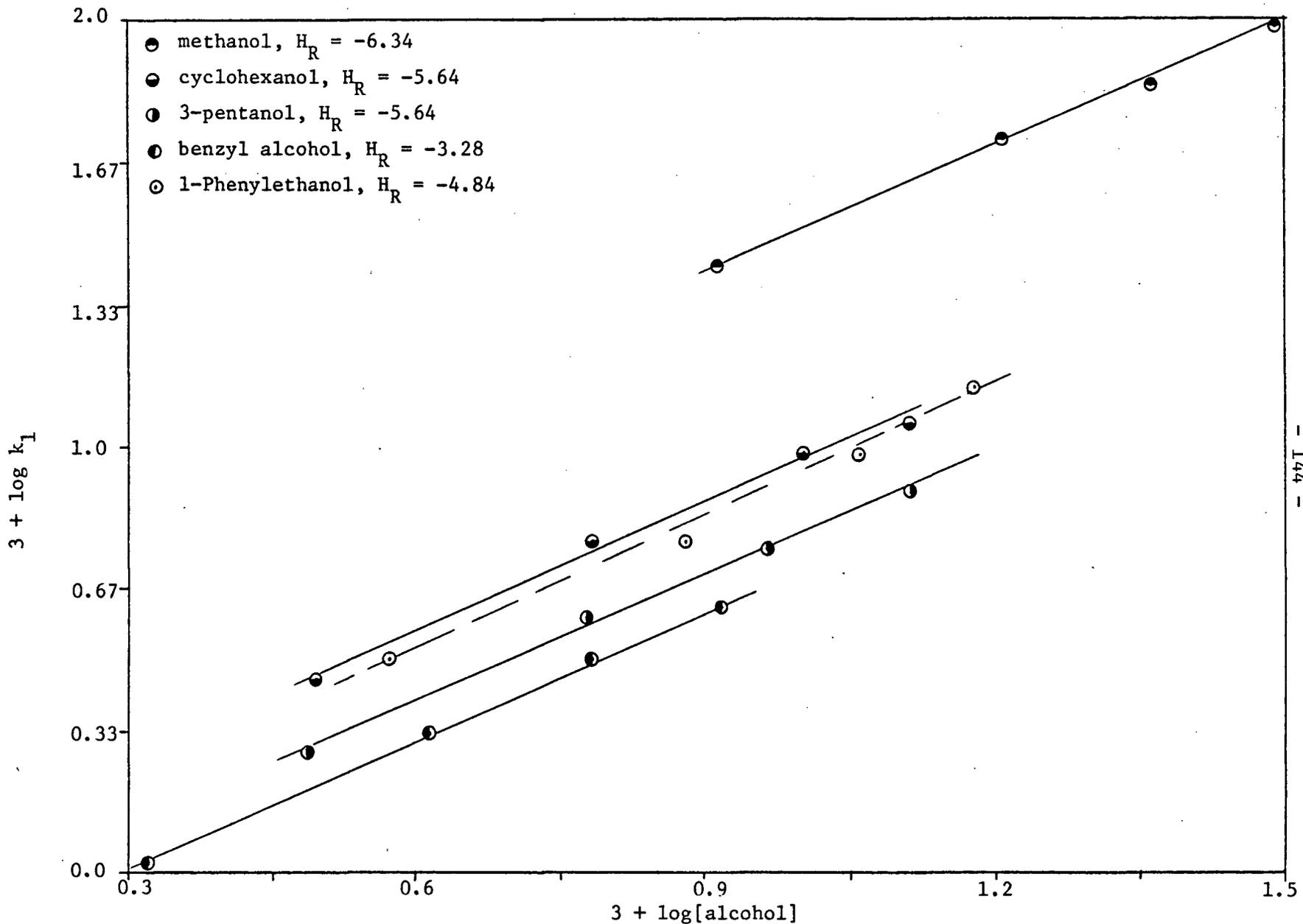


Figure 30. $\log k_1$ vs. $\log[\text{alcohol}]$ for the oxidation of a variety of alcohols.

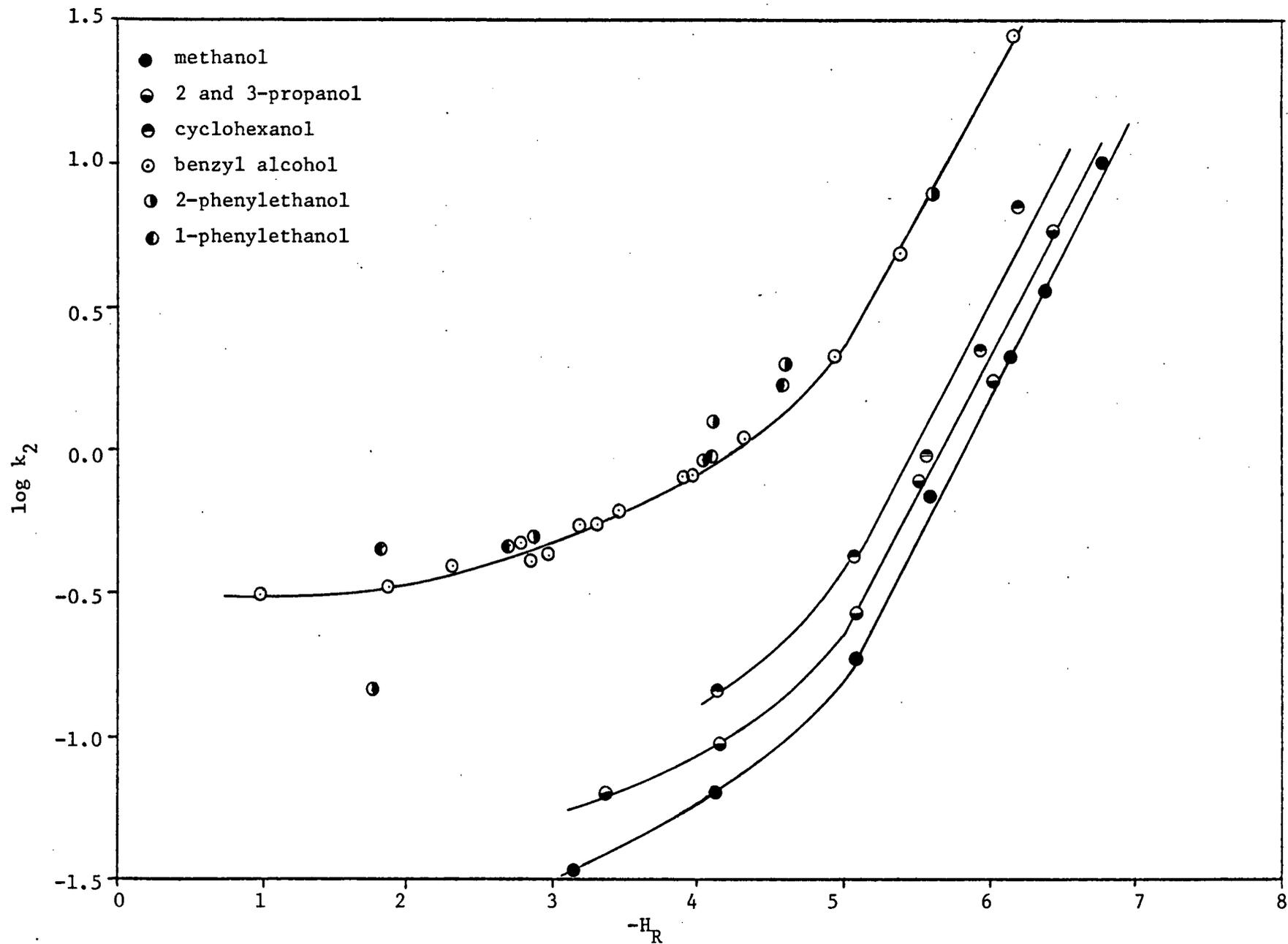


Figure 31. Variation of oxidation rate with acidity for the oxidation of alcohols in TFA-water.

governs the observed acid catalysis and this has been demonstrated to be due to oxidation by permanganyl ion. At lower acidities, however, the acid catalysis correlates with h_o . This is clearly illustrated by the case of benzyl alcohol where it is possible to measure oxidation rates in the highly aqueous region. The dependence upon H_o is believed to be due to oxidation by permanganic acid, $HMnO_4$, (refer to Section 4.3, page 115, where it is demonstrated that oxidations by permanganic acid should correlate with H_o). Apparently permanganic acid is a weak oxidant relative to permanganyl ion since it only functions as an oxidant towards easily oxidizable functional groups such as hydroxyl.

Table 35 shows that appreciable kinetic isotope effects are observed when methanol- d_4 was used in place of methanol. This indicates that the carbon-hydrogen bond is cleaved in the rate-determining step. The carbon-hydrogen bond is probably cleaved homolytically since 1- and 2-phenylethanol have almost identical oxidation rates. If a hydride transfer mechanism were operative as Barter and Littler⁵⁰ have proposed for the oxidation of cyclohexanol in sulfuric acid-water medium, 1-phenylethanol should be oxidized at a much faster rate. (Note: 1-phenylethanol yields exclusively acetophenone but 2-phenylethanol yields phenylacetaldehyde and phenylacetic acid and minute amounts of benzoic acid.)

Again there is no effect of added salts upon the oxidation rate (see Figure 32). The approximate ρ^+ for the oxidation of substituted benzyl alcohol is -1 (trials 884-890).

Table 35. Isotope Effects in the Permanganate Oxidation of Alcohols.

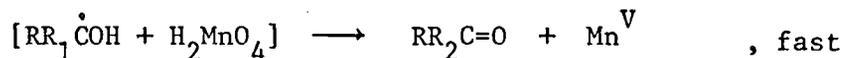
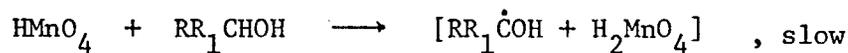
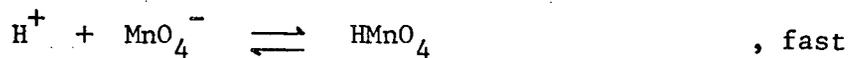
Substrate	$-H_R$	$k(D_2O)/k(H_2O)^a$	k_H/k_D^b
Benzyl alcohol	0.12	1.7	3.5
Methanol	3.76		10.4
	4.38		8.3
	5.01	0.9	7.1
	6.09		10.0
	6.59		9.1
	7.10		6.8

^a Solvent systems made up from $CF_3CO_2H-H_2O$ and $CF_3CO_2H-D_2O$.

^b $k_H/k_D = k_2(\text{benzyl alcohol})/k_2(\text{benzyl alcohol-}\alpha\text{-d}_2)$
 and $k_H/k_D = k_2(\text{methanol})/k_2(\text{methanol-d}_4)$.

The transition state can be considered to result from one molecule of oxidant and one molecule of alcohol, where some positive charge develops on the carbon atom containing the hydroxyl group. Mechanisms consistent with all the before mentioned observations, with the product studies of Table 3, and with the stoichiometries of Table 5 can be outlined as follows:

(a) TFA concentration less than seven molar,



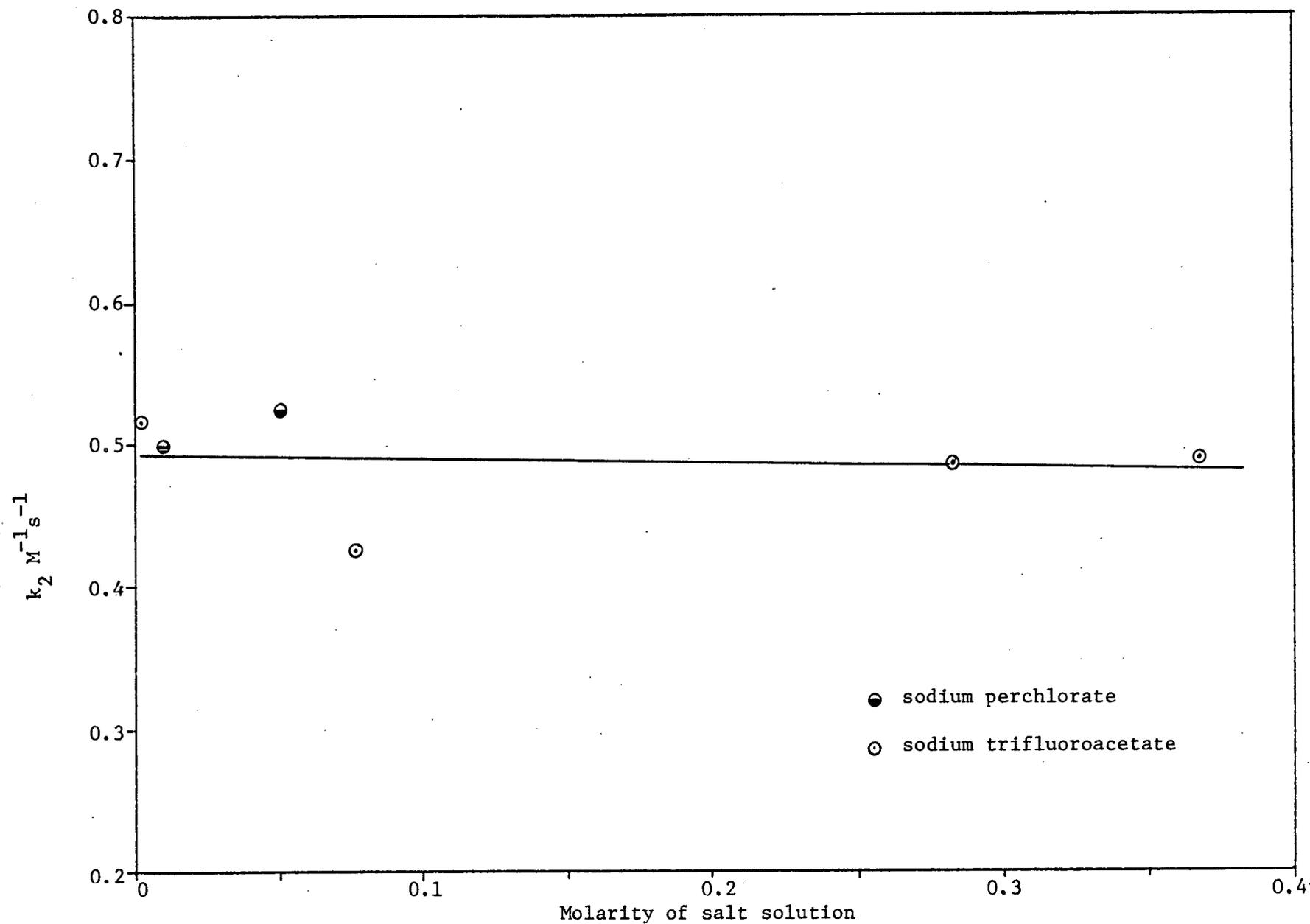
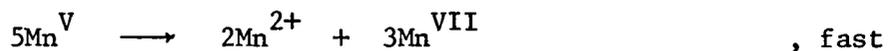
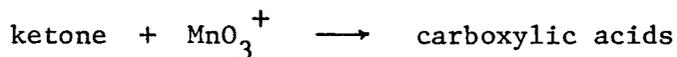
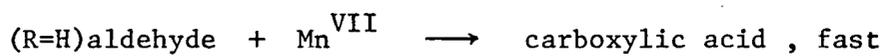
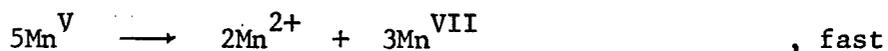
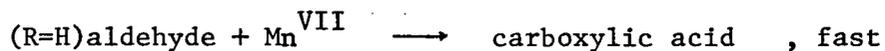
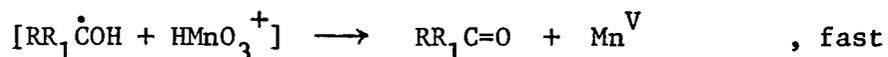
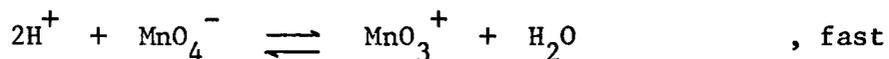


Figure 32. Salt effects on the permanganate oxidation of methanol. (Trials 812-825).

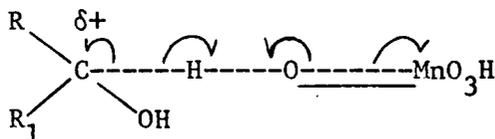


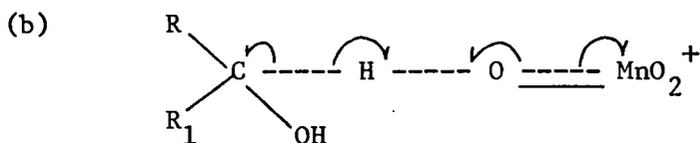
(b) TFA concentrations more than seven molar,



The transition states can be depicted as outlined below.

(a)





Considerable research has been directed towards elucidating the mechanism of the permanganate oxidation of alcohols, but as outlined in the Introduction the emphasis has been on the basic or weakly acidic regions.^{5,51} Some of the observations made in this investigation substantiate previous reports: (a) substantial primary isotope effects were observed in the oxidation of cyclohexanol-1-d₁;⁵⁰ (b) a large number of oxidations show acid catalyses which are governed by H₀;^{48-50,52} (c) substituent effects for the oxidation of tri- and di-arylcabinols have negative values of ρ⁺ indicating positive charge development in the transition state.⁴⁸

From the present mechanistic investigation of the oxidation of arenes and alkanes it became apparent that aromatic ring oxidation differs mechanistically from alkane oxidation. The oxidant, permanganyl ion, preferentially degrades aromatic rings via rate-determining electrophilic attack at ring carbon. This process shows no primary isotope effect.

Benzyl alcohol is a rather unique substrate which can be used to demonstrate that not only does ring attack proceed with no isotope effect but also that only permanganyl ion is capable of electrophilic ring attack. Table 36 presents the data for the oxidation of both benzyl alcohol and benzyl alcohol-α-d₂. It can be seen that when side-chain oxidation is inhibited by the presence of deuterium that the

Table 36. Kinetic Isotope Effects in the Oxidation of Benzyl Alcohol

$-H_R$	$H_2O, k_H/k_D^a$	$D_2O, k_H/k_D^b$	$d_2, k(D_2O)/k(H_2O)^c$	$h_2, k(D_2O)/k(H_2O)^d$
0.12	3.5	2.6	1.7	1.3
0.87	2.2	1.6	1.8	1.3
2.81	1.1	0.9	1.6	1.2
4.37	0.9	0.9	1.1	1.1
6.46	1.0	1.1	1.0	1.1
7.21	1.3	1.1	1.1	1.0

^a A medium made from $CF_2CO_3H-H_2O$, $k_H/k_D = k_2$ (benzyl alcohol)/ k_2 (benzyl alcohol- α - d_2).

^b A medium made from $CF_2CO_3H-D_2O$, k_H/k_D as defined in (a).

^c Substrate was benzyl alcohol- α - d_2 , $k(D_2O)/k(H_2O) = k_2$ (medium made from $CF_2CO_3H-D_2O$)/ k_2 (medium made from $CF_2CO_3H-H_2O$, k_2 is the oxidation rate of the substrate).

^d Substrate was benzyl alcohol, $k(D_2O)/k(H_2O)$ as defined in (c).

solvent isotope effect increases. This is consistent only with permanganyl ion being the electrophilic-ring oxidant since the rate changes parallel the pK changes for the generation of permanganyl ion when D_2O is substituted for H_2O . Further, it can be seen that as conditions are changed to maximize side chain attack (using H_2O and benzyl alcohol) that the primary isotope effect is at a maximum. This is in accord with both permanganyl ion and permanganic acid oxidizing the side chain via rate-determining carbon-hydrogen bond scission. It will be noted that as the acidity increases the selectivity imposed by deuterium is lost. This is due to ring attack becoming predominant when larger amounts of permanganyl ion are generated. (The solvent becomes richer in protium as the acidity increases since CF_3CO_2H was used to prepare the solutions.)

4.6 Oxidation of Aldehydes

The data for the oxidation of formaldehyde and benzaldehyde are presented in Appendix C, trials 1091-1164.

The excellent fit of the time-absorbance data with the pseudo first-order rate equation for up to two half-lives of permanganate confirms a first-order dependence upon permanganate. Figure 33 illustrates that the order with respect to substrate was first-order in both cases. The order with respect to acidity, as Figure 34 illustrates, was variable, as was also the case for alcohols. The resulting rate law can be expressed in a form parallel to that observed for alcohols except that a third term has been added to account for the

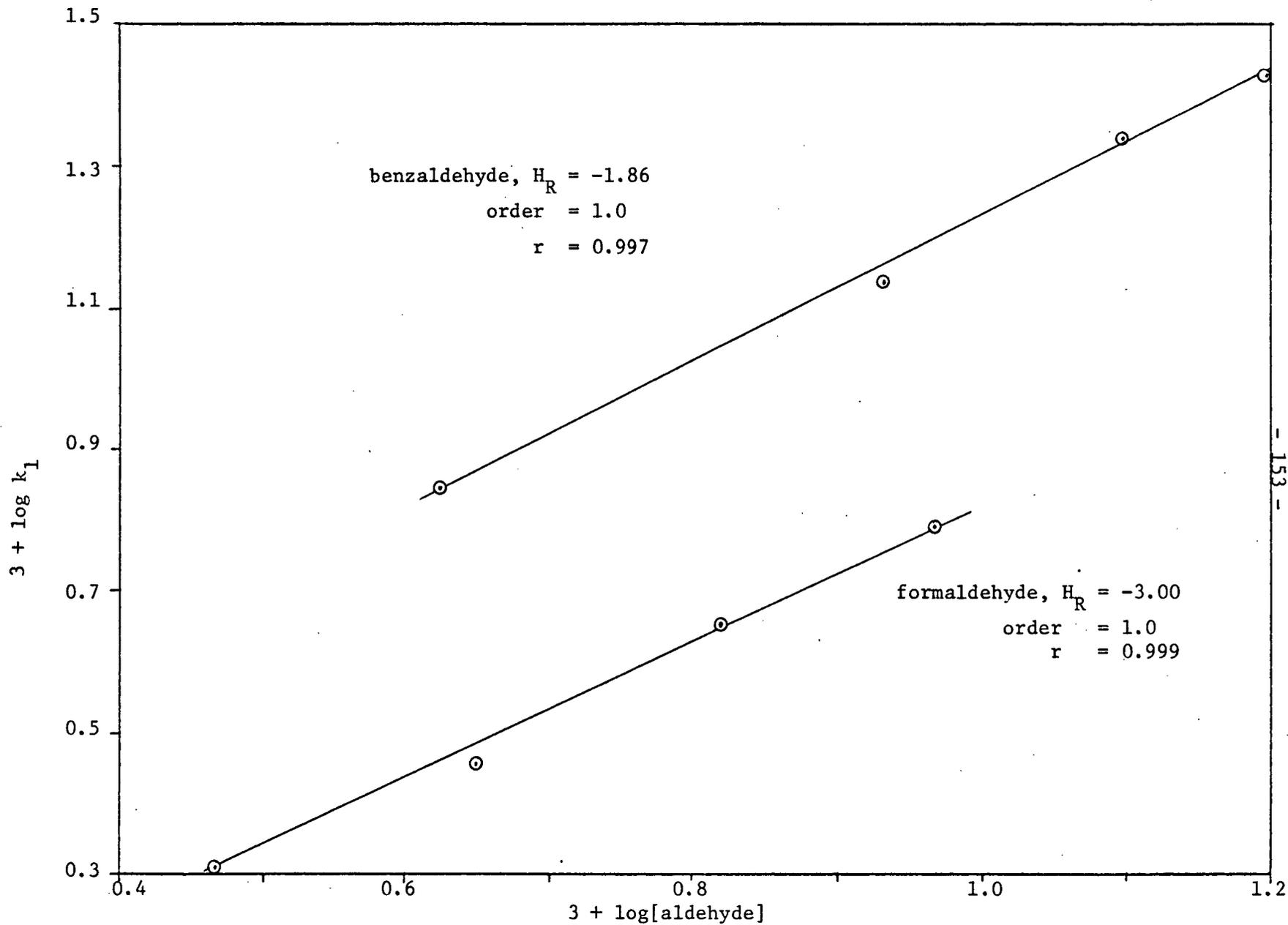


Figure 33. $\log k_1$ vs. $\log[\text{aldehyde}]$ for the oxidation of formaldehyde and benzaldehyde.

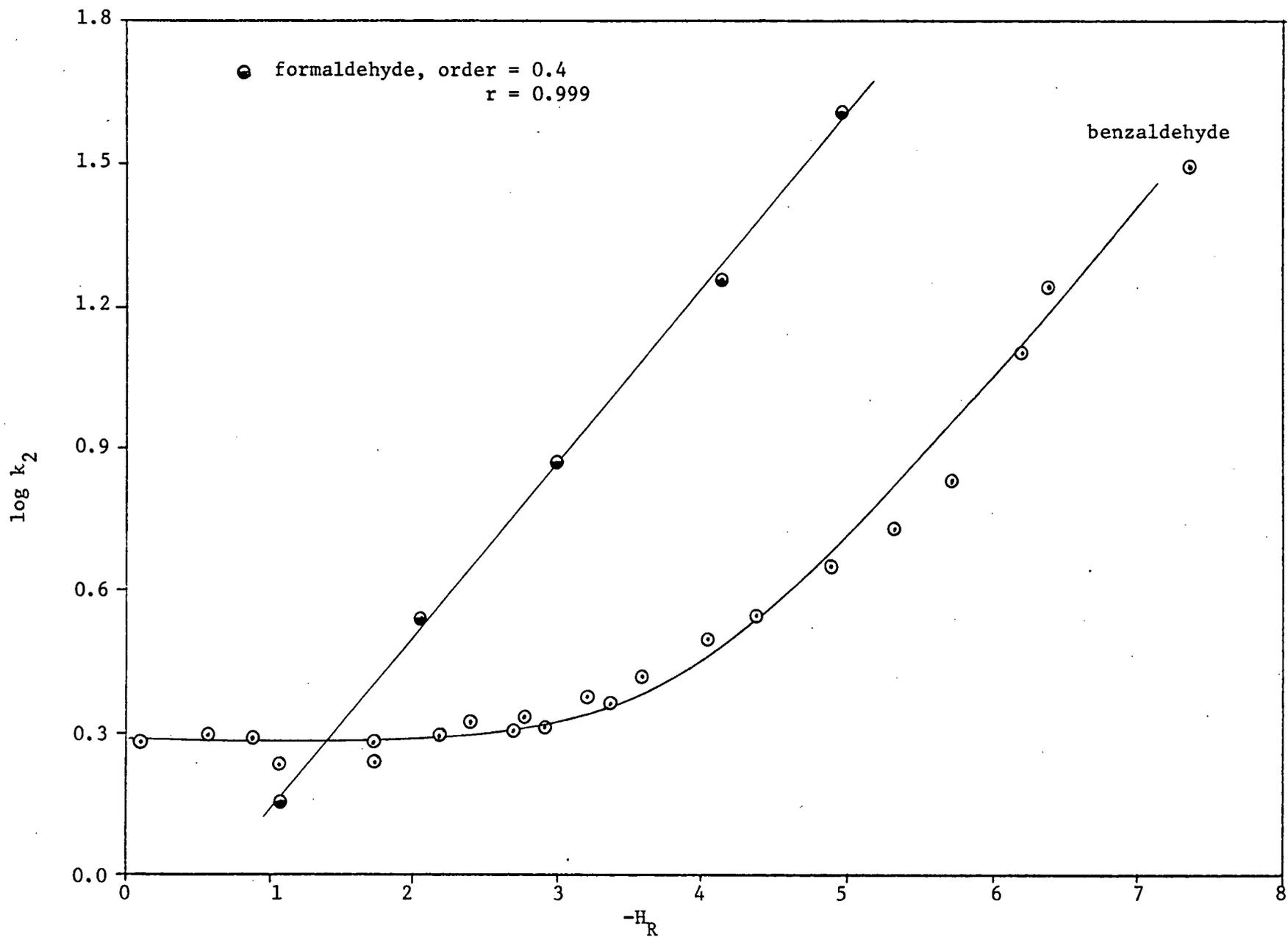


Figure 34. Log k_2 vs. H_R for the oxidation of formaldehyde and benzaldehyde

participation by permanganate ion.

$$-d[\text{MnO}_4^-]/dt = k_2[\text{aldehyde}][\text{MnO}_4^-] + k_3[\text{MnO}_4^-][\text{aldehyde}]h_o + k_3'[\text{aldehyde}][\text{MnO}_4^-]h_R$$

If electron withdrawing substituents are present the oxidation rate decreases ($\rho^+ = -0.5$, trials 1109-1116). A solvent isotope effect of $k(\text{D}_2\text{O})/k(\text{H}_2\text{O}) = 1.5$ at $H_R = -1.86$ was observed. These results indicate that the transition state resulting from one molecule of oxidant and one of aldehyde develops some positive charge and that permanganate ion is one of the oxidants. All of the evidence is consistent with mechanisms parallel to those observed for alcohols in the regions where either H_o or H_R govern the oxidation.

4.7 Oxidation of Ketones

The data for the oxidation of a variety of ketones are contained in Appendix C, trials 1004 to 1090 and 1175 to 1255.

The order with respect to permanganate was not constant for the series of compounds investigated. The oxidations of acetone, cyclohexanone, benzophenone, and trifluoroacetophenone were clearly first-order with respect to permanganate for more than two half-lives of permanganate, as the good to excellent fits with the pseudo first-order equation indicate. 2,4-Pentanedione and acetophenone were clearly zero order in permanganate but 3-pentanone was neither zero order nor first order. 2-Pentanone had a considerably better correlation with the first-order equation but should be considered as a borderline case.

Although the correlations ranged about 0.99 definite curvature was observed in all plots rather than random scatter about the least square line. Figures 35 and 36 depict typical zero-order and first-order plots.

The order with respect to substrate (see Table 37 and Figure 37) is first-order in all cases where clear dependence upon either the pseudo first-order or the zero-order equation is observed. 2-Pentanone and 3-pentanone indicate substrate orders in excess of one but this is caused by failure to find a proper equation to treat the time-absorbance data. The acid dependence is neither upon H_0 nor upon H_R , as the data in Table 37 show.

It is known in the chromic acid oxidation of ketones that when enolization becomes rate-determining the order in oxidant changes from first to zero order.^{137,138} Also, studies by Gero on the enol content of ketones have established the following order, ranging from highest enol content to the lowest; 2,4-pentanedione >> acetophenone > 3-pentanone > cyclohexanone > 2-pentanone > acetone.¹³⁹ In this kinetic investigation the two ketones which have the largest enol content, according to Gero, are oxidized via zero-order kinetics but those with lower enol contents than 3-pentanone show first-order dependence upon permanganate. Thus the change observed from first-order to zero-order in permanganate can be attributed to differences in the degree of enolization.

The product studies and the stoichiometries listed in Tables 3 and 5 indicate that ketones are degraded via carbon-carbon bond cleavage to yield acids.

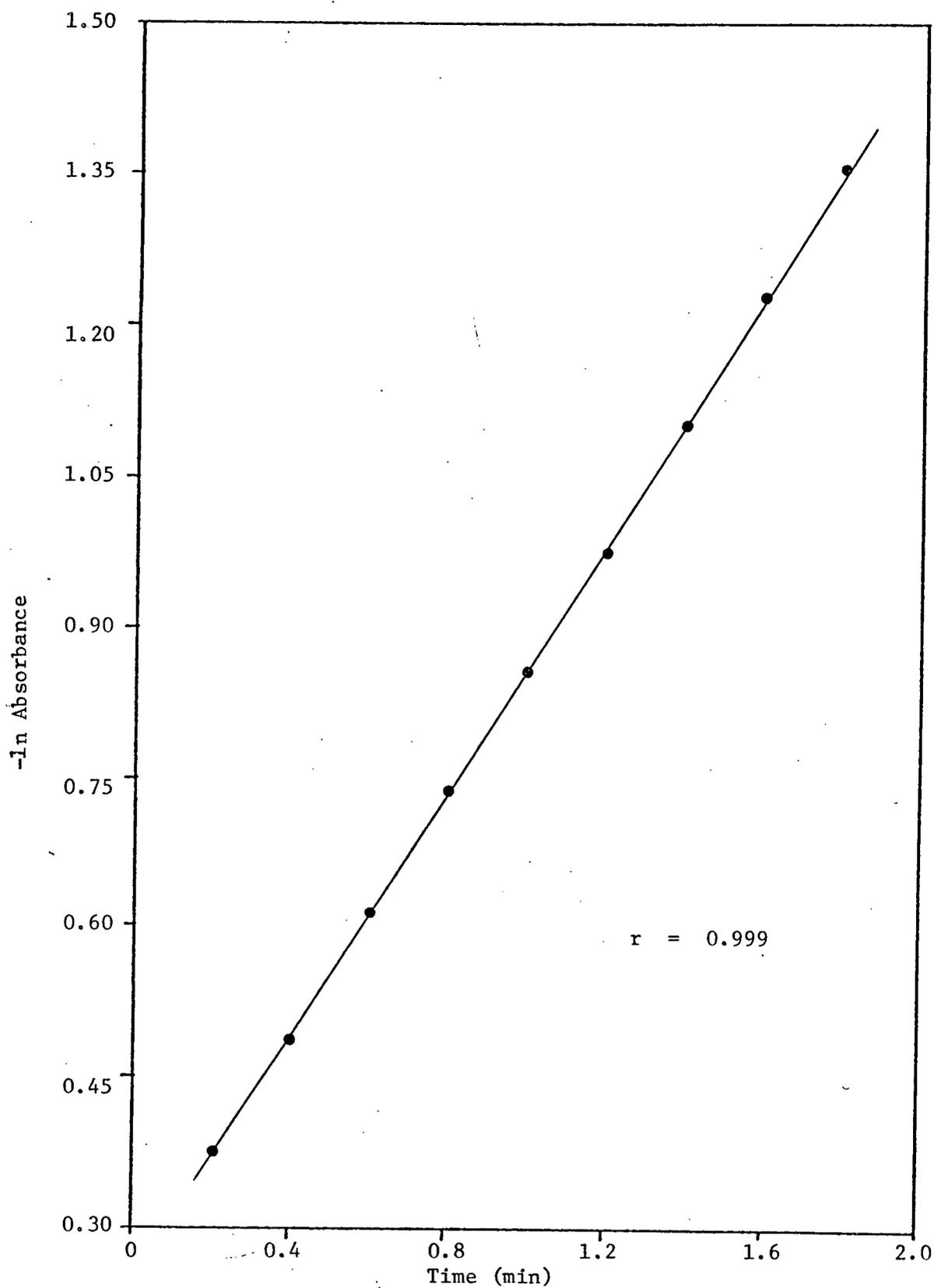


Figure 35. Typical pseudo first-order plot for the oxidation of cyclohexanone. (Trial 1069). Absorbance changed from 0.721 to 0.231.

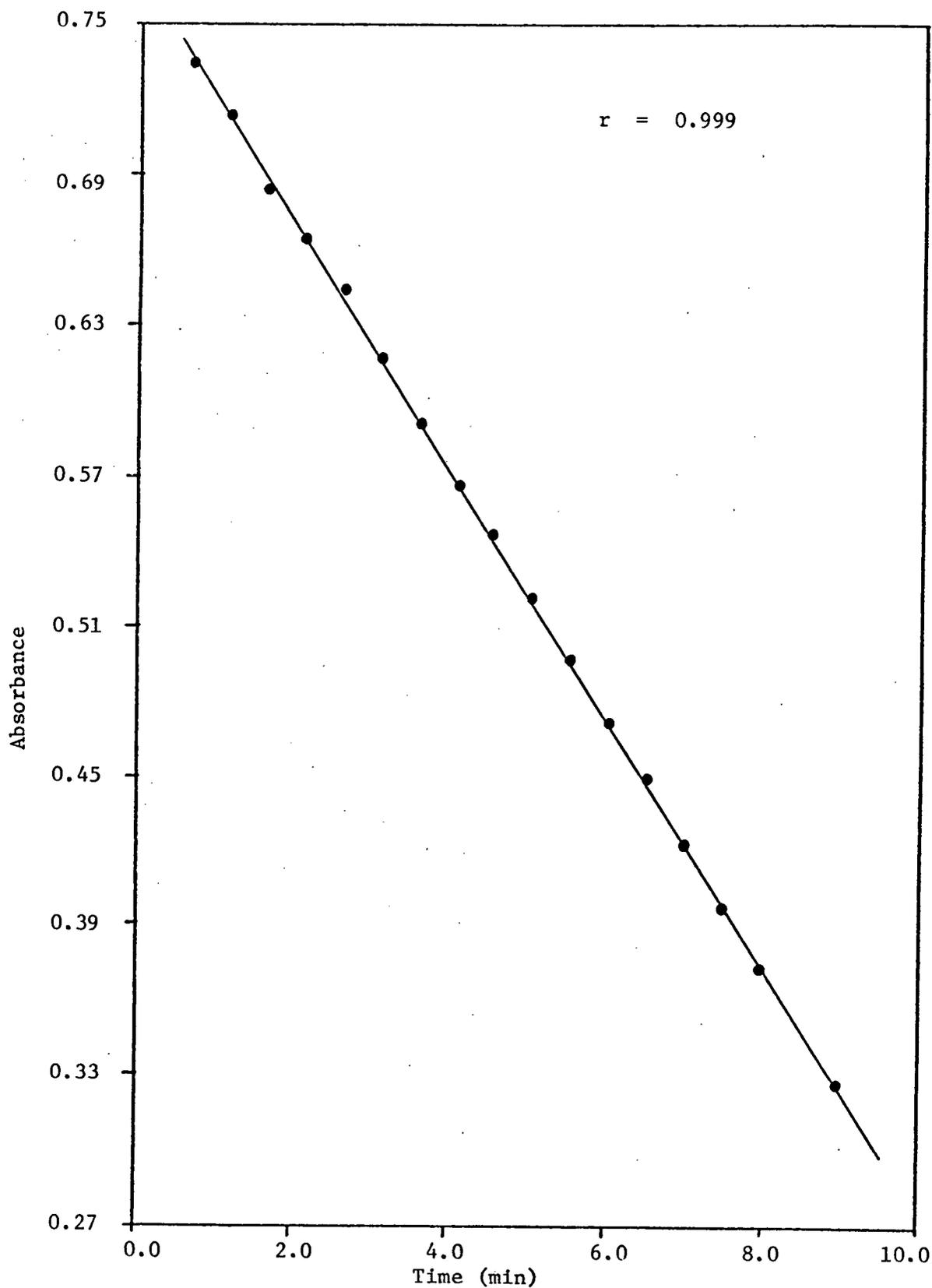


Figure 36. Typical zero order plot for the oxidation of acetophenone. (trial 1238).

Table 37. Order of Reactants in the Permanganate^a Oxidation of Ketones in TFA-Water.

Substrate	Order of substrate	r	Trials	Order in h_R	r	Order in h_o	r
Acetone	1.0	0.976	1009-1012				
	1.1	0.993	1013-1016				
			1004-1016	0.5	0.993		
2-Pentanone	1.4	.990	1035-1039				
			1017-1053	0.7 ^b	0.996		
2,4-Pentanedione	1.0	0.994	1203-1209				
			1197-1209	0.1	0.992	0.3	0.94
Benzophenone	1.1	0.988	1077-1080	-		-	
Trifluoroacetophenone	1.1	0.998	1085-1090				
			1081-1090	0.8	0.999		
Acetophenone	1.0	0.999	1236-1243				
			1232-1247	0.8	0.998		
Cyclohexanone	1.1	0.995	1057-1061				
			1054-1070	0.6 ^c	0.97		
3-Pentanone	1.6	0.999	1179-1186				

Note: Error in orders are \pm 5%.

^a First-order in permanganate except for acetophenone and 2,4-pentanedione where the order with respect to permanganate was zero.

^b Only those trials where $-H_R > 6.6$ and $T = 25.0^\circ$ have been considered.

^c Only those trials where $-H_R > 6.0$ and $T = 25.0^\circ$ have been considered.

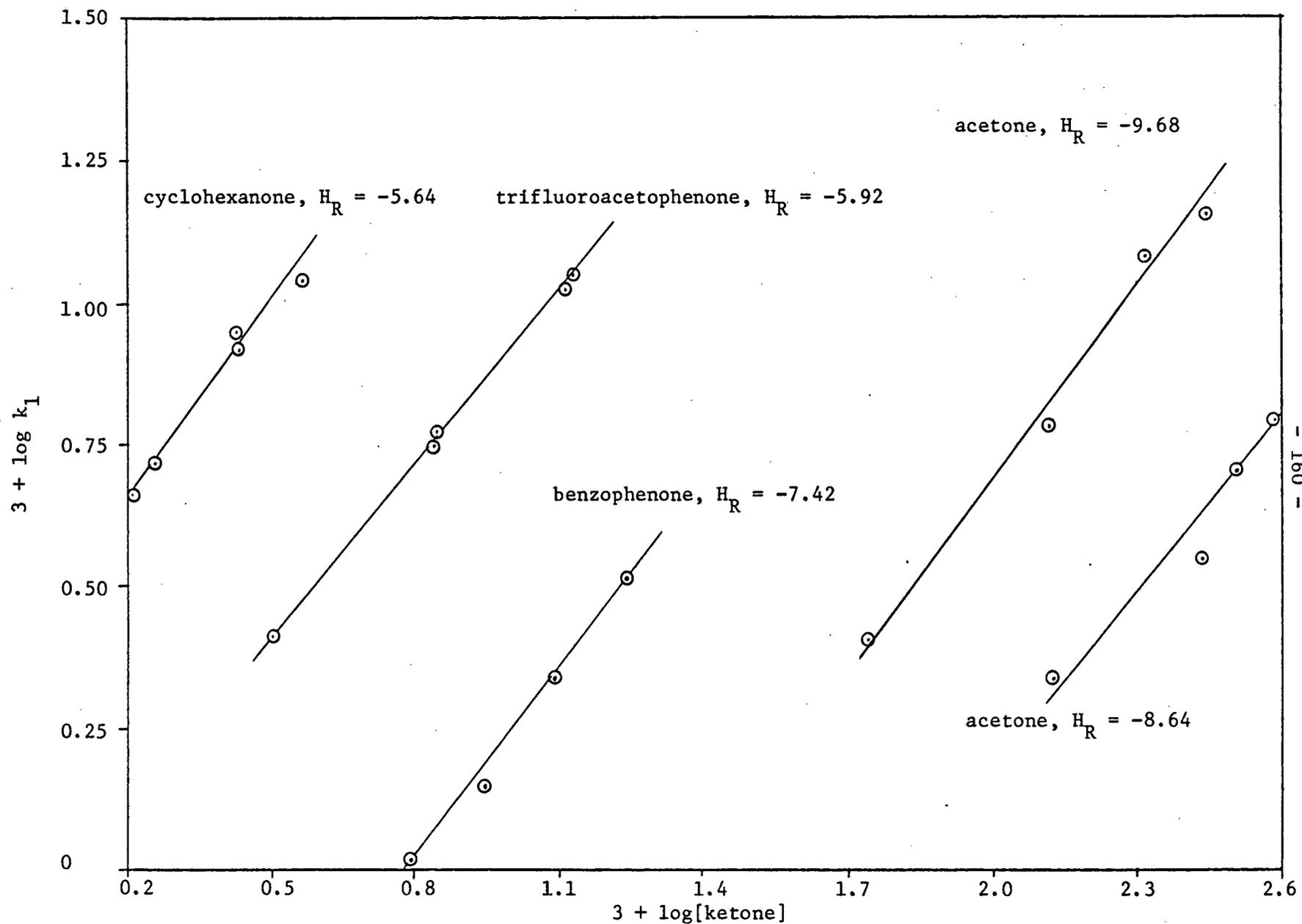


Figure 37. $\log k_1$ vs. $\log[\text{ketone}]$ for the oxidation of a variety of ketones.

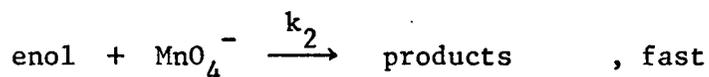
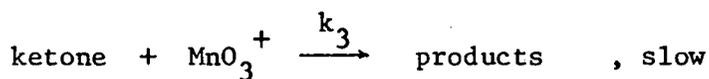
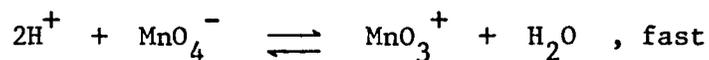
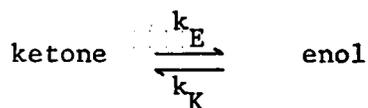
The oxidation of 2,4-pentanedione, which is extremely fast even in the aqueous region, and the observation that very little acid catalysis is observed for this compound (see Table 37) is a consequence of it readily enolizing and the enol being rapidly oxidized by permanganate ion.

The experimental rate law for ketones can be expressed in the following composite form:

$$-d[\text{MnO}_4^-]/dt = k_1[\text{ketone}] + k_3[\text{ketone}][\text{MnO}_4^-]h_R$$

The first term accounts for the oxidation of the enol by permanganate ion since it is the predominant oxidant. The second term accounts for the degradation of the ketone (in the keto form) by permanganyl ion.

A mechanism which accounts for the experimental observations can be expressed as;



Using a steady-state approximation for the enol content the following rate law results.

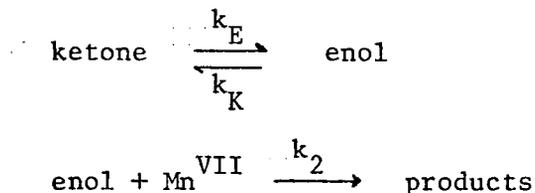
$$r = k_3[\text{ketone}][\text{MnO}_4^-]h_R + \frac{k_E k_2[\text{ketone}][\text{MnO}_4^-]}{k_K + k_2[\text{MnO}_4^-]}$$

Since it is known that permanganate ion rapidly oxidizes enols it can be assumed that $k_2[\text{MnO}_4^-] \gg k_K$. The rate equation then reduces to,

$$r = \frac{k_E}{k_K} [\text{ketone}] + k_3[\text{ketone}][\text{MnO}_4^-]h_R$$

This derived rate law is similar to the experimental rate law. The observed change in order of oxidant can be explained as follows: If the ketone does not readily enolize the major oxidative pathway is the degradation of the ketone by permanganyl ion (the first-order case) but if the ketone readily enolizes then the enol pathway becomes predominant (the zero-order case). The deviations from either of the two known acidity functions are probably due to varying degrees of oxidation by all three possible oxidants (MnO_4^- , HMnO_4 , and MnO_3^+) each of which has a different acidity dependence.

An alternate mechanism can be proposed which accounts for the experimental facts:



The derived rate law is shown below, which results from the steady-state approximation on enol.

$$r = \frac{k_E k_2 [\text{ketone}] [\text{Mn}^{\text{VII}}]}{k_K + k_2 [\text{Mn}^{\text{VII}}]}$$

when $k_K \gg k_2 [\text{Mn}^{\text{VII}}]$, $r = \frac{k_E k_2}{k_E} [\text{ketone}] [\text{Mn}^{\text{VII}}]$

when $k_K \ll k_2 [\text{Mn}^{\text{VII}}]$, $r = k_E [\text{ketone}]$

This satisfies the change from zero to first-order dependence upon permanganate and this type of rate law has been shown to indeed apply to chromic acid oxidations of ketones.^{137,138} But because of the extremely fast rate for the oxidation of 2,4-pentanedione, which clearly involves enolization, it can be concluded that $k_2 [\text{Mn}^{\text{VII}}]$ will always be greater than k_K . (In the highly aqueous region where the 2,4-pentanedione oxidations were performed permanganate ion, the weakest of the three oxidants, is the predominant species.) Thus whenever the oxidation proceeds via the enol route a zero-order dependence upon permanganate should be observed. Therefore, this latter mechanism cannot account for the first-order dependence upon permanganate for some of the ketones.

4.8 Oxidation of Formic Acid

The kinetic data for the oxidation of formic acid are presented in Appendix C, trials 1165-1174.

The excellent correlation of the time-absorbance data with the pseudo first-order equation indicates first-order dependence upon permanganate. The order with respect to substrate concentration, as is depicted in Figure 38, is first order. The acid dependence, depicted

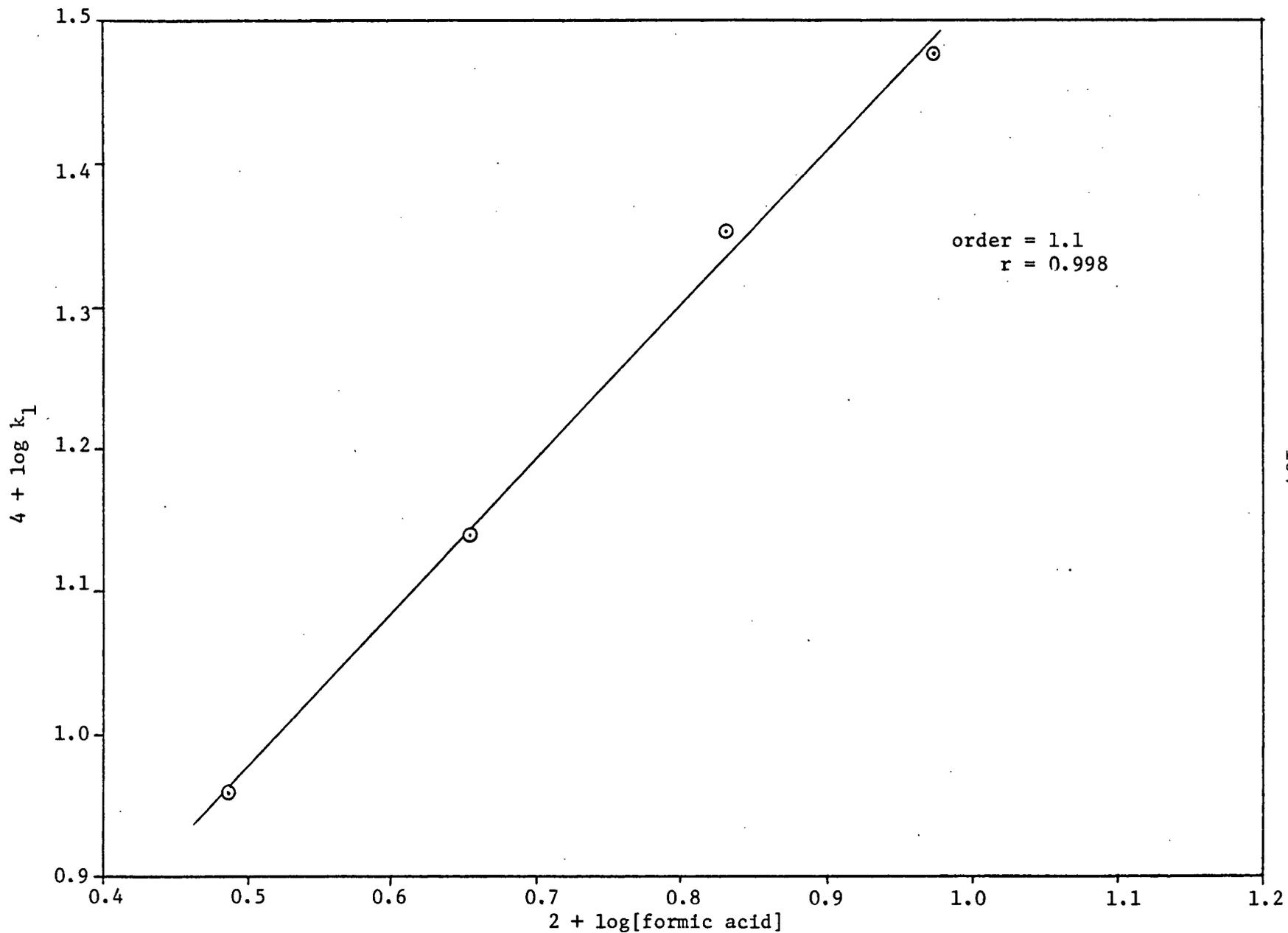


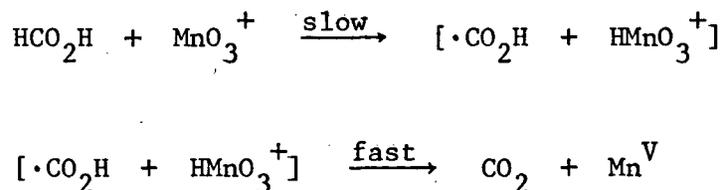
Figure 38. $\log k_1$ vs. $\log[\text{formic acid}]$ for the oxidation of formic acid.

in Figure 39, is upon h_R with an order of one. The resulting rate law can be expressed as;

$$-d[\text{MnO}_4^-]/dt = k_3[\text{MnO}_4^-][\text{HCO}_2\text{H}]h_R$$

The active oxidant appears to be permanganyl ion, as indicated by the rate dependence upon h_R .

The mechanism of the formic acid oxidation can be expressed as;



This scheme is analogous to that proposed by other researchers.⁶³

4.9 Oxidation by Permanganate in Benzene

After Starks⁷⁰ showed that permanganate could be used as an oxidant in organic solvents such as benzene by phase transfer using quaternary alkyl ammonium cations it was decided to examine the mechanism of this permanganate oxidation in benzene. The kinetic data are contained in Appendix D, trials 1256-1285.

The species present in the benzene layer was identified as a one to one salt of the cation and permanganate ion as it was possible to isolate this salt in good yields (see Tables 11 and 12 and Section 3.11). This compound can be used to readily oxidize alkenes, alkynes, alcohols, and aldehydes to carboxylic acids. These oxidations show first-order

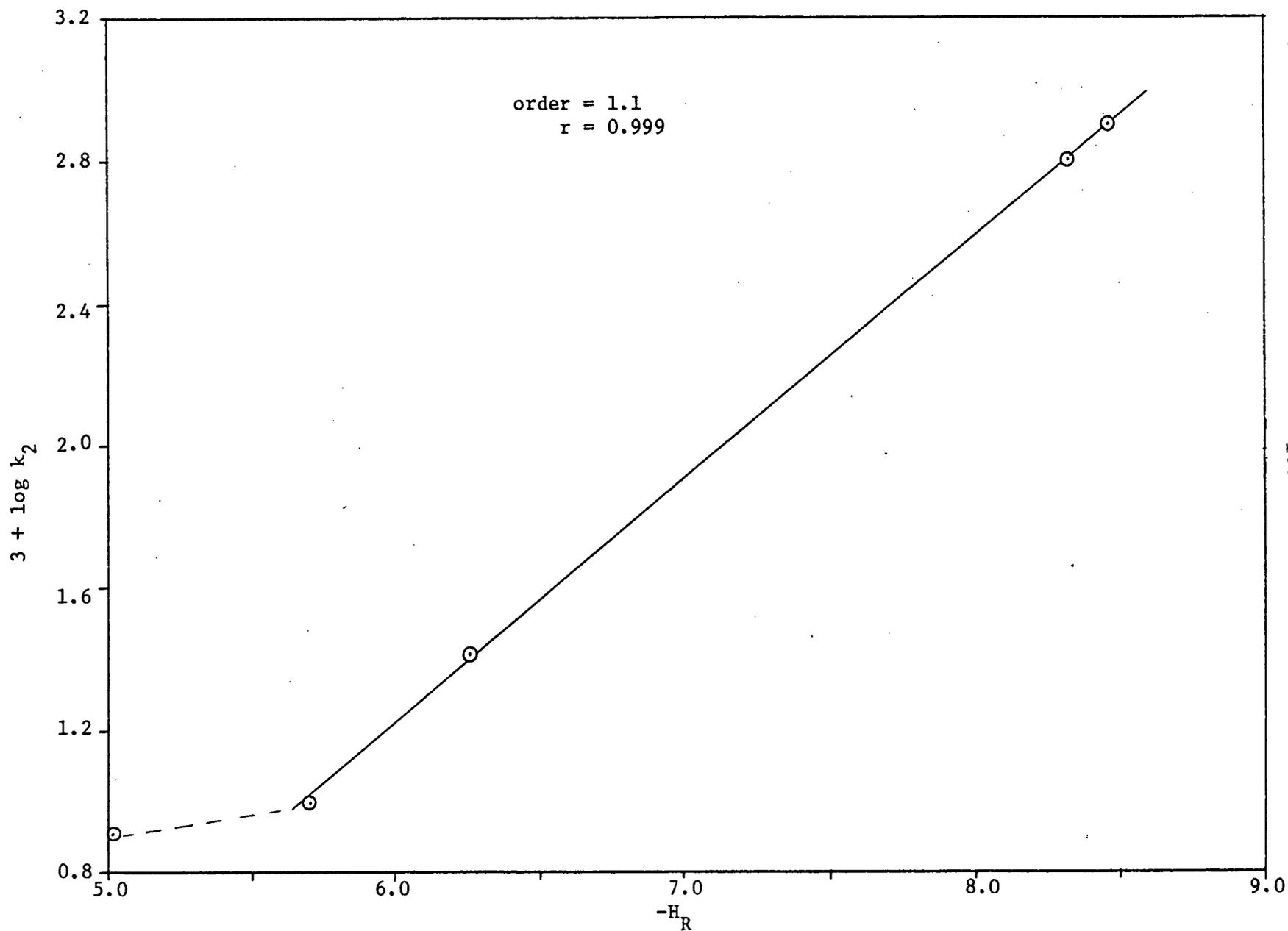


Figure 39. $\log k_2$ vs. H_R for the oxidation of formic acid.

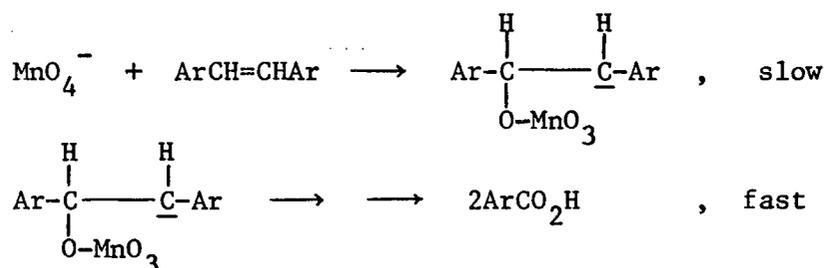
dependence upon permanganate ion as the good correlations with the pseudo first-order equation illustrates. The constancy of the k_2 values in Appendix D confirms a first-order dependence upon substrate concentration. It was not possible to examine any acid or base catalysis since such additions resulted in rapid and complete decomposition of Mn^{VII} .

The effect of substituents, as depicted in Figure 40, shows that electron-withdrawing substituents increase the oxidation rate. Such substituent effects, although unusual for an oxidation process, have been observed for some basic permanganate oxidations of arenes.¹⁴⁰

The rate law is;

$$-d[MnO_4^-]/dt = k_2[\text{substrate}][MnO_4^-]$$

The mechanism of this oxidation can be visualized as the following for stilbenes;



The only products detected from the oxidation of tolan, stilbene, benzyl alcohol, and benzaldehyde was benzoic acid. The yield was quite low if based on permanganate consumed and thus the reaction would seem to have very little synthetic value. However, the tetra-(n-hexyl)ammonium permanganate salt can be isolated and stored without

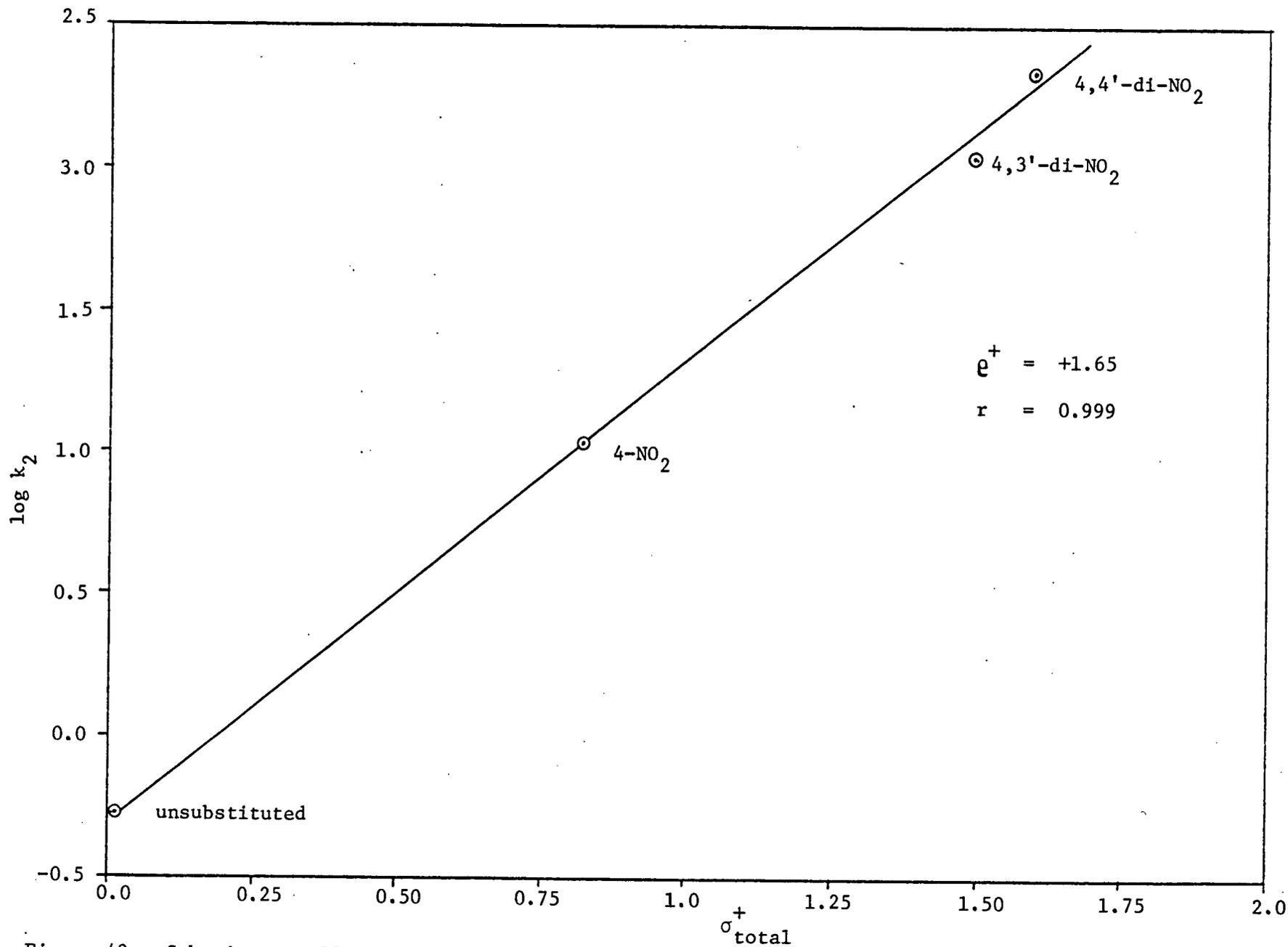


Figure 40. Substituent effects on the permanganate oxidation of trans-stilbenes in a medium of benzene. σ_{total}^+ vs. $\log k_2$.

appreciable decomposition and it is possible that this organic solvent-soluble salt could have some future application.

5. CONCLUSIONS

The data presented indicate that three manganese(VII) species can be generated in TFA-water. Their proportions depend upon the solvent composition and their role as oxidants depends upon the nature of the reductant. Labile compounds such as aldehydes and enols are appreciably oxidized by permanganate ion and by permanganic acid. Somewhat less labile compounds such as alcohols are oxidized mostly by permanganic acid in TFA-water solutions less than 7 molar in TFA. Inert substrates such as ketones (those which do not readily enolize), alkanes, acids, and arenes are oxidized by the more vigorous oxidant permanganyl cation. In regions more acidic than 7 molar TFA, regardless of the reductant, permanganyl cation appears to be the major oxidant.

The oxidations previously discussed have the following general characteristics.

(i) Permanganate oxidations in TFA-water solutions that correlate with H_R involve permanganyl ion as the oxidant.

(ii) Oxidations in TFA-water solutions that deviate appreciably from H_R and tend to correlate with H_O involve permanganic acid as one of the oxidants.

(iii) Permanganic acid is not an important oxidant in solutions more acidic than 7 molar TFA.

(iv) Aromatic rings are degraded only by permanganyl cation, which acts as an electrophile. The mechanism postulated for these types of oxidations involves phenolic compounds as intermediates.

(v) Primary kinetic isotope effects are observed only for oxidations where the major oxidative pathway does not involve aromatic ring attack. Solvent isotope effects are observed for a wide variety of substrates and this is due to the solvent's effect upon the permanganate ion-permanganyl ion equilibrium.

(vi) The activation parameters change with increased TFA content showing smaller enthalpy values but larger negative entropy values. This could be indicative of increased solvation of the partially positively-charged transition state by TFA.

(vii) No salt effects were observed for any of the substrates examined.

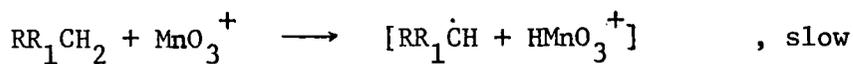
(viii) The substituent studies indicate that the substrates examined develop some positive charge in the transition state.

(ix) In all cases the rate law showed first-order dependence upon substrate concentration. The order with respect to the oxidant was first-order except when enolizable ketones were the reductants. In these cases the order in oxidant was zero.

(x) In all cases except arene oxidation the rate-determining step can be considered to involve homolytic carbon-hydrogen bond cleavage.

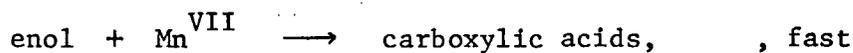
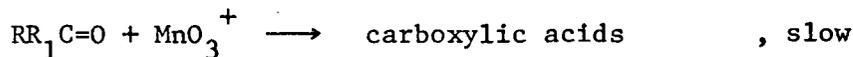
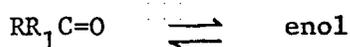
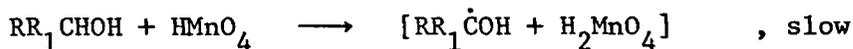
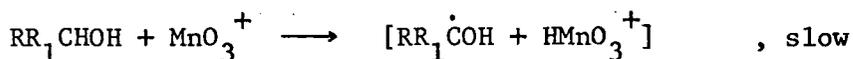
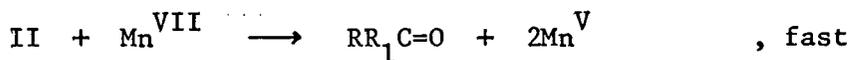
The following oxidative sequences for arenes and alkanes accommodate all of the kinetic results. Note: The final inorganic product can be either manganese(II), manganese dioxide, or a mixture of both, depending on the nature of the reductant.

(a) Oxidation of Alkanes

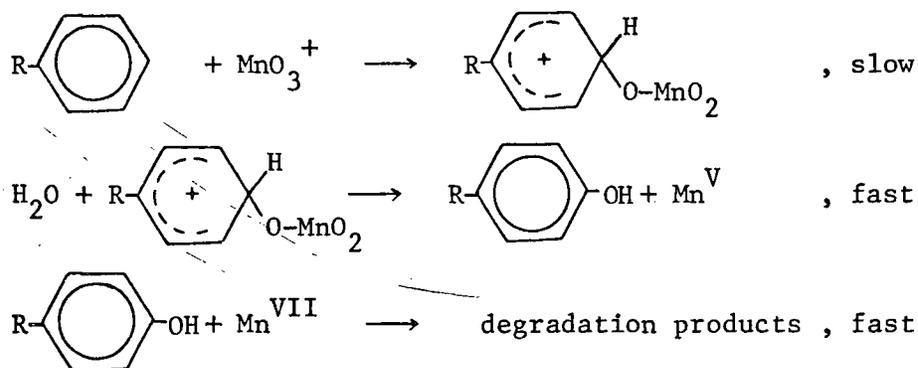


(I)

(II)



(b) Oxidation of Arenes (ring attack)



The use of TFA-water medium to perform homogeneous permanganate oxidations of organic substrates appears to have little synthetic value since carboxylic acids and unidentifiable degradation products were the only products obtained. This complication probably arises from the medium generating the vigorous oxidant, permanganyl ion (MnO_3^+).

The use of tetra(n-hexyl)ammonium permanganate extends the utility of permanganate as an oxidant to homogeneous organic systems. Unfortunately this technique makes inefficient use of the oxidant.

6. SUGGESTIONS FOR FURTHER STUDY

The mechanistic investigation of the oxidation of organic substrates by permanganate in TFA-water medium appears to be complete, but several interesting areas were touched upon which warrant further investigation. The tetra(n-hexyl)ammonium permanganate salt which is soluble only in organic solvents could have considerable potential as an oxidant if a solvent system could be found in which it is stable. The preliminary kinetic and product analysis indicate that a wide range of functional groups can be oxidized with very little aromatic ring degradation.

The mechanism of aromatic nitration should be re-examined in order to explain the presence of phenolic products which could result from electrophilic attack on arenes by the oxygen atoms of the ambident nitronium ion (NO_2^+).

APPENDIX A

The tables listed in this appendix present the original spectrophotometric data for the ionization of carbinols in TFA-water solutions. The acid content is expressed in terms of molarity (M).

The numbers listed were obtained by performing the following calculations.

$[R^+]$ = Absorbance observed, corrected for blanks = Abs.

$[ROH]$ = Final absorbance of fully ionized carbinol - Abs.

$$Q = [R^+]/[ROH]$$

$pH \equiv H_R$ in dilute solutions; used to determine pK_R of the anchor compounds. The pH values used to determine the average pK_R are marked with an asterisk.

$pK_{R+} = H_R + \log Q$ for those solutions which overlapped with the next indicator used. The H_R values used to generate the pK_{R+} of successive indicators are marked with an asterisk.

- denotes the absorbance value used for the fully ionized species.

(H_R) - independent H_R values from the other anchor indicator.

APPENDIX A

4,4',4''-Trimethoxy TPC average $pK_{R^+} = +0.92$

M	pH	Abs.	Q	log Q	pK_{R^+}	H_R
0.068	1.29*	0.1920	0.429	-0.368*	0.92	1.29
0.072	1.28*	0.1928	0.431	-0.365*	0.92	1.29
0.144	1.04	0.3012	0.889	-0.051	0.92	0.97
0.140	1.03	0.3042	0.906	-0.043	0.92	0.96
0.270		0.4274	2.011	0.303	0.92	0.62
0.540		0.5450	5.743	0.759	0.92	0.16
0.800		0.6005	15.241	1.183	0.92	-0.26
1.07		0.6266	47.113	1.673	-	-
1.31		0.6399 ⁻				
0.069	1.30*	0.2292	0.410	-0.387*	0.92	1.31
0.070	1.32*	0.2076	0.358	-0.447*	0.92	1.37
0.130	1.06*	0.3410	0.763	-0.118*	0.92	1.04
0.130	1.02*	0.3754	0.909	-0.041*	0.92	0.96
0.256		0.5382	2.153	0.333	0.92	0.59
0.260		0.5080	1.813	0.258	0.92	0.66
0.261		0.5318	2.074	0.317	0.92	0.60
0.270		0.5222	1.962	0.293	0.92	0.63
0.515		0.6950	7.457	0.873	0.92	0.05
0.525		0.6661	5.455	0.737	0.92	0.18
0.770		0.7362	14.158	1.151	0.92	-0.23
1.04		0.7780	76.275			
1.292		0.7882 ⁻				

APPENDIX A

4-Methyl-4',4''-dimethoxytriphenylcarbinol $pK_{R^+} = -0.28$

M	pH	Abs.	Q	log Q	pK_{R^+}	H_R (H_R)
0.069	1.28	0.004	0.006	-2.221		
0.069	1.28	0.008	0.012	-1.918	-0.64	
0.130	1.01*	0.0326	0.051	-1.291*	-0.28	1.01 (1.04)
0.130	1.01*	0.0308	0.048	-1.317*	-0.31	1.04 (0.96)
0.261	0.76*	0.0742	0.125	-0.905*	-0.25	0.63 (0.60)
0.544		0.1725	0.347	-0.460		0.18 (0.16)
0.796		0.2740	0.692	-0.160		-0.12(-0.26)
1.08		0.3630	1.183	0.073		-0.35
1.33		0.4451	1.981	0.297		-0.58
1.61		0.5088	3.160	0.500		-0.78
1.85		0.5580	4.991	0.698		-0.98
2.11		0.5858	6.974	0.843		-1.12
2.34		0.6159	11.427	1.058		-1.34
2.86		0.6480	29.725	1.473		-1.75
3.10		0.6470	28.377	1.453		-1.71
3.40		0.6680				
3.92		0.6698 ⁻				

APPENDIX A

4,4'-Dimethoxytriphenylmethyl chloride $pK_{R+} = -0.97$

M	H_R^*	Abs.	Q	log Q	pK_{R+}	H_R
0.515		0.0356	0.052	-1.284		+0.31
0.770		0.0724	0.112	-0.952		-0.02
1.290	-0.55	0.1840	0.343	-0.464	-1.01	-0.51
1.810	-0.92	0.3567	0.982	-0.008	-1.00	-0.96
2.32	-1.32	0.5032	2.321	0.366	-0.95	-1.34
2.84	-1.70	0.6278	6.809	0.833	-0.97	-1.80
3.32		0.6820	17.947	1.254		-2.22
3.85		0.7111	79.899	1.903		-2.87
4.37		0.7182				
4.90		0.7298				
		0.7200 ⁻				

APPENDIX A

4,4',4''-Trimethyltriphenylcarbinol $pK_{R^+} = -2.81$

M	$-H_R^*$	Abs.	Q	log Q	$-pK_{R^+}$	$-H_R$
2.86	1.82	0.0719	0.087	-1.063	2.88	1.75
3.16	2.06	0.1347	0.175	-0.756	2.82	2.05
3.36	2.26	0.2273	0.336	-0.473	2.73	2.34
3.60		0.3708	0.697	-0.157		2.65
3.88		0.4948	1.212	+0.084		2.89
4.46		0.7260	4.102	+0.613		3.42
4.92		0.7850	6.653	+0.823		3.63
5.42		0.8550	17.813	1.251		4.06
5.96		0.8762	32.694			
6.48		0.8910				
7.12		0.9010				
7.52		0.9060				
8.52		0.9140				
		0.9030 ⁻				

APPENDIX A

4-Methoxytriphenylcarbinol $pK_{R+} = -3.18$

M	$-H_R^*$	Abs.	Q	Log Q	$-pK_{R+}$	$-H_R$
2.86	1.78	0.0305	0.044	-1.360	3.14	1.82
3.34	2.28	0.0784	0.121	-0.916	3.20	2.26
3.87	2.88	0.1969	0.369	-0.433	3.31	2.75
4.45	3.41	0.3770	1.068	0.029	3.39 ⁺	3.21
4.87	3.59	0.5460	2.967	0.472	3.12	3.65
5.15	3.79	0.6004	4.633	0.666	3.12	3.85
5.42	4.06	0.6482	7.924	0.899	3.16	4.08
5.44		0.6420	7.133	0.853		4.03
6.00		0.6844	15.009	1.176		4.36
6.50		0.7093	34.266	1.535		
7.00		0.7239				
7.50		0.7270				
8.02		0.7352				
8.55		0.7390				
		0.7300 ⁻				

⁺ not used for pK_R

APPENDIX A

4,4'-Dimethyltriphenylcarbinol $pK_{R+} = -3.78$

M	$-H_R^*$	Abs.	Q	Log Q	$-pK_{R+}$	$-H_R$
3.88		0.0720	0.138	-0.860		2.92
4.44	3.20	0.1404	0.310	-0.509	3.71	3.27
4.73	3.51	0.2039	0.523	-0.282	3.79	3.50
4.96	3.74	0.2681	0.823	-0.085	3.83	3.70
5.23	3.93	0.3419	1.356	0.132	3.80	3.91
5.48	4.07	0.3899	1.910	0.281	3.79	4.06
5.70		0.4552	3.280	0.516		4.30
6.07		0.5170	6.714	0.827		4.61
6.48		0.5461	11.401	1.057		4.84
7.00		0.5800	41.429	1.617		
7.53		0.5910				
8.10		0.5939				
8.57		0.5942				
		0.5940 ⁻				

APPENDIX A

4,4'-Diethoxydiphenylcarbinol $pK_{R^+} = -5.77$

M	$-H_R^*$	Abs.	Q	Log Q	$-pK_{R^+}$	$-H_R$
5.47		0.0280	0.025	-1.602		
6.00	4.53	0.0586	0.054	-1.269	5.80 ⁺	4.50
6.47	4.83	0.1161	0.113	-0.948	5.77	4.82
7.07		0.2105	0.225	-0.648		5.12
7.28		0.2940	0.345	-0.463		5.31
7.47		0.3798	0.495	-0.305		5.47
7.79		0.4830	0.727	-0.138		5.63
8.03		0.5899	1.059	0.025		5.80
8.30		0.6678	1.394	0.144		5.91
8.53		0.7800	2.125	0.327		6.10
8.87		0.8898	3.460	0.539		6.31
9.07		0.9702	5.488	0.739		6.51
9.33		1.008	7.252	0.860		6.63
9.57		1.061	12.337	1.091		6.86
9.83		1.100	24.404	1.369		7.14
10.10		1.113				
10.57		1.147 ⁻				
11.05		1.166				

+ not used for $-pK_{R^+}$

APPENDIX A

Triphenylcarbinol $pK_{R+} = -6.25$

M	$-H_R^*$	Abs.	Q	Log Q	$-pK_{R+}$	$-H_R$
7.10	5.14	0.0377	0.066	-1.181	6.32	5.07
7.57	5.53	0.0794	0.150	-0.825	6.33	5.43
7.80	5.64	0.1206	0.246	-0.608	6.24	5.64
8.07	5.84	0.1739	0.399	-0.399	6.24	5.85
8.33	5.94	0.2392	0.645	-0.190	6.14	6.06
8.67	6.20	0.3189	1.095	0.040	6.16	6.29
8.81		0.3771	1.619	0.209		6.46
9.17		0.4549	2.933	0.467		6.72
9.47		0.5112	5.174	0.714		6.96
9.57		0.5478	8.807	0.945		7.20
10.20		0.6039	99.00	1.996		
10.67		0.6178				
11.27		0.6101				
		0.6100 ⁻				

APPENDIX A

4,4',4''-Trichlorotriphenylcarbinol $pK_{R+} = -7.94$

M	$-H_R^*$	Abs.	Q	Log Q	$-pK_{R+}$	$-H_R$
9.13	6.54	0.0273	0.031	-1.516		6.42
9.33	6.72	0.0470	0.054	-1.270	7.99	6.67
9.53	6.90	0.0815	0.097	-1.018	7.92	6.93
9.87	7.20	0.1535	0.200	-0.700	7.91	7.24
10.10		0.2898	0.458	-0.339		7.60
10.27		0.3500	0.612	-0.213		7.73
10.40		0.4331	0.886	-0.053		7.89
10.53		0.5578	1.532	0.185		8.13
10.60		0.6400	2.270	0.356		8.30
10.80		0.7114	3.378	0.529		8.47
10.93		0.7760	5.315	0.726		8.67
11.00		0.8030	6.748	0.829		8.77
11.10		0.8458	11.100	1.045		8.99
11.23		0.8660	15.464	1.189		9.13
11.67		0.9120				
12.20		0.9220				
12.70		0.9310				

APPENDIX A

4-Nitrotriphenylcarbinol $pK_{R^+} = -9.56$

M	$-H_R^*$	Abs.	Q	Log Q	$-pK_{R^+}$	$-H_R$
10.57		0.0354	0.087	-1.049		8.51
10.83	8.60	0.0428	0.110	-0.959	9.56	8.60
11.07	8.91	0.0786	0.222	-0.653	9.56	8.91
11.37		0.0865	0.250	-0.601		8.96
11.67		0.1554	0.551	-0.259		9.30
11.93		0.2704	1.673	0.224		9.78
12.20		0.3326	3.346	0.525		10.09
12.43		0.3753	6.619	0.821		10.38
12.63		0.3984	11.857	1.074		10.63
13.03		0.4312				
13.07		0.4320 ^{- a}				

^a Addition of H_2SO_4 gave no further increase so it appears to be fully ionized at this point.

APPENDIX B

Oxidation in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$

No.	[Substrate] $\times 10^3$	$-\text{H}_\text{O}$	$-\text{H}_\text{R}$	$k_1 \times 10^3 \text{ s}^{-1}$	$k_2 \text{ M}^{-1} \text{ s}^{-1}$	r
n-Pentane						
1	3.10	3.72	7.49	17.89	5.76	.999
2	"			17.97	5.79	"
3	"			17.07	5.50	"
4	2.325			11.48	4.94	"
5	"			12.77	5.49	"
6	"			12.48	5.35	"
7	1.55			7.74	5.00	"
8	"			5.07	3.27	.990
9	"			4.84	3.11	.980
10	3.10	3.50	6.95	5.35	1.73	.999
11	"			5.98	1.93	"
12	"			6.16	1.98	"
13	2.325			4.09	1.76	"
14	"			4.52	1.94	"
15	"			4.67	2.01	"
16	1.55			1.68	1.08	.980
17	"			1.41	0.910	.975
18	"			1.27	0.820	.970
19	0.775			0.843	1.09	.950
20	"			0.801	1.03	.970
21	"			0.806	1.04	.965
22	3.10	3.01	5.90	1.45	0.467	.999
23	"			1.45	0.467	"
24	"			1.31	0.423	"
25	2.325			0.658	0.283	"
26	"			0.610	0.262	.975
27	"			0.646	0.278	.999
28	1.55			0.443	0.286	.990
29	"			0.418	0.270	.970
30	"			0.476	0.307	.998
31	0.775			0.194	0.251	.980
32	"			0.183	0.236	.965
33	"			0.199	0.258	.975
34	3.10	2.53	4.90	0.251	0.0810	.999
35	"			0.289	0.0930	"
36	"			0.256	0.0825	"
37	"			0.235	0.0759	"
38	"			0.284	0.0915	"
39	"			0.242	0.0780	"
40	2.325			0.264	0.113	"
41	"			0.248	0.106	"
42	"			0.228	0.0979	"
43	"			0.216	0.0926	"

APPENDIX B

No.	[Substrate] x 10 ³	-H _O	-H _R	k ₁ x 10 ³ s ⁻¹	k ₂ M ⁻¹ s ⁻¹	r
44	"			0.214	0.0920	.999
45	"			0.199	0.0855	"
46	1.55			0.150	0.0969	"
47	"			0.144	0.0929	"
48	"			0.155	0.100	"
49	0.775			0.0719	0.0930	"
50	"			0.0722	0.0934	.997
51	"			0.0652	0.0841	.947
52	3.10	2.19	4.25	0.0900	0.0290	.999
53	"			0.0872	0.0282	"
54	"			0.0846	0.0273	"
55	2.325			0.0852	0.0366	"
56	"			0.0937	0.0402	"
57	"			0.0887	0.0381	"
58	1.55			0.0710	0.0458	"
59	"			0.0709	0.0457	"
60	"			0.0713	0.0460	"
61	0.775			0.0423	0.0546	.997
62	"			0.0459	0.0592	"
63	"			0.0452	0.0584	"
64	"	3.72	7.49	0.350	0.452	.970
65	"			0.340	0.440	.954
	iso-Pentane					
66	3.10	2.55	4.93	1.16	0.375	.999
67	"			1.18	0.380	"
68	2.325			1.36	0.586	"
69	2.325			1.41	0.603	"
70	1.55			0.859	0.554	"
71	"			0.876	0.565	"
72	0.775			0.356	0.461	.990
73	"			0.348	0.451	"
74	3.10	3.01	5.90	0.78	2.18	.999
75	"			7.31	2.36	"
76	2.325			3.54	1.52	"
77	"			3.60	1.54	"
78	1.55			0.957	0.617	"
79	"			1.02	0.660	"
80	0.775			0.151	0.195	.945
81	"			0.155	0.200	.955
82	3.10	3.37	6.80	11.2	3.64	.999
83	"			13.1	4.24	"
84	2.325			7.02	3.02	"
85	"			5.94	2.55	"

APPENDIX B

No.	[Substrate] x 10 ³	-H _O	-H _R	k ₁ x 10 ³ s ⁻¹	k ₂ M ⁻¹ s ⁻¹	r
86	1.55			2.61	1.68	.999
87	"			2.51	1.62	"
88	0.775			0.383	4.95	.985
89	"			0.432	5.59	.980
90	3.10	3.78	7.52	25.0	8.36	.999
91	"			24.0	7.75	"
92	2.325			15.8	6.77	"
93	"			15.7	6.74	"
94	1.55			4.10	2.64	.965
95	"			4.34	2.80	.970
96	0.775			1.81	2.34	.934
97	"			1.76	2.77	.942
98	3.10	3.78	7.52	119.0	38.4	.985
99	2.325			84.1	36.2	.999
100	"			84.4	36.3	"
101	1.55			47.1	30.4	"
102	"			42.7	27.5	"
103	0.775			7.54	9.74	"
104	"			4.27	5.51	.980
105	3.10	3.37	6.80	17.4	5.60	.999
106	"			16.9	5.44	"
107	2.325			15.1	6.49	"
108	"			15.0	6.46	"
109	1.55			5.29	3.41	"
110	"			5.83	3.76	"
111	0.775			0.623	0.804	.980
112	"			0.839	1.08	.985
113	3.10	3.19	6.10	5.84	1.88	.999
114	"			6.50	2.10	"
115	2.325			4.50	1.93	"
116	"			4.34	1.87	"
117	1.55			2.12	1.36	"
118	"			2.24	1.44	"
119	0.775			0.890	1.15	"
120	"			0.962	1.24	"
121	3.10	2.55	4.93	1.14	0.367	.999
122	"			1.22	0.393	"
123	2.325			0.660	0.284	"
124	"			0.660	0.284	"
125	1.55			0.643	0.415	"
126	"			0.694	0.444	"
127	0.775			0.337	0.435	"
128	"			0.346	0.446	"

APPENDIX C

All of the rate data contained in this section have been corrected for blank decomposition. Some trials, because of low substrate concentration, were analyzed by a second-order technique and as such no k_1 was reported. Trials 1197-1255 were analyzed by a zero-order technique; all the rest were calculated by the pseudo first-order method.

Unless otherwise stated all reactions were performed at 25.0° in a medium of trifluoroacetic acid (TFA) and water. All the alcohol reactions were carried out immediately after stock solutions were prepared unless otherwise designated. All the tables should be read in the accepted manner, i.e. Table value = actual rate constant $\times 10^x$ where x and units are given in the header.

Several notations will be found under the heading substrate which mean the following:

D₂O - a medium of TFA-D₂O.

STFA - designated molar strength of sodium trifluoroacetate added.

MP - designated molar strength of potassium perchlorate added.

B.Alc. - benzyl alcohol.

B.Ald. - benzaldehyde.

time - time interval before alcohol solution was used.

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
129	Ethane	8.50	8.680	38.0	4.38	.999
130	"	"	"	36.5	4.21	"
131	"	"	7.483	42.6	5.69	"
132	"	"	"	44.0	5.88	"
133	"	"	3.443	15.0	4.35	"
134	"	"	"	15.3	4.45	"
135	Propionitrile	"	124.9	0.305	0.00244	.983
136	"	"	"	0.304	0.00243	.975
137	Nitroethane	"	124.0	0.729	0.00588	.980
138	"	"	"	0.705	0.00569	.998
139	Propionic acid	"	48.01	0.607	0.0127	.999
140	"	"	"	0.710	0.0148	"
141	Propane	7.08	34.91	22.2	0.635	"
142	"	"	"	21.2	0.606	"
143	"	"	17.76	13.2	0.743	"
144	"	"	"	15.2	0.855	"
145	"	"	44.83	26.6	0.594	"
146	"	"	"	23.3	0.520	"
147	"	"	39.30	23.9	0.609	"
148	"	"	"	24.6	0.627	"
149	n-Butane	7.08	34.36	45.5	1.33	"
150	"	"	"	49.1	1.43	"
151	"	"	33.76	44.3	1.31	"
152	"	"	"	47.4	1.41	"
153	"	"	2.787	3.35	1.20	"
154	"	"	45.99	7.30	1.59	"
155	"	"	"	6.38	1.39	"
156	n-Pentane	7.86	3.127	18.6	5.96	"
157	"	"	"	19.3	6.17	"
158	"	6.27	3.11	0.321	0.103	"
159	"	"	26.47	2.28	0.0976	"
160	"	5.65	31.13	0.813	0.0261	"
161	"	7.10	15.59	13.0	0.836	"
162	"	"	"	13.9	0.894	"
163	"	6.96	5.99	3.38	0.564	"
164	"	"	"	3.38	0.564	"
165	"	"	18.71	10.3	0.551	"
166	"	"	8.98	5.15	0.574	"
167	"	"	"	4.95	0.552	"
168	"	"	13.47	7.29	0.541	"
169	"	"	"	7.33	0.544	"
170	"	38.4°	7.52	6.250	18.0	2.87
171	"	"	"	"	20.5	3.28
172	"	31.8°	"	7.812	18.3	2.35

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r	
173	n-Pentane	19.8°	7.52	7.812	10.3	1.32	.999
174	"	25.2°	"	6.250	8.92	1.43	"
175	"	25.4°	"	"	10.5	1.68	"
176	"	14.0°	"	7.812	7.56	0.968	"
177	"	"	"	"	7.52	0.963	"
178	"		6.70	7.812	3.98	0.510	"
179	"		"	"	4.02	0.515	"
180	"		7.74	15.63	-	3.88	"
181	"		"	"	-	3.88	"
182	"		8.00	3.12	-	20.2	"
183	"		"	"	-	21.3	"
184	"		"	"	-	19.4	"
185	n-Hexane		6.42	13.77	4.93	0.358	"
186	"		"	9.91	3.51	0.354	"
187	"		"	"	3.53	0.356	"
188	"		"	6.61	2.64	0.399	"
189	"		"	"	2.65	0.400	"
190	"		"	3.305	1.39	0.421	"
191	"		"	"	1.39	0.419	"
192	"		6.96	13.77	17.9	1.30	"
193	"		"	9.91	11.3	1.14	"
194	"		"	"	10.6	1.07	"
195	"		"	6.61	7.22	1.09	"
196	"		"	"	7.44	1.13	"
197	"		"	3.305	3.23	0.976	"
198	"		"	"	3.81	1.15	"
199	"		7.30	4.13	13.4	3.25	"
200	"		"	1.983	6.40	3.22	"
201	"		8.26	1.652	39.3	23.8	"
202	"	25.0°	6.66	13.77	12.8	0.930	"
203	"	21.4°	"	"	5.99	0.435	"
204	"	15.6°	"	"	5.10	0.370	"
205	"		7.86	2.754	37.1	13.5	"
206	"		"	"	37.0	13.4	"
207	"	D ₂ O	6.93	5.509	7.20	1.31	"
208	"	"	"	"	9.35	1.70	"
209	"	H ₂ O	"	8.263	10.8	1.30	"
210	"	"	"	"	12.5	1.52	"
211	"	38.5°	7.77	4.132	45.3	11.0	"
212	"	"	"	"	43.6	10.6	"
213	"	31.8°	"	3.443	29.9	8.68	"
214	"	20.0°	"	"	19.2	5.59	"
215	"	25.4°	"	4.132	28.0	6.77	"
216	"	"	"	"	27.6	6.67	"
217	"	14.0°	"	"	19.0	4.60	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r	
218	n-Hexane	13.9°	7.77	4.132	18.3	4.42	.999
219	"		7.74	8.260	-	9.73	"
220	"		"	"	-	9.28	"
221	"		8.00	1.380	-	41.0	"
222	"		"	"	-	35.9	"
223	"		"	"	-	35.3	"
224	n-Heptane		7.86	3.68	64.4	17.5	"
225	"		"	"	68.0	18.5	"
226	"		7.20	6.82	29.2	4.28	"
227	"		"	"	31.1	4.56	"
228	"		6.81	12.28	18.0	1.46	"
229	"		"	8.84	11.3	1.28	"
230	"		"	"	11.6	1.31	"
231	"		"	5.89	6.94	1.18	"
232	"		"	"	7.40	1.26	"
233	"		"	2.95	3.62	1.23	"
234	"		6.42	12.28	6.09	0.496	"
235	"		"	"	6.18	0.504	"
236	"	25.0°	6.66	12.28	10.3	0.838	"
237	"	21.4°	"	"	4.89	0.398	"
238	"	15.6°	"	"	4.21	0.343	"
239	"		7.86	2.456	39.9	16.2	"
240	"		7.74	7.37	-	10.7	"
241	"		"	"	-	10.2	"
242	"		8.00	1.23	-	52.8	"
243	"		"	"	-	50.2	"
244	"		"	"	-	46.8	"
245	n-Octane		7.74	4.928	-	15.3	"
246	"		"	"	-	14.9	"
247	"		8.00	1.11	-	65.7	"
248	"		"	"	-	66.6	"
249	"		"	"	-	60.6	"
250	n-Nonane		7.86	2.014	63.3	31.4	"
251	"		"	"	67.3	33.4	"
252	"		7.74	3.021	-	19.6	"
253	"		"	"	-	19.1	"
254	"		8.00	0.850	-	93.0	"
255	"		"	"	-	91.3	"
256	"		"	"	-	86.3	"
257	n-Decane		7.74	1.847	-	26.6	"
258	"		"	"	-	28.2	"
259	"		8.00	0.740	-	103.0	"
260	"		"	"	-	101.0	"
261	"		"	"	-	107.0	"
262	n-Undecane		7.74	1.705	-	33.8	"
263	"		"	"	-	33.1	"
264	"		8.00	0.680	-	131.0	"
265	"		"	"	-	126.0	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r	
266	n-Undecane	8.00	0.680	-	124.0	.999	
267	n-Dodecane	7.86	1.582	85.0	53.7	"	
268	"	"	"	86.8	54.9	"	
269	"	38.2°	7.41	2.37	70.1	29.6	"
270	"	"	"	"	79.7	33.6	"
271	"	31.1°	"	1.98	39.9	20.1	"
272	"	24.9°	7.41	0.40	5.79	14.5	"
273	"	19.4°	"	"	4.95	12.4	"
274	"	14.0°	"	"	3.69	9.23	"
275	"	7.74	0.791	-	39.9	"	
276	"	"	"	-	39.1	"	
277	"	8.00	0.630	-	153.0	"	
278	"	"	"	-	138.0	"	
279	"	"	"	-	162.0	"	
280	n-Tridecane	7.74	0.738	-	58.2	"	
281	"	"	"	-	54.5	"	
282	"	8.00	0.370	-	167.0	"	
283	"	"	"	-	155.0	"	
284	"	"	"	-	164.0	"	
285	Isopentane	5.71	15.50	3.90	0.257	"	
286	"	"	11.16	2.11	0.189	"	
287	"	"	"	2.30	0.206	"	
288	"	"	7.44	1.44	0.193	"	
289	"	"	"	1.67	0.224	"	
290	"	"	3.720	0.771	0.207	"	
291	"	6.00	15.50	7.77	0.502	"	
292	"	"	11.16	4.19	0.376	"	
293	"	"	"	4.67	0.419	"	
294	"	"	7.440	2.53	0.339	"	
295	"	"	"	2.95	0.397	"	
296	"	"	3.720	1.09	0.294	"	
297	"	"	"	1.13	0.382	"	
298	"	6.33	15.50	16.6	1.07	"	
299	"	"	11.16	9.28	0.825	"	
300	"	"	"	10.3	0.922	"	
301	"	"	7.440	7.03	0.944	"	
302	"	"	"	7.54	1.01	"	
303	"	"	3.720	3.12	0.839	"	
304	"	"	"	3.86	1.04	"	
305	"	6.64	7.751	16.2	2.09	"	
306	"	"	5.581	9.96	1.79	"	
307	"	"	"	10.6	1.90	"	
308	"	"	3.720	6.32	1.70	"	
309	"	"	"	7.09	1.91	"	
310	"	"	1.860	3.45	1.86	"	

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
311	Isopentane		6.64	1.860	4.21	2.26	.999
312	"	25.0°	6.66	6.20	17.2	2.77	"
313	"	21.2°	"	"	7.91	1.28	"
314	"	15.6°	"	"	6.08	0.981	"
315	"	12.5°	"	"	3.64	0.587	"
316	"	H ₂ O	5.95	9.282	3.19	0.343	"
317	"	"	"	"	3.71	0.400	"
318	"	D ₂ O	"	"	3.74	0.403	"
319	"	"	"	"	4.17	0.449	"
320	"		4.08	7.730	0.2130	0.0276	"
321	"		4.80	7.730	0.483	0.0624	"
322	Neopentane		7.90	30.80	6.31	0.205	"
323	"		"	"	6.32	0.205	"
324	"		8.44	34.50	14.1	0.408	"
325	"		"	"	14.6	0.422	"
326	"		"	"	15.1	0.437	"
327	"		8.96	31.23	42.5	1.36	"
328	"		"	"	39.0	1.25	"
329	"		"	"	44.1	1.41	"
330	"		8.70	50.89	42.9	0.843	"
331	"		"	"	43.3	0.851	.997
332	"		"	"	43.7	0.858	.999
333	"		"	35.00	26.4	0.755	"
334	"		"	"	24.7	0.705	"
335	"		"	23.09	18.0	0.779	"
336	"		"	"	17.5	0.757	"
337	Cyclopentane		7.52	7.71	55.9	7.24	"
338	"		"	"	48.9	6.34	"
339	"		6.52	19.28	15.7	0.813	"
340	"		"	"	15.9	0.825	"
341	"		6.26	28.91	11.4	0.394	"
342	"		"	20.82	7.91	0.380	"
343	"		"	"	7.52	0.361	"
344	"		"	13.88	5.29	0.381	"
345	"		"	"	4.99	0.360	"
346	"		"	9.25	3.80	0.411	"
347	"		"	"	3.44	0.371	"
348	"		5.72	19.28	2.47	0.128	"
349	"		"	"	2.77	0.144	"
350	"	38.6°	7.02	7.71	30.2	3.91	"
351	"	"	"	"	26.6	3.46	"
352	"	31.8°	"	9.638	27.5	2.85	"
353	"	25.0°	"	7.71	17.6	2.28	"
354	"	"	"	"	16.4	2.12	"

APPENDIX C

No.	Substrate	-H _R	[S]x10 ³	k ₁ x10 ³ s ⁻¹	k ₂ M ⁻¹ s ⁻¹	r	
355	Cyclopentane	19.9°	7.02	9.638	16.8	1.74	.999
356	"	14.0°	"	"	12.2	1.27	"
357	"	"	"	"	11.9	1.23	"
358	"		6.90	19.28	42.7	2.21	"
359	"		"	"	41.2	2.14	"
360	Cyclohexane		6.42	8.332	3.20	0.384	"
361	"		"	5.999	2.55	0.426	"
362	"		"	"	2.47	0.412	"
363	"		"	3.999	1.79	0.447	"
364	"		"	"	1.77	0.442	"
365	"		"	2.00	1.01	0.503	"
366	"		6.96	8.332	10.7	1.28	"
367	"		"	5.999	8.46	1.41	"
368	"		"	"	8.26	1.38	"
369	"		"	3.999	5.40	1.35	"
370	"		"	"	5.89	1.47	"
371	"		"	2.000	3.30	1.65	"
372	"		"	"	3.20	1.60	"
373	"		7.30	8.332	32.7	3.92	"
374	"		"	5.999	22.2	3.70	"
375	"		"	"	22.2	3.70	"
376	"		"	3.999	15.0	3.74	"
377	"		"	"	16.4	4.10	"
378	"		"	2.000	7.60	3.80	"
379	"		"	"	7.93	3.97	"
380	"		8.26	2.00	60.7	30.4	"
381	"	25.0°	6.66	16.66	14.3	0.860	"
382	"	21.4°	"	"	8.81	0.529	"
383	"	15.6"	"	"	5.22	0.313	"
384	Cyclohexane-d ₁₂	25.0°	"	29.17	5.41	0.185	"
385	"	"	"	"	6.85	0.235	"
386	Cyclohexane		6.80	16.66	12.9	0.772	"
387	"		"	"	12.5	0.748	"
388	"		6.74	"	12.9	0.773	"
389	"		"	"	13.1	0.789	"
390	Cyclohexane-d ₁₂		"	"	3.00	0.180	"
391	Cyclohexane		6.38	16.66	5.25	0.315	"
392	Cyclohexane-d ₁₂		"	"	1.13	0.0678	"
393	"		"	"	1.10	0.0657	"
394	Cyclohexane		6.12	16.66	2.62	0.157	"
395	Cyclohexane-d ₁₂		"	"	0.496	0.0298	"
396	"		7.91	4.166	17.3	4.15	"
397	Cyclohexane		"	2.083	34.6	16.6	"
398	"		7.70	4.166	32.7	7.84	"
399	Cyclohexane-d ₁₂		"	8.332	11.4	1.37	"
400	"		7.40	13.33	11.2	0.837	"
401	"		"	"	12.9	0.971	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
402	Cyclohexane	7.40	6.665	28.4	4.26	.999
403	"	"	"	28.4	4.26	"
404	Cyclohexane-d ₁₂	6.96	13.33	2.67	0.191	"
405	"	"	"	5.36	0.402	"
406	Cyclohexane	"	"	16.4	1.23	"
407	"	"	"	16.2	1.22	"
408	"	6.77	1.33	1.01	0.755	"
409	"	"	"	1.09	0.826	"
410	"	"	4.23	2.86	0.675	"
411	"	"	"	3.38	0.799	"
412	"	"	8.00	5.71	0.714	"
413	"	"	"	5.74	0.718	"
414	"	"	10.66	7.41	0.695	"
415	"	"	"	7.67	0.720	"
416	"	6.77	13.33	9.64	0.723	"
417	"	"	16.00	10.8	0.674	"
418	"	"	"	11.3	0.704	"
419	"	"	24.00	15.9	0.661	"
420	"	"	"	16.4	0.684	"
421	"	"	26.66	19.1	0.715	"
422	"	"	"	18.3	0.686	"
423	"	"	33.33	21.5	0.649	"
424	"	6.93	9.998	13.3	1.33	"
425	"	"	"	14.3	1.43	"
426	"	D ₂ O	6.665	9.77	1.47	"
427	"	"	"	9.26	1.40	"
428	"	38.5°	7.70	3.333	39.2	11.8
429	"	31.8°	"	4.166	45.2	10.8
430	"	25.3°	"	4.999	43.4	8.68
431	"	"	"	"	44.9	8.98
432	"	19.9°	"	4.166	29.1	6.98
433	"	13.9°	"	"	22.3	5.35
434	"	6.90	8.33	13.6	1.63	"
435	"	"	"	13.1	1.58	"
436	Cycloheptane	6.80	4.46	22.9	5.13	"
437	"	"	"	23.2	5.21	"
438	"	6.36	11.89	27.7	2.33	"
439	"	"	8.562	18.0	2.11	"
440	"	"	"	18.7	2.18	"
441	"	"	5.708	12.2	2.14	"
442	"	"	"	12.8	2.25	"
443	"	"	2.854	6.47	2.27	"
444	"	"	"	6.48	2.27	"
445	"	5.37	2.975	0.899	0.302	"
446	"	5.82	"	2.08	0.698	"

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
447	Cycloheptane		5.82	2.975	2.13	0.717	.999
448	"		6.09	5.946	7.11	1.20	"
449	"		"	"	7.43	1.25	"
450	"	38.4°	7.20	2.973	68.8	23.1	"
451	"	"	"	"	67.6	22.7	"
452	"	31.8°	"	3.716	68.7	18.5	"
453	"	19.9°	"	"	44.5	12.0	"
454	"	25.3°	"	2.973	41.5	14.0	"
455	"	"	"	"	44.3	14.9	"
456	"	14.0°	"	"	27.3	9.19	"
457	"	"	"	"	27.2	9.15	"
458	"		6.90	7.45	63.4	8.51	"
459	"		"	"	61.5	8.26	"
460	"	0.36 STFA	5.58	3.716	2.32	0.625	"
461	"	" "	"	"	2.38	0.640	"
462	"	0.28 STFA	5.60	"	2.45	0.660	"
463	"	" "	"	"	2.29	0.616	"
464	"	0.07 STFA	5.64	"	2.15	0.578	"
465	"	" "	"	"	2.31	0.623	"
466	Cyclooctane		6.80	2.01	30.6	15.2	"
467	"		"	4.012	52.9	13.2	"
468	"		"	"	54.8	13.7	"
469	"		6.36	8.024	57.9	7.22	"
470	"		"	5.777	39.1	6.78	"
471	"		"	"	39.1	6.78	"
472	"		"	3.852	26.9	6.98	"
473	"		"	"	28.0	7.27	"
474	"		"	1.926	12.4	6.45	"
475	"		"	"	12.4	6.43	"
476	"		5.82	2.675	5.75	2.15	"
477	"		"	"	5.44	2.03	"
478	"		6.09	5.349	20.2	3.77	"
479	"		"	"	20.5	3.83	"
480	"	38.6°	6.80	1.377	37.3	27.9	"
481	"	"	"	"	38.7	29.0	"
482	"	31.8°	"	"	23.1	17.3	"
483	"	19.9°	"	"	16.9	12.7	"
484	"	25.2°	"	"	19.2	14.4	"
485	"	"	"	"	20.0	15.0	"
486	"	14.0°	"	"	12.5	9.38	"
487	"	"	"	"	12.1	9.01	"
488	"		6.90	3.34	78.6	23.5	"
489	"		"	"	76.9	23.0	"
490	Benzene	D ₂ O	5.78	22.28	26.3	1.18	"
491	"	"	"	"	26.7	1.20	"

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
492	Benzene	H ₂ O	4.80	20.50	1.52	0.0741	.999
493	"		"	"	1.45	0.0709	"
494	"		5.40	20.50	6.06	0.296	.998
495	"		"	"	5.97	0.291	.999
496	"		5.84	5.74	4.82	0.839	"
497	"		"	"	4.84	0.843	"
498	"		"	9.72	8.45	0.869	"
499	"		"	"	8.45	0.869	"
500	"		"	13.94	11.5	0.822	"
501	"		"	"	11.1	0.798	"
502	"		"	20.50	18.4	0.895	"
503	"		6.30	16.20	54.3	3.35	"
504	"		"	"	55.0	3.40	"
505	"		6.64	5.06	58.3	11.5	"
506	Chlorobenzene		"	17.69	40.7	2.30	"
507	Fluorobenzene		"	4.80	22.3	4.64	"
508	Nitrobenzene		"	44.00	3.82	0.00868	"
509	Benzoic acid		"	32.06	5.41	0.169	.997
510	Anisole		4.16	0.35	32.0	91.3	.999
511	Benzene		"	30.37	4.65	0.0153	"
512	Toluene		"	16.94	16.6	0.977	"
513	Ethylbenzene		"	5.88	7.36	1.25	"
514	Cumene		"	3.23	5.04	1.56	"
515	t-Butylbenzene		"	2.91	4.15	1.43	"
516	Fluorobenzene		5.64	28.78	5.90	0.205	"
517	Chlorobenzene		"	26.54	2.22	0.0838	"
518	Benzene	38.5°	5.70	20.25	20.9	1.03	"
519	"	"	"	"	21.1	1.04	"
520	"	31.8°	"	"	16.5	0.813	"
521	"	19.9°	"	"	9.25	0.457	"
522	"	25.3°	"	"	12.4	0.610	"
523	"	"	"	"	12.4	0.612	"
524	"	13.9°	"	20.25	9.10	0.449	"
525	"	"	"	"	9.55	0.472	.998
526	"	0.048 MP	5.64	10.12	6.43	0.636	.999
527	"	0.026 MP	5.60	"	6.30	0.623	"
528	"	0.36 STFA	5.58	"	6.68	0.660	"
529	"	" "	"	"	7.51	0.742	"
530	"	0.07 STFA	5.64	"	7.12	0.704	.997
531	"	" "	"	"	7.25	0.716	.999
532	"	0.29 STFA	5.60	"	6.41	0.633	"
533	"	" "	"	"	6.51	0.643	"
534	"		4.80	20.25	1.44	0.0712	.998
535	"		4.08	"	0.365	0.0180	.999
536	"		"	"	0.336	0.0166	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
537	Toluene	2.88	4.24	0.719	0.170	.999
538	"	"	6.78	1.39	0.205	"
539	"	"	"	1.13	0.167	"
540	"	"	10.20	1.56	0.153	"
541	"	"	"	1.46	0.143	"
542	"	"	13.60	2.03	0.149	"
543	"	"	"	2.37	0.174	"
544	"	3.48	4.24	1.70	0.402	"
545	"	"	6.78	2.74	0.404	"
546	"	"	"	2.74	0.404	"
547	"	"	10.20	4.22	0.414	"
548	"	"	"	4.14	0.406	"
549	"	"	13.60	4.78	0.351	"
550	"	"	"	5.41	0.396	"
551	"	3.84	4.24	2.72	0.642	"
552	"	"	6.78	4.88	0.721	"
553	"	"	"	4.72	0.696	"
554	"	"	10.20	7.73	0.758	"
555	"	"	"	7.73	0.758	"
556	"	"	13.60	9.58	0.705	"
557	"	"	"	9.58	0.705	"
558	"	4.32	2.12	3.71	1.78	"
559	"	"	3.39	5.95	1.76	"
560	"	"	"	6.11	1.80	"
561	"	"	5.10	8.53	1.67	"
562	"	"	"	8.28	1.62	"
563	"	"	6.80	11.3	1.66	"
564	"	"	"	12.3	1.81	"
565	"	4.84	2.12	10.9	5.13	"
566	"	"	3.39	14.7	4.34	"
567	"	"	"	15.0	4.42	"
568	"	"	5.10	20.6	4.04	"
569	"	"	"	19.1	3.74	"
570	"	"	6.80	27.3	4.01	"
571	"	"	"	27.6	4.06	"
572	"	2.90	4.24	0.620	0.146	"
573	"	"	6.78	1.08	0.160	"
574	"	"	"	1.07	0.158	"
575	"	"	10.20	1.71	0.168	"
576	"	"	"	1.82	0.178	"
577	"	"	13.60	2.56	0.188	"
578	"	"	"	2.69	0.197	"
579	"	3.42	4.24	1.45	0.341	"
580	"	"	6.78	2.79	0.412	"
581	"	"	"	3.07	0.454	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 \text{ s}^{-1}$	$k_2 M^{-1} \text{ s}^{-1}$	r
582	Toluene	3.42	10.20	4.42	0.434	.999
583	"	"	"	4.41	0.433	"
584	"	"	13.60	5.77	0.424	"
585	"	"	"	5.64	0.415	"
586	"	3.82	4.24	2.88	0.679	"
587	"	"	6.78	5.23	0.771	"
588	"	"	"	5.31	0.783	"
589	"	"	10.20	6.42	0.630	"
590	"	"	"	7.93	0.778	"
591	"	"	13.60	1.05	0.772	"
592	"	"	"	1.05	0.772	"
593	"	4.19	2.12	3.39	1.60	"
594	"	"	3.39	5.74	1.69	"
595	"	"	"	5.69	1.68	"
596	"	"	5.10	8.37	1.64	"
597	"	"	"	8.63	1.69	"
598	"	4.19	6.80	10.9	1.60	"
599	"	"	"	11.3	1.66	"
600	"	4.70	2.12	7.76	3.66	"
601	"	"	4.24	14.6	3.44	"
602	"	"	5.10	17.0	3.34	"
603	"	"	"	17.9	3.51	"
604	"	"	6.80	22.4	3.30	"
605	"	"	"	22.9	3.37	"
606	"	4.08	8.846	9.67	2.04	"
607	"	"	"	10.7	2.08	"
608	p-Nitrotoluene	"	22.06	2.73	1.09	"
609	"	"	"	2.43	1.04	"
610	m-Toluic acid	"	25.64	1.13	0.642	"
611	"	"	"	1.26	0.692	"
612	m-Nitrotoluene	"	33.23	3.27	0.993	"
613	"	"	"	4.30	1.11	"
614	m-Chlorotoluene	"	6.051	1.46	1.38	"
615	"	"	"	1.54	1.41	"
616	Ethylbenzene	4.50	5.88	1.74	2.95	"
617	"	"	"	1.70	2.88	"
618	Toluene-d ₈	"	5.99	1.56	2.60	"
619	"	"	"	1.50	2.50	"
620	"	"	3.74	0.952	2.54	"
621	Toluene	"	6.77	1.56	2.31	"
622	"	"	"	1.59	2.34	"
623	"	3.07	3.387	0.797	0.235	"
624	"	"	"	0.633	0.187	"
625	Toluene-d ₈	"	3.404	0.681	0.200	"
626	"	"	"	0.601	0.177	"
627	Ethylbenzene	"	3.234	1.27	0.391	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 \text{ s}^{-1}$	$k_2 M^{-1} \text{ s}^{-1}$	r
628	Cumene	3.07	3.235	1.24	0.382	.999
629	Toluene	3.39	3.387	1.26	0.372	"
630	"	"	"	1.20	0.355	"
631	Toluene-d ₈	"	3.404	1.28	0.375	"
632	"	"	"	1.27	0.373	"
633	Ethylbenzene	"	3.675	2.25	0.611	"
634	Cumene	"	2.588	1.58	0.609	"
635	"	"	"	1.42	0.554	"
636	Toluene	3.88	3.387	2.63	0.777	"
637	"	"	"	2.58	0.761	"
638	Toluene-d ₈	"	8.510	6.57	0.771	"
639	Ethylbenzene	"	2.940	3.15	1.07	"
640	Cumene	"	2.588	2.91	1.12	"
641	"	"	"	2.93	1.13	"
642	Toluene	4.44	7.114	13.2	1.86	"
643	Toluene-d ₈	"	6.808	13.5	1.99	"
644	Ethylbenzene	"	5.879	15.2	2.59	"
645	Cumene	"	3.235	8.18	2.53	"
646	Toluene	4.82	3.387	14.4	4.26	"
647	"	"	"	14.5	4.28	"
648	Toluene-d ₈	"	3.404	14.4	4.23	"
649	"	"	"	14.3	4.21	"
650	Ethylbenzene	"	2.940	15.5	5.27	"
651	"	"	"	15.8	5.37	"
652	Cumene	"	3.235	19.1	5.91	"
653	Toluene	5.29	1.694	21.5	12.7	"
654	"	"	"	23.2	13.7	"
655	Toluene-d ₈	"	1.702	22.7	13.3	"
656	"	"	"	22.7	13.4	"
657	Toluene	5.70	0.339	11.6	34.3	"
658	"	"	"	11.6	34.3	"
659	Toluene-d ₈	"	0.340	13.0	38.3	"
660	"	"	"	12.1	35.6	"
661	Toluene	4.42	3.387	5.40	1.59	"
662	"	"	"	5.14	1.52	"
663	"	"	6.775	10.6	1.56	"
664	"	"	"	10.9	1.62	"
665	"	"	13.55	23.1	1.71	"
666	"	"	"	23.7	1.75	"
667	"	"	20.33	32.1	1.58	"
668	"	"	"	32.0	1.57	"
669	Toluene-d ₈	"	3.404	5.47	1.61	"
670	"	"	"	5.61	1.65	"
671	"	"	6.808	10.7	1.57	"
672	"	"	"	10.7	1.57	"
673	"	"	13.62	22.4	1.65	"

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
674	Toluene-d ₈		4.42	13.62	22.5	1.65	.999
675	"		"	20.43	32.8	1.61	"
676	"		"	"	33.6	1.64	"
677	Toluene-d ₈ ,	D ₂ O	4.83	4.255	42.2	9.91	"
678	"	"	"	8.510	75.2	8.83	"
679	Toluene,	D ₂ O	"	4.234	41.1	9.71	"
680	"	"	"	8.469	79.1	9.34	"
681	m-Nitrotoluene		5.40	14.69	2.19	0.149	"
682	m-Toluic acid		"	17.74	2.68	0.151	"
683	p-Toluic acid		"	25.39	1.81	0.0714	"
684	m-Nitrotoluene		"	14.69	2.60	0.177	.995
685	p-Bromotoluene		"	5.001	3.90	0.780	.999
686	"		"	"	4.22	0.844	"
687	p-Nitrotoluene		"	17.95	4.75	0.0264	"
688	"		"	"	3.66	0.0204	.992
689	m-Bromotoluene		"	7.746	24.0	3.10	.999
690	"		"	"	24.0	3.10	"
691	m-Chlorotoluene		"	9.144	30.0	3.20	"
692	"		"	"	30.2	3.30	"
693	Toluene		"	6.241	107.0	17.1	"
694	"		"	"	116.0	18.6	"
695	"	14.7°	4.26	5.10	4.99	0.978	"
696	"	"	"	"	4.72	0.926	"
697	"	20.4°	"	"	6.34	1.24	"
698	"	"	"	"	5.81	1.14	"
699	"	25.0°	"	"	9.30	1.82	"
700	"	"	"	"	9.37	1.84	"
701	"	31.6°	"	"	12.8	2.51	"
702	"	"	"	"	11.7	2.30	"
703	"	36.2°	"	"	10.5	2.06	"
704	"	"	"	"	12.8	2.52	"
705	Toluene	15.0°	4.13	5.10	4.83	0.947	"
706	"	"	"	"	3.63	0.711	"
707	"	20.0°	"	"	5.63	1.10	"
708	"	"	"	"	5.89	1.16	"
709	"	25.0°	"	"	9.29	1.82	"
710	"	"	"	"	9.39	1.84	"
711	"	30.0°	"	"	10.5	2.06	"
712	"	"	"	"	10.3	2.01	"
713	"	35.0°	"	"	9.67	1.90	"
714	"	"	"	"	10.2	1.99	"
715	"		2.90	16.94	2.79	0.165	"
716	Toluene-d ₈		2.34	5.08	0.270	0.0532	"
717	Toluene-α-d ₃		"	"	0.307	0.0604	"
718	Toluene		"	"	0.288	0.0566	"

APPENDIX C.

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
719	Toluene-d ₈		3.52	6.77	3.00	0.450	.998
720	"		"	"	3.17	0.469	.999
721	Toluene- α -d ₃		"	"	2.91	0.429	"
722	"		"	"	2.91	0.430	"
723	Toluene		"	"	2.92	0.432	"
724	"		"	"	2.96	0.437	"
725	"		4.44	3.39	5.40	1.59	"
726	"		"	"	5.54	1.63	"
727	Toluene-d ₈		"	"	5.25	1.55	"
728	"		"	"	5.55	1.64	"
729	Toluene- α -d ₃		"	"	5.25	1.55	"
730	"		"	"	5.23	1.54	"
731	Toluene		5.28	1.69	21.0	12.4	"
732	"		"	"	20.8	12.3	"
733	Toluene- α -d ₃		"	"	19.0	11.2	"
734	"		"	"	19.1	11.3	"
735	Toluene-d ₈		"	"	20.2	12.0	"
736	"		"	"	20.2	12.0	"
737	Toluene		4.47	6.775	15.5	2.28	"
738	"		"	"	15.2	2.24	"
739	"	D ₂ O	"	"	31.7	4.69	"
740	"	"	"	"	31.1	4.59	"
741	Toluene	37.4°	5.17	1.694	22.4	13.2	"
742	"	"	"	"	22.0	13.0	"
743	"	31.5°	"	4.234	43.4	10.3	"
744	"	20.0°	"	"	28.0	6.59	"
745	"	25.0°	"	1.694	16.1	9.47	"
746	"	"	"	"	16.5	9.74	"
747	"	14.0°	"	3.388	19.4	5.73	"
748	"	"	"	"	20.1	5.93	"
749	"	37.4°	2.52	4.234	0.821	0.194	"
750	"	31.6°	"	"	0.646	0.153	"
751	"	25.0°	"	5.081	0.462	0.0910	"
752	"	19.9°	"	4.234	0.231	0.0545	"
753	"	14.1°	"	5.081	0.230	0.0453	"
754	Toluene		3.18	4.23	1.73	0.408	"
755	"		"	"	1.90	0.448	"
756	Ethylbenzene		"	3.67	2.35	0.640	"
757	"		"	"	2.29	0.655	"
758	Cumene		"	1.94	1.19	0.611	"
759	"		"	"	1.28	0.659	"
760	<u>t</u> -Butylbenzene		"	1.74	0.786	0.452	"
761	"		"	"	0.799	0.459	"
762	Toluene		5.39	4.23	85.3	20.2	"
763	"		5.39	"	95.6	22.6	"
764	Ethylbenzene		"	2.20	74.5	33.9	"
765	"		"	"	70.0	31.8	"

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
766	Cumene		5.39	1.94	63.7	32.8	.999
767	"		"	"	65.8	33.9	"
768	t-Butylbenzene		"	1.74	50.8	29.2	"
769	"		"	"	52.4	30.1	"
770	Methanol		6.34	8.233	28.9	3.51	"
771	"		"	16.47	53.2	3.23	"
772	"		"	24.70	73.9	2.99	"
773	"		"	32.93	90.0	2.73	"
774	Methanol	15 min	6.34	164.7	76.2	0.463	"
775	"	45 min	"	"	38.2	0.232	"
776	"	75 min	"	"	21.0	0.127	"
777	"	7 min	"	82.33	53.2	0.646	"
778	"	30 min	"	"	30.3	0.368	"
779	"	60 min	"	"	16.7	0.203	"
780	Methanol		5.64	16.47	11.3	0.683	"
781	"		"	"	11.0	0.668	"
782	"		4.08	41.17	2.24	0.0545	"
783	"		5.01	41.17	8.03	0.195	"
784	"		"	"	8.33	0.202	"
785	"		3.26	82.33	1.87	0.0227	"
786	"		"	41.17	1.03	0.0249	"
787	"		6.15	8.233	22.3	2.71	"
788	"		"	"	19.6	2.38	"
789	"		6.84	8.233	90.7	11.0	"
790	"		"	"	80.5	9.78	"
791	Methanol	37.4°	3.18	200.1	9.48	0.0474	"
792	"	31.6°	"	"	7.17	0.0359	"
793	"	25.0°	"	"	3.80	0.0190	"
794	"	19.8°	"	"	2.99	0.0149	"
795	"	14.1°	"	"	1.77	0.00886	"
796	Methanol-d ₄		4.38	88.92	0.891	0.0100	"
797	Methanol		"	44.46	3.68	0.0828	"
798	"		7.10	4.446	72.1	16.2	"
799	Methanol-d ₄		"	8.892	21.2	2.38	"
800	Methanol		6.09	11.13	22.6	2.03	"
801	Methanol-d ₄		"	22.23	4.46	0.201	"
802	"		5.01	44.46	1.24	0.0278	"
803	Methanol		"	22.23	4.23	0.190	"
804	Methanol-d ₄		3.76	200.1	0.451	0.00225	"
805	Methanol		"	100.5	2.35	0.0234	"
806	"		6.59	11.12	56.3	5.06	"
807	Methanol-d ₄		"	22.23	12.5	0.559	"
808	Methanol		5.01	35.57	5.87	0.165	"
809	"		"	"	6.70	0.188	"
810	"	D ₂ O	"	"	7.33	0.206	"
811	"	"	"	"	7.06	0.199	"
812	Methanol	0.019 MP	5.44	66.99	33.2	0.499	"

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
813	Methanol	0.019 MP	5.44	66.99	31.7	0.475	.999
814	"	0.05 MP	"	"	32.1	0.481	"
815	"	" "	"	"	35.3	0.530	"
816	"	0.026 MP	5.40	"	32.2	0.483	"
817	"	" "	"	"	35.7	0.535	"
818	"	0.36 STFA	5.38	"	31.1	0.466	"
819	"	" "	"	"	28.3	0.425	"
820	"	0.07 STFA	5.44	"	27.1	0.406	"
821	"	" "	"	"	29.1	0.436	"
822	"	0.28 STFA	5.40	"	31.3	0.470	"
823	"	" "	"	"	32.9	0.493	"
824	2-Pentanol		3.26	30.64	1.73	0.0563	"
825	"		"	"	1.71	0.0557	"
826	"		5.01	"	7.57	0.247	"
827	"		5.64	12.26	7.39	0.603	"
828	"		"	9.192	5.51	0.599	"
829	"		"	6.128	3.84	0.627	"
830	"		"	3.064	2.15	0.700	"
831	"		4.08	30.64	2.96	0.0967	"
832	"		"	"	2.90	0.0947	"
833	"		6.15	6.128	9.77	1.59	"
834	"		"	"	10.2	1.67	"
835	"		6.84	3.064	18.1	5.91	"
836	"		"	"	17.7	5.77	"
837	3-Pentanol		3.26	30.83	1.90	0.0617	"
838	"		"	"	1.83	0.0594	"
839	"		5.64	12.33	7.62	0.618	"
840	"		"	9.250	5.72	0.618	"
841	"		"	6.167	3.85	0.625	"
842	"		"	3.083	2.05	0.664	"
843	"		4.08	30.83	3.11	0.101	"
844	"		"	"	3.19	0.104	"
845	"		5.01	30.83	7.83	0.254	"
846	"		"	"	8.00	0.260	"
847	"		6.15	6.167	10.2	1.65	"
848	"		6.84	3.083	17.6	5.70	"
849	"		"	"	18.3	5.95	"
850	"	38.1°	5.84	6.66	8.69	1.30	"
851	"	"	"	"	9.48	1.42	"
852	"	31.0°	"	8.33	8.24	0.990	"
853	"	19.5°	"	"	6.00	0.720	"
854	"	25.0°	"	"	6.61	0.793	"
855	"	"	"	"	6.91	0.830	"
856	"	14.0°	"	"	3.52	0.422	"
857	"	"	"	"	3.39	0.407	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r	
858	Cyclohexanol		5.64	3.203	2.76	0.860	"
859	"		"	6.406	5.58	0.871	"
860	"		"	9.609	8.49	0.883	"
861	"		"	12.81	11.1	0.866	"
862	"		4.08	16.01	2.52	0.157	"
863	"		"	"	2.44	0.152	"
864	"		5.01	"	6.25	0.391	"
865	"		"	"	6.59	0.411	"
866	"		6.15	6.406	15.3	2.39	"
867	"		"	"	15.2	2.37	"
868	"		6.84	3.203	27.7	8.65	"
869	"	38.0°	5.40	10.38	9.69	0.933	"
870	"	38.2°	"	"	8.98	0.865	"
871	"	30.9°	"	17.30	13.6	0.784	"
872	"	19.4°	"	"	9.37	0.542	"
873	"	25.0°	"	"	10.9	0.632	"
874	"	24.9°	"	"	10.5	0.606	"
875	"	13.8°	"	"	5.36	0.310	"
876	"	14.0°	"	"	5.22	0.302	"
877	Benzyl alcohol		2.90	8.67	3.34	0.386	"
878	"		2.76	6.94	3.04	0.438	"
879	"		"	"	3.01	0.433	"
880	"		1.00	20.81	5.85	0.281	"
881	"		"	"	5.81	0.279	"
882	"		1.81	"	6.57	0.316	"
883	"		"	"	6.67	0.321	"
884	"		3.28	8.671	4.35	0.502	"
885	"		"	6.243	3.37	0.539	"
886	"		"	4.162	2.16	0.519	"
887	"		"	2.081	1.04	0.499	"
888	p-Nitro B.Alc.		"	4.756	0.589	0.124	"
889	m-Nitro B.Alc.		"	12.56	1.46	0.117	"
890	"		"	"	1.44	0.114	"
891	Benzyl alcohol		2.87	10.41	4.24	0.408	"
892	"		"	"	4.14	0.398	"
893	Benzyl alcohol	D ₂ O	"	"	5.69	0.547	"
894	"	"	"	"	6.05	0.581	"
895	"		2.33	34.69	14.5	0.419	"
896	"		"	"	15.5	0.446	"
897	"		2.79	17.34	7.70	0.444	"
898	"		"	"	8.00	0.461	"
899	"		3.20	"	9.27	0.535	"
900	"		"	"	9.53	0.549	"
901	"		3.60	"	11.4	0.658	"
902	"		"	"	11.9	0.685	"
903	"		4.09	"	15.4	0.885	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
904	Benzyl alcohol	4.09	17.34	15.5	0.893	.999
905	"	4.50	13.87	17.0	1.22	"
906	"	"	"	17.6	1.22	"
907	"	4.94	10.41	21.5	2.07	"
908	"	"	"	22.0	2.11	"
909	"	5.40	"	38.8	3.73	"
910	"	"	"	40.7	3.91	"
911	"	5.74	3.47	22.9	6.59	"
912	"	"	"	24.3	7.00	"
913	"	6.20	4.35	96.3	22.2	"
914	"	"	"	95.6	22.0	"
915	"	2.35	34.69	15.0	0.433	"
916	"	"	"	15.0	0.432	"
917	"	1.71	"	12.8	0.370	"
918	"	"	"	13.0	0.375	"
919	"	0.98	17.34	5.79	0.334	"
920	"	"	"	5.67	0.327	"
921	"	0.60	"	5.04	0.291	"
922	"	0.12	"	4.59	0.265	"
923	"	37.5°	3.58	27.66	25.5	0.921
924	"	"	"	"	27.5	0.994
925	"	31.4°	"	25.94	18.3	0.705
926	"	20.0°	"	"	10.8	0.417
927	"	25.0°	"	34.55	19.0	0.550
928	"	"	"	"	19.2	0.555
929	"	14.1°	"	"	10.4	0.301
930	"	14.1°	"	"	10.1	0.293
931	"	37.4°	6.72	0.9104	60.9	66.9
932	"	31.4°	"	0.867	63.9	73.7
933	"	25.0°	"	1.734	125.0	72.0
934	"	"	"	"	119.0	68.8
935	"	20.0°	"	0.867	31.1	35.9
936	"	14.0°	"	1.734	54.9	31.7
937	"	"	"	"	49.8	28.7
938	"	4.41	"	"	15.3	0.879
939	"	"	"	"	15.3	0.880
940	Benzyl alcohol- α -d ₂	0.84	21.28	2.07	0.0969	"
941	"	"	"	1.96	0.0919	"
942	Benzyl alcohol	"	21.68	3.92	0.181	"
943	"	"	"	4.90	0.226	"
944	Benzyl alcohol D ₂ O	9.90	"	5.66	0.261	"
945	"	"	"	6.01	0.277	"
946	Benzyl alcohol- α -d ₂ , D ₂ O	"	21.28	3.63	0.171	"
947	"	"	"	3.58	0.168	"
948	Benzyl alcohol- α -d ₂	2.76	34.06	12.0	0.353	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 \text{ s}^{-1}$	$k_2 M^{-1} \text{ s}^{-1}$	r
949	Benzyl alcohol- α -d ₂	2.76	34.06	12.3	0.361	.999
950	Benzyl alcohol	"	34.69	13.3	0.384	"
951	"	"	"	14.9	0.430	"
952	" D ₂ O	2.86	"	16.7	0.482	"
953	" "	"	"	17.0	0.491	"
954	Benzyl alcohol- α -d ₂ , D ₂ O	"	34.06	18.9	0.555	"
955	" "	"	"	19.2	0.565	"
956	Benzyl alcohol- α -d ₂	0.12	21.28	1.12	0.0528	"
957	"	"	"	1.10	0.0515	"
958	Benzyl alcohol	"	21.68	4.08	0.188	"
959	"	"	"	3.74	0.173	"
960	" D ₂ O	"	"	5.08	0.234	"
961	" "	"	"	4.87	0.225	"
962	Benzyl alcohol- α -d ₂ , D ₂ O	"	21.28	1.84	0.0867	"
963	" "	"	"	1.91	0.0899	"
964	Benzyl alcohol- α -d ₂	6.48	4.26	222.0	52.2	"
965	"	"	"	218.0	51.2	"
966	Benzyl alcohol	"	4.34	223.0	51.5	"
967	"	"	"	221.0	50.9	"
968	" D ₂ O	6.44	0.867	48.1	55.5	"
969	" "	"	"	50.0	57.6	"
970	Benzyl alcohol- α -d ₂ , D ₂ O	"	0.851	41.9	49.2	"
971	" "	"	"	43.1	50.7	"
972	Benzyl alcohol- α -d ₂	7.24	"	198.0	233.0	"
973	"	"	"	189.0	222.0	"
974	Benzyl alcohol	"	0.867	241.0	278.0	"
975	"	"	"	259.0	298.0	"
976	" D ₂ O	7.18	"	239.0	276.0	"
977	" "	"	"	238.0	275.0	"
978	Benzyl alcohol- α -d ₂ , D ₂ O	"	0.851	216.0	254.0	"
979	" "	"	"	210.0	247.0	"
980	Benzyl alcohol- α -d ₂	4.40	"	10.2	1.20	"
981	"	"	"	10.1	1.19	"
982	Benzyl alcohol	"	0.867	9.44	1.09	"
983	"	"	"	9.42	1.09	"
984	" D ₂ O	4.34	"	10.3	1.19	"
985	" "	"	"	10.1	1.17	"
986	Benzyl alcohol- α -d ₂ , D ₂ O	"	0.851	10.8	1.27	"
987	" "	"	"	11.1	1.30	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r	
988	1-Phenylethanol	1.85	11.26	5.50	0.489	.999	
989	"	4.84	7.507	12.6	1.68	"	
990	"	2.82	3.754	1.47	0.393	"	
991	"	4.16	3.754	3.09	0.823	"	
992	"	"	15.02	12.6	0.839	"	
993	"	"	11.26	8.88	0.789	"	
994	"	"	7.507	5.66	0.754	"	
995	2-Phenylethanol	4.10	7.535	6.07	0.805	"	
996	"	"	11.30	9.15	0.810	"	
997	"	"	15.07	12.9	0.856	"	
998	"	1.85	15.07	1.57	0.104	.998	
999	"	4.84	7.535	16.1	2.14	.999	
1000	"	4.16	"	8.38	1.11	"	
1001	"	5.70	15.07	116.0	7.67	"	
1002	"	"	"	131.0	8.69	"	
1003	"	2.82	"	5.29	0.351	"	
1004	Acetone	8.76	61.27	1.12	0.0183	"	
1005	"	6.66	"	0.162	0.00264	.992	
1006	"	7.42	"	0.360	0.00588	.998	
1007	"	5.64	"	0.0384	0.000627	.842	
1008	"	9.42	"	3.52	0.0574	.996	
1009	"	8.64	133.5	2.20	0.0165	.995	
1010	"	"	264.4	3.53	0.0133	.999	
1011	"	"	392.8	6.56	0.0167	"	
1012	"	"	328.9	5.06	0.0154	"	
1013	"	9.68	53.71	2.58	0.0480	.997	
1014	"	"	133.5	6.25	0.0468	"	
1015	"	"	212.3	13.1	0.0615	"	
1016	"	"	264.4	14.1	0.0533	.983	
1017	2-Pentanone	8.76	22.07	16.0	0.726	.999	
1018	"	"	30.90	24.2	0.783	"	
1019	"	"	44.14	33.0	0.748	"	
1020	"	6.66	33.95	1.04	0.0307	"	
1021	"	7.42	42.45	3.85	0.0908	"	
1022	"	5.64	"	0.528	0.0124	"	
1023	"	9.42	8.49	28.7	3.38	"	
1024	"	38.2°	8.86	10.19	2.47	"	
1025	"	"	"	34.6	3.39	"	
1026	"	31.2°	"	12.73	1.30	"	
1027	"	19.5°	"	16.98	0.946	"	
1028	"	25.0°	"	"	1.12	"	
1029	"	"	"	21.8	1.28	"	
1030	"	13.9°	"	9.93	0.585	"	
1031	"	14.0°	"	12.0	0.704	"	
1032	"	"	6.33	33.96	2.02	0.0594	"

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r	
1033	2-Pentanone	6.33	33.96	1.83	0.0538	.999	
1034	"	7.40	"	3.35	0.0985	"	
1035	"	8.04	"	13.2	0.387	"	
1036	"	"	24.45	6.49	0.266	"	
1037	"	"	"	7.09	0.290	"	
1038	"	"	16.30	4.04	0.248	"	
1039	"	"	10.87	2.45	0.225	"	
1040	"	8.92	10.19	10.3	1.01	"	
1041	"	"	"	9.59	0.941	"	
1042	"	6.70	50.63	1.28	0.0253	"	
1043	"	"	"	1.27	0.0251	"	
1044	"	7.90	8.49	1.61	0.189	"	
1045	"	"	"	1.48	0.174	.995	
1046	"	7.41	84.05	7.27	0.0864	.999	
1047	"	"	"	6.65	0.0791	"	
1048	"	"	67.38	5.51	0.0817	"	
1049	"	"	"	5.56	0.0825	"	
1050	"	"	33.96	3.04	0.0896	"	
1051	"	"	"	3.07	0.0903	"	
1052	"	"	16.98	1.54	0.0904	"	
1053	"	"	"	1.49	0.0879	"	
1054	Cyclohexanone	6.90	18.30	16.1	0.880	"	
1055	"	6.24	"	7.85	0.429	"	
1056	"	"	"	7.99	0.437	"	
1057	"	5.64	36.60	11.5	0.315	"	
1058	"	"	26.35	8.27	0.314	"	
1059	"	"	"	7.34	0.279	"	
1060	"	"	17.57	5.04	0.287	"	
1061	"	"	11.71	3.36	0.287	"	
1062	"	5.16	36.60	8.18	0.223	"	
1063	"	"	"	8.55	0.234	"	
1064	"	D ₂ O	8.07	10.07	35.3	3.50	.996
1065	"	38.0°	6.34	10.98	14.0	1.27	.999
1066	"	38.2°	"	"	13.4	1.22	"
1067	"	31.1°	"	18.30	15.0	0.820	"
1068	"	19.4°	"	"	7.40	0.404	"
1069	"	24.9°	"	"	10.5	0.571	"
1070	"	25.1°	"	"	10.3	0.565	"
1071	"	14.0°	"	"	4.36	0.238	"
1072	"	"	"	"	4.39	0.240	"
1073	"	7.41	"	49.7	2.72	.997	
1074	"	"	"	49.8	2.72	.999	
1075	Benzophenone	6.66	14.77	5.46	0.370	.985	
1076	"	"	3.32	0.836	0.252	.995	
1077	"	7.42	18.01	32.5	1.80	.992	

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
1078	Benzophenone	7.42	12.61	21.6	1.71	.994
1079	"	"	6.30	11.0	1.74	.991
1080	"	"	9.01	13.5	1.50	.993
1081	Trifluoroaceto- phenone	5.66	13.45	7.49	0.557	.998
1082	"	6.62	"	43.0	3.20	"
108e	"	"	"	45.6	3.39	.999
1084	"	6.74	20.17	76.7	3.80	.996
1085	"	5.92	13.45	12.9	0.962	.997
1086	"	"	"	11.0	0.815	.995
1087	"	"	6.72	5.60	0.833	.999
1088	"	"	"	6.13	0.912	"
1089	"	"	3.36	2.40	0.714	"
1090	"	"	"	2.70	0.803	"
1091	Formaldehyde	4.98	1.83	70.8	38.7	"
1092	"	"	"	73.5	40.2	.998
1093	"	3.00	9.14	63.3	6.92	.999
1094	"	"	6.58	47.0	7.15	"
1095	"	"	"	45.2	6.87	"
1096	"	"	4.39	29.2	6.65	"
1097	"	"	"	31.2	7.10	"
1098	"	"	2.92	20.0	6.83	"
1099	"	"	"	20.3	6.96	"
1100	"	4.16	3.65	62.9	17.2	"
1101	"	"	"	67.8	18.6	"
1102	"	2.04	7.30	26.1	3.57	"
1103	"	"	"	25.8	3.53	"
1104	"	1.03	10.90	15.3	1.40	"
1105	"	"	"	15.9	1.45	"
1106	Benzaldehyde	2.90	8.830	18.2	2.07	"
1107	"	2.76	3.534	7.39	2.09	"
1108	"	"	"	7.34	2.08	.994
1109	"	1.00	10.60	1.91	1.81	.992
1110	"	"	"	1.99	1.88	.999
1111	<u>p</u> -Chloro B.ald.	2.16	1.606	1.63	1.02	"
1112	<u>p</u> -Nitro B.ald.	"	2.105	1.90	0.901	"
1113	Benzaldehyde	"	1.699	3.53	2.08	"
1114	"	"	"	3.40	2.00	"
1115	<u>m</u> -Methyl B.ald.	2.16	1.468	2.20	1.50	"
1116	"	"	"	2.50	1.71	"
1117	Benzaldehyde	3.28	1.767	4.10	2.32	.996
1118	"	"	"	4.22	2.39	.997
1119	"	1.86	16.67	28.4	1.71	.999
1120	"	"	12.72	23.0	1.81	.997
1121	"	"	"	23.1	1.82	.999

APPENDIX C

No.	Substrate	$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
1122	Benzaldehyde	1.86	8.482	13.8	1.62	.997
1123	"	"	"	14.2	1.68	.999
1124	"	"	4.241	7.35	1.73	"
1125	"	"	"	7.44	1.76	.997
1126	"	1.86	10.60	20.1	1.89	.999
1127	"	"	"	20.4	1.92	"
1128	"	"	7.066	20.4	2.89	.997
1129	"	"	"	20.1	2.84	"
1130	"	2.33	3.53	7.71	2.19	.998
1131	"	"	"	7.92	2.25	.999
1132	"	2.79	"	8.00	2.27	"
1133	"	"	"	8.10	2.29	"
1134	"	3.20	3.53	8.78	2.49	.996
1135	"	"	"	8.93	2.53	"
1136	"	3.60	3.53	9.60	2.72	"
1137	"	"	"	9.88	2.80	"
1138	"	4.09	"	10.5	2.99	.997
1139	"	"	"	10.7	3.02	"
1140	"	4.50	"	11.5	3.26	.998
1141	"	"	"	11.7	3.30	"
1142	"	4.94	"	15.9	4.52	.997
1143	"	"	"	15.7	4.44	"
1144	"	5.40	"	18.3	5.19	.996
1145	"	"	"	18.6	5.26	.995
1146	"	5.75	"	24.1	6.83	.997
1147	"	"	"	25.0	7.08	"
1148	"	6.20	4.42	59.9	13.5	.999
1149	"	"	"	56.1	12.7	"
1150	"	2.35	7.07	16.2	2.29	.997
1151	"	"	"	16.6	2.34	.996
1152	"	1.71	6.71	13.1	1.95	.997
1153	"	"	"	12.6	1.88	"
1154	"	0.98	7.07	15.1	2.13	"
1155	"	"	"	15.4	2.17	"
1156	"	0.60	"	14.8	2.10	"
1157	"	"	"	13.6	1.93	.999
1158	"	0.12	"	13.7	1.94	.997
1159	"	"	"	13.6	1.93	.998
1160	"	6.34	1.77	32.1	18.2	.997
1161	"	"	"	32.7	18.5	"
1162	"	7.62	"	54.7	30.9	.999
1163	"	"	"	55.9	31.6	"
1164	"	no TFA	7.07	1.26	0.178	.997
1165	Formic acid	4.98	23.9	0.179	0.00747	.980
1166	"	5.70	46.75	0.387	0.00828	.999
1167	"	8.42	46.70	27.8	0.582	"

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
1168	Formic acid		8.42	46.70	29.0	0.607	.999
1169	"		6.26	68.42	2.19	0.0319	"
1170	"		"	95.03	2.98	0.0314	"
1171	"		"	45.61	1.37	0.0299	"
1172	"		"	30.41	0.898	0.0295	"
1173	"		8.50	119.3	82.9	0.695	"
1174	"		"	"	79.5	0.666	.998
1175	3-Pentanone		6.90	25.58	3.55	0.139	.993
1176	"		"	"	3.73	0.146	"
1177	"		7.90	8.53	4.23	0.496	.991
1178	"		"	"	3.71	0.435	"
1179	"		7.41	29.84	17.4	0.582	.999
1180	"		"	"	17.4	0.584	"
1181	"		"	20.46	9.68	0.473	"
1182	"		"	"	9.83	0.480	"
1183	"		"	17.90	7.80	0.436	"
1184	"		"	"	8.03	0.448	"
1185	"		"	8.53	2.43	0.285	.992
1186	"		"	"	2.57	0.301	.993
1187	"	14.6°	7.90	17.05	9.94	0.583	.994
1188	"	14.8°	"	"	9.63	0.565	"
1189	"	20.6°	"	"	11.9	0.698	"
1190	"	"	"	"	12.4	0.728	"
1191	"	30.2°	"	"	15.9	0.930	.997
1192	"	"	"	"	16.7	0.979	"
1193	"	37.6°	"	"	22.3	1.31	"
1194	"	37.4°	"	"	21.3	1.25	.998
1195	"	25.0°	"	"	14.0	0.819	.997
1196	"	"	"	"	13.8	0.812	.996
1197	Benzene,	D ₂ O	6.96	5.013	139.0	27.7	.999
1198	"	"	"	"	147.0	29.3	"
1199	"	H ₂ O	"	"	140.0	28.0	"
1200	"	"	"	"	133.0	26.5	"
1201	"	D ₂ O	6.15	"	15.1	3.01	.998
1202	"	"	"	"	15.3	3.06	"
1203	"	H ₂ O	6.26	"	13.9	2.76	"
1204	"	"	"	"	13.7	2.74	.997
1205	"	D ₂ O	5.67	20.50	11.6	0.565	.999
1206	"	"	"	"	11.2	0.545	.994
1207	"	H ₂ O	5.64	"	9.89	0.482	.997
1208	"	"	"	"	9.70	0.473	.995
1209	Cyclohexane,	D ₂ O	6.15	33.32	7.84	0.235	.999
1210	"	"	"	"	7.78	0.234	"
1211	"	H ₂ O	6.26	"	7.08	0.212	"
1212	"	"	"	"	6.84	0.205	"

APPENDIX C

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^3 s^{-1}$	$k_2 M^{-1} s^{-1}$	r
1213	Cyclohexane,	H ₂ O	6.98	16.66	27.5	1.65	.999
1214	"	"	"	"	28.9	1.72	"
1215	"	D ₂ O	6.96	"	25.9	1.55	"
1216	"	"	"	"	25.2	1.51	"
1306	"	TFAD, D ₂ O	6.10	11.66	0.00683	0.585	"
1307	"	"	7.48	8.33	0.140	16.8	.997

No.	Substrate		$-H_R$	$[S] \times 10^3$	$k_1 \times 10^7 M s^{-1}$	$k_2 \times 10^5 s^{-1}$	r
1217	2,4-Pentanedione		1.02	1.75	172.0	984.0	.998
1218	"		1.02	"	172.0	983.0	"
1219	"		2.86	"	254.0	145.0	.997
1220	"		"	"	242.0	138.0	"
1221	"		-0.05	3.50	246.0	703.0	.979
1222	"		"	"	245.0	700.0	.996
1223	"		-0.41	1.68	116.0	691.0	.999
1224	"		"	"	117.0	698.0	.996
1225	"		"	2.52	172.0	701.0	"
1226	"		"	"	176.0	697.0	.995
1227	"		"	3.78	259.0	684.0	.991
1228	"		"	"	270.0	714.0	.996
1229	"		"	5.24	337.0	643.0	.999
1230	3-Pentanone		6.70	25.58	5.04	1.97	.995
1231	"		"	"	5.08	1.98	.994
1232	"		7.90	8.53	8.23	9.65	.978
1233	"		"	"	6.91	8.10	.991
1234	"		7.41	29.84	26.2	8.78	.981
1235	"		"	"	25.9	8.67	.979
1236	"		"	20.46	13.7	6.71	.973
1237	"		"	"	13.5	6.62	.971
1238	"		"	17.90	10.9	6.08	.975
1239	"		"	"	10.4	5.81	.978
1240	"		"	8.53	4.58	5.37	.975
1241	"		"	"	5.06	5.93	.978
1242	"	14.6°	7.90	17.05	17.6	10.3	.981
1243	"	14.8°	"	"	16.2	9.50	.985
1244	"	20.6°	"	"	18.7	11.0	.979
1245	"	"	"	"	18.2	10.7	.984
1246	"	30.2°	"	"	20.2	11.9	.978
1247	"	"	"	"	19.9	11.7	"
1248	"	37.6°	"	"	23.8	13.9	.969

APPENDIX C

No.	Substrate	-H _R	[S]x10 ³	k ₁ x10 ⁷ Ms ⁻¹	k ₂ x10 ⁵ s ⁻¹	r	
1249	3-Pentanone	37.4°	7.90	17.05	22.7	13.3	.969
1250	"	25.0°	"	"	18.8	11.0	.980
1251	"	"	"	"	18.5	10.8	"
1252	Acetophenone		5.66	23.10	1.53	0.660	.999
1253	"		"	"	1.74	0.759	.997
1254	"		6.62	15.40	5.47	3.55	.999
1255	"		6.62	"	5.43	3.53	"
1256	"		6.74	23.10	9.38	4.06	"
1257	"		"	"	8.84	3.83	.994
1258	"		"	7.70	3.38	4.38	.999
1259	"		"	"	3.21	4.16	"
1260	"		"	15.40	6.02	3.91	"
1261	"		"	"	6.24	4.05	"
1262	"		"	38.51	15.2	3.95	.996
1263	"		"	"	14.8	3.85	.997
1264	"		5.92	23.10	2.08	0.898	.999
1265	"		"	"	2.18	0.942	"
1266	"	25.0°	6.41	15.40	3.32	2.16	"
1267	"	"	"	"	3.37	2.19	"
1268	"	37.6°	"	30.80	12.4	4.02	"
1269	"	37.4°	"	"	11.5	3.75	"
1270	"	30.2°	"	"	8.75	2.84	"
1271	"	"	"	"	8.78	2.85	"
1272	"	20.6°	"	"	5.08	1.65	"
1273	"	"	"	"	5.21	1.69	"
1274	"	14.7°	"	"	3.96	1.29	"
1275	"	14.8°	"	"	3.85	1.25	"

APPENDIX D

Permanganate in Benzene^a

No.	Substrate	[S]x10 ³	k ₁ x10 ³ s ⁻¹	k ₂ M ⁻¹ s ⁻¹	r
1276	<u>trans</u> -Stilbene	2.27	1.020	0.449	.999
1277	"	3.72	1.641	0.441	"
1278	"	"	1.612	0.433	"
1279	"	2.27	1.037	0.457	"
1280	"	1.29	0.591	0.458	"
1281	"	"	0.611	0.474	"
1282	<u>cis</u> -Stilbene	4.32	0.4065	0.0941	"
1283	"	"	0.4028	0.0932	"
1284	"	3.59	0.3065	0.0854	"
1285	"	"	0.3129	0.0872	"
1286	"	0.884	0.0842	0.0953	"
1287	<u>trans</u> -Stilbene	3.72	1.616	0.434	"
1288	"	"	1.650	0.444	"
1289	Tolan	41.56	0.3257	0.00784	"
1290	"	"	0.3666	0.00882	"
1291	<u>p,p'</u> -Dinitro- <u>trans</u> -stilbene	0.353	84.90	240.5	.980
1292	"	"	61.99	175.6	.998
1293	<u>m,p'</u> -Dinitro- <u>trans</u> -stilbene	0.128	14.62	114.2	"
1294	"	"	12.55	98.05	.999
1295	<u>p</u> -Nitro- <u>trans</u> -stilbene	1.687	16.61	9.84	"
1296	"	"	16.51	9.79	"
1297	"	1.012	11.51	11.4	"
1298	"	"	11.12	11.0	"
1299	Benzyl alcohol	5.4776	0.661	0.121	"
1300	"	"	0.772	0.141	"
1301	Benzaldehyde	4.542	8.01	1.764	"
1302	<u>p</u> -Nitrobenzyl alcohol*	0.716	31.2	43.5	.910
1303	"	"	15.9	22.2	.960
1304	<u>p</u> -Nitrobenzaldehyde*	1.679	15.2	9.05	.985
1305	"	"	16.1	9.61	.999

^a All rates corrected for blank corrections.

* These rates are very approximate because of very large infinite time absorbances.

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