

MECHANISM OF THE CHROMIC ACID
OXIDATION OF ALCOHOLS

by

DONALD GARRY LEE

B.A., University of Saskatchewan, 1958

M.A., University of Saskatchewan, 1960

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
CHEMISTRY

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

March, 1963

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia,
Vancouver 8, Canada.

Date May 1/63

The University of British Columbia

FACULTY OF GRADUATE STUDIES

PROGRAMME OF THE

FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

DONALD GARRY LEE

PUBLICATIONS

Rearrangement Studies with C^{14} , X. Ethanol- $2-C^{14}$ from the Irradiation of ethanol- $1-C^{14}$ with Co^{60} Gamma Rays. Can. J. Chem. 38, 2315 (1960) C.C. Lee and D.G. Lee

2-Phenylethyl- $2-C^{14}$ Iodide from the Irradiation of 2-Phenylethyl- $1-C^{14}$ Iodide with Cobalt-60 Gamma Rays. Radiation Research 17, 536 (1962) C.C. Lee, D.G. Lee, and I.S. Bhardwaj

Rearrangement Studies with C^{14} , XIII. The Thermal Decomposition of $1-C^{14}$ -2-Butyl Chlorosulphite. Tetrahedron 18, 1395 (1962) C.C. Lee, J.W. Clayton, D.G. Lee and A.J. Finlayson

B.A., The University of Saskatchewan, 1958
M.A., The University of Saskatchewan, 1960

MONDAY, APRIL 29th, 1963, AT 9:30 A.M.
IN ROOM 261, CHEMISTRY BUILDING

COMMITTEE IN CHARGE

Chairman: F.H. Soward

W.A. Bryce	R.E. Pincock
W.R. Cullen	R. Stewart
C.A. McDowell	D.S. Scott

External Examiner: F.H. Westheimer

Harvard University

MECHANISM OF THE CHROMIC ACID

OXIDATION OF ALCOHOLS

ABSTRACT

The relative rates of chromic acid oxidation of eight aryltrifluoromethylcarbinols were determined in 77.2% acetic acid medium. The primary deuterium isotope effects of these alcohols ranged from 7.40 for *p*-tolyltrifluoromethylcarbinol to 12.93 for 3,5-dinitrophenyltrifluoromethylcarbinol at 25°. The rates fitted a Hammett plot best when modified σ^+ substituent values were used and a modified "rho" value of -1.01 was observed.

The rates of oxidation of several halogenated-2-propanols as well as their corresponding 2-d analogues were also determined in 77.2% acetic acid and in 50.1% sulfuric acid. Results indicated that while the isotope effect varied with changes in the nature of the alcohol being oxidized, it was constant for a particular alcohol in solutions of varying acidity.

The thermodynamic parameters for the oxidation of two different alcohols under a variety of conditions were determined and found to be approximately the same, $\Delta H^\ddagger = 9$ kcal/mole, $\Delta S^\ddagger = -40$ cal/mole deg.

An extensive investigation of the oxidation of alcohols in sulfuric acid solutions ranging from 5 to 95% was conducted and a spectroscopic study was made of the behaviour of chromium VI in this entire region.

A σ^* value was obtained for the CF₃ group and this was used to determine the "true rate constant", $k = k_{\text{obs}}/K$, for the chromic acid oxidation of a series of primary alcohols. A Taft $\sigma^* - \rho^*$ plot then yielded a ρ^* value of -0.92 for the rate determining step of this reaction.

A spectroscopic investigation of the variation of the pK_a of chromic acid with changes in the identity of the mineral acid solvents was made, and the results were applied to explain observed variations in the rate of oxidation of isopropyl alcohol in solutions of different mineral acids all having the same acidity.

The results are best explained in terms of a unimolecular decomposition of a chromate ester via a cyclic transition state.

GRADUATE STUDIES

Field of Study: Physical Organic Chemistry

Topics in Physical Chemistry	R.F. Snider
	J.A.R. Coope
Topics in Organic Chemistry	R.A. Bonnett
	R. Stewart
	J. Kutney
Physical Organic Chemistry	R. Stewart
	R.E. Pincock
Inorganic Reaction Mechanisms	J. Halpern
Organic Reaction Mechanisms	R.E. Pincock

Related Studies:

Differential Equations	S.A. Jennings
Light	J.J. Veit

ABSTRACT

The relative rates of chromic acid oxidation of eight aryltrifluoromethylcarbinols were determined in 77.2% acetic acid medium. The primary deuterium isotope effects for these alcohols ranged from 7.40 for *p*-tolyltrifluoromethylcarbinol to 12.93 for 3,5-dinitrophenyltrifluoromethylcarbinol at 25°. The rates fitted a Hammett plot best when modified σ^+ substituent values were used and a modified "rho" value of -1.01 was observed.

The rates of oxidation of several halogenated-2-propanols as well as their corresponding 2-d analogues were also determined in 77.2% acetic acid and in 50.1% sulfuric acid. Results indicated that while the isotope effect varied with changes in the nature of the alcohol being oxidized, it was constant for a particular alcohol in solutions of varying acidity.

The thermodynamic parameters for the oxidation of two different alcohols under a variety of conditions were determined and found to be approximately the same, $\Delta H^\ddagger = 9$ kcal/mole, $\Delta S^\ddagger = -40$ cal/mole deg.

An extensive investigation of the oxidation of alcohols in sulfuric acid solutions ranging from 5 to 95% was conducted and a spectroscopic study was made

of the behavior of chromium VI in this entire region.

A σ^* value was obtained for the CF_3 group and this was used to determine the "true rate constant", $k = k_{\text{obs}}/K$, for the chromic acid oxidation of a series of primary alcohols. A Taft $\sigma^* - \rho^*$ plot then yielded a ρ^* value of -0.92 for the rate determining step of this reaction.

A spectroscopic investigation of the variation of the pKa of chromic acid with changes in the identity of the mineral acid solvents was made, and the results were applied to explain observed variations in the rate of oxidation of isopropyl alcohol in solutions of different mineral acids all having the same acidity.

The H_0 acidity function for nitric and phosphoric acid systems with a 1:1 molar ratio of sodium perchlorate was also determined.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. Ross Stewart for his guidance during the course of this research and for his constructive criticism during the preparation of this thesis.

Grateful acknowledgment is also made to the University of British Columbia for the award of two Teaching Assistantships (1960-61 and 1961-62), and to the National Research Council of Canada for the award of a Studentship (1961-62).

TABLE OF CONTENTS

	Page
I. HISTORICAL INTRODUCTION	
1. Chromic Acid Oxidation of Organic Compounds	1
2. Chromic Acid Oxidation of Alcohols	3
3. Primary Kinetic Isotope Effects	24
II. SCOPE OF THE PRESENT INVESTIGATION	36
III. EXPERIMENTAL	39
1. Materials	
(i) Alcohols	39
(ii) Inorganic Reagents	53
(iii) Indicators	54
2. Kinetic Methods	55
(i) Iodometric Method	56
(ii) Spectrophotometric Method	64
3. Consideration of the Acid Chromate-Bichromate Equilibrium	64
4. Product Analysis	65
5. Determination of pKa Values for H_2CrO_4	67
6. Acidity Function for the Phosphoric Acid-Sodium Perchlorate System	72
7. Acidity Function for the Nitric Acid-Sodium Perchlorate System	79
8. Determination of the Chromate Ester Equilibrium Constant for 2-Methoxy-ethanol and 2,2,2-Trifluoroethanol	80

IV. RESULTS AND DISCUSSION

1. Oxidation of Fluoro Alcohols in 77.2% Acetic Acid	85
2. Oxidation of some Halogenated 2-propanols in 50.1% Sulfuric Acid	101
3. Variation in the Magnitude of Isotope Effects with Changes in Acidity	107
4. Thermodynamic Parameters	109
5. Oxidation in Concentrated Sulfuric Acid Solutions	113
6. Determination of the e^* Value for the CF_3 Group	136
7. Determination of the "True Rate Constant", $k_2 = k_{obs}/K$, for the Chromic Acid Oxidation of some Primary Alcohols	138
8. Acidity Functions for Nitric and Phosphoric Acid Solutions with Added Sodium Perchlorate	143
9. Variation in the pK_a of Chromic Acid with Changes in the Identity of the Mineral Acid Solvent	149
10. Variation in Rate of Chromic Acid Oxidations with Changes in the Identity of the Mineral Acid Solvent	166

V. CONCLUSION	175
---------------	-----

VI. SUGGESTIONS FOR FURTHER RESEARCH	181
--------------------------------------	-----

VII. APPENDIX	183
---------------	-----

VIII. BIBLIOGRAPHY	184
--------------------	-----

TABLES

I. Variation in Theoretical Isotope Effects with Temperature	28
II. Data for Rate Plots	59
III. Acidity of Solutions Containing a 1:1 Molar Ratio of H_3PO_4 to NaClO_4	74
IV. Acidity of Solutions Containing a 1:1 Molar Ratio of HNO_3 to NaClO_4	75
V. Data for Figure 10	84
VI. Oxidation of Fluoro alcohols in 77.2% Acetic Acid	86
VII. Variation in Rate of Oxidation of Phenyltrifluoromethylcarbinols in 77.2% Acetic with H_2O	101
VIII. Rates of Oxidation of Substituted 2-Propanols in 50.1% Sulfuric Acid	104
IX. Deuterium Isotope Effects for the Oxidation of Isopropyl Alcohol in Perchloric Acid Solutions of Varying Acidities	108
X. Heats and Entropies of Activation for the Oxidation of Substituted 2-Propanols Under Various Conditions	110
XI. Rates Used in Calculation of Thermodynamic Parameters	111
XII. Extinction Coefficients of Chromium VI in Sulfuric Acid Solutions	117
XIII. Oxidation of $\text{CF}_3\text{CROHCH}_3$ by Chromium VI in Sulfuric Acid Solutions at 25.0°C .	123
XIV. Oxidation of $\text{CH}_3\text{CROHCH}_3$ in Sulfuric Acid Solutions	124
XV. Oxidation of 1,1,1,3,3,3-hexafluoro-2-propanol in Sulfuric Acid Solutions	125

XVI. Oxidation of Substituted Methanols in 3.82M HClO ₄	139
XVII. Calculation of the "True Rate Constants", $k_2 = k_{\text{obs}}/K$ for some Substituted Methanols in Aqueous Perchloric Acid Solutions	141
XVIII. Acidities of Solutions Containing a 1:1 Molar Ratio of Phosphoric Acid and Sodium Perchlorate	144
XIX. Acidities of Solutions Containing a 1:1 Molar Ratio of Nitric Acid and Sodium Perchlorate	145
XX. Comparison of the pKa of H ₂ CrO ₄ in Aqueous Solution of Various Mineral Acids and the Point of Slope Change in a Plot of log k v.s. H ₀ for these Acids	151
XXI. Spectral Data for the Acid Chromate Ion in Various Mineral Acids	153
XXII. Spectral Data for Chromic Acid in Various Mineral Acids	154
XXIII. Rate of Oxidation of Isopropyl Alcohol in Mineral Acids of a Given Acidity (H ₀ = -2.5)	155
XXIV. Rates of Oxidation of Isopropyl Alcohol in Sulfuric Acid Solutions	169
XXV. Rates of Oxidation of Isopropyl Alcohol in Perchloric Acid Solutions	170
XXVI. Rates of Oxidation of Isopropyl Alcohol in Phosphoric Acid Solutions	170
XXVII. Rates of Oxidation of Isopropyl Alcohol in Hydrochloric Acid Solutions	171
XXVIII. Rates of Oxidation of Isopropyl Alcohol in Nitric Acid Solutions	172

XXIX. Rates of Oxidation of Isopropyl Alcohol in Solutions Containing a 1:1 Molar Ratio of H_3PO_4 to NaClO_4	173
XXX. Rates of Oxidation of Isopropyl Alcohol in Solutions Containing a 1:1 Molar Ratio of HNO_3 to NaClO_4	173

FIGURES

1. Typical Second Order Rate Plots for the Oxidation of Substituted Phenyltrifluoromethylcarbinols in 77.2% Acetic Acid	57
2. Typical First Order Rate Plots for the Oxidation of Isopropyl Alcohol	58
3. pKa of H_2CrO_4 in H_2SO_4	69
4. pKa of H_2CrO_4 in HClO_4	69
5. pKa of H_2CrO_4 in HCl	70
6. pKa of H_2CrO_4 in HNO_3	70
7. pKa of H_2CrO_4 in H_3PO_4 - NaClO_4	71
8. Ionization of Indicators in H_3PO_4 - NaClO_4 Solutions	77
9. Ionization of Indicators in HNO_3 - NaClO_4 Solutions	78
10. Chromate Ester Equilibrium Constants	83
11. Hammett σ^+ - ρ^+ Plot for the Chromic Acid Oxidation of Substituted Phenyltrifluoromethylcarbinols in 77% Acetic Acid	89
12. Hammett σ^- - ρ^- Plot for the Chromic Acid Oxidation of Substituted Phenyltrifluoromethylcarbinols in 77% Acetic Acid	90
13. Relationship Between the Rate of Oxidation of Trifluoromethylcarbinols in 77% Acetic Acid and the Primary Deuterium Isotope Effect	96
14. Linear Relationship Between Rate and Acidity for the Oxidation of Phenyltrifluoromethylcarbinol in 77.2% Acetic Acid	100
15. Taft σ^* - ρ^* Plot for the Oxidation of Substituted 2-Propanols in 50.1% H_2SO_4	106

16. Thermodynamic Parameters	112
17. Extinction Coefficients for Chromium VI in Sulfuric Acid Solutions	116
18. U. V. Spectra of Chromium VI in H_2SO_4 Solutions	118
19. Attempted Determination of the pKa for p-Toluic Acid in Acetic Acid-Sulfuric Acid Media	120
20. Relationship Between H_0 and the Rate of Oxidation of three 2-Propanols in Sulfuric Acid Solutions	122
21. Oxidation of 1,1,1-Trifluoro-2-propanol in 57.6% H_2SO_4	129
22. Oxidation of 1,1,1-Trifluoro-2-propanol in 63.9% H_2SO_4	130
23. Oxidation of 1,1,1-Trifluoro-2-propanol in 68.5% H_2SO_4	131
24. Oxidation of 1,1,1-Trifluoro-2-propanol in 76.4% H_2SO_4	132
25. Oxidation of 1,1,1-Trifluoro-2-propanol in 85.7% H_2SO_4	133
26. Oxidation of 1,1,1-Trifluoro-2-propanol in 95.3% H_2SO_4	134
27. Relationship Between $K_{obs.}$ for the Oxidation of Substituted Methanols and the σ^* Value for the Substituents	142
28. Relationship Between the True Rate Constant, $k_2 = k_{obs}/K$ and σ^* Values	142
29. Comparison of the H_0 Function for a 1:1 Molar Ratio of H_3PO_4 and $NaClO_4$ with that for H_3PO_4	146

30. Comparison of the H_0 Function for a 1:1 Molar Ratio of HNO_3 and $NaClO_4$ with that for HNO_3	147
31. Ultraviolet Spectrum of Chromium VI in 3.50 M $HClO_4$	156
32. Ultraviolet Spectrum of Chromium VI in 3.10 M H_2SO_4	157
33. Ultraviolet Spectrum of Chromium VI in 3.60 M HCl	158
34. Ultraviolet Spectrum of Chromium VI in 3.00 M H_3PO_4	159
35. "pKa" of $HCrSO_7$	165
36. "pKa" of $HCrO_3Cl$	165
37. Chromic Acid Oxidation of Isopropyl Alcohol in Aqueous Solutions of Mineral Acids	168

I. HISTORICAL INTRODUCTION

1. CHROMIC ACID OXIDATION OF ORGANIC COMPOUNDS

While chromic acid has long been used as an oxidizing agent in preparative organic chemistry it is only in comparatively recent years that kinetic or mechanistic investigations have been conducted. Since the first kinetic studies performed by Westheimer and Novick (1) on the chromic acid oxidation of isopropyl alcohol, investigations have been carried out on the mechanism of oxidation of hydrocarbons (2-11), aldehydes (12-17), ketones (18, 19) carboxylic acids (20, 21), ethers (22), olefins (23) and glycols (24-26), as well as alcohols. The latter group will be discussed in detail later. In addition to the two most commonly used solvents, water and acetic acid, the reaction has been studied in acetic anhydride (15), propionic acid (23), propionic anhydride (23), benzene (27), pyridine (27, 28), aqueous acetone (29), and concentrated sulfuric acid (30, 31, 31).

While the details of the reaction vary considerably from one type of compound to another and from one solvent to another several very general features can be observed. In all cases studied the reaction was found to be acid catalyzed, with the rate being proportional to some power of h_0 (12, 20, 31). Also

in all studies reported to date but one it has been observed that electron withdrawing groups attached to the organic substrates slow down the rate of reaction while electron donating groups increase the rate (20, 27, 32). The one exception in this case is the oxidation of substituted benzaldehydes in 91% acetic acid where Wiberg and Mill found a "rho" value of +1.02 (12). Roček, on the other hand, has reported that the chromic acid oxidation of a series of substituted acetaldehydes gives a "rho*" value of -1.2 (14, 33). Finally, for a given acidity it has been found that reactions in acetic acid are always faster than the corresponding reactions in aqueous solution (34), and that increasing the proportion of acetic acid in mixed acetic acid-water solvents usually results in a corresponding increase in rate (35, 36).

Since the investigations of this reaction have been so extensive and of such a large variety no attempt will be made in this thesis at a comprehensive review of all the literature. Instead attention will be directed to the oxidation of alcohols by this reagent, and only such material that directly pertains to this reaction will be included.

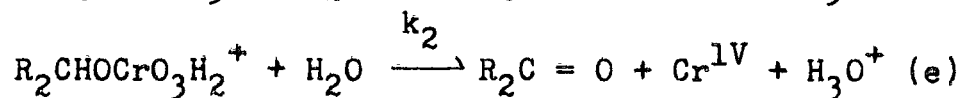
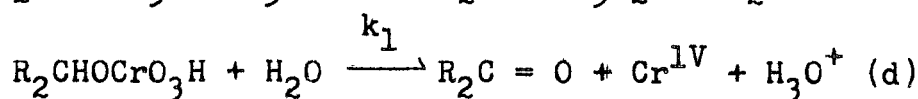
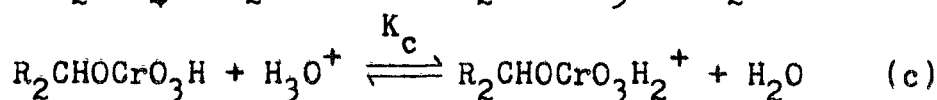
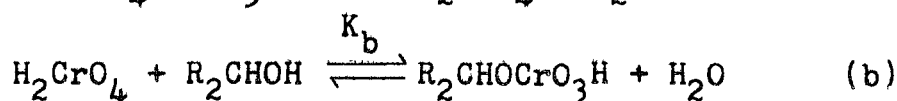
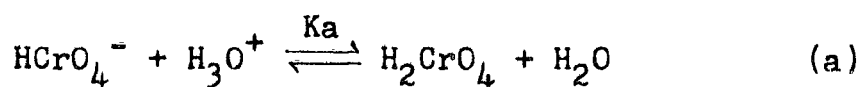
2. CHROMIC ACID OXIDATION OF ALCOHOLS

The literature on this reaction was reviewed by Westheimer (37) in 1949, and again by Waters (38) in 1958. In addition to these two review articles Wiberg (2) and Kwart (39) have both recently published extensive résumés of the literature pertaining to this subject.

In a series of investigations over a period of some seventeen years, Westheimer and coworkers have made a detailed study of the mechanism of the chromic acid oxidation of isopropyl alcohol. The results they have obtained indicate that the reaction is first order in H^+ concentration in dilute acid solutions and second order in H^+ concentration in more acidic solutions (1); that the initial reactions involves a 2-electron change (40); that in dilute acidic aqueous solutions the only active oxidizing species is $HCrO_4^-$ (1); that isopropyl alcohol is oxidized much more rapidly than diisopropyl ether (22); that the rate determining step involves fission of the α -carbon-hydrogen bond ($k_H/k_D = 6.6$) (41); that although similar in many other respects the reaction in 86.5% acetic acid is 250 times as fast as in water of a corresponding acidity (34); and that the reaction is faster in acidic solutions of D_2O than in solutions of H_2O

containing the same concentration of acid ($k_{D_2O}/k_{H_2O} = 2.44$ for the portion of the reaction which is first order in H^+ concentration and $k_{D_2O}/k_{H_2O} = 6.26$ for the portion of the reaction which is second order in H^+ concentration) (22).

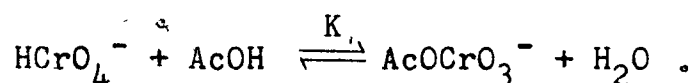
These data together with the observation that a chromate ester of isopropyl alcohol could be prepared in water and extracted into benzene, and further that addition of water or bases such as pyridene caused the ester to decompose to acetone and chromium III (42) led Westheimer to propose a mechanism in which the isopropyl chromate ester was an intermediate.



This mechanism seemed to amply explain all the observed features of the reaction and Westheimer was also able to use it to explain why chromic acid oxidations were faster in acetic acid medium than in water and why addition of chloride ion decreased the

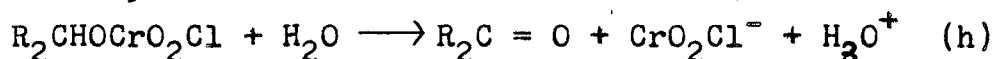
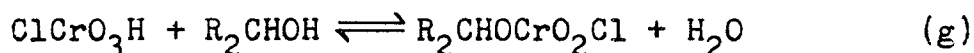
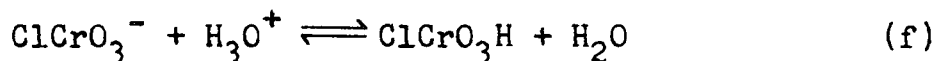
rate of reaction (34). He suggested that the position of the equilibrium in equation (a) would be shifted to the right due to a lowering of the dielectric constant in acetic acid and that the position of the equilibrium in equation (b) would be shifted to the right due to a simple mass action effect. These two effects together were assumed to be sufficient to overcome any reduction in the rate of ester decomposition caused by a lowering of the dielectric constant.

Westheimer's first suggestion that the pKa of chromic acid would be different in acetic acid than in aqueous medium bears further consideration. If the proper H₂ acidity functions were used the pKa of H₂CrO₄ should be the same in both media. However it is possible that chromic acid does not exist as the same species in these two solvents, i.e. an acetate ligand may be incorporated into the coordination shell of the chromium or a mixed anhydride may be formed. One would then be comparing the pKa's of two different species such as HO₂CrO₂OH and HO₂CrO₂OAc. These two species might easily have different pKa's. In fact, Klaning and Symons (43) have recently measured the equilibrium constant for the formation of such a mixed anhydride;



K was found to be 4.5. A simple calculation then shows that in 86.5% acetic acid 90% of the total Chromium VI present is in the form of the mixed anhydride. Hence, if HOCrO_2OAc were a more active oxidizing reagent than H_2CrO_4 the rate enhancement found in acetic acid would be explained.

Further, in explaining the reduction in rate caused by addition of chloride ions Westheimer found it necessary to invoke the formation of chlorochromate ions (34).



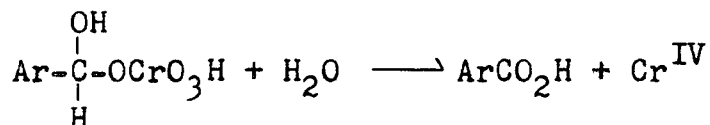
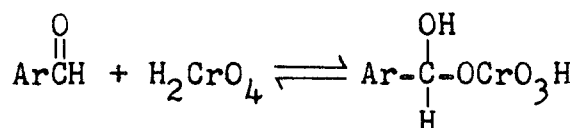
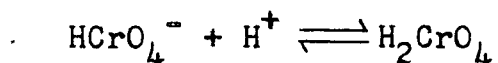
He contended that while incorporation of chloride in this way would not have much effect on the position of the esterification equilibrium it would lower the pKa of the acid and thus shift the equilibrium in (f) as compared with (a) to the right. Although there would also be an effect on reaction (h) it was thought that it would not be of as great a magnitude as the effect on the pKa of the acid.

The ester mechanism has also been used by Wiberg and Mill (12), and by Graham and Westheimer (13) to account satisfactorily for the kinetic results observed when benzaldehyde is oxidized by chromic

acid. The rate law in this case was found to be,

$$V = k [\text{RCHO}] [\text{HCrO}_4^-] h_0$$

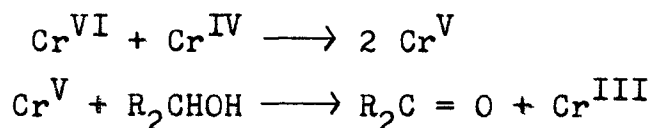
and a "rho" value of +1.02 was observed. The mechanism proposed involved a pre-equilibrium ester formation by reaction of one molecule of H_2CrO_4 with a molecule of aldehyde.



As has been previously mentioned this is the only reported instance in which electron attracting substituents increase the rate of oxidation, and there has been considerable discussion concerning it in the literature. Roček (33), in light of the negative "rho*" value of -1.2 which he observed for the oxidation of four substituted acetaldehydes has suggested that the positive "rho" observed by Wiberg and Mill might be due to the fact that it is the aldehyde hydrates which are being oxidized. If the "rho" for the hydration equilibrium were strongly

positive it would cancel the negative "rho" for oxidation. In reply to this criticism Wiberg and Evans (2) have estimated from a comparison with the permanganate oxidation of aldehydes that the "rho" for hydration is approximately unity. This implies that the "rho" for the rest of the reaction is almost zero. In addition these authors point out that it is possible to reconcile a negative "rho" value with a rate determining proton abstraction step in two ways. Firstly, if the activated complex strongly resembled the products, resonance stabilization of the acid by electron donating groups would lead to an enhanced rate. Secondly, it must be borne in mind that in addition to a proton loss two electrons must also be transferred to the oxidant, and it is conceivable that the effect of substituents could be mainly concerned with the electron transfer.

The exact fate of the chromium IV species produced by these mechanisms is as yet unknown. Westheimer originally postulated that one chromium IV species would combine with a chromium VI species to give two chromium V species which could then react further with alcohol by 2-electron changes.



Evidence favoring this type of a sequence has come from a study of the oxidation of phenyl-t-butylcarbinol by chromic acid (44). The products of this reaction are phenyl t-butyl ketone, benzaldehyde and t-butylalcohol. Since the yield of cleavage products (benzaldehyde and t-butylalcohol) was sharply reduced by addition of Ce^{+++} or Mn^{++} to the reaction medium it was postulated that the cleavage products resulted from an oxidation of the phenyl-t-butylcarbinol by intermediate Cr^{V} and Cr^{IV} species. In the presence of Mn^{++} or Ce^{+++} the intermediate chromium species would be reduced before they could participate in a cleavage reaction.

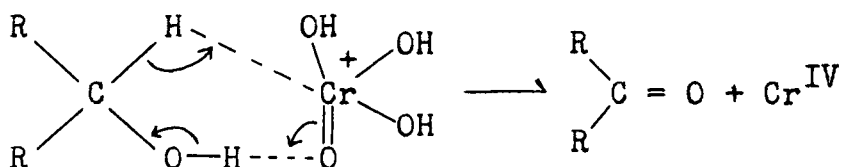
Further, the maximum yield of cleavage products in the absence of Ce^{+++} or Mn^{++} was about 67% indicating that the most likely active intermediate was Cr^{V} and not Cr^{IV} . If the latter species were responsible for the cleavage reaction a maximum yield of only 33% would be expected. Subsequent work by Kaplan (45) on the competitive oxidation of 2-propanol and 2-propanol-2-t has indicated that rupture of the α -carbon-hydrogen bond is also the rate-determining step for the oxidation of 2-propanol by the intermediate chromium species.

More recently Wiberg and Richardson (16) have made a study of the oxidation of aldehydes by Cr^{V} and

Cr^{IV} . Since these chromium species are unstable under reaction conditions they were studied by two new and probably very useful techniques, namely the competitive oxidation of a mixture of organic compounds and the oxidation of a compound which will give different products for different reaction paths. The general result derived from the competitive studies was that the oxidation by the intermediate chromium species exhibited a "rho" value of the same sign and of approximately the same magnitude as that observed for chromium VI oxidation (+0.45 for $\text{Cr}^{\text{IV}}-\text{Cr}^{\text{V}}$ c.f. + 0.77 for Cr^{VI}). This indicates a possibility that both the intermediate species and the Cr^{VI} may react by similar mechanisms. Results obtained from the oxidation of triphenylacetaldehyde on the other hand, indicate that about one-third of the reaction proceeded via a path that did not involve an ester intermediate.

Although the results of many subsequent investigations such as substituent effects on oxidation rates of a group of arylmethylcarbinols (27) and the relative oxidation rates of axial and equatorial cyclanols (46, 47) were also explained in terms of the ester mechanism, Roček and Krupička in 1958 proposed a different mechanism involving hydride ion transfer from the α -carbon atom with simultaneous

proton loss by the hydroxyl (31).



Their reasons for favoring this mechanism as opposed to the ester mechanism were five fold: (i) the rate of oxidation of hydrocarbons, where no ester formation is possible, is also much greater in acetic acid than in aqueous medium of the same acidity; (ii) the log of the rate constant was found to be linear with H_0 indicating, according to the Zucker-Hammett hypothesis (48), that the transition state did not contain a molecule of water; (iii) the effect of substituents on the rate of oxidation of alcohols could be more easily explained on the basis of a rate determining hydride ion transfer; (iv) the catalytic effect of pyridine reported by Halloway, Cohen, and Westheimer (42) could not be duplicated; and (v) a hydride abstraction mechanism more easily explained why cyclic alcohols with axial hydroxyls were more readily oxidized than their equatorial epimers.

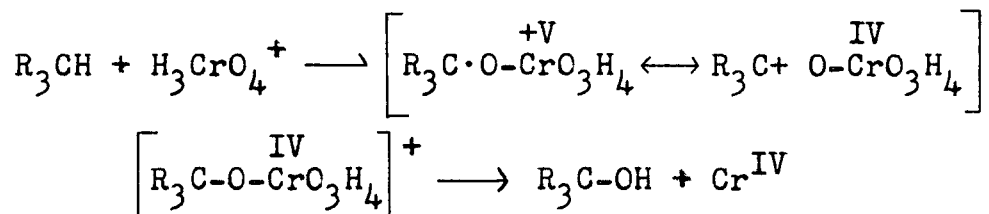
Each of these points requires further elaboration.

The increase in rate of oxidation of hydrocarbons in acetic acid as compared to aqueous solutions of the same acidity could be due, as has been discussed, to the formation of a different more active species of chromium VI in this medium. Or it could be due

simply to the fact that the reaction is general acid catalyzed. In addition Wiberg and Evans (2) have observed that in the oxidation of hydrocarbons the rate of reaction is dependent on the total chromium VI concentration, while the rate of oxidation of alcohols and aldehydes is dependent only on the concentration of HCrO_4^- . This implies that quite a different mechanism is operative in the case of hydrocarbons. In fact Wiberg and Evans have suggested that the mechanism may be different for different hydrocarbons with diphenylmethane reacting via hydrogen atom abstraction while p-methoxydiphenylmethane and pp'-dimethoxydiphenylmethane react via hydride abstraction. Wiberg and Foster (3) have also reported that the oxidation of (+)-3-methylheptane in 91% acetic acid gives (+)-3-methyl-3-heptanol with 70-80% retention of configuration. The mechanism they proposed for this reaction involved hydrogen abstraction by Cr^{VI} with the radical and Cr^{V} recombining to form an ester of Cr^{IV} which subsequently decomposes by chromium-oxygen bond cleavage to give optically active products.

More recently Roček (4) has briefly summarized some features of the chromic acid oxidation of hydrocarbons which indicate that in some cases the intermediate appears to have properties similar to a

carbonium ion while in other instances it appears to have the characteristics of a free radical. Accordingly he has proposed a mechanism which envisages the intermediate as a mesomeric hybrid of a carbonium ion-Cr^{IV} complex and a radical-Cr^V complex.



Since the Zucker-Hammett hypothesis has not been found to be universally applicable (48), Roček and Krupička's observation that the log of the rate

constant was linear with H_0 loses much of its significance. Further Graham and Westheimer (13) have pointed out that if one writes out the entire rate expressions for both the ester mechanism and the hydride ion mechanism they are identical except for possible differences in the activity coefficients for the two activated complexes. Roček (32) has however been reluctant to accept these arguments, contending that a linear rate-acidity relationship for the ester mechanism required an unlikely similarity between the terms

$$\frac{f_{H_2CrO_4} f_{ROH}}{f_{ROCrO_3H_2^+} \cdots H_2O} \text{ and } \frac{f_B}{f_{BH^+}}$$

while the hydride ion mechanism requires a more likely similarity between the terms

$$\frac{f_{\text{H}_2\text{CrO}_4} f_{\text{ROH}}}{f_{\text{H}_3\text{CrO}_4^+ \cdots \text{ROH}}} \quad \text{and} \quad \frac{f_{\text{B}}}{f_{\text{BH}^+}}$$

With respect to this point it should be mentioned that Bunnett (49) has recently developed a method of treating the relationship between reaction rates, H_0 values and the activity of water in such a way that one can estimate semi-empirically the number of water molecules involved in the transition state of a reaction. According to this treatment reactions which occur by hydride abstraction with no participation of H_2O generally have negative "w" values in the range of -2 to -7, while reactions in which water acts as a base to abstract protons generally exhibit a positive "w" value of +3 or greater. Although the treatment is fairly new and has not yet been widely tested Bunnett has nevertheless substantiated it with a wide variety of reactions and it would appear that the treatment can be applied with considerable confidence. Thus Kwart (39) has recently recast Roček and Krupička's data in terms of this new treatment and found that a plot of $(\log k + H_0)$ v.s. $\log a_{\text{H}_2\text{O}}$ gave a straight line with $w = +0.49$. Since the

the reaction under conditions where it is first order in H^+ and $(2.5)^2 = 6.25$ under conditions where it is second order in H^+ . This is in good agreement with the factors of 2.4 and 6.3 found by Westheimer. These results are not in accord with Roček's hydride transfer mechanism since it would involve a simultaneous O-D bond rupture when the reaction was carried out in D_2O . Since such a O-D bond rupture has been shown to result in a decrease in the rate of bromine oxidation of 2-propanol by a factor of 1.49 (77) one would not expect as large a rate increase as Westheimer observed. Further, the large difference in the rate of oxidation between isopropyl alcohol and diisopropyl ether indicates that a direct hydride abstraction without O-H or O-D cleavage is unlikely.

Perhaps the strongest point in Roček and Krupička's criticism of the ester mechanism is the observation which Kwart and Francis (27) had previously made, that the rate constants for the oxidation of a series of arylmethylcarbinols fitted a Hammett relationship with a "rho" value of -1.01. If the rate-determining step involved proton abstraction a negative charge would be built up on the α -carbon in the transition state. Such a transition state would predict a positive "rho" value. However if the reaction went by hydride transfer the carbon would bear

a positive charge in the transition state and the reaction would be expected to exhibit a negative "rho" value. Kwart and Francis have justified the negative rho value with the ester mechanism by suggesting that the substituents have a much stronger effect on the position of the ester equilibrium than they do on the rate-determining step. i.e. The complete rate expression for the ester mechanism at moderate acidities is

$$= k_2 K_e [H_2CrO_4] [ROH] h_o$$

Kwart and Francis claimed that the substituents would have a greater effect on K_e than on k_2 . However, Klaning and Symons (43, 52) have shown that the position of the chromate ester equilibrium is not greatly affected by changes in the structure of the alcohol. In addition, results will be presented later which indicate that a Taft $\sigma^* - \rho^*$ plot for the true rate constant ($k_2 = k_{obs}/K_e$) still exhibits a negative "rho*" value. Although this observation raises grave doubts as to the validity of Kwart and Francis' original explanation Westheimer (22) and Wiberg (2) have recently presented an alternative explanation which can be reconciled to the ester mechanism. By a comparison with the permanganate oxidation of aromatic aldehydes which Wiberg and Stewart (53) have shown to involve a rate-determining

proton removal step, as well as a negative "rho" value, Westheimer and Wiberg have argued that the substituents have a greater effect upon the withdrawal of two electrons by the oxidant, than upon the removal of the proton which accompanies the reaction.

Since Roček and Krupička's report that pyridene does not catalyze the oxidation of isopropyl alcohol Westheimer and Chang (54) have re-examined their evidence and have come to the conclusion that the reaction is, in fact, not catalyzed by the addition of pyridene. The rate catalysis first reported by Holloway, Cohen and Westheimer (55) was found to be in error due to the method used in determining acidities of perchloric acid solutions containing dissolved pyridinium perchlorate on one hand and sodium perchlorate on the other.

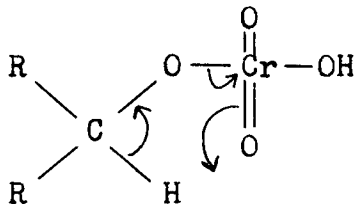
The final objection to the ester mechanism which Roček and Krupička raised concerned the relative rates of oxidation of epimeric steroidal alcohols. In the hydroxy-chalestane series it is found that regardless if the hydroxyl is in the 1, 2, 3, 4, 6 or 7-position the epimer which contains the axial hydroxyl is oxidized by chromic acid at a faster rate (46). Since axial hydroxyls are more hindered than equatorial hydroxyls Barton (47) had suggested that the faster

rate for the axial epimers resulted from a rate-determining step involving nucleophilic attack of the α -hydrogen by water. However, it is also well known that axial hydroxyls are much more difficult to esterify (47) and this would tend to shift the position of the ester equilibrium to the left. Hence there exists a paradox between this explanation and the suggestion made by Kwart and Francis (27) that the position of the ester equilibrium determines the relative rates of oxidation of a series of arylmethylcarbinols. Roček's hydride transfer mechanism, on the other hand, more easily explains the observed rates of oxidation of such epimeric hydroxycholestanes.

Another explanation for the relative rates of oxidation of epimeric hydroxycholestanes, as well as those for a series of alkylated cyclohexanols is that the axial alcohols are oxidized faster because formation of the ketone is favored by relief of steric strain (46, 56). Such an explanation assumes that the transition state for the reaction has considerable carbonyl character. In this way steric strain in the tetrahedral ground state would be relieved on passing to a trigonal transition state. However, Kwart (57) has objected to this explanation, pointing out that there is no parallel between the rates of

oxidation of cyclic alcohols and the stability of the resulting carbonyl products. For example, cyclopentanol is oxidized only slightly faster than cyclohexanol while there is a vast difference in the relative carbonyl stability of cyclopentanone and cyclohexanone (39), and with 7-hydroxyborane which on oxidation gives a ketone with a very small valence angle the rate is only reduced to one-third that of cyclopentanol.

The alternative mechanism proposed by Kwart and Francis (58) envisages a chromate ester transition state in which proton abstraction occurs by way of a concerted cyclic process.



Acceleration of the rate of oxidation due to steric effects is attributed to restrictions in the freedom of rotation of the chromate ester, i.e. in those reactions in which acceleration due to steric effects is observed the rotation of the ester is restricted in such a way that the acceptor oxygen spends more time in the vicinity of the hydrogen and thus increases the statistical probability that a reaction will occur. Kwart and Francis have successfully

applied this mechanism to explain the relative rates of oxidation of a series of alkylated cyclohexanols (57) as well as a large number of 1, 2-diols (24).

The main criticism of this mechanism has come from Roček (32). His first contention that such a mechanism should not give a good $\log k$ v.s. H_0 plot is not well founded, as has been indicated in previous discussion. On the other hand, his second objection that one would not expect a reaction which required proton transfer to the chromium part of the ester to be accelerated by protonation of this very part, is a valid criticism of the mechanism. However, a slight modification of the mechanism to allow for internal hydride ion transfer as opposed to internal proton transfer would overcome this objection. In addition the observed negative "rho" value for the reaction would also be more easily explained on the basis of such an internal hydride ion transfer mechanism.

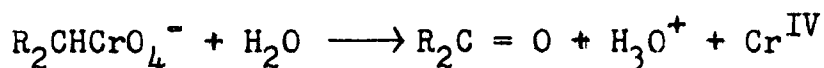
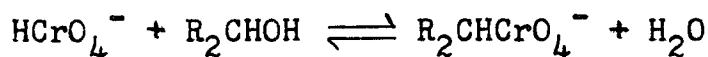
The work of Kwart, Lord and Corey (24) on the oxidation of 1, 2-diols, as well as that reported by Chang and Westheimer (25) and by Roček and Westheimer (26) has proven to be very illuminating because the observed results indicate very strongly that chromate esters function as intermediates in this reaction. Roček (32) was the first to point out that if a 1, 2-

diol gave rise to a cyclic ester, the total amount of esterified alcohol would be much greater than in the case of a monohydric alcohol and this should lead to enhancement of the rate. Although Roček in his initial investigation failed to find any acceleration in the rate of oxidation of ethylene glycol as compared to ethanol it has since been found by Chang and Westheimer (25) that pinacol is more rapidly oxidized than pinacol monomethyl ether. In addition it has been observed that exo-exo-2,3-camphanediol and endo-endo-2,3-camphanediol are both more readily oxidized than exo-endo-2,3-camphanediol (24), and that 1,2-cis-cyclopentanediol and 1,2-cis-cyclohexanediol are both oxidized faster than the corresponding trans-compounds as is the case for cis and trans-1,2-dimethyl-1,2-cyclopentanediol (26). In each instance it has been concluded that the cis-diols are oxidized at a faster rate because they can form cyclic chromate esters, while the geometry of the corresponding trans compounds prevents formation of such cyclic esters.

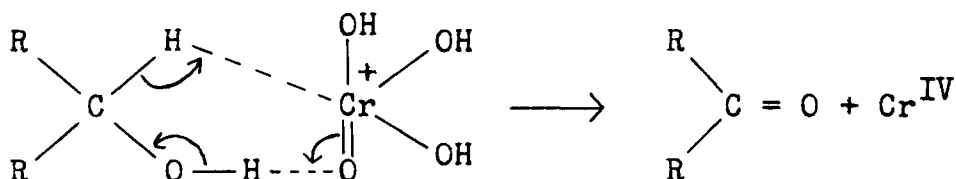
In conclusion, it can be seen from a review of the literature concerning chromic acid oxidations of alcohols that there exists four different suggested mechanisms for this reaction:

(i) The original Westheimer ester mechanism which assumed the formation of a chromate ester in a rapid

reversible equilibrium step followed by proton transfer to an external nucleophile such as water in the rate-determining step (37).

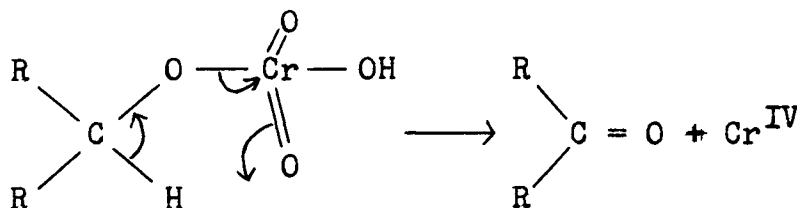
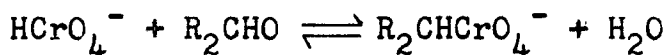


(ii) A hydride ion transfer mechanism proposed by Roček and Krupička (31);

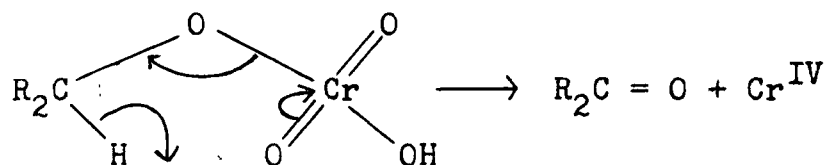


This mechanism has been shown to be quite improbable by studies in D_2O (13) and by the results obtained in the oxidation of 1,2-diols which involve participation of the chromate ester (24).

(iii) A modification of the ester mechanism which postulates a cyclic intramolecular proton transfer in the ester molecule (58);



(iv) A cyclic intramolecular hydride transfer which Littler (51) has very briefly indicated as a possibility.



3. PRIMARY KINETIC ISOTOPE EFFECTS

Primary deuterium isotope effects have often been used as an aid in the elucidation of the mechanism of chemical reactions (59). Theoretical predictions indicate that if the rate controlling step of a reaction involves fission of a carbon-hydrogen bond the rate of the reaction should be slower in cases where one of the heavier isotopes of hydrogen (deuterium or tritium) forms the bond than when the lightest isotope (protium) forms the bond (60). (While this reasoning can as easily be applied to cases where hydrogen is bonded to elements other than carbon, it will be sufficient to consider only carbon-hydrogen bonds in this discussion.)

A typical example of the use of this effect as a diagnostic tool in mechanism studies can be found in the chromic acid oxidation of secondary alcohols. One of the earliest postulated mechanisms of this reaction suggested that the rate-determining step involved

hydride transfer from the hydroxyl group of the alcohol (61). Although there existed at the time some evidence for the plausibility of such a reaction it was shown to be incorrect when Westheimer and Nicolaides (37) observed that the reaction exhibited a primary deuterium isotope effect. This indicated that the rate-determining step involved carbon-hydrogen bond fission and led Westheimer to propose the previously discussed ester mechanism for this reaction.

As has been indicated by Bell (62a) and others there are two main reasons why reactions involving carbon-deuterium bond fission should be slower than corresponding reactions involving carbon-protium bonds;

(i) the relatively large mass difference between these two isotopes and (ii) the possibility of deviations from classical mechanics leading to quantum mechanical tunnelling. The mass difference manifests itself mainly in a difference in zero-point energies for the C-H and C-D bonds, i.e. the lowest energy level for any bond corresponds to $1/2 h\nu$, where h is Planck's constant and ν is the vibrational stretching frequency of the bond in question. The vibrational stretching frequency is in turn inversely dependent on the square root of

the reduced mass according to the Hooke's law expression,

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{u}} \quad \text{where } k \text{ is the force constant. For}$$

example, if one considers two molecules A-H and A-D the ratio of the vibrational stretching frequencies for the protium and deuterium bond is given by

$$\frac{\nu_{A-H}}{\nu_{A-D}} = \sqrt{\frac{m_D(m_A+m_H)}{m_H(m_A+m_D)}}$$

For large molecular weight molecules m_A is so much greater than m_H and m_D that the terms in the brackets cancel leaving one with the ratio $\frac{\nu_{A-H}}{\nu_{A-D}} = \sqrt{\frac{m_D}{m_H}} = \sqrt{2}$.

Hence, from the observation that the carbon-hydrogen stretching frequency for the α -hydrogen in 2-propanol is at 2900 cm^{-1} (63) one would predict that the carbon-deuterium frequency in 2-deuterio-2-propanol would be at $2900 \times 1/1.414 = 2050 \text{ cm}^{-1}$. This agrees favorably with the observed value of 2100 cm^{-1} (64) and gives a difference in the zero point energies for these two bonds of 1.15 kcal/mole .

The ratio k_H/k_D can then be calculated by application of the theory of absolute rates which predicts that the specific rate of a reaction should be given by the following expression (65a);

$$k = \frac{KT}{h} \frac{F_{\#}}{F_x F_y} e^{-E_0/RT}$$

Where K is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, $F_{\#}$ is the partition function for the activated complex, F_x and F_y are the partition functions for the reacting molecules, R is the gas constant and E_0 is the zero point energy of the bond being broken in the reaction. If one neglects possible differences in the energies of the corresponding transition states the ratio k_H/k_D should be $e^{\Delta E/RT}$. Thus, for the case of oxidation of isopropyl alcohol where ΔE was calculated to be 1.15 kcal/mole this predicts a primary kinetic isotope effect of 6.9 at 25°C. This is in agreement with value observed experimentally (41).

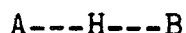
Since temperature appears in the denominator of the exponential used to calculate the isotope effect it can be seen that smaller effects should be observed at higher temperatures while the converse should be true at lower temperatures. The maximal isotope effects predicted for various temperatures are listed in Table I.

TABLE I
VARIATION IN THEORETICAL ISOTOPE
EFFECTS WITH TEMPERATURE

Temperature ($^{\circ}\text{C}$)	$k_{\text{H}}/k_{\text{D}}$ *
0	10
25	8.34
50	7.14
75	6.75
100	5.56
125	5.00
150	4.54

* These values were obtained from their reciprocals listed in reference (66).

It is, however, possible to observe effects to be much smaller than those listed in Table I, even when the rate-determining step of a reaction involves carbon-hydrogen bond fission, since a linear transition state such as



may have a "symmetrical" mode of vibration involving movement of H as well as A and B (67). If the hydrogen moves the deuterio transition state will have a lower zero point energy than the corresponding protio transition state and the over-all result will be a

decrease in the observed isotope effect. Only in the case where the so-called "symmetrical" vibration involves no motion of the hydrogen atom will the maximal predicted isotope effect be observed. Thornton has recently suggested an application of these ideas to show whether the transition state is product-like or reactant-like (68).

It has also been suggested by Melander (66) that an alternative explanation of small isotope effects may be found in a consideration of the carbon-hydrogen bending frequencies. If the bending frequencies were to increase on passing to the transition state the isotope effect due to differences in the zero point energies of the stretching frequencies would be partially cancelled. In addition if the bending frequencies were decreased in the transition state it would lead to the observation of unusually large isotope effects. There have, in fact, been several reports of reactions exhibiting isotope effects of a magnitude greater than the values listed in Table I. These include the chromic acid oxidation of phenyl-tert-butylcarbinol in 86.5% acetic acid ($k_H/k_D = 8.5$ to 14.4 at 0°C) (44), the reaction of methyl radicals with toluene ($k_H/k_D = 8.9$ at 122°C) (69), ($k_H/k_D = 9.9$ at 120°C) (59), the reaction of lithium cyclohexylamine

with ethylbenzene ($k_H/k_D = 12^{+3}$ at 49.9°C) (70), the abstraction of hydrogen atoms from acetic $-\alpha\text{-d}_1$ acid by methyl radicals ($k_H/k_D = 8.3$ at 120°C) (59), the abstraction of hydrogen atoms from cyclohexane- d_1 by methyl radicals ($k_H/k_D = 6.9$ at 120°C) (59), and the oxidation of aryltrifluoromethylcarbinols with basic permanganate ($k_H/k_D = 16$ at 25°C) (71).

The largest primary deuterium isotope effects reported to date have been observed in the oxidation of fluorinated alcohols by basic permanganate (71, 72). For this reaction values of k_H/k_D from 12.0 to 19.5, depending on the substrate oxidized and on the conditions of the reaction, have been observed at 25°C . While tunnelling has been cited as a possible explanation for the large effects it has also been suggested that they might be due to a loss of the bending carbon-hydrogen motion in the transition state, or perhaps to an unusual consecutive process which produces a cumulative isotope effect. It is of interest, however, to note that the value of $16.1^{+1.1}$ obtained for the permanganate oxidation of m-bromophenyltrifluoromethylcarbinol, p-tolyltrifluoromethylcarbinol and phenyltrifluoromethylcarbinol at a pH of 13.3 is in good agreement with the theoretical isotope effect of 17.2 predicted for the case

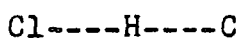
where the carbon-hydrogen bond loses both stretching and bending frequencies in the transition state (66). Further Stewart and Van der Linden (71) have pointed out that the rate-determining step of the reaction involves interaction of two anions and that this could lead to a transition state containing two widely separated molecules. In the involvement of such an extended transition state may lie an explanation of the loss of bending frequencies in this reaction.

Another possible explanation of unusually large deuterium isotope effects is the operation of a phenomenon commonly called "proton tunnelling". In fact, Bell (62b) has stated that, "In any kinetic treatment (of isotope effects) which is sufficiently refined to take into account the zero-point energy of the transition state it is not justifiable to neglect the tunnel effect." This effect arises from the quantum mechanical conclusion that all particles have, besides a corpuscular nature, a wave-like nature with a De Broglie wavelength of $\lambda = h/mv$ where m is the mass of the particle and v is its velocity. Since the mass of the particle appears in the denominator of this expression it is to be expected that the effect will be more pronounced for lighter

particles, in particular it should be greater for protons than for deuterons. Further, it is well known that particles with a wave-like nature do not obey the laws of classical mechanics and that there is a finite possibility that a quantum mechanical particle will be found in regions, which according to classical theory, are completely forbidden (73). Thus classically the only way that a chemical reaction can occur is for a particle to hurdle the potential energy barrier. However, quantum mechanical considerations lead to the conclusion that it is possible for a particle of low mass to also penetrate the barrier. Since the mass of a proton is only one-half as great as that of a deuteron this effect could also contribute to the isotope effect of a reaction involving proton transfer. (The same considerations would also apply to reactions involving hydride ion, or hydrogen atom transfers.) Evidence of a contribution from this source to the observed isotope effect has come from the work of Bell, Fendley and Hulett (74, 75) and Shiner and Smith (76).

Before concluding this discussion of primary kinetic isotope effects two other aspects of this field should be mentioned briefly; (i) the variation of isotope effects with rates in a series of analogous

reactions and (ii) the suggested use of substituent effects on isotope effects to distinguish between proton and hydride transfer reactions (77). With respect to the former feature it has been observed in at least three reactions (the side chain halogenation of toluene (78), the chromic acid oxidation of some methyl carbinols (39), and the decarboxylation of β -keto acids in benzene (79)) that isotope effects become larger with decreasing reaction rates. The reason for this relationship would seem to be that the reactions which have the highest activation energy also have the most symmetrical transition state. For example, in the chlorination of substituted toluenes studied by Wiberg and Slaugh (78) the transition state is probably linear



and since the isotope effect is smaller than seven in all cases the so-called "symmetrical" vibration must involve considerable motion of the hydrogen. However since the isotope effect varies from 3.22 to 4.86 to 5.08 for the reaction of N-Bromosuccinimide with *p*-methoxytoluene- d_1 , toluene- d_1 , and *p*-chloro-toluene- d_1 , respectively, it has been suggested that the transition state is modified as one moves along this series to involve less and less movement of the

hydrogen in the "symmetrical" vibration (67).

The second suggestion that substituent effects on isotope effects can be used to distinguish between proton and hydride transfer reactions has been advanced by Swain and coworkers (77, 79). They have presented theoretical reasons for suspecting that the bonding in the transition state of a proton transfer reaction is "weaker, longer, more ionic and more polarizable" than the bonding in the transition state of a hydride ion transfer. A somewhat oversimplified statement of the theoretical considerations that led these authors to propose this difference in transition state bonding for the two reactions is that in a hydride transfer between electron deficient centers the two electrons of the hydride can be accommodated in the lowest σ -orbital, while for the case of proton transfer between two electron rich centers an antibonding orbital must also be occupied. This leads, for proton transfer reactions, to a more polarizable transition state which should be more sensitive to substituent effects. As supporting experimental evidence these authors cite the carbon-hydrogen and oxygen-hydrogen isotope effects for the oxidation of 2-propanol and 1-fluoro-2-propanol by bromine. The carbon-hydrogen isotope effect is

almost the same for both alcohols while the oxygen-hydrogen isotope effect is 38% greater for 1-fluoro-2-propanol, suggesting that the mechanism involves hydride transfer from the carbon with simultaneous proton abstraction from the oxygen (77). Also they present data showing that the isotope effect observed in the decarboxylation of several substituted benzoylacetic acids is variable, indicating that the rate-determining step in this reaction involves proton and not hydride transfer.

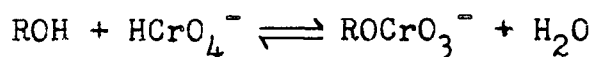
Although this theory could eventually prove to be a useful diagnostic tool one cannot make extensive use of it until more experimental evidence in its support has been presented. Further, it should be noted that Littler (51) has recently offered a brief criticism of the mechanism suggested by Swain and coworkers for the bromine oxidation of alcohols, and that the results of the decarboxylation experiments could as easily be incorporated into the more general theory which predicts a parallel between the magnitude of the isotope effects and the activation energies in an analogous series of reactions (59).

II SCOPE OF THE PRESENT INVESTIGATION

The discovery by Stewart and Van der Linden (71) that unusually large isotope effects were observed when a group of aryltrifluoromethylcarbinols were oxidized by permanganate in basic medium gave the initial impetus to this investigation. In light of this discovery it was decided to determine if extraordinary isotope effects were also observed when these alcohols were oxidized by chromic acid. An initial investigation revealed that although the isotope effects observed in the chromic acid oxidations were not as large as those reported for permanganate oxidations the magnitude varied considerably when different substituents were introduced into the aromatic nucleus. In order to study this phenomena in more detail it was decided to synthesize some additional fluorinated secondary alcohols, both aromatic and aliphatic. Isotope effects for the oxidation of various fluoroalcohols in 77.2% acetic acid and 50.1% sulfuric acid were investigated, although due to solubility difficulties with sulfuric acid only aliphatic alcohols could be used in this medium.

During the investigation of these isotope effects it became apparent that some of the fluoro-

alcohols possessed properties such that they could be used effectively to test certain postulates concerning the mechanism of chromic acid oxidations, particularly in very acidic regions. Hence a study of the oxidation mechanism in concentrated sulfuric acid solutions was undertaken. Further, the publication by Klaning and Symons (43) of a large number of equilibrium constants for equilibriums of the type



led to a decision to determine the "true" rate constant ($k_2 = k_{\text{obs}}/K_e$) for the chromic acid oxidation of a number of primary aliphatic alcohols.

Finally, it was observed that if one plotted $\log k_{\text{obs}}$ against H_0 for the oxidation of isopropyl alcohol in perchloric acid solutions of various concentrations a sharp change in the slope of the plot was observed at approximately the same point that Bailey, Carrington, Lott and Symons (80) had determined to be the pK_a of H_2CrO_4 in this medium. Further investigation revealed that the pK_a of chromic acid varied considerably when it was determined in different mineral acids and that in each case the change in slope of the plot occurred at approximately the same point as the observed pK_a .

The detailed results and experimental procedures along with a discussion of the implications that can

be derived from the results of this investigation will be presented in the following pages of this thesis.

III EXPERIMENTAL

1. MATERIALS

(i) Alcohols:

All liquid fluoro and chloro-alcohols were purified by use of an Aerograph Model A-90P Chromatograph before use in kinetic experiments. A ten foot Ucon Polar column was found to be most suitable for these compounds. The alcohols used in this investigation conveniently fit into three groups; those available commercially, those previously synthesized in this laboratory and those prepared during the course of this investigation.

The following alcohols were obtained from commercial sources: isopropyl alcohol, 1, 3-dichloro-2-propanol, 1-chloro-2-propanol, ethanol, 2-methoxyethanol, 2-chloroethanol, methanol, n-propanol (Eastman Organic Chemical Company) 1,3-difluoro-2-propanol, 1,1,1-trifluoro-2-propanol, 1,1,1-trifluoro-2-methyl-2-propanol (Columbia Organic Chemical Co.), 1,1,1,3,3,3-hexafluoro-2-propanol (obtained as a gift from S. Andreades, E.I. du Pont de Nemours and Co., Research Department Wilmington, Delaware).

The following fluoro alcohols had previously been prepared in these laboratories (81, 82): p-

methoxyphenyltrifluoromethylcarbinol, p-tolyltrifluoromethylcarbinol, p-tolyltrifluoromethylcarbinol- α -d, phenyltrifluoromethylcarbinol, phenyltrifluoromethylcarbinol- α -d, m-bromophenyltrifluoromethylcarbinol, m-bromophenyltrifluoromethylcarbinol- α -d and m-nitrophenyltrifluoromethylcarbinol. During the present investigation several of these compounds were re-synthesized and good agreement with all the reported physical constants was found except in the case of m-nitrophenyltrifluoromethylcarbinol where the melting point was found to be 51.2-52.2°C instead of the reported 47-48°C.

The preparations of other alcohols which were synthesized especially for this investigation are given below.

2-Propanol-2-d. Following the procedure of Leo and Westheimer (41) dry acetone (5 gm., 0.086 moles) in 20 ml. of dry ether was added dropwise to a stirred solution of lithium aluminum deuteride (1.05 gm., 0.025 moles) in 50 ml of dry ether at -80°C. The mixture was allowed to warm slowly to room temperature and the complex was decomposed with dil. sulfuric acid. The heterogeneous reaction mixture was then distilled through a 12" glass column and the azeotrope of 2-propanol-2-d and water which distilled at 70-90°C was collected. This was dissolved in ether and dried

over anhydrous magnesium sulfate. After evaporation of the ether the resulting clear solution was distilled from 0.2 gm. of calcium oxide to give 2-propanol-2-d (3.1 gm., 0.052 mole, 60%) b.p. = 81-82.3°C.

1-Fluoro-2-propanol. Chloroacetone (41.2 gm., 0.5 mole) was added dropwise to a well stirred mixture of potassium hydrogen fluoride (87 gm., 1 mole) and 60 ml. of diethylene glycol in a 250 ml. three necked flask fitted with a dropping funnel, a stirrer and a still head; the flask at the time being immersed in an oil bath at 160°C. As the addition proceeded a colorless liquid distilled off at 80-95°C. This was collected, dried over anhydrous magnesium sulfate and redistilled through a 12" glass column to give fore run (3 gm.) b.p. 50-75°C, fluoroacetone (9.9 gm., 0.13 mole, 26%) b.p. = 75-80°C, n_{max} (liquid) 1730 cm^{-1} ($\text{C} = \text{O}$) and unreacted chloroacetone (32.6 gm.) b.p. 80-120°C.

Lithium aluminum hydride (1 gm., 0.026 mole) in 50 ml. of ether was added dropwise to a stirred solution of fluoroacetone (5.0 gm., 0.068 mole) in 20 ml. of ether at -80°C. The mixture was allowed to warm slowly to room temperature and finally refluxed gently for 30 min., after which the complex

was decomposed with dil. sulfuric acid. The aqueous phase was separated and extracted twice with 20 ml. portions of ether. These extracts were added to the ethereal phase and dried over anhydrous magnesium sulfate. Evaporation of the ether gave a dark oil which on distillation yielded 1-fluoro-2-propanol (1 gm., 0.013 mole, 19%) b.p. = $103 - 104^{\circ}\text{C}$, (lit. (83) $103-105^{\circ}\text{C}$)

1-Fluoro-2-propanol-2-d. Fluoroacetone was reduced with lithium aluminium deuteride in the manner described above for the preparation of 1-fluoro-2-propanol. Both compounds had exactly the same boiling point and gave identical retention times on the vapor phase chromatograph.

1,3-Dichloro-2-propanol-2-d. 1,3-Dichloro-2-propanol was oxidized by chromic acid in the manner described by Conant and Quayle (84). The crude product, 1,3-dichloroacetone, was extracted from the aqueous solution with ether, dried over anhydrous magnesium sulfate and distilled under reduced pressure (b.p. = $43^{\circ}/0.6\text{ m m.}$). One gram of this material was dissolved in ether and purified by vapor phase chromatography to insure that it would be completely free of the starting alcohol. The melting point of the final product was $45-46^{\circ}\text{C}$ (lit(85a) 45°C). This

pure ketone was reduced in ether with a slight excess of lithium aluminum deuteride to give 1,3-dichloro-2-propanol-2-d in 90% yield. The product was characterized by comparing its retention time on a vapor phase chromatography column with that of 1,3-dichloro-2-propanol under identical conditions and through a comparison of the nuclear magnetic resonance spectra of these two compounds.

1-Chloro-3-fluoro-2-propanol. A stirred mixture of epichlorohydrin (250 gm.), potassium hydrogen fluoride (235 gm.) and diethylene glycol (250 gm.) was refluxed for four hours. The crude product was then distilled under reduced pressure (b.p. 50-120/40 m m.) and then redistilled through a 12" column at standard pressure. The fraction distilling at 140-155°C was collected and a small portion was purified by vapor phase chromatography. $n_D^{20} = 1.4320$ (lit.(83) $n_D^{28} = 1.4269$). The nuclear magnetic resonance spectra of this product was also consistent with the assumed structure.

1,3-Difluoro-2-propanol-2-d. Commercial 1,3-difluoro-2-propanol was oxidized to 1,3-difluoroacetone with chromic acid in the manner described by Bergmann and Cohen (83). The crude product was continuously extracted from the reaction mixture with ether, dried over anhydrous magnesium sulphate and distilled under

reduced pressure. $\nu_{\text{max.}}$ at 1750 cm^{-1} . One gram of this material was purified by vapor phase chromatography and reduced in ether with a slight excess of lithium aluminum deuteride to give 1,3-difluoro-2-propanol in 70% yield. The product was characterized by comparing its retention time on a vapor phase chromatography column with that of 1,3-difluoro-2-propanol under identical conditions and through a comparison of the nuclear magnetic resonance spectra of these two compounds.

1,1,1,3,3,3-Hexafluoro-2-propanol-2-d. Ten gm. of potassium dichromate was dissolved in 500 ml. of 97% sulfuric acid contained in a three necked flask fitted with a dropping funnel, a reflux condenser, a nitrogen bubbler and a magnetic stirrer. The top of the reflux condenser was connected by means of rubber tubing to four traps. The first and fourth traps in the series were cooled in liquid nitrogen while the second and third were cooled with a mixture of dry ice in acetone. The second and third traps also contained an excess of lithium aluminum deuteride dissolved in dry ether. The solution was stirred continuously throughout the preparation and a gentle flow of nitrogen through the system was maintained.

1,1,1,3,3,3-Hexafluoro-2-propanol (5.0 gm., 0.030 mole)

was then added dropwise to the chromic acid solution and the colorless gas which came off was collected in the first trap. After all the alcohol had been added the contents of the flask were warmed to 60°C for 2 hrs. When the contents of the first trap were then allowed to warm slowly to room temperature the gas (1,1,1,3,3,3-hexafluoroacetone) bubbled slowly into the lithium aluminum deuteride solution in traps two and three. Any gas not reacting with the lithium aluminum deuteride was collected in trap four and recycled. Finally, the ethereal solutions in traps two and three were allowed to warm slowly to room temperature and the complex was decomposed with dil. sulfuric acid. The aqueous solution was separated and extracted continuously with ether for 48 hours. The ethereal solutions were then all collected, dried over anhydrous magnesium sulfate and distilled through a 12" column. Aside from a large amount of ether the main fraction collected was 1,1,1,3,3,3-hexafluoro-2-propanol-2-d (3.2 gm., 0.019 mole, 63%). This compound had exactly the same retention time on a vapor phase chromatography column as 1,1,1,3,3,3-hexafluoro-2-propanol supplied by S. Andreades of E.I. du Pont de Nemours and Co. and nuclear magnetic spectroscopy indicated that it contained less than 4% protium

alcohol. The properties of this compound correspond closely with those reported by Dr. M. Mocek who had previously prepared 1,1,1,3,3,3-hexafluoro-2-propanol-2-d by a similar but independent method in these laboratories (72).

m-Methylphenyltrifluoromethylcarbinol. Commercial m-Bromotoluene (Eastman Organic Chemicals) (49 gm., 0.286 moles) dissolved in 40 ml. of dry ether was added to magnesium turnings (7 gm., 0.286 moles) under anhydrous conditions. After the reaction has been started by warming the mixture slightly 70 ml. of dry ether was added and at the completion of the reaction a further 150 ml. of ether was added. Then trifluoroacetic acid (10.5 gm., 0.092 moles) in 25 ml. of ether was added dropwise over a period of two hours. After refluxing for one hour the complex was decomposed in 10% sulfuric acid. The product (m-tolyl trifluoromethyl ketone) was extracted from the aqueous solution with ether, dried over anhydrous magnesium sulfate and distilled. B.p. = 58°C/8 m m. Yield; 8.5 gm., 0.045 moles, 49%. $\nu_{\text{max.}}(\text{liq.}) 1717 \text{ cm}^{-1} (\text{C} = \text{O})$.

This ketone (6.0 gm., 0.032 moles) was dissolved in 20 ml. of dry ether and lithium aluminum hydride (0.38 gm., 0.01 moles) in 20 ml. of dry ether was added slowly under anhydrous conditions. After

refluxing for one hour the complex was decomposed with dil. sulfuric acid and the product was extracted with ether, washed with water and dried over anhydrous magnesium sulfate. Distillation yielded 3.5 gm

(0.0184 moles, 57%) of m-tolyltrifluoromethylcarbinol.

B.p. = 95°C/14 m m. (Found: C, 57.0%; H, 3.6%.

$C_9H_7OF_3$ required C, 57.4%; H, 3.7%.)

p-tert-Butylphenyltrifluoromethylcarbinol. Starting

from p-tert-butylbromobenzene (b.p. = 104-107°C/14 m m.,

lit.(87) 103/10 m m.) p-tert-butylphenyltrifluoro-

methylcarbinol (m.p. = 75.0 - 75.5°C) was prepared by

the same procedure used to synthesize m-methylphenyl-

trifluoromethylcarbinol. (Found: C, 61.6%; H, 6.13%.

$C_{12}H_{15}OF_3$ requires: C, 62.0%; H, 6.52%.)

B-Naphthyltrifluoromethylcarbinol. Magnesium (2.4 gm.,

0.1 moles) was placed in a flame dried three necked

flask fitted with two dropping funnels, a reflux

condenser and a magnetic stirrer. Methyl iodide

(0.5 gm) dissolved in 10 ml. of dry ether was added

through the first funnel and after the reaction had

started β -bromonaphthylene (Eastman Organic Chemicals)

(13 gm., 0.063 moles) dissolved in 50 ml. of dry ether

was added slowly. The mixture was refluxed for one-

half an hour after which 100 ml. of dry ether was

added. This was followed by the dropwise addition of

trifluoroacetic acid (1.82 gm., 0.016 moles) dissolved in 20 ml. of dry ether. After the addition was complete the solution was refluxed for two hours and then decomposed with cold dil. sulfuric acid, extracted with ether and dried over anhydrous magnesium sulfate. The product (β -naphthyl trifluoromethyl ketone) was distilled under reduced pressure (b.p. = $88^{\circ}\text{C}/1.1$ m m.) and crystallized from low boiling petroleum ether. $\nu_{\text{max.}}$ (CHCl_3) 1706 cm^{-1} ($\text{C}=\text{O}$). Yield; 5.0 gm., 0.013 moles, 80%.

This ketone (2.5 gm., 0.011 mole) was dissolved in 50 ml. of dry ether and added slowly to ethereal lithium aluminum hydride (0.25 gm., 0.0066 moles) under anhydrous conditions. The viscous solution was refluxed for one hour, decomposed with dil. sulfuric acid and extracted with ether. The ethereal extracts were washed with dilute sodium bicarbonate, dried over anhydrous magnesium sulfate and evaporated. The resulting oil was recrystallized from petroleum ether yielding a fine white crystalline compound. M.p = $83-84^{\circ}\text{C}$. A mixed melting point with naphthylene gave a depression of 20°C . (Found: C, 63.4%; H, 3.64%. Required for $\text{C}_{12}\text{H}_9\text{OF}_3$; C, 63.76%; H, 4.01%.)
p Chlorophenyltrifluoromethylcarbinol. Starting from 1-bromo-4-chlorobenzene (Eastman Organic Chemicals)

p-chlorophenyltrifluoromethylcarbinol (b.p. = 117-119°C/22 m m.) was prepared by the same procedure used to synthesize m-tolyltrifluoromethylcarbinol. (Found: C, 44.9%; H, 2.63%. Required for $C_8H_6OF_3Cl$: C, 45.6% H, 2.87%).

m-Nitrophenyltrifluoromethylcarbinol- α -d. m-Nitrophenyl trifluoromethyl ketone was prepared by the method reported by Van der Linden (81). This ketone was reduced, as described below, with lithium diethoxyaluminumdeuteride using the procedure developed by Brown and Tsukamoto (88).

Ethanol (1.84 gm., 0.040 moles) in 25 ml. of ether was slowly added to a stirred solution of lithium aluminum deuteride (0.87 gm., 0.0201 moles) dissolved in 50 ml. of dry ether at -80°C. This entire solution was then added slowly to a stirred solution of m-nitrophenyl trifluoromethyl ketone (9.05 gm., 0.041 moles) in 50 ml. of dry ether at -80°C. After the addition which took 1.5 hours the mixture was allowed to warm slowly to room temperature and the complex was decomposed with cold dil. sulfuric acid. The aqueous solution was extracted with ether; the ethereal extract was dried over anhydrous magnesium sulfate and then evaporated leaving a brown oil which distilled at 122°C/0.4 mm. This product was re-

crystallized several times from benzene and petroleum ether to give pale yellow crystals. M.p. = 51.5-52.5°C. (Found: C, 43.1%; H, 2.00%, N, 6.28%. Required for $C_8H_5NO_3F_3$: C, 43.2%; H, 2.72%, N, 6.32%.)

3,5-Dinitrophenyltrifluoromethylcarbinol. Fuming nitric acid (Sp. gr. 1.15) was added dropwise to a stirred solution of trifluoroacetophenone (Columbia Organic Chemicals) (38.4 gm., 0.216 moles) in 150 ml. of concentrated sulfuric acid. External cooling was applied to maintain a temperature of 60-80°C during the addition. The mixture was then heated on a steam bath for four hours. This was followed by cooling and the addition of another 40 ml. of fuming nitric acid. The mixture was again heated on a steam bath for four hours and finally at 130-150°C for four hours. The reaction mixture was then poured into crushed ice and extracted with ether. The ethereal extract was dried over anhydrous magnesium sulfate and evaporated leaving a yellow oil which was distilled under reduced pressure. The distillation yielded 2 gm. fore-run, 10.6 gm. m nitrophenyl trifluoromethyl ketone (b.p. = 90°C/.95 m m.) and 3,5-dinitrophenyl trifluoromethyl ketone (b.p. = 120-127/.95 m m.) (32.4 gm., 0.123 moles, 57%). ν_{\max} . (film) 1733 cm^{-1} (C = O). Hydrolysis of this compound with dil. sodium

hydroxide yielded 3,5-dinitrobenzoic acid (m.p. = 203-205°C, lit.(85b) 204-205°C).

Attempted recrystallization of the crude 3,5-dinitrophenyl trifluoromethyl ketone from most common solvents such as ether, petroleum ether and chloroform yielded a stable white solid which showed no carbonyl band in the infrared, but exhibited peaks at 3490 and 3270 cm^{-1} . (m.p. = 85.0-85.5°C). It was concluded that this compound was 3,5-dinitrophenyl trifluoromethyl ketone hydrate. (Found: C, 32.52%; H, 2.13%; N, 9.22%. Required for $\text{C}_8\text{H}_5\text{N}_2\text{O}_6\text{F}_3$; C, 34.01%; H, 1.78%; N, 9.94%.) The nuclear magnetic resonance spectra of this compound was also consistent with the assignment of this structure. This compound was also easily hydrolyzed to 3,5-dinitrobenzoic acid in dil. sodium hydroxide.

Dehydration of 3,5-dinitrophenyl trifluoromethyl ketone hydrate by phosphorous pentoxide at 50°C yielded the corresponding ketone (m.p. 77-78°C). $\nu_{\text{max.}} (\text{CHCl}_3) 1737 \text{ cm}^{-1}$ (C = O). (Found: C, 35.8%; H, 1.28%; N, 10.27%. Required for $\text{C}_8\text{H}_3\text{N}_2\text{O}_5\text{F}_3$: C, 36.4%; H, 1.14%; N, 10.60%.)

Recrystallization of the crude 3,5-dinitrophenyl trifluoromethyl ketone from ethanol yielded a white crystalline compound (m.p. = 70-71°C) which showed no

absorption in the carbonyl region of the infrared spectra nor any in the region from 3200 to 3500 cm^{-1} . where the hydrate absorbs. (Found: C, 29.85%; H, 1.53%; N, 10.96%; O, 26.35%; F, 0.00%; M.W. = 243.) This compound was resistant to basic hydrolysis and as yet its exact structure has not been determined.

3,5-Dinitrophenyltrifluoromethylcarbinol was prepared from crude 3,5-dinitrophenyl trifluoromethyl ketone by reduction with lithium tri-t-butoxyaluminumhydride in diglyme (89).

tert-Butyl alcohol (12.33 gm., 0.166 moles) dissolved in 25 ml. of dry diglyme was added dropwise to a stirred solution of lithium aluminum hydride (2.11 gm.; 0.055 moles) in 50 ml. of dry diglyme. This complete solution was then added dropwise to 3,5-dinitrophenyl trifluoromethyl ketone (14.6 gm., 0.056 moles) in 50 ml. of dry diglyme at -80°C . After the addition was complete the solution was warmed slowly to room temperature, decomposed in dilute sulfuric acid and extracted with ether. The ethereal extract was dried over anhydrous magnesium sulfate and evaporated leaving a yellow oil. Distillation of the oil yielded 3,5-dinitrophenyltrifluoromethylcarbinol (b.p. = $108-174^{\circ}\text{C}/8\text{ m m.}$), (9.2 gm., 0.0346 moles, 63%). This product was further purified by recrystal-

lization from carbon tetrachloride. The resulting fine white crystalline compound gave an infrared spectrum similar to m-nitrophenyltrifluoromethylcarbinol and a nuclear magnetic resonance spectra consistent with the assumed structure. (M.p. = 76-77°C). (Found: C, 36.16%; H, 1.72%, N, 10.54%. Required for $C_8H_3N_2O_5F_3$: 36.10%; H, 1.89%; N, 10.53%.)

3,5-Dinitrophenyltrifluoromethylcarbinol- α -d. This compound was prepared by the reduction of 3,5-dinitrophenyl trifluoromethyl ketone with lithium tri-*t*-butoxyaluminumdueteride as described above. (M.p. = 76.77°C.) (Found: C, 36.07%; H, 1.78%, 10.78%. Required for $C_8H_2DN_2O_5F_3$: C, 36.00%; H, 1.89%; N, 10.50%.) The nuclear magnetic resonance spectrum was also consistent with the assignment of this structure.

(ii) Inorganic Reagents

Chromic acid stock solutions were made up by dissolving weighed amounts of potassium dichromate (Mallinckrodt, Analytical Reagent Grade, Primary Standard) in definite volumes of distilled water. Sulfuric acid solutions were prepared from commercial 95-98% sulfuric acid (Fisher Certified Reagent). The concentrations of these solutions were determined by titrating weighed amounts of each solution with

standardized sodium hydroxide.

Perchloric acid solutions were prepared from commercial 70% perchloric acid (B.D.H.). These solutions were also standardized by titration with sodium hydroxide solutions of known concentration.

Nitric acid solutions were prepared from commercial 73% nitric acid (B.D.H. Micro Analytical Reagent), and standardized with sodium hydroxide.

Hydrochloric acid solutions were prepared from commercial 35.4% hydrochloric acid (B.D.H. Analar), and standardized with sodium hydroxide.

Phosphoric acid solutions were prepared from commercial 85% O-phosphoric acid (Fisher Certified Reagent), and standardized with sodium hydroxide.

Sodium Perchlorate. Commercial sodium perchlorate (G. Frederick Smith Chemical Co. Columbus Ohio) was recrystallized several times from water and dried for 10 days at 120°C.

Acetic Acid. Glacial acetic acid (Nichols Chemical Co.) was purified by distillation under reduced pressure from potassium dichromate and sulfuric acid (12). B.p. = 41°C/25 m m.

(iii) Indicators. The indicators used in this investigation (p-nitroaniline, o-nitroaniline, 4-chloro-2-nitroaniline and p -nitrodiphenylamine) were all

obtained commercially and recrystallized from ethanol to constant melting points. The melting points were all found to agree favorably with the values reported in the literature (90).

p-Toluic acid was obtained commercially (Eastman Organic Chemicals) and recrystallized several times from hot water (m.p. = 178-179, lit.(85c) 179.6)

2. KINETIC METHODS. Oxidation rates were obtained by following the disappearance of Cr^{VI} during the course of a reaction. The concentration of Cr^{VI} was determined either iodometrically or spectrophotometrically. In cases where the alcohol was present in several fold excess a plot of $\log [\text{Cr}^{\text{VI}}]$ against time was prepared and the first order rate constants were obtained from the slope. These first order rate constants were converted to the corresponding second order rate constants by dividing through by the concentration of the alcohol. In cases where the alcohol and Cr^{VI} were present in stoichiometric proportions a plot of the reciprocal of $[\text{Cr}^{\text{VI}}]$ against time yielded the second order rate constant directly.

With the exceptions of oxidations in very concentrated or very dilute solutions good straight line plots to at least 70% completion were obtained by both methods for all rate constants reported.

(See Figs. 1 and 2, and Table 2.) In very dilute acid concentrations initial reaction rates were used since it was found that the pH increased slightly as the reaction proceeded. In very concentrated acid (68.5% H_2SO_4 or greater) it was found that the optical density of the solution at 349 $\text{m}\mu$. increased for a few minutes after addition of the alcohol and then decreased exponentially to give a good first order plot. This has been interpreted as evidence for ester formation by a slowly established equilibrium prior to the rate-determining step and will be discussed in detail later.

Typical kinetic runs were carried out as follows:

(i) Iodometric method. Fifty ml. of a $4.035 \times 10^{-3}\text{M}$ acetic acid solution of phenyltrifluoromethylcarbinol were mixed with 20 ml. of 71% perchloric acid and thermostated at $25.0 \pm 0.1^\circ\text{C}$ for 10 min. A fast delivery pipet was then used to add 4.94 ml. of 0.01361 M potassium dichromate to this solution and 4.92 ml. aliquots were withdrawn at intervals. The aliquots were quenched by adding them to 15 ml. of 5% sodium bicarbonate solution containing a large excess of potassium iodide. Two ml. of 6M sulfuric acid were added and the solution was set aside to develop for three minutes. The I_2 formed was then titrated with standardized thiosulfate using Thyodene as an indicator.

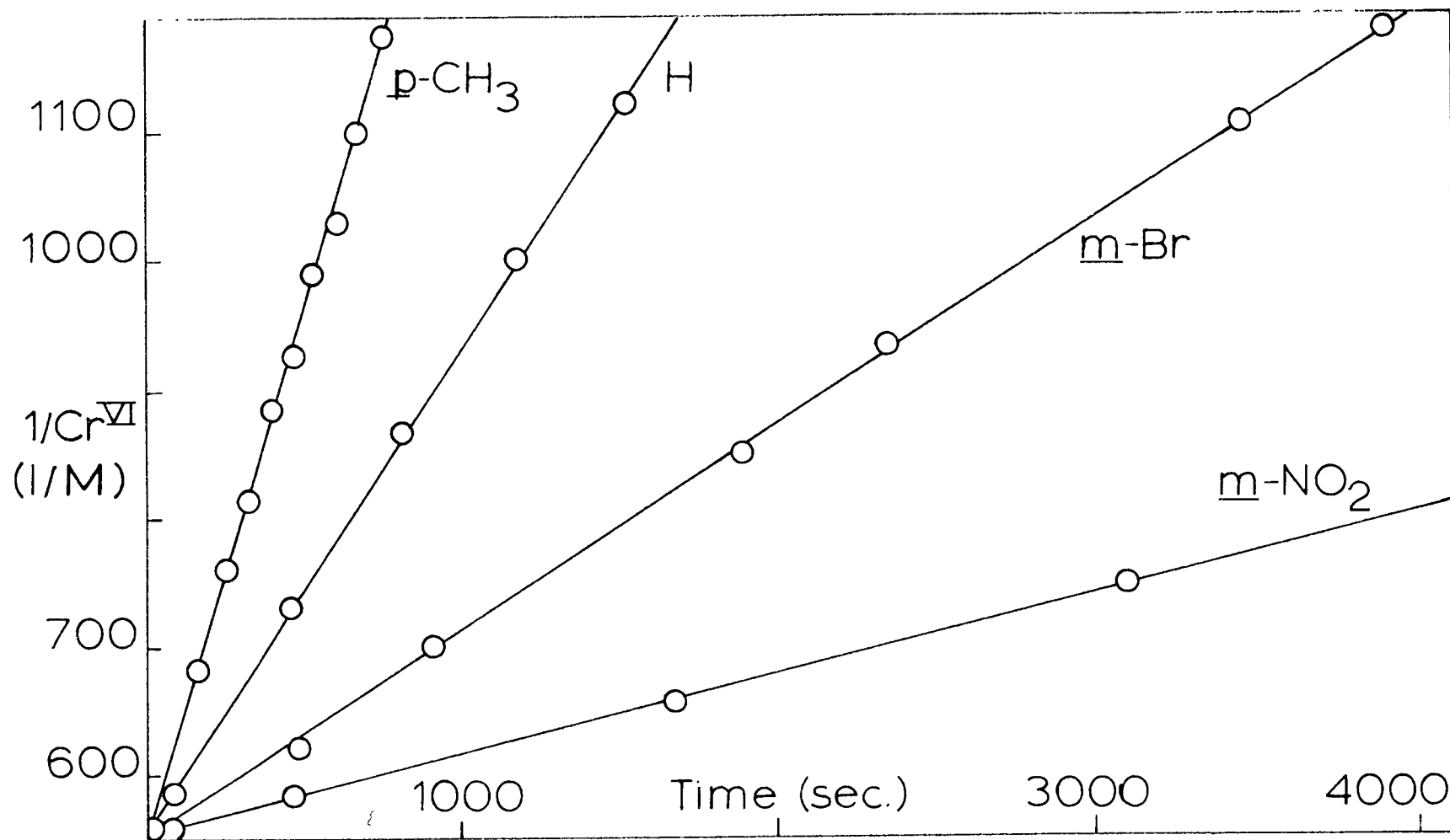


Fig.1 Typical rate plots for the oxidation of aryltrifluoromethylcarbinols in 77.2% acetic acid.

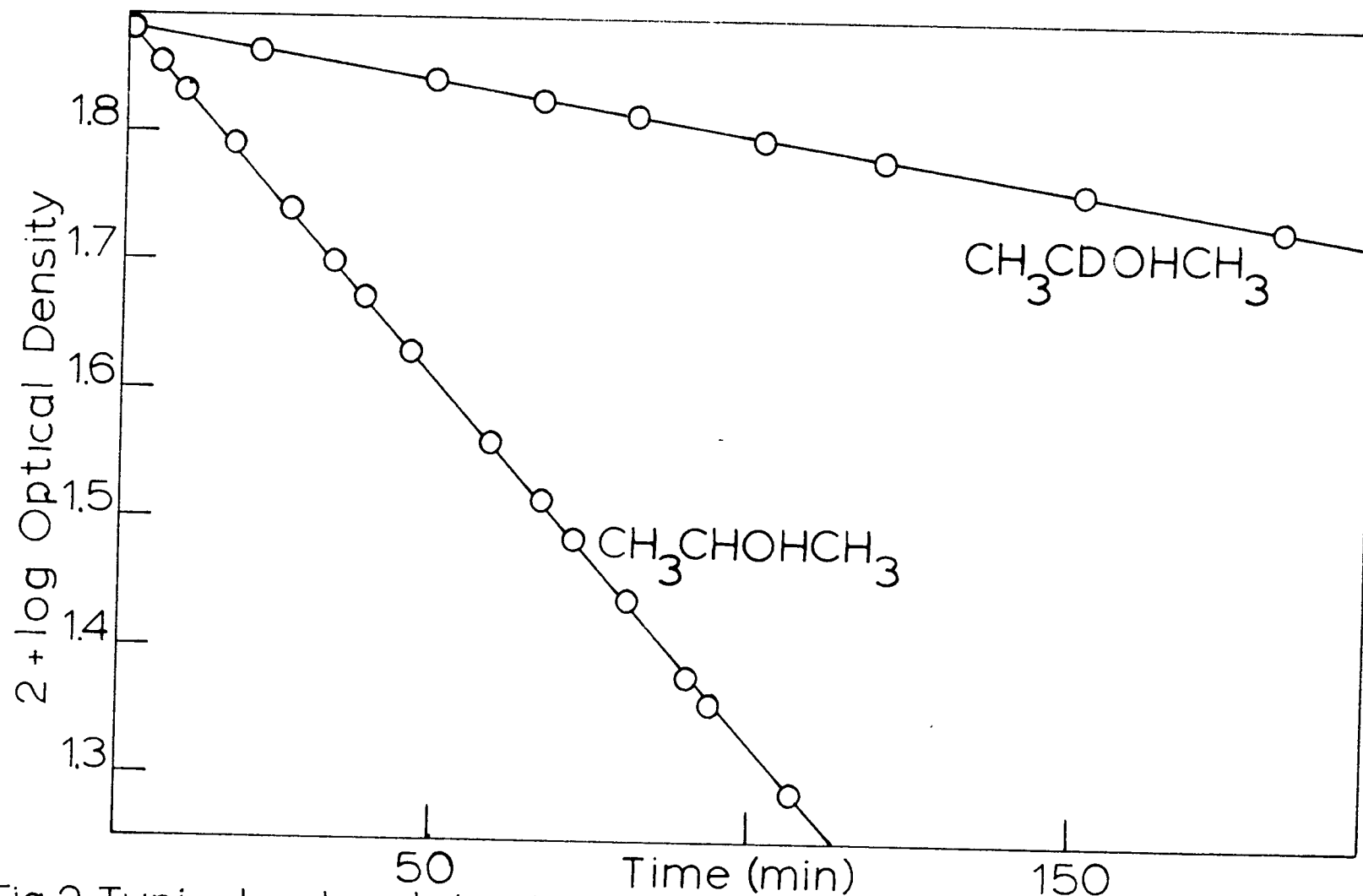


Fig.2 Typical rate plots for the oxidation of isopropyl alcohol in 0.463M HClO_4 .

TABLE II

DATA FOR PLOTS IN FIGURES 1 AND 2

(a) Oxidation of *p*-methylphenyltrifluoromethylcarbinol
in 77.2% acetic acid. $H_o = -2.82$, $T = 25.0^\circ\text{C}$.

Time (sec.)	Milliliters of 6.64×10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$	$1/[\text{Cr}^{\text{VI}}]$ (1/M)
90	3.43	648
165	3.21	683
245	2.92	762
320	2.74	814
400	2.50	888
470	2.40	926
530	2.24	994
610	2.16	1030
670	2.02	1100
760	1.89	1177
850	1.75	1272
960	1.66	1340

(b) Oxidation of phenyltrifluoromethylcarbinol in 77.2%
acetic acid. $H_o = -2.28$, $T = 25^\circ\text{C}$.

Time (sec.)	Milliliters of 6.42×10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$	$1/[\text{Cr}^{\text{VI}}]$ (1/M)
90	3.92	588
453	3.13	870

815	2.65	870
1175	2.30	1005
1525	2.05	1125
1920	1.81	1275
2265	1.64	1410
2650	1.48	1500
3250	1.30	1775
4155	1.10	2100

(c) Oxidation of m-bromophenyltrifluoromethylcarbinol
in 77.2% acetic acid. $H_o = -2.82$, $T = 25.0^\circ\text{C}$.

Time (sec.) Milliliters of $6.64 \times 10^{-3} \text{ M Na}_2\text{S}_2\text{O}_3$ $1/[\text{Cr}^{\text{IV}}] \text{ (1/M)}$

70	3.88	574
490	3.58	621
915	3.18	700
1320	2.93	759
1890	2.61	852
2345	2.38	936
2915	2.23	996
3440	2.01	1108
3900	1.88	1185

(d) Oxidation of m-nitrophenyltrifluoromethylcarbinol
in 77.2% acetic acid. $H_o = -2.82$, $T = 25.0^\circ\text{C}$.

Time (sec.)	Milliliter of $6.65 \times 10^{-3} \text{ M Na}_2\text{S}_2\text{O}_3$	$1/[\text{Cr}^{\text{VI}}]$ (1/M)
85	3.99	558
465	3.80	585
1670	3.38	657
3090	2.96	750
4260	2.66	834
5580	2.41	922
6810	2.20	10090
7995	2.00	11100
9120	1.81	12280
10140	1.73	12830

(e) Oxidation of isopropyl alcohol in 0.463 M HClO_4 .
 $T = 25.0^\circ\text{C}$, $\lambda = 4440 \text{ \AA}$, $[\text{alcohol}] = 0.129 \text{ M}$.

Time (min.)	Optical Density Observed	Optical Density Corrected	$2 + \log \text{O.D.}$
0.0	.765	.765	1.884
0.5	.756	.756	1.879
1.2	.750	.750	1.875
2.1	.741	.740	1.869
3.0	.738	.737	1.868
5.1	.720	.716	1.855
9.78	.682	.677	1.831

17.1	.621	.615	1.789
20.5	.602	.595	1.775
26.7	.559	.550	1.740
33.3	.511	.500	1.699
38.5	.481	.470	1.672
45.9	.440	.426	1.629
58.3	.378	.363	1.560
66.2	.344	.328	1.516
71.7	.323	.306	1.486
80.0	.294	.275	1.439
89.5	.260	.240	1.380
93.9	.248	.228	1.358
106.5	.212	.191	1.281
116.0	.192	.170	1.230
121.8	.178	.155	1.190
133.5	.155	.130	1.111
146.1	.139	.114	1.057
159.8	.118	.093	0.969

(f) Oxidation of 2-propanol-2-d in 0.463 M HClO_4 . $T = 23^\circ\text{C}$, $\lambda = 4440\text{\AA}$, $[\text{alcohol}] = 0.127 \text{ M}$.

Time (min.)	Optical Density		$2 + \log \text{O.D.}$
	Observed	Corrected	
0	.763	.763	1.883
1	.758	.758	1.880
2	.753	.753	1.877

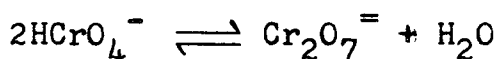
12	.740	.740	1.869
21	.730	.730	1.863
31	.728	.728	1.862
48	.695	.694	1.841
66	.674	.672	1.827
81	.657	.655	1.816
102	.630	.626	1.797
120	.610	.605	1.782
151	.579	.574	1.759
182	.541	.535	1.731
256	.470	.460	1.663
287	.450	.440	1.644
311	.429	.419	1.622
373	.380	.367	1.565
396	.365	.351	1.545
436	.340	.325	1.512
450	.330	.315	1.498
632	.235	.217	1.337
653	.227	.210	1.322
685	.212	.193	1.286

Standardization of the thiosulfate was accomplished by following an identical procedure with deletion of the alcohol.

(ii) Spectrophotometric Method. Three ml. of $3.42 \times 10^{-3} \text{ M Cr}^{\text{VI}}$ solution in 0.463 M HClO_4 were pipetted into a one cm. silica cell and thermostated at $25.0 \pm 0.1^\circ \text{C}$ in the cell compartment of a Beckmann model D.U. spectrophotometer. Isopropyl alcohol (.03 ml., 3.92×10^{-4} moles) was then added from a microliter syringe fitted with a Chaney adapter. The solution was mixed thoroughly and the optical density at 4440 \AA was determined at intervals. The optical density at this wave length was corrected for Cr^{III} absorption by use of a previously prepared calibration curve and a plot of $\log [\text{Cr}^{\text{VI}}]$ against time was prepared. (For oxidations utilizing a lower concentration of Cr^{VI} the peak at 3490 \AA could be used and no correction to the observed optical density was required.)

3. CONSIDERATION OF THE ACID CHROMATE-BICHROMATE EQUILIBRIUM

Westheimer and Novick (1) have established that the active chromium species in the oxidation of isopropyl alcohol is HCrO_4^- and that this species exists in equilibrium with bichromate.



The magnitude of the equilibrium constant in dilute aqueous solutions is such that the amount of chromium in the bichromate form is appreciable only at fairly high concentrations and Westheimer has observed that in dilute solutions (0.0005 - 0.005M) the rate is proportional to the gross Cr^{VI} concentration (37). Although no further investigation of this equilibrium was conducted during the present work, an attempt to minimize any deviations arising from this effect was made by using concentrations of Cr^{VI} that were always lower than 0.005M and in cases where rates were used for comparison purposes attempts were made to keep the Cr^{VI} concentration constant throughout the whole series.

4. PRODUCT ANALYSIS

It is well known that chromic acid oxidizes secondary alcohols smoothly to the corresponding ketones with little or no carbon-carbon bond fission (37). Since the concentration of reactants was low in all of the kinetic experiments conducted in this investigation, it was found to be extremely difficult to isolate and identify the products of these reactions. However, when the concentrations of the reactants were increased to a preparative scale it was found that both the aromatic and the aliphatic secondary alcohols gave

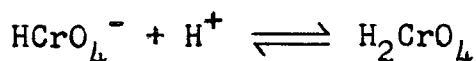
almost quantitative yields of the corresponding ketones. The good second order rate plots obtained also indicate that few side reactions are taking place. In the case where pseudo first order rate plots were obtained by using large excesses of alcohol it is very probable, as Best, Littler and Waters (19) have indicated, that the initial product does not react further with oxidant. This is so because the reacting alcohol is always present in much larger concentrations than any possible products.

Oxidation of primary alcohols yield as initial products aldehydes, which are likely to be more reactive than the alcohols themselves. Thus, strictly speaking, one can only calculate the rate of oxidation of a primary alcohol if the rate of oxidation of the corresponding aldehyde is known. This problem has been considered by Roček (32) who found that if a large excess of alcohol was used the rate constants calculated from the initial slope of the $\log [\text{Cr}^{\text{VI}}]$ v.s. time curve agreed well with the rate obtained from the equation for consecutive reactions (rates for the aldehydes being known). In this investigation the rate constants for primary alcohols were all obtained from the initial slope of the $\log [\text{Cr}^{\text{VI}}]$ v.s. time plot since the rates of oxidation of the corresponding aldehydes under these conditions were

not known.

5. DETERMINATION OF PKa VALUES FOR H_2CrO_4

For the equilibrium



the pKa is defined in the following way:

$$K_a = \frac{a_{\text{HCrO}_4^-} \cdot a_{\text{H}^+}}{a_{\text{H}_2\text{CrO}_4}} = \frac{C_{\text{HCrO}_4^-} \cdot C_{\text{H}^+} \cdot f_{\text{HCrO}_4^-} \cdot f_{\text{H}^+}}{C_{\text{H}_2\text{CrO}_4} \cdot f_{\text{H}_2\text{CrO}_4}}$$

$$\text{pKa} = \log \frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}} - \log \frac{a_{\text{H}^+} \cdot f_{\text{HCrO}_4^-}}{f_{\text{H}_2\text{CrO}_4}}$$

In dilute solutions the last term on the right becomes pH. In more concentrated acid solutions it is commonly denoted as H_- (91).

$$\text{i.e. } H_- = \log \frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}} - \text{pKa}$$

From this equation it can be seen that a plot of $\frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}}$ against H_- should give a straight line

of unit slope and an intercept at the pKa. The ratio

$\frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}}$ was determined, following the method of

Symons et al (80) by measuring the extinction coefficient of Cr^{VI} at one or more wave lengths over a

wide range of acidities. Then if $\epsilon_{\text{H}_2\text{CrO}_4}$ is the extinction coefficient of a solution of H_2CrO_4 at a particular wave length and $\epsilon_{\text{HCrO}_4^-}$ is the extinction coefficient of a solution of HCrO_4^- at the same wave length

$$\frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}} = \frac{\epsilon_{\text{HCrO}_4^-} - \epsilon}{\epsilon - \epsilon_{\text{H}_2\text{CrO}_4}}$$

where ϵ is the extinction coefficient of a solution containing both H_2CrO_4 and HCrO_4^- (91). The particular wavelength at which measurements were made was chosen from a comparison of the spectra of the two species such that a maximum change in the extinction coefficient was obtained.

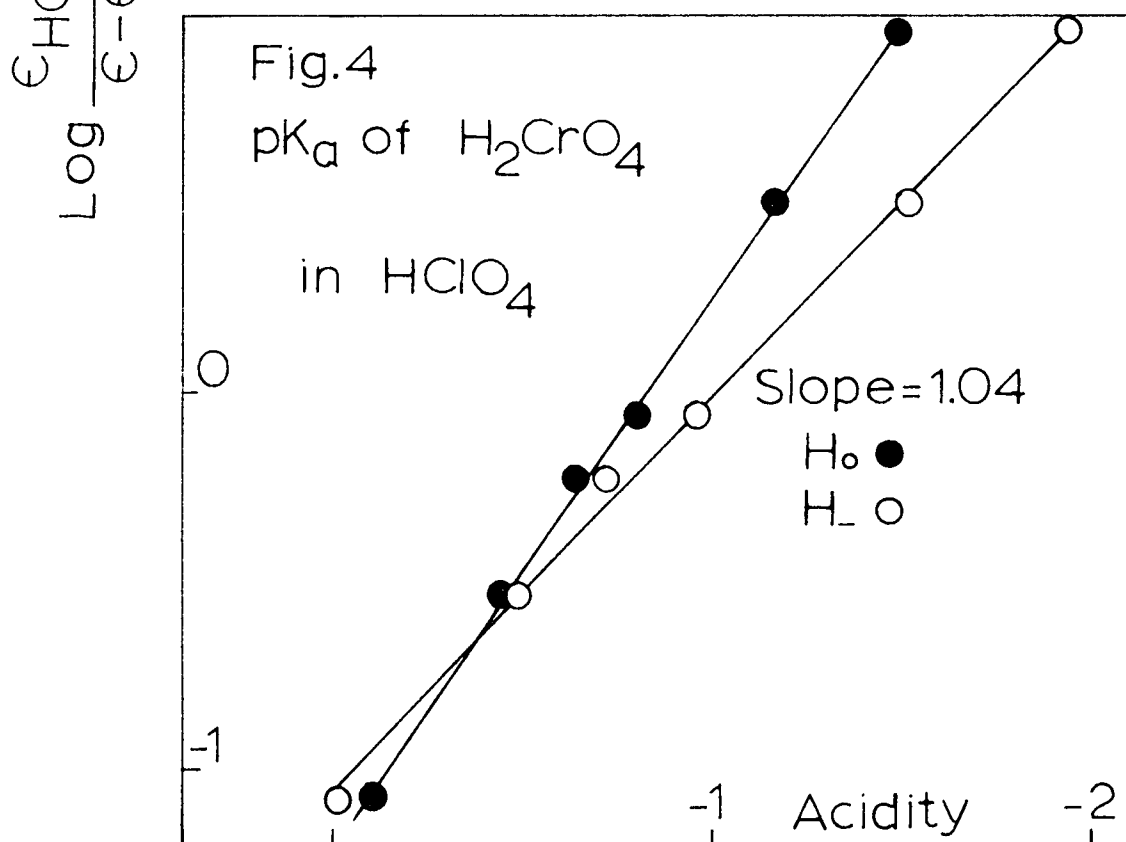
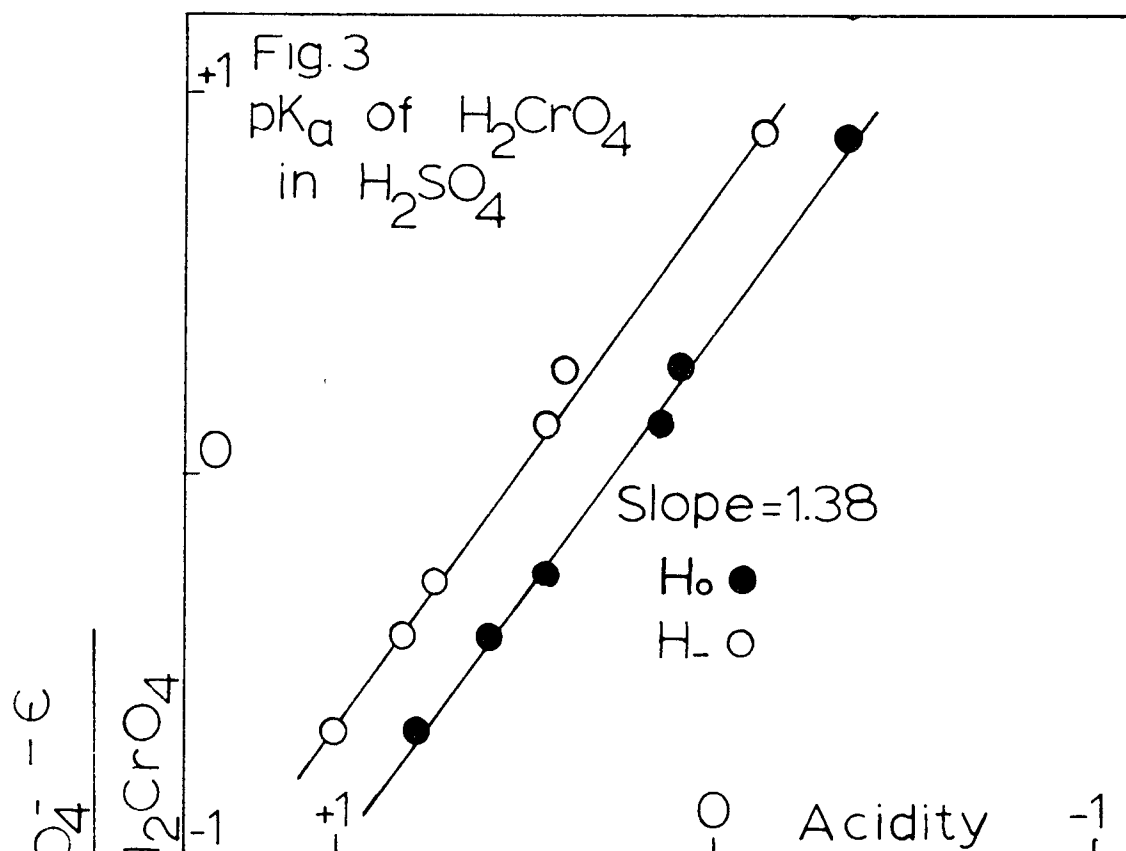
For perchloric acid, sulfuric acid and hydrochloric acid solutions a plot of

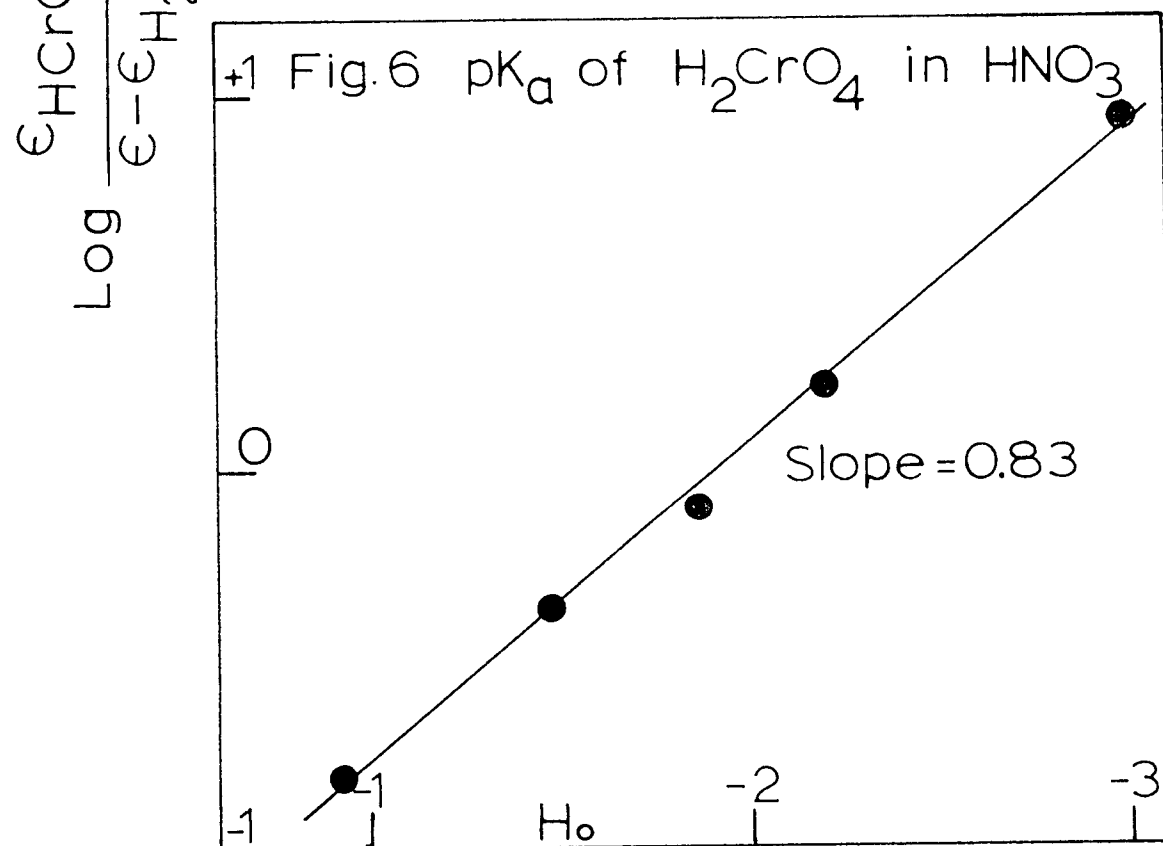
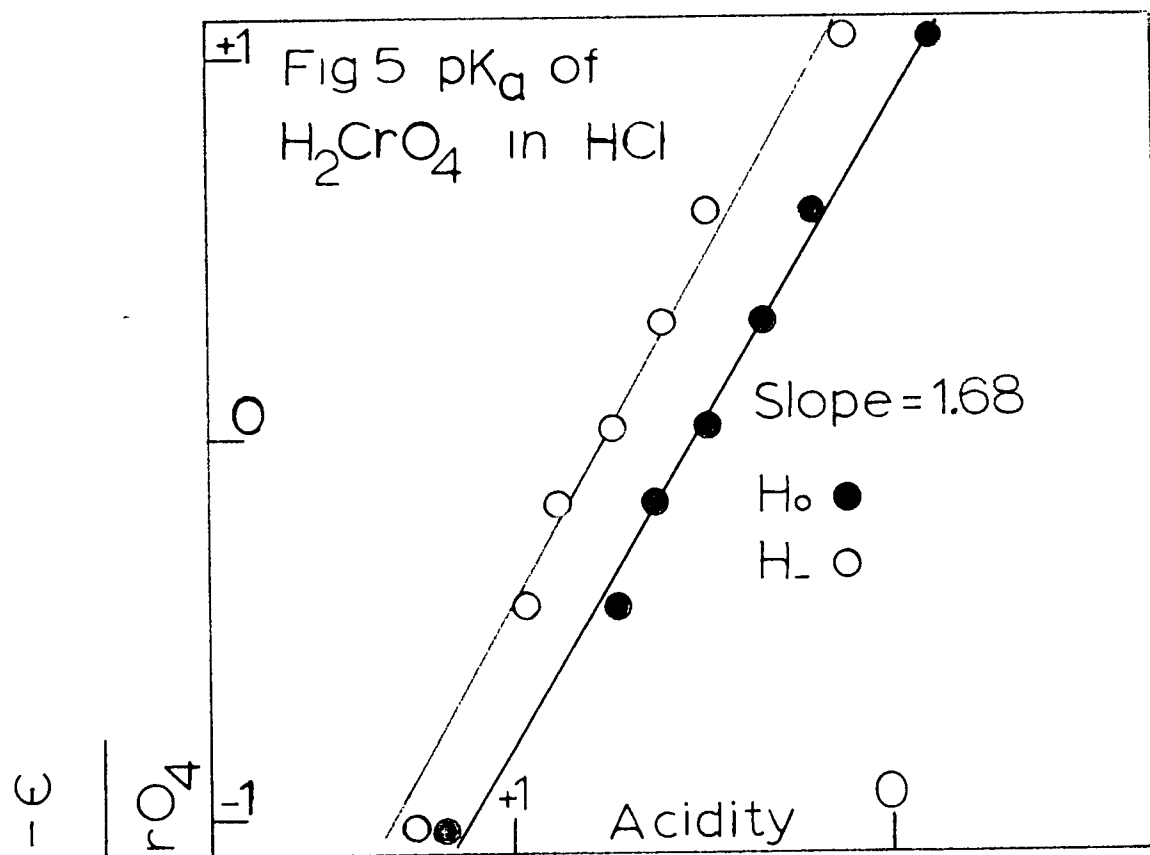
$$\log \frac{\epsilon_{\text{HCrO}_4^-} - \epsilon}{\epsilon - \epsilon_{\text{H}_2\text{CrO}_4}}$$

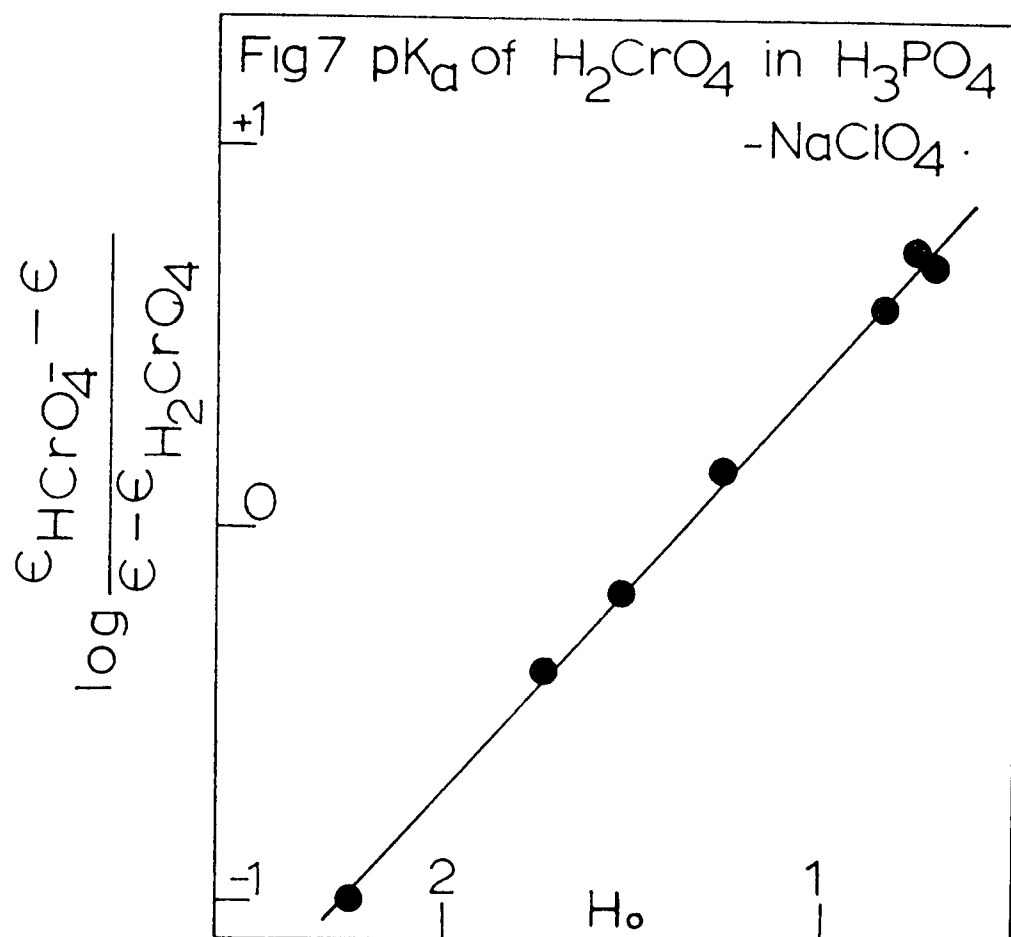
against H_+ was then prepared and the pK_a was obtained from the zero intercept. (See Figs. 3, 4 and 5.) For solutions of phosphoric acid and nitric acid where no H_+ functions are available a plot of

$$\log \frac{\epsilon_{\text{HCrO}_4^-} - \epsilon}{\epsilon - \epsilon_{\text{H}_2\text{CrO}_4}}$$

against H_0 was used for the pK_a determination. (See Figs. 6 and 7). It is to be expected that the use of H_0 instead of H_+ would not introduce too great an error in the







value obtained, since in the cases where both the H_- and H_0 functions are known for a particular medium they do not deviate greatly in reasonably dilute solutions. This is evident from a consideration of Figs. 3, 4 and 5 where both the H_0 and H_- scales have been used.

The H_0 functions used were those reported by Paul and Long (91) while the H_- functions were obtained from a report by Boyd (92, 93). The pK_a was also determined in phosphoric acid containing a 1:1 molar ratio of sodium perchlorate (Fig. 7). Since no acidity function was available for this medium it was determined in these laboratories. Its determination is presented in the next section.

It should be noted that although theory predicts the plots in Figs. 3-7 should have a slope of unity, most of the plots differ considerably from this. The reason for this is thought to be due to the same phenomenon that causes the values of the pK_a to change from medium to medium and which will be discussed later.

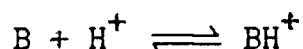
6. ACIDITY FUNCTION FOR THE PHOSPHORIC ACID-SODIUM PERCHLORATE SYSTEM

While glass electrode pH measurements may be

used to determine the acidity of dilute acid solutions the acidity of more concentrated solutions is generally defined in terms of the H_0 function originally conceived by Hammett and Deyrup (90). The determination of this function makes use of uncharged bases as indicators and is defined by the equation;

$$H_0 = pK_{BH^+} - \log \frac{C_{BH^+}}{C_B}$$

where pK_{BH^+} is the equilibrium constant for the reaction



This concept, which has now become quite general (91), involves the use of weaker and weaker bases as indicators as the acidity of the solution increases.

In the present determination of the acidity of solutions containing a 1:1 molar ratio of phosphoric acid and sodium perchlorate the indicators used were *p*-nitroaniline, *o*-nitroaniline and 4-chloro-2-nitroaniline (Fig. 9). The ratio $\frac{C_{BH^+}}{C_B}$ was determined spectroscopically using an absorption peak due to the unprotinated base. A stock solution containing 4.57 M phosphoric acid and 4.57 M sodium perchlorate was prepared by dissolving 280.0 gm. $NaClO_4$ in 381 ml. of 6 M H_3PO_4 and diluting the resulting mixture with water to exactly 500 ml. This solution was then diluted to give a series of solutions of varying

TABLE III
ACIDITY OF SOLUTIONS CONTAINING
A 1:1 MOLAR RATIO OF H_3PO_4 to NaClO_4

Molarity	O.D.	$C_{\text{BH}^+}/C_{\text{B}}$	H_0
(a) <u>p</u> -Nitroaniline, $\text{pK} = 0.99$, $\lambda_{\text{max}} = 380$			
0.0	.766		
0.0457	.660	0.161	1.78
0.0914	.596	0.286	1.53
0.183	.503	0.525	1.27
0.457	.317	1.415	0.84
0.914	.175	3.39	0.46
1.83	.060	11.82	-0.08
(b) <u>o</u> -Nitroaniline, $\text{pK} = -0.20$, $\lambda_{\text{max}} = 412$			
0.0	.660		
0.457	.610	0.0823	0.84
0.730	.570	0.175	0.57
0.914	.542	0.216	0.46
1.83	.373	0.802	-0.08
2.74	.185	2.57	-0.60
3.66	.064	9.30	-1.17
(c) 4-Chloro-3-nitroaniline, $\text{pK} = -0.95$, $\lambda_{\text{max}} = 425$			
0.0	.648		
1.83	.574	0.130	-0.08
2.74	.438	0.479	-0.60

3.66	.246	1.630	-1.17
4.57	.105	5.17	-1.66

TABLE IV

ACIDITY OF SOLUTIONS CONTAINING A 1:1 MOLAR

RATIO OF HNO_3 to NaClO_4

Molarity	O.D.	$C_{\text{BH}^+}/C_{\text{B}}$	H_0
(a) <u>p</u> -Nitroaniline, $\text{pK}_a = 1.00$, $\lambda_{\text{max}} = 383$			
0.0	.741		
0.0139	.652	0.136	1.89
0.0232	.618	0.198	1.68
0.0464	.529	0.401	1.38
0.0928	.396	0.870	1.06
0.186	.249	1.97	0.705
0.371	.124	5.05	0.297
0.464	.095	6.81	0.167
(b) <u>o</u> -Nitroaniline, $\text{pK}_a = -0.28$, $\lambda_{\text{max}} = 383$			
0.0	.675		
0.0928	.645	0.0460	1.060
0.1856	.609	0.109	0.705
0.464	.497	0.358	0.167
0.812	.373	0.809	-0.20
1.218	.246	1.74	-0.53
2.030	.109	5.17	-1.00

2.676	.044	14.40	-1.45
-------	------	-------	-------

(c) 4-Chloro-2-nitroaniline*, pKa = -0.98, λ_{\max} = 429

0.0	.680		
0.464	.641	0.0605	-1.218
0.812	.591	0.150	-0.824
1.218	.511	0.330	-0.481
1.338	.481	0.415	-0.382
1.784	.381	0.786	-0.105
2.03	.321	1.12	-1.00
2.23	.283	1.40	-1.16
2.44	.208	2.27	-1.29
2.68	.192	2.55	-1.45
3.12	.125	4.44	-1.60
3.57	.072	8.42	-1.85
4.06	.030	21.7	-2.25

* For this indicator the optical density at this wave length increased with time in the more concentrated acid solutions. Hence all readings were extrapolated to zero time.

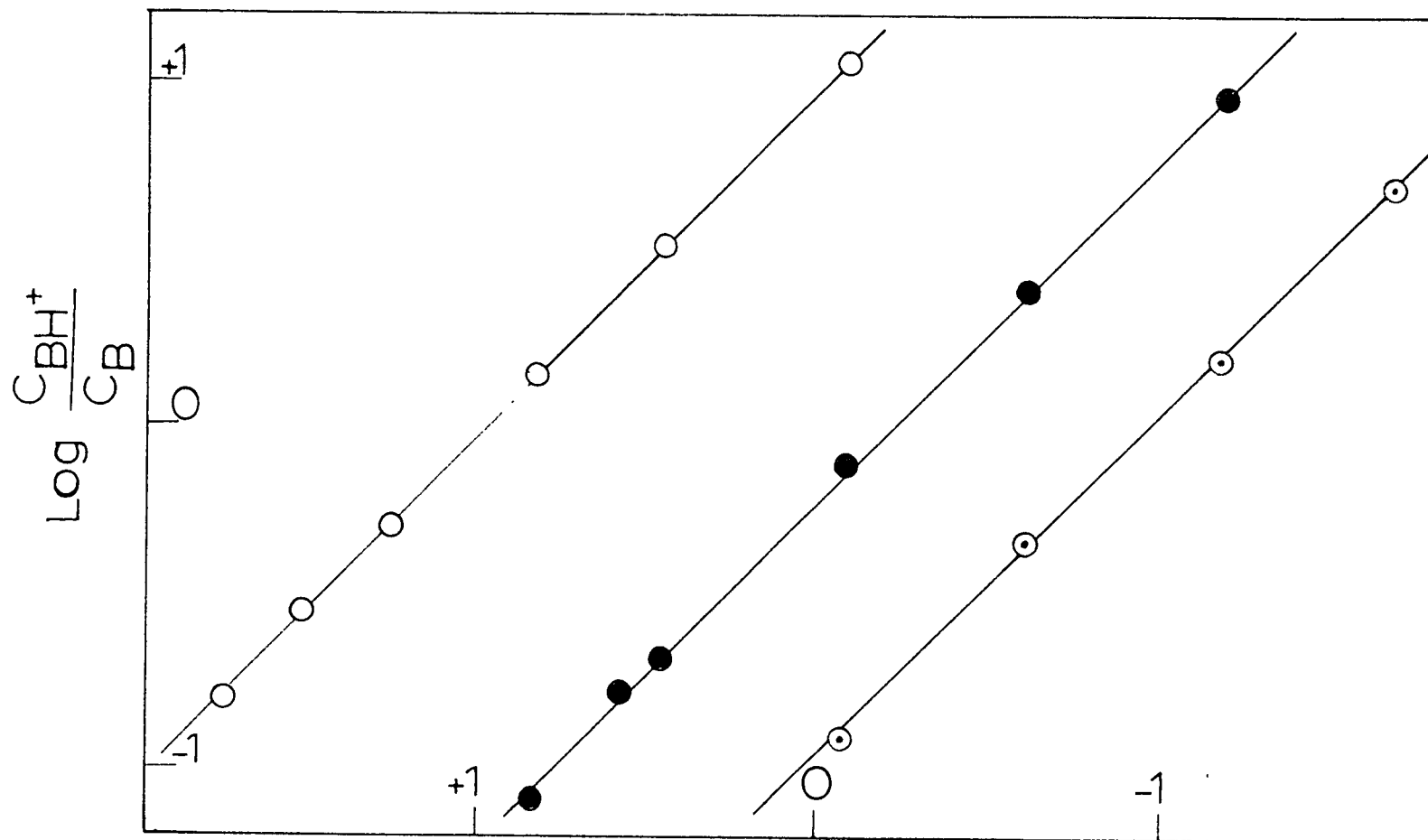


Fig.8 Ionization of indicators in H_3PO_4 - $NaClO_4$ solutions.
 o,p-nitroaniline. ●,o-nitroaniline. ◉, 4-chloro-2-nitroaniline.

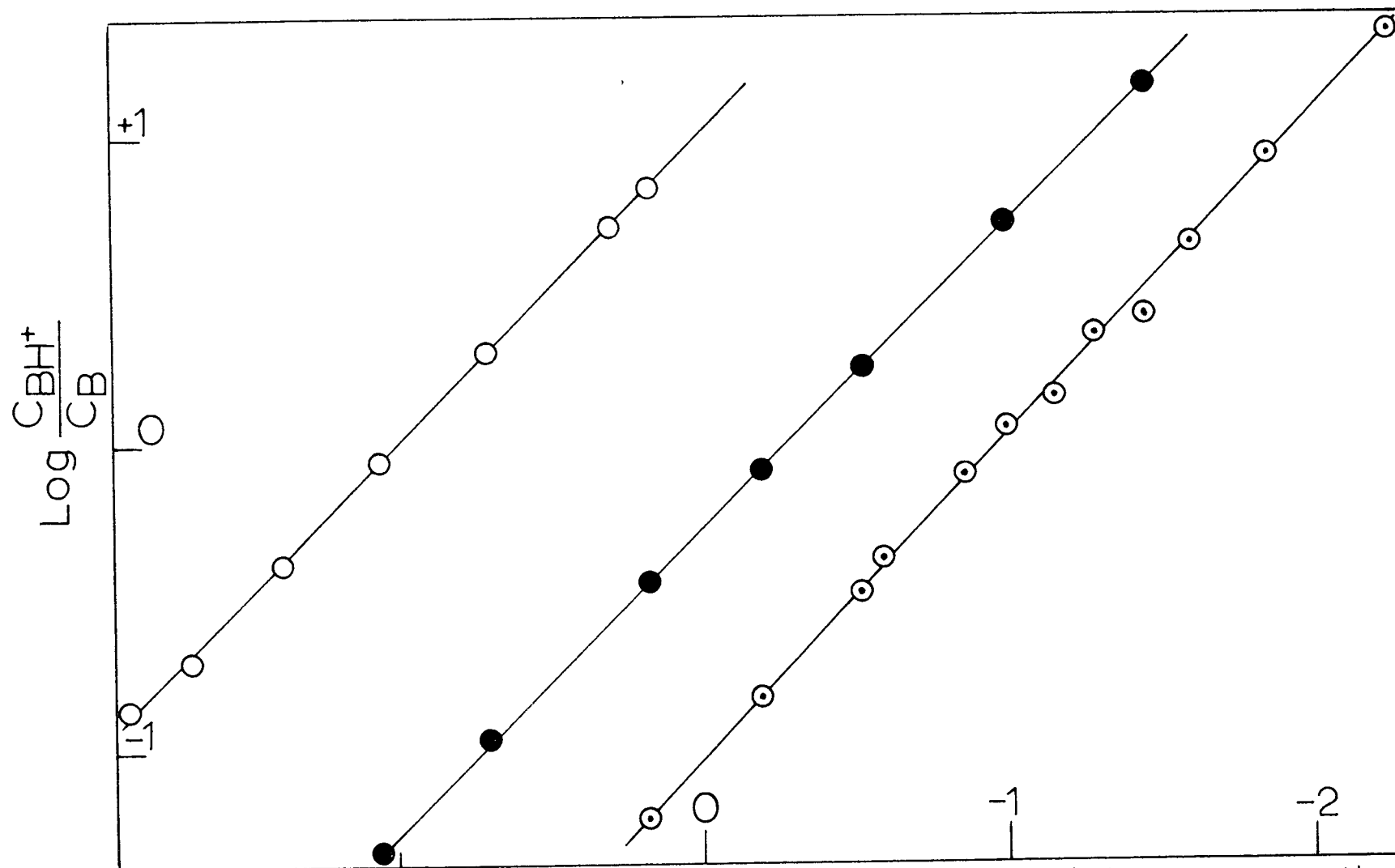


Fig.9 Ionization of indicators in $\text{HNO}_3\text{-NaClO}_4$ solutions. *o,p*-nitroaniline. ●, *o*-nitroaniline. ◐, 4-chloro-2-nitroaniline.

concentrations. Fifty microliters of an alcoholic solution of indicator was then added to each of one dozen five ml. volumetric flasks. The flasks were then filled to the mark with solutions of concentrations varying from pure water to 5.47 M acid. In addition one flask was filled to the mark with 70% sulfuric acid. The visible and ultraviolet spectrum of the indicator in water was then determined to select the best wave length at which to work and the optical density of each solution at this particular wave length was measured on a Beckman D.U. Spectrophotometer.

The data obtained have been tabulated in Table III. In dilute solutions the H_0 determined from p-nitroaniline solutions was found to agree to within 0.03 units with pH measurements made with a glass electrode on a Beckman Model G. pH meter.

7. ACIDITY FUNCTION FOR THE NITRIC ACID-SODIUM PERCHLORATE SYSTEM

The H_0 acidity function for a medium containing a 1:1 molar ratio of nitric acid and sodium perchlorate was also determined by the same methods just described for the phosphoric acid-sodium perchlorate system. The indicators used for this function were also p-nitroaniline, o-nitroaniline and 4-chloro-3-nitroaniline

(See Fig. 9). The data obtained is presented in Table IV. The H_0 values for very dilute solutions were found to agree to within 0.01 units with pH measurements made with a glass electrode on a Beckmann Model G pH meter.

8. DETERMINATION OF THE CHROMATE ESTER EQUILIBRIUM CONSTANT FOR 2-METHOXYETHANOL AND 2,2,2-TRIFLUOROETHANOL

Equilibria of the type, $ROH + HCrO_4^- \rightleftharpoons ROCrO_3^- + H_2O$ have previously been studied spectroscopically by Klaning and Symons (43, 52). Their experimental procedure involved measuring the optical density of chromium VI in aqueous acidic solutions containing varying amounts of an alcohol. If activity coefficients can be neglected the following relationship between the difference in optical density (Δd) and the equilibrium constant (K_e) can be derived:

$$\Delta d [H_2O] / [ROH] = \Delta \epsilon K_e l [Cr^{VI}] - K_e \Delta d \quad (I)$$

where $\Delta \epsilon$ is the difference in extinction coefficient between $HCrO_4^-$ and $ROCrO_3^-$ at 375 m μ . and l is the length of the cell used. Accordingly the slope of a plot of $\Delta d [H_2O] / [ROH]$ against Δd should equal $-K_e$.

While Klänig and Symons have determined the equilibrium constant for a large number of alcohols it was found necessary to determine this constant for two additional alcohols, 2-methoxyethanol and 2,2,2-

trifluoroethanol. For comparison purposes the equilibrium constant for isopropyl alcohol was also determined. The results obtained are presented in graphical form in Fig. 10. The value of 8.2 for isopropyl alcohol obtained in this investigation agrees very well with the value of 8.2 reported by Klänning and Symons. By use of identical methods the equilibrium constant for 2-methoxyethanol was found to be 8.3.

The determination of K_e for 2,2,2-trifluoroethanol was complicated to some extent by two factors; (i) the equilibrium constant is only about one-sixth as large as that for the two other alcohols and (ii) the difference in extinction coefficients for the ester of this alcohol and HCrO_4^- is apparently somewhat smaller than in the other cases. As can be seen from Fig. 10, the changes in optical density were not large enough to permit an accurate slope to be drawn. Hence, a different approach involving the use of the intercept of the line was employed in this case. From equation (I) it can be seen that the value of the intercept should be equal to $\Delta\epsilon K_e l [\text{Cr}^{\text{VI}}]$. The only unknown in this term is $\Delta\epsilon$. Thus an attempt to measure the extinction coefficient of the ester was made following the procedure of Westheimer et al

(42). An aqueous acidic solution of 2,2,2-trifluoroethanol was extracted with benzene. The organic layer containing extracted ester and alcohol was dried briefly over CaCl_2 and the optical density was determined at 375 m μ . The amount of ester present was determined from the decrease of chromium VI concentration in the aqueous layer. This decrease in concentration was calculated from measurements of the optical density of the aqueous solution before and after extraction with benzene and a consideration of the volume change occurring during the extraction. By this method, the molar extinction coefficient of the ester was determined to be approximately 1150 at 375 m μ . From this $\Delta\epsilon$ was calculated to be 310 and the K_e value was determined to be 1.29.

While it is apparent that this number may contain considerable error it is fortunate that the conclusions derived from it are not very sensitive to the accuracy of this particular result. Thus it can be seen from a consideration of the calculations to be presented in Sec. IV. that the same general conclusions would be obtained even if this result contained an error of several hundred percent. Indeed the same conclusions would be derived if this result were disregarded altogether.

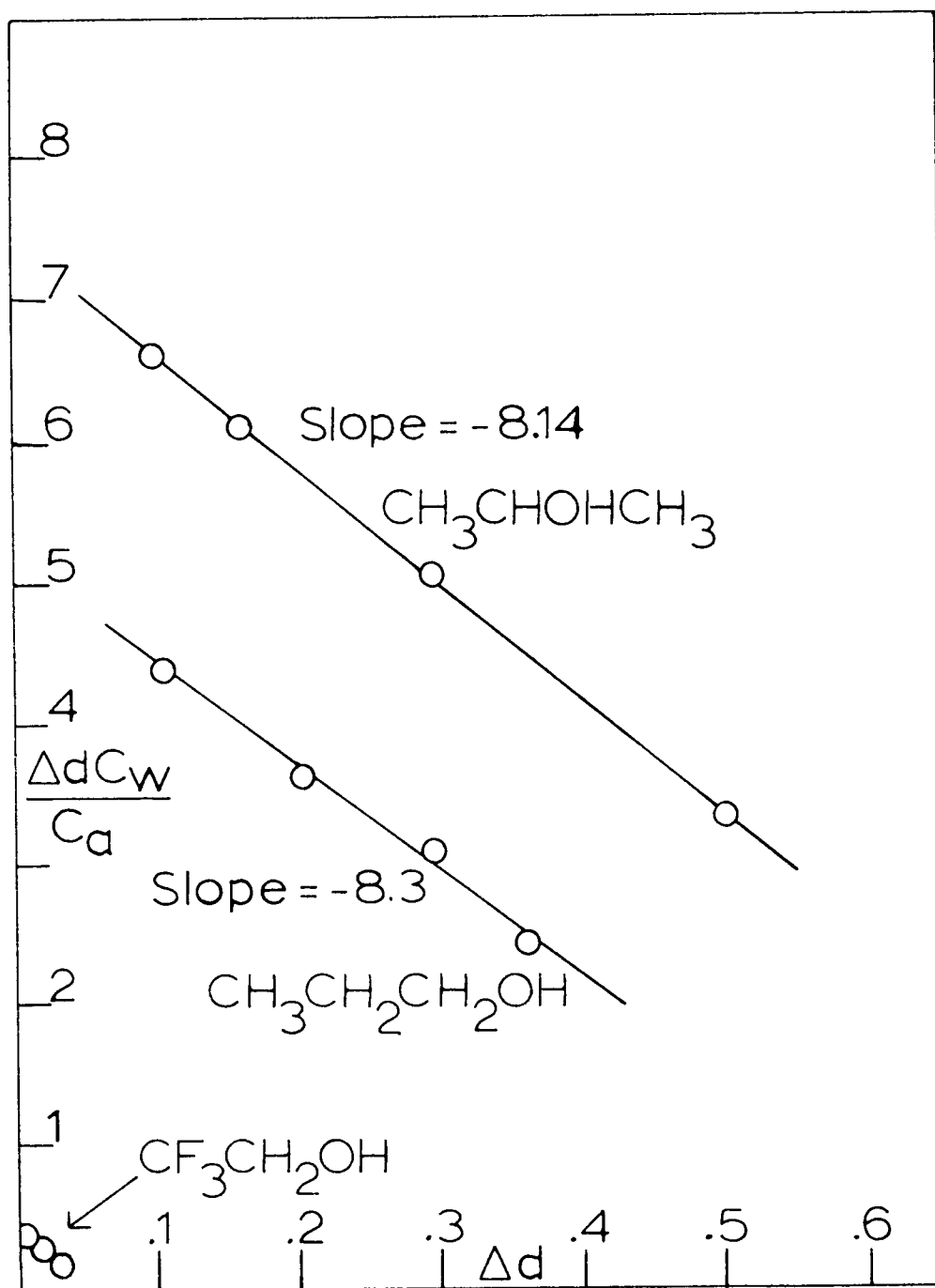
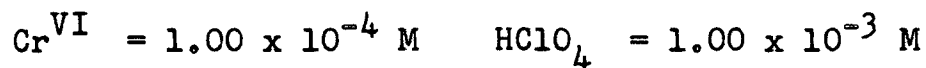


Fig.10 Chromate ester equilibrium Constants

TABLE V

DATA FOR FIGURE 10



[Alcohol]	[H ₂ O]	O.D.	Δd	$\Delta d \times [\text{H}_2\text{O}] / [\text{ROH}]$
-----------	--------------------	------	------------	---

(a) Isopropyl Alcohol

0.0		.820		
0.785	52.0	.920	.100	6.64
1.31	50.0	.980	.160	6.10
2.62	44.9	1.116	.296	5.09
3.92	39.9	1.200	.380	3.77
5.24	34.7	1.320	.500	3.31

(b) 2-Methoxyethanol

0.0		.820		
1.27	50.2	.930	.110	4.35
2.54	44.6	1.026	.206	3.62
3.81	39.3	1.119	.299	3.08
5.08	34.2	1.182	.362	2.44

(c) 2,2,2-Trifluoroethanol

0.0		.820		
1.37	50.2	.830	0.010	.36
4.12	40.1	.843	0.023	.22
6.87	29.0	.855	0.035	.15

IV RESULTS AND DISCUSSION

1. OXIDATION OF FLUORO ALCOHOLS IN 77.2% ACETIC ACID

The rates of oxidation of eight aryltrifluoromethylcarbinols were determined at 25°C in a 77.2% acetic acid solution containing 3.20 M perchloric acid. The deuterium isotope effects for five of these alcohols were also determined. In addition the rates of oxidation of five substituted 2-propanols along with the deuterium isotope effects for three of these were determined for comparison purposes. The results are presented in Table VI. A Hammett plot using modified σ^+ values for both the protio and deuterio compounds is shown in Fig. 11, and the same plot using the original Hammett σ values is shown in Fig. 12.

Although the correlation coefficients are approximately the same for both plots (0.985 and 0.990 respectively) an examination of Figures 11 and 12 reveals that there is a definite break in the slope of the plot obtained when the original Hammett values are used. Such a break is not apparent for the plot in Fig. 11 where the modified σ^+ values are used. As a further aid in deciding whether the rates of oxidation were better correlated with σ or σ^+ values attempts were made to determine the rates of oxidation of *p*-methoxyphenyltrifluoromethylcarbinol

TABLE VI

OXIDATION OF FLUORO ALCOHOLS IN 77.2% ACETIC ACID,

3.20 M HClO_4 ($H_o = -2.82$), $T = 25^\circ\text{C}$

Alcohol	No.	$[\text{Cr}^{\text{VI}}]$ ($\text{M} \times 10^3$)	$[\text{alc.}]$ ($\text{M} \times 10^3$)	k_2 ($1 \text{ moles}^{-1} \text{ sec}^{-1}$)	k_H/k_D
p-t-Butylphenyl-trifluoromethylcarbinol	56	1.79	2.68	.574	
	57	"	"	.544	
p-Methylphenyl-trifluoromethylcarbinol	44	"	"	.534	
	55	"	"	.537	
	105	"	"	.564	
	111	"	"	.540	
p-Methylphenyl-trifluoromethylcarbinol- α -d	107	"	"	.0727	$7.40 \pm .20$
	109	"	"	.0740	
	110	"	"	.0747	
	115	"	"	.0706	
m-Methylphenyl-trifluoromethylcarbinol	64	"	"	.350	
	68	"	"	.340	
Phenyltrifluoromethylcarbinol	82	"	"	.259	
	89	"	"	.250	
	41	"	15.3	.258	
Phenyltrifluoromethylcarbinol- α -d	39	"	16.1	.0310	$8.53 \pm .15$
	90	"	2.68	.0294	
	92	"	"	.0297	

p-Chlorophenyl-	80	1.79	2.68	.174	
trifluoromethyl-					
carbinol	81	"	"	.174	
m-Bromophenyl-	42	"	"	.119	
trifluoromethyl-					
carbinol	60	"	"	.106	
	61	"	"	.110	
	91	"	"	.109	
m-Bromophenyl-	66	"	"	.0117	9.80 \pm .20
trifluoromethyl-					
carbinol- α -d	72	"	"	.0111	
	75	"	20.8	.0113	
m-Nitrophenyl-	47	"	2.68	.0494	
trifluoromethyl-					
carbinol	62	"	"	.0514	
	101	"	"	.0484	
	78	"	14.06	.0453	
	119	"	17.22	.0444	
	113	"	15.96	.0474	
m-Nitrophenyl-	117	"	17.28	.00360	12.20 \pm .20
trifluoromethyl-					
carbinol- α -d	118	"	18.69	.00367	
3,5-Dinitro-	138	"	17.65	.0116	
phenyltrifluoro-					
methylcarbinol	143	"	12.81	.0118	
3,5-Dinitro-	132	"	55.10	.00100	12.93 \pm .78
phenyltrifluoro-					
methylcarbinol-	139	"	10.92	.000834	
α -d					

Isopropyl alcohol	175	1.29	1.93	4730*	
	176	"	"	5380*	
1-Fluoro-2- propanol	187	1.37	2.06	15.4	
	188	"	"	15.2	
1,3-Difluoro- 2-propanol	178	"	30.2	.429	
	179	"	30.2	.425	
1,3-Difluoro- 2-propanol-2-d	180	"	30.0	.0407	10.50 ⁺ .10
1,1,1-Trifluoro- 2-propanol	181	"	26.0	.0292	
	182	"	37.2	.0302	
1,1,1-Trifluoro- 2-propanol-2-d	183	"	25.8	.00263	11.29 ⁺ .20
1,1,1,3,3,3- Hexafluoro-2- propanol	189	0.685	31.6	.0000245	
	190	0.685	25.3	.0000220	
	194	0.633	63.3	.0000285	
	193	0.818	158	.0000169	
	576	1.03	190	.0000160	
	577	1.08	238	.0000158	
1,1,1,3,3,3- Hexafluoro-2- propanol-2-d	578	1.47	79.5	.00000322	7.8 ⁺ .5
	579	1.14	249	.00000210	

* Approximate rate only

Fig.11 Hammett plot for the chromic acid oxidation of substituted phenyltrifluoromethylcarbinols in 77% acetic acid.

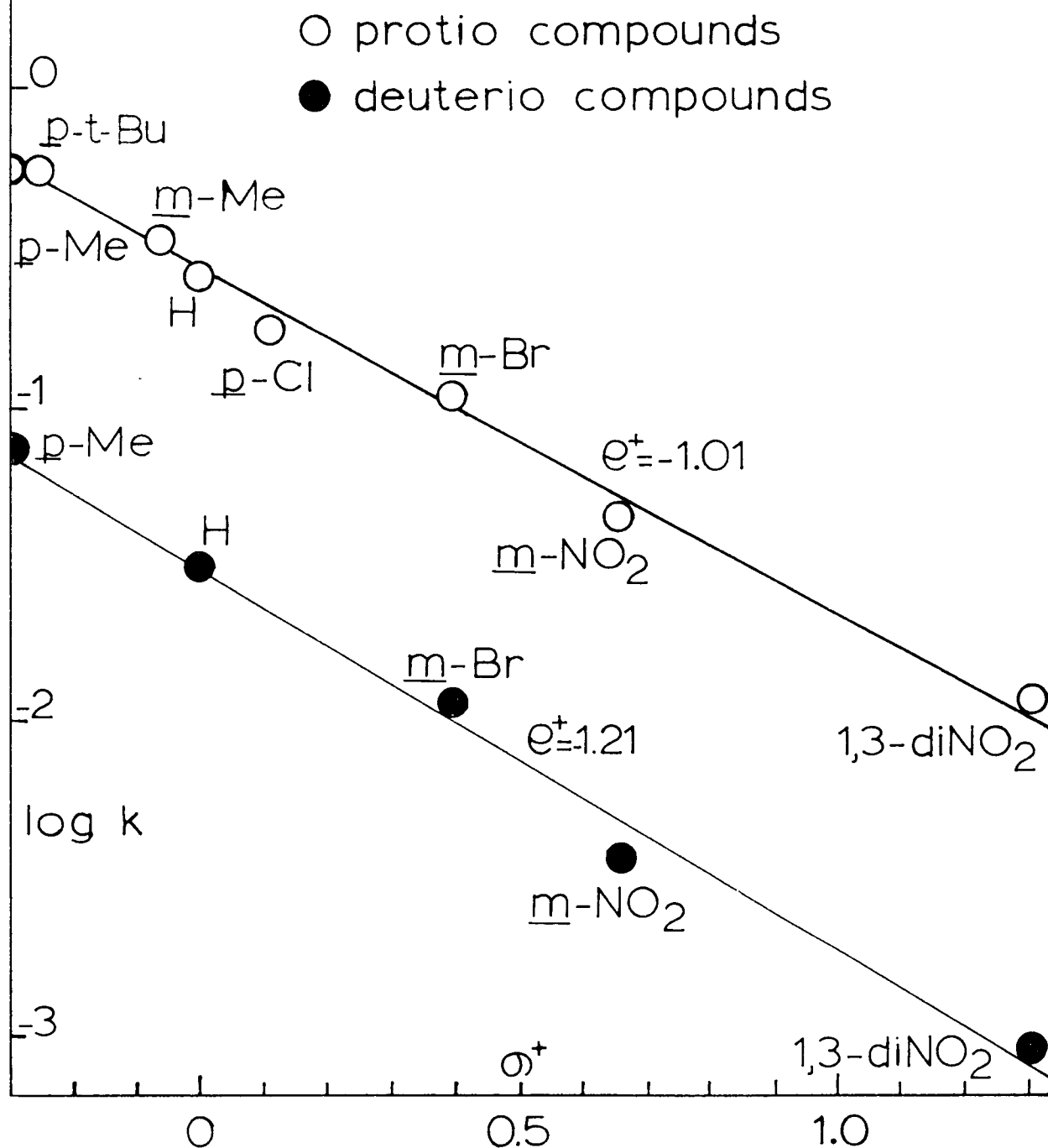
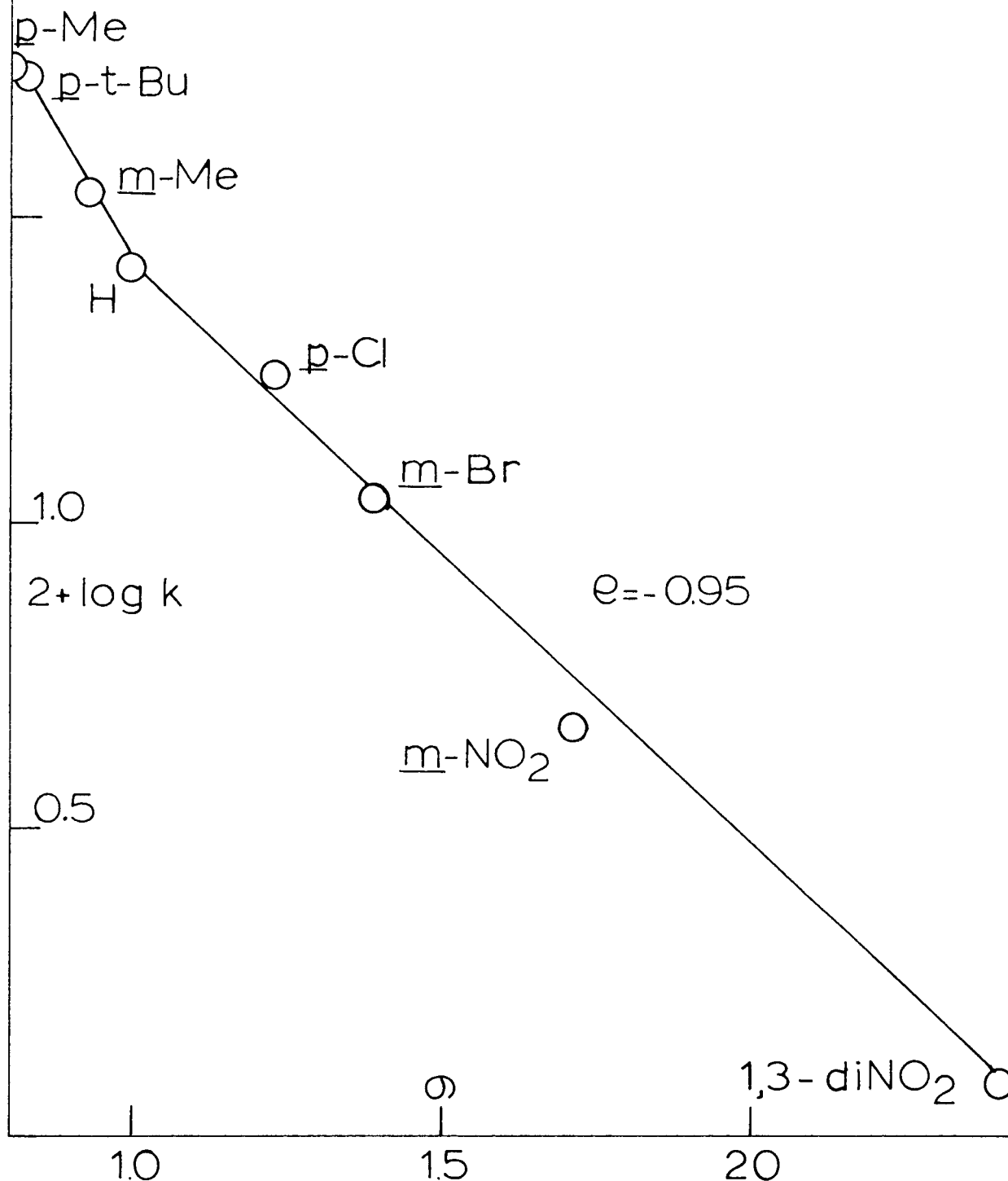


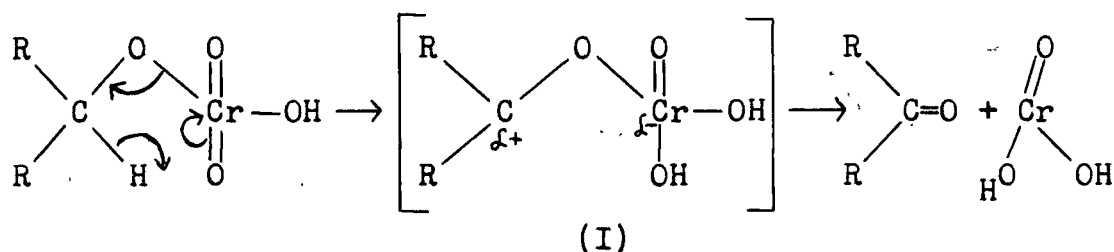
Fig.12 Hammett plot for the chromic acid oxidation of substituted phenyltrifluoromethylcarbinols in 77% acetic acid.



and β -naphthyltrifluoromethylcarbinol. Since the difference between σ and σ^+ values for the p-methoxy and the α -naphthyl group are greater than for any of the other groups they are most useful in differentiating between reactions which follow σ^+ values and those which follow σ values. Unfortunately both of these alcohols reduced chromium VI at a very fast rate in the medium used. This can be attributed to the oxidation of these compounds at sites other than the hydroxylated carbon since it was later found that both anisole and naphthalene were very rapidly oxidized under these conditions.

A modified "rho" value of -1.01 was calculated from the slope of the plot in Fig. 11. While other interpretations (22,27) have been suggested for the negative "rho" values observed in the oxidation of alcohols by chromic acid the most direct explanation for the fact that any reaction exhibits a negative ρ^+ value is that considerable positive charge is located on the α -carbon atom in the transition state. Further, the observation of very pronounced isotope effects demands that any proposed mechanism include as a rate-determining step, fission of the α -carbon-hydrogen bond. Taken together these two observations suggest that hydride abstraction is taking place. However,

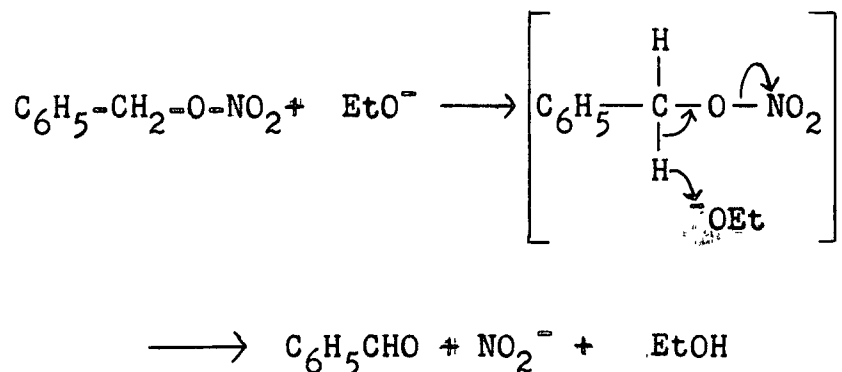
the results reported by Westheimer et al (22) on the oxidation of isopropyl alcohol in D_2O indicate that the original hydride ion mechanism proposed by Roček and Krupička (31) cannot be correct. Also the evidence available in the literature, particularly the evidence obtained from studies of the oxidation of diols (24, 25, 26) strongly indicates that the chromate esters play the role of intermediates in this reaction. All of these considerations are satisfactorily met by a mechanism which employs as a rate-determining step decomposition of the chromate ester by internal hydride ion transfer.



It can be argued that since mechanisms such as the one above involve essentially the movement of electrons in a cycle the effect of substituents should be the same regardless of the direction of electron flow. However, the very pronounced isotope effect observed definitely indicates that fission of the α -carbon-hydrogen bond is rate-determining. Hence stretching of this bond probably initiates the reaction

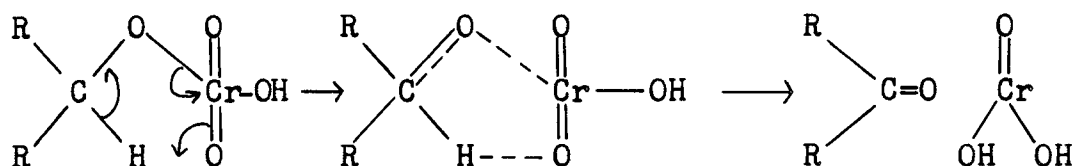
and the transition state must be similar to (I). If the mechanism involves simultaneous fission of the oxygen-chromium and the carbon-hydrogen bonds the effect of substituents would still be more pronounced on the carbon-hydrogen bond since it is physically closer to the substituents.

Such an effect has been elegantly illustrated by Buncl and Bourns (95) in their work on the decomposition of benzyl nitrate by ethoxide ions.



This reaction shows a deuterium isotope effect of 5.04 at 60°C and an N¹⁵ isotope effect of 1.0196 at 30°C indicating that the carbon-hydrogen and the nitrogen-oxygen bonds are broken simultaneously in the course of the reaction. In this case it is evident that the hydrogen is being abstracted as a proton and the large positive "rho" value of +3.40 indicates that the effect of substituents is more intimately concerned with cleavage of the α-carbon-hydrogen bond than the more remote oxygen-nitrogen bond.

In the case of a cyclic chromate ester decomposition movement of electrons in the reverse direction to that shown in the reaction sequence involving (I) would result in a proton transfer mechanism identical with the one proposed by Kwart and Francis (50).



However, the negative "rho" values observed in this and other investigations (27, 32) for the chromic acid oxidation of alcohols are not, in light of the benzyl nitrate results, compatible with a rate-determining proton transfer. Moreover, as Roček (32) has indicated, one would not expect that protonation of the chromium part of the ester would lead to rate enhancement if the rate-determining step also involved internal proton transfer to this part of the molecule. The hydride transfer mechanism, on the other hand, readily accommodates this observed feature of the reaction. In addition it will be shown that the other results obtained in this investigation can also be easily explained on the basis of such a mechanism.

With the exception of 1,1,1,3,3,3-hexafluoro-2-propanol an approximately linear relationship exists

between the rates of oxidation of trifluoromethylcarbinols and the observed isotope effects. This relationship, which is illustrated in Fig. 13 fits in well with the suggestion first made by Wiberg (59) that there should be a general correlation between rates and isotope effects within a group of analogous reactions, slow rates being accompanied by large isotope effects. Wiberg based his predictions on the experimental observation that the isotope effects in the side chain halogenation of para substituted toluenes varied from 3.22 to 5.11 at 77°C. Since the largest of these isotope effects is somewhat smaller than the maximum effect predicted from a consideration of zero-point energies of the carbon-hydrogen and carbon-deuterium bonds, the variation with rate was explained in terms of factors which could be related to C-H stretching frequencies (59, 67).

In the present case, however, even the smallest isotope effect observed is larger than the maximal effect predicted from a consideration of carbon-hydrogen stretching frequencies. While it is not clear from the present results whether the large isotope effects are due to loss of bending frequencies in the transition state or to a tunnel effect it is interesting to note that a correlation between rate

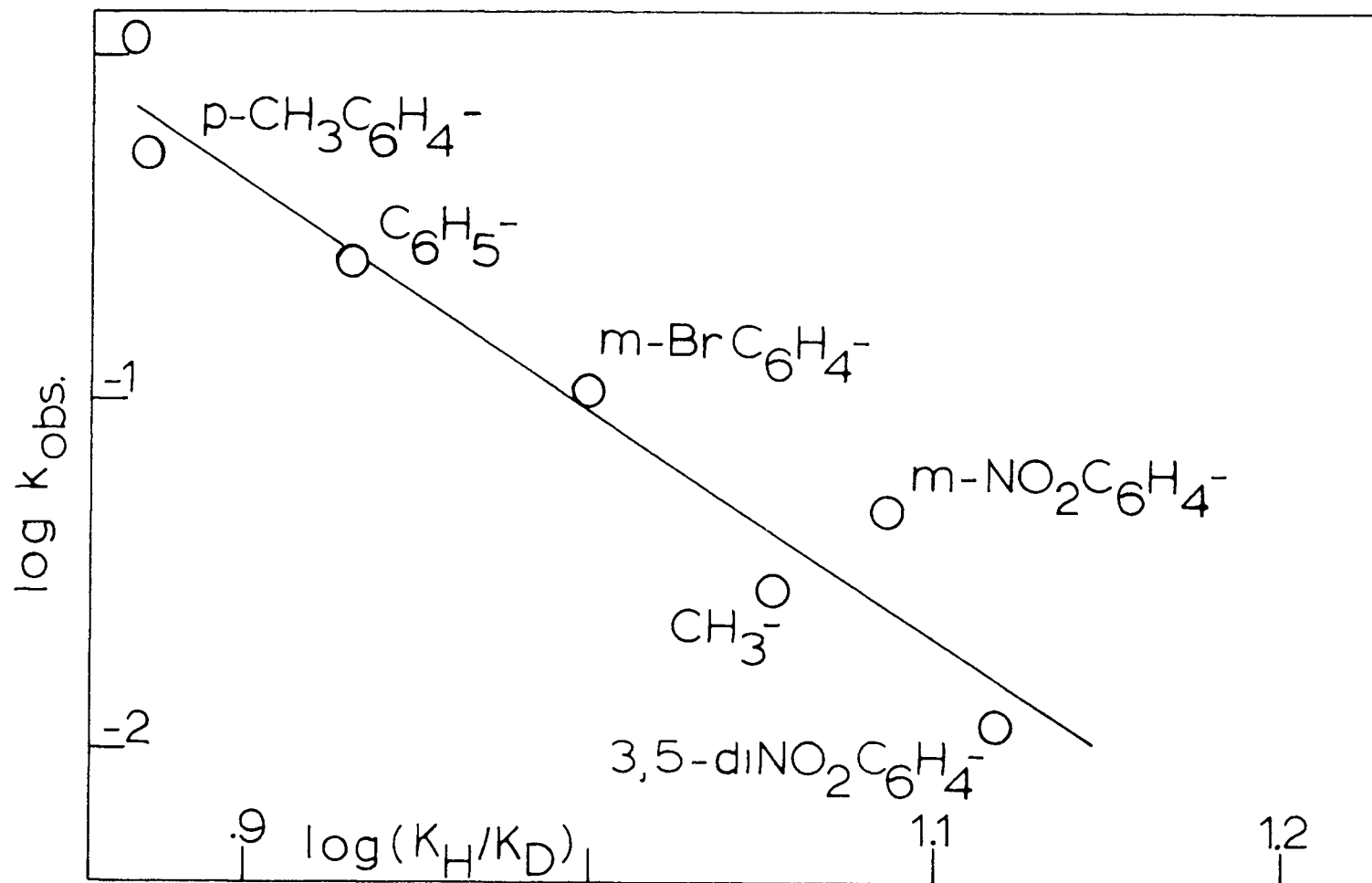


Fig.13 Relationship between the rate of oxidation of trifluoromethylcarbinols in 77.2% acetic acid and the primary deuterium isotope effects.

and isotope effect still exists. Such a correlation was not observed by Stewart and Van der Linden (71) in the permanganate oxidation of these alcohols since the "rho" value for that reaction was almost zero. It does appear however that large isotope effects are intimately connected with the trifluoromethyl group or at least with the presence of strongly electron withdrawing groups adjacent to the site of oxidation.

The isotope effect observed for the chromic acid oxidation of 1,1,1,3,3,3-hexafluoro-2-propanol is anomalous in that it is only 7.8 while the rate of oxidation of this compound is the slowest in the series. This low isotope effect is not likely to be due to impurities in the deuterio compound since it was carefully purified by vapor phase chromatography before use. Further it was found that the properties of this compound prepared independently by two different workers in this laboratory agreed well and that the same isotope effect was observed for each sample. The deuterium content of these samples was easily checked by nuclear magnetic resonance spectroscopy and found to be above 97%. The small amount of protio compound present gave the rate plot a steep initial slope. However, over an extended period of time good straight line kinetics were observed. Also it was noted that

the rate of reaction of this compound depended to some extent on the concentration of the alcohol present, being $0.025 \text{ l. moles}^{-1} \text{ sec.}^{-1}$ at an alcohol concentration $.6\text{M.}$ and only $0.016 \text{ l. moles}^{-1} \text{ sec.}^{-1}$ at an alcohol concentration of 1.0M. This may be due to an effect of the solvent that is observed for alcohol concentrations as large as this.

The lower than expected isotope effect may be a manifestation of experimental conditions since it is possible in this case that the intermediate chromium V and chromium IV species are reacting to a considerable extent with the solvent i.e. the reducing potential of 1,1,1,3,3,3-hexafluoro-2-propanol may not be much greater than that of acetic acid, and since the concentration of the solvent is so much greater than that of the alcohol a considerable amount of side reaction may be occurring. Kaplan's work has shown that an isotope effect is also observed for these intermediate species in the oxidation of 2-propanol-2- t . Hence the overall result of the reduction of these species by solvent would be a decrease in the magnitude of the observed isotope effect.

The rate of oxidation of phenyltrifluoromethylcarbinol was found to be linear with h_0 as indicated by the plot in Fig. 14. The acidity data, reported in

Table VII was obtained by a comparative method using *p*-nitrodiphenylamine and 4-chloro-2-nitroaniline as indicators. (The *pK*_a's of these indicators were assumed to be -2.48 and -1.03 respectively (91).) This observed linearity with *h*_o is in accord with the rate law observed for the oxidation of isopropyl alcohol (34) and benzaldehyde (12) in acetic acid.

$$v = K [R_2CHOH] [HCrO_4^-] h_o$$

The "rho" value observed for the oxidation of the aryltrifluoromethylcarbinols is also identical with the value observed for the corresponding oxidation of arylmethylcarbinols in acetic acid (27). Hence it is probable that the trifluoromethyl alcohols are oxidized via a reaction path similar to the one followed by their hydrocarbon analogs.

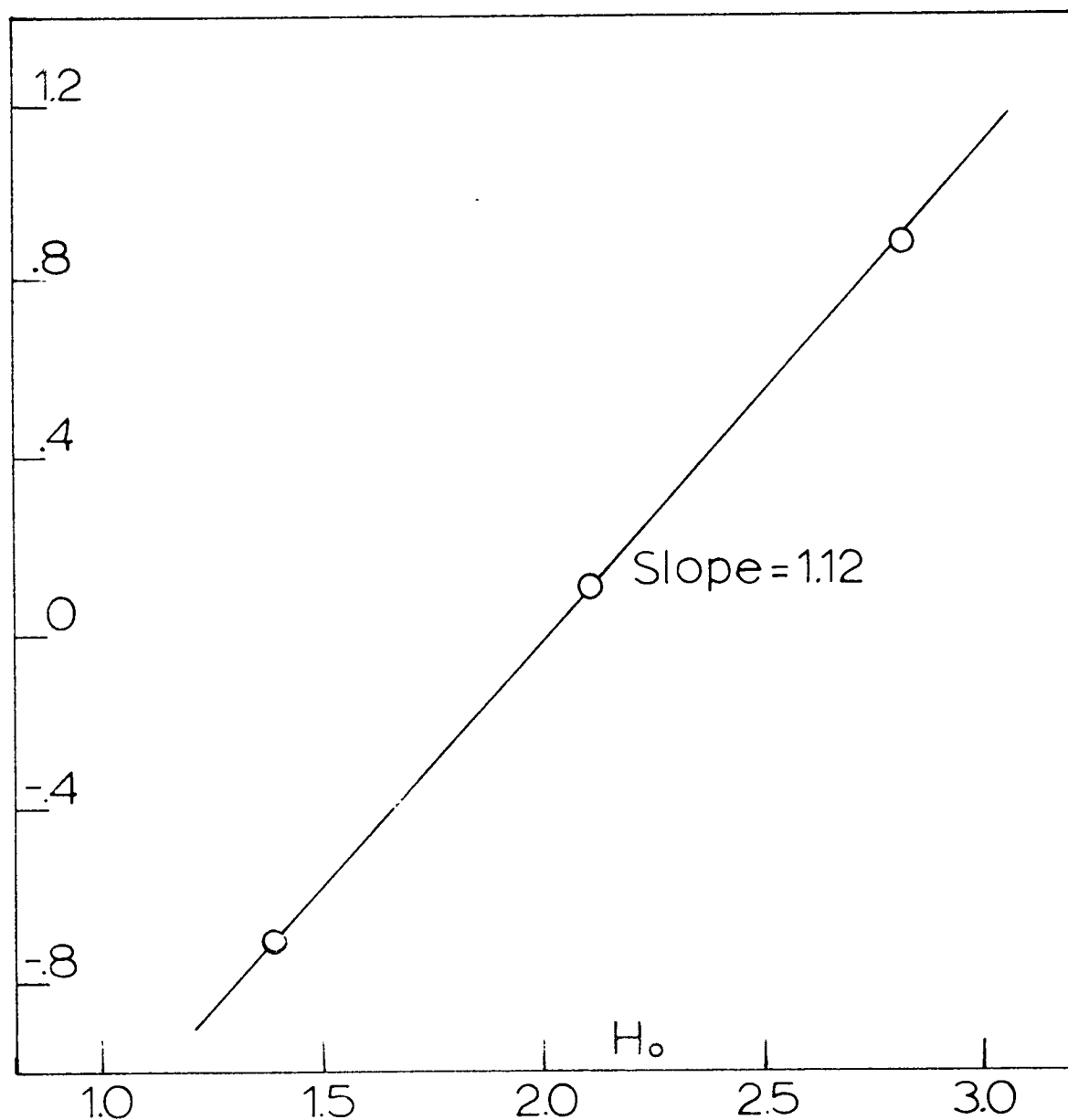


Fig.14 Linear relationship between rate and acidity for the oxidation of phenyl-trifluoromethylcarbinol in 77.2% acetic acid.

TABLE VII
 VARIATION IN RATE OF OXIDATION OF
 PHENYLTRIFLUOROMETHYLCARBINOL IN 77.2%
 ACETIC ACID WITH H₂O

No	$\frac{\text{HClO}_4}{(\text{M})}$	H ₂ O	k ₂
82	3.20	-2.82	.259
89	"	"	.250
41	"	"	.258
155	2.47	-2.12	.0433
159	"	"	.0440
156	1.83	-1.40	.0059
157	"	"	.0066

2. OXIDATION OF SOME HALOGENATED 2-PROPANOLS IN 50.1% SULFURIC ACID

The oxidation of isopropyl alcohol by chromic acid in sulfuric acid medium bears a resemblance to the corresponding reaction in acetic acid solutions in so far as the same rate law is obtained and an isotope effect of approximately the same magnitude is observed (34, 37). (One notable difference is the slower rate of oxidation in sulfuric acid media of the same acidity.)

It was of interest, therefore, to determine the rates of oxidation and the isotope effects for some of the fluorinated alcohols in sulfuric acid media. A solution of 50.1% H_2SO_4 by weight was chosen because this was the highest acidity at which the isotope effect for the oxidation of isopropyl alcohol could be accurately determined. A preliminary investigation indicated, however, that a study of the oxidation of aryltrifluoromethylcarbinols in sulfuric acid solutions was not feasible because of the low solubility of these alcohols in aqueous acidic media. The halogenated-2-propanols, on the other hand possessed suitable solubility characteristics and the rates of oxidation of seven such alcohols were determined. In addition the deuterium isotope effects were determined for five of these compounds.

It was expected, in analogy with the results obtained in 77.2% acetic acid, that the isotope effects in sulfuric acid would increase as the rate of oxidation decreased. However, as the results in Table VIII indicate, the isotope effect for 1,3-dichloro-2-propanol and 1,3-difluoro-2-propanol were even lower than the effect observed for 2-propanol. The reason for the lower isotope effects observed for these two compounds may, however, be due to the

occurrence of a small amount of halogen hydrolysis in sulfuric acid media. The hydrolysis product, a primary alcohol, would be oxidized immediately under these conditions with no isotope effect. This would lead to the observation of an isotope effect somewhat diminished in magnitude. Hydrolysis was probably not observed in 77.2% acetic acid solutions since the rate of oxidation was much faster in that medium and a slow rate of hydrolysis would not have an observable effect on the results.

In any event it is apparent that carbon-hydrogen bond fission constitutes the rate-determining step for the chromic acid oxidation of all alcohols studied in both 77.2% acetic acid and in 50.1% sulfuric acid solutions. A Taft σ^* - ρ^* plot shown in Fig. 15 gives a ρ^* value of -0.94 for the reactions in 50.1% sulfuric acid. This is comparable in magnitude with the value of -1.01 obtained for ρ^+ in 77.2% acetic acid and indicates that the reaction paths are probably similar, at least in some respects, in both media. Results which will be presented in part IV of this section indicate that the heats and entropies of activation for the oxidation of 1,1,1-trifluoro-2-propanol are almost identical in both sulfuric and acetic acid media. This also lends weight to the idea that the

TABLE VIII

RATES OF OXIDATION OF SUBSTITUTED 2-PROPANOLS IN 50.1%

SULFURIC ACID, $[\text{Cr}^{\text{VI}}] = 1.03 \times 10^{-3} \text{ M}$, $T = 25^\circ\text{C}$

Alcohol	No.	$[\text{Alc.}]$ ($\text{M} \times 10^2$)	k_1 ($\text{sec}^{-1} \times 10^3$)	k_2 ($1 \text{ moles}^{-1} \text{ sec}^{-1}$)	$k_{\text{H}}/k_{\text{D}}$
Isopropyl alcohol	393	1.31	55.2	4.21	
	394	"	55.8	4.26	
	395	"	53.1	4.06	
Isopropyl alcohol-2-d	486	3.43	23.4	0.683	6.44
	487	2.14	14.4	0.673	
	488	1.29	8.09	0.626	
1-Chloro-2- propanol	482	1.19	7.59	0.636	
	483	1.87	11.6	0.620	
	485	3.30	20.4	0.619	
1-Fluoro-2- propanol	542	2.60	9.65	0.371	
	543	1.30	5.05	0.388	
	544	2.17	8.46	0.390	
1-Fluoro-2- propanol-2-d	545	2.14	1.05	0.0491	7.56
	546	1.29	0.676	0.0524	
1,3-Dichloro- 2-propanol	491	1.76	0.925	0.0525	
	489	1.41	0.719	0.0510	
	490	1.06	0.580	0.0545	

1,3-Dichloro-2-propanol-2-d	496	3.43	0.306	0.00893	5.85
	497	1.75	0.161	0.00920	
1-Chloro-3-Fluoro-2-propanol	504	1.93	0.800	0.0414	
	505	1.15	0.439	0.0382	
1,3-Difluoro-2-propanol	478	1.29	0.256	0.0198	
	479	2.13	0.411	0.0193	
	480	4.30	0.839	0.0195	
1,3-Difluoro-2-propanol-2-d	510	2.14	0.0599	0.00280	6.92
	511	4.28	0.122	0.00285	
1,1,1-Trifluoro-2-propanol	465	3.74	0.0436	0.00116	
	494	3.72	0.0421	0.00113	
	495	7.44	0.0907	0.00122	
1,1,1-Trifluoro-2-propanol-2-d	469	7.74	0.00865	0.000112	10.54
	485	3.69	0.00370	9.000110	

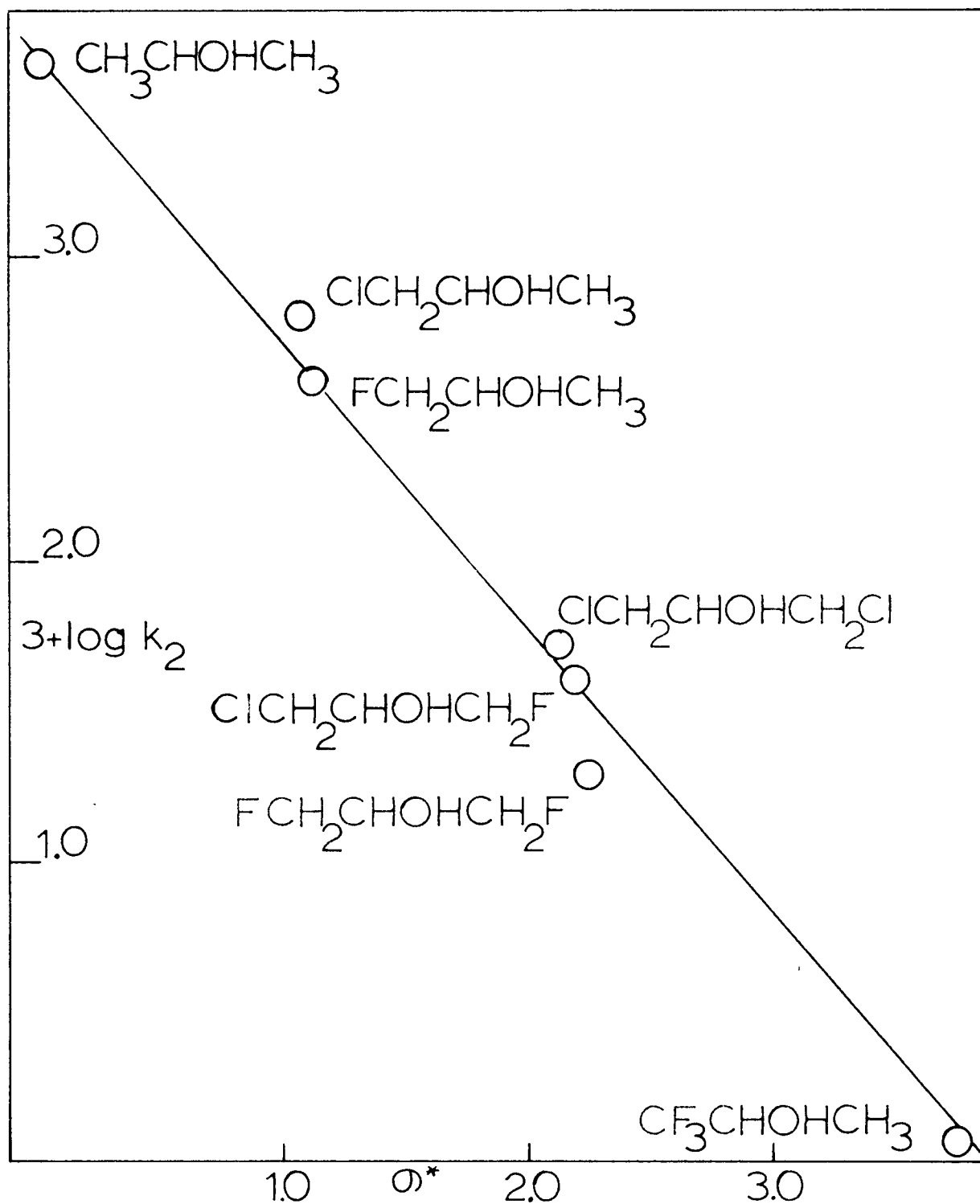


Fig.15 Taft ρ^*-e^* plot for the oxidation of substituted 2-propanols in 50.1% H_2SO_4 .

reaction mechanisms are similar but not identical in both media. A complete explanation for the marked increase of rate in acetic acid solutions remains unobtainable at the present time.

3. VARIATION IN THE MAGNITUDE OF ISOTOPE EFFECTS WITH CHANGES IN ACIDITY

The magnitude of the isotope effect was found to correlate with changes in rates of oxidation caused by introduction of substituents into the structure of the alcohol. It therefore seemed possible that changes in the magnitude of the isotope effect might also be observed when the rate of reaction was varied by changing the acidity of the medium. Hence the relative rates of oxidation of 2-propanol and 2-propanol-2-d were determined in perchloric acid solutions of varying concentrations. The results, which are presented in Table IX indicate that within experimental error no change in isotope effect is observed when the rate of the reaction is changed by alterations in the acidity of the medium. (in dilute HClO_4).

From these results it would seem that the introduction of substituents into the substrate can cause a change in the shape of the potential energy barrier while a change in acidity of the medium does not change the shape of the barrier; it merely in-

TABLE IX
DEUTERIUM ISOTOPE EFFECTS FOR THE
OXIDATION OF ISOPROPYL ALCOHOL IN PERCHLORIC
ACID SOLUTION OF VARYING ACIDITIES
($T = 25^{\circ}\text{C}$, $[\text{Cr}^{\text{VI}}] = 3.4 \times 10^{-3} \text{ M}$)

$[\text{HClO}_4]$ (M)	H_O	k_H ($1 \text{ moles}^{-1} \text{sec}^{-1} \times 10^2$)	k_D	k_H/k_D
0.463	+0.20	.159	0.0259	6.2
0.93	-0.18	.713	0.1037	6.9
2.08	-0.82	5.76	0.943	6.1
2.63	-1.05	14.1	2.25	6.3
3.82	-1.62	65.6	10.4	5.9
4.52	-1.99	171	26.2	6.5

creases the equilibrium concentration of the reacting species.

4. THERMODYNAMIC PARAMETERS

The variation of the reaction rate with temperature can be utilized to obtain the heat and entropy of activation, respectively ΔH^\ddagger and ΔS^\ddagger .

The equation

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

as derived from transition state theory would predict that if $\log k_2/T^\circ K$ was plotted against $1000/T^\circ K$ (over a limited temperature range), the slope of the straight line and the intercept would give respectively ΔH^\ddagger and ΔS^\ddagger (65b).

The rate constants for the oxidation of 1,1,1-trifluoro-2-propanol and isopropyl alcohol under various conditions were determined at several temperatures. As indicated in Fig. 16 plots of $\log k_2/T^\circ K$ against $1000/T^\circ K$ gave good straight lines from which the heat and entropy of activation for each of these reactions was calculated. The values determined for these two thermodynamic parameters are recorded in Table X, while the rates for the reactions at various

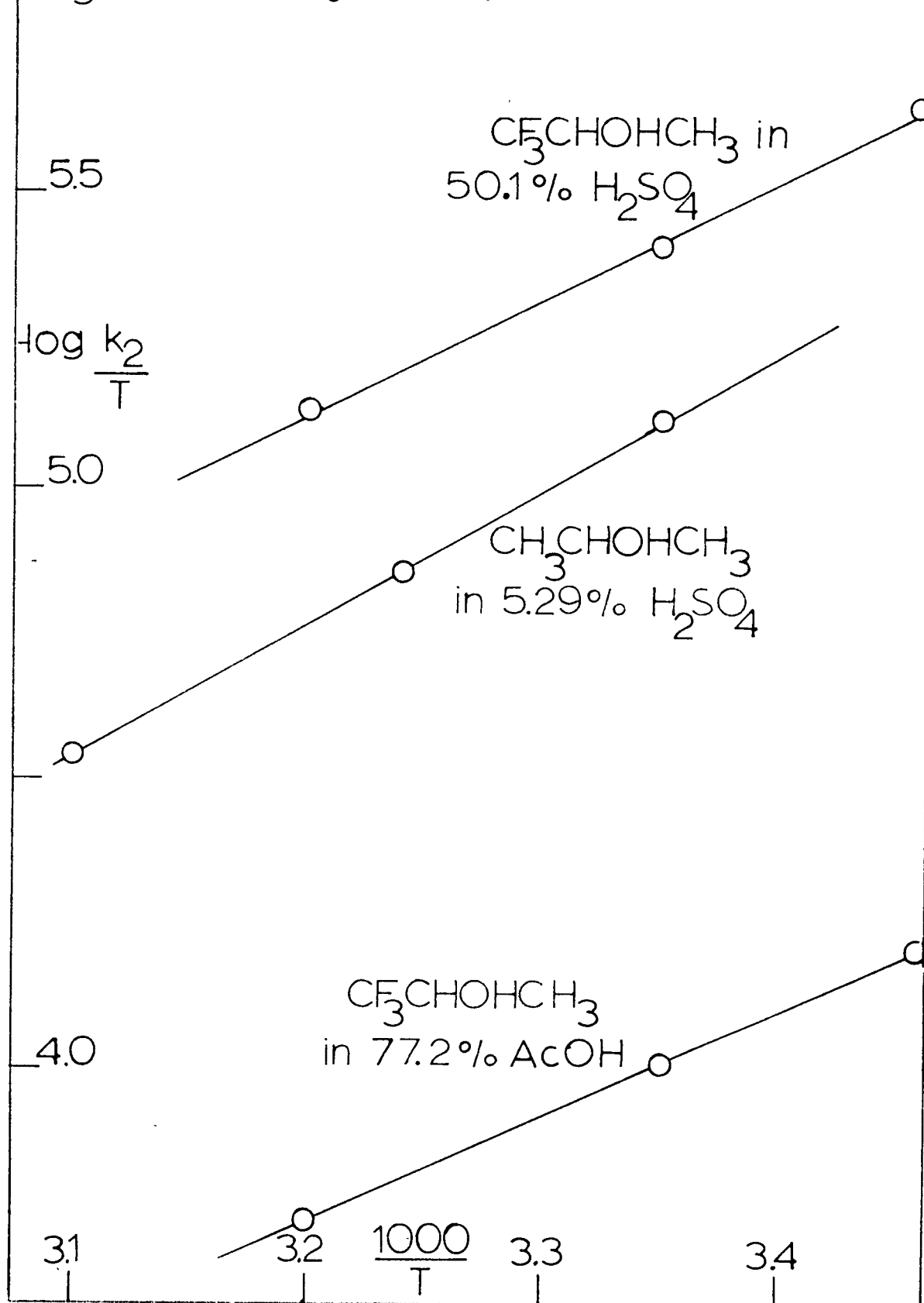
TABLE X
HEATS AND ENTROPIES OF ACTIVATION FOR THE
OXIDATION OF SUBSTITUTED 2-PROPANOLS
UNDER VARIOUS CONDITIONS

Compound	Conditions	$\Delta H^\#$	$\Delta S^\#$
		(kcal/mole)	(cal/mole deg.)
1,1,1-Trifluoro-2-propanol	50.1% H_2SO_4	8.93	-42.0
1,1,1-Trifluoro-2-propanol	77.2% Acetic Acid	8.15	-38.1
	3.20 M $HClO_4$		
Isopropyl alcohol	5.29% H_2SO_4	10.38	-35.7

TABLE XI
RATES USED IN CALCULATION OF
THERMODYNAMIC PARAMETERS

	No.	T(°C)	$[Cr^{VI}]$ ($M \times 10^3$)	$[alc.]$ ($M \times 10^2$)	k_1 ($sec^{-1} \times 10^3$)	k_2 ($l \text{ moles}^{-1} sec^{-1}$)
Isopropyl alcohol in 5.29% H_2SO_4	344	50.0	3.40	42.1	3.94	0.00935
	349	35.8	3.90	42.1	1.84	0.00437
	334	25.0	4.10	12.9	0.296	0.00230
1,1,1-Trifluoro- 2-propanol in 50.1% H_2SO_4	537	16.4	1.03	3.73	0.0248	0.000667
	465	25.0	"	3.74	0.0436	0.00116
	494	"	"	3.72	0.0421	0.00113
	495	"	"	7.44	0.0907	0.00122
	536	39.5	"	3.72	0.0874	0.00232
1,1,1-Trifluoro- 2-propanol in 77.2% Acetic Acid, 3.20 M $HClO_4$	186	16.4	1.37	3.72	.677	0.0182
	181	25.0	"	2.60	.760	0.0292
	182	"	"	3.72	1.12	0.0302
	184	39.5	"	3.72	2.12	0.0570

Fig.16 Thermodynamic parameters.



temperatures are given in Table XI.

While it is possible to explain the large negative entropy of activation observed for these reactions in a number of ways it is certainly consistent with the cyclic transition state that has been postulated for these reactions. It is also of interest to note that the thermodynamic parameters for chromic acid oxidations in acid medium are very similar to those reported for acid permanganate oxidations in sulfuric acid media (72).

5. OXIDATIONS IN CONCENTRATED SULFURIC ACID SOLUTIONS

It is known that the rate of oxidation of many organic compounds by chromic acid in sulfuric acid media is maximal in solutions containing 60-75% H_2SO_4 by weight (21, 30, 31). Pungor and Trompler (30) claim that an explanation for this maximal rate of oxidation of methanol, ethanol and formic acid in 73% H_2SO_4 may lie in a consideration of the stability of chromium IV in various solutions of sulfuric acid. Roček and Krupička on the other hand have suggested that the rate versus acidity plot for the oxidation of isopropyl alcohol may change from a slope of about unity to one of zero at about 55% H_2SO_4 due to a protonation of the alcohol at this point. The former explanation requires that rates of oxidation of all

compounds be maximal at the same point, while the latter demands that the point of slope change vary with the pK_{BH^+} of the compounds.

Roček has also reported that the rates of oxidation of several carboxylic acids in acetic acid-sulfuric acid mixtures show a break in the rate versus acidity plot at an H_0 of about -3.6 (20). This is only 0.3 units less than the H_0 of 55% sulfuric acid. He has also presented results which he claims indicates that the hydrocarbon n-heptane does not show a rate maximal at this point. However the experimental evidence presented for this compound is very weak and could be interpreted either way. While it is not probable that compounds of as widely different structures as 2-propanol and p-toluic acid would have similar pK_{BH^+} 's, it is possible since they are both oxygenated hydrocarbons.

Another possible explanation, suggested by Roček for the occurrence of this break in the rate versus acidity plot, involves the protonation of chromic acid at this point. While this possibility was rejected on the basis of the aforementioned results obtained for the oxidation of n-heptane, a spectroscopic study conducted in the present investigation showed that there was indeed a change in the nature

of the chromium species at an H_0 of about -6.4 . Fig. 17 shows a plot of the extinction coefficients of chromium VI at various wave lengths against the acidity of a series of sulfuric acid solutions. The plot shows a well defined sigmoidal curve with a mid-point at $H_0 = +0.3$. This has previously been ascribed to an equilibrium of the type $HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4$ (80). Another change in the spectra is also observed at about $H_0 = -6.4$. This change is not as pronounced since still another change appears at only a slightly higher acidity. One possible explanation may be that protonation of H_2CrO_4 is followed at only slightly higher acidities by a sulphonation step. The visible and ultraviolet spectra of chromium VI in sulfuric acid solutions of various strengths is shown in Fig. 18.

Further, Roček's suggestion that the observed crest in the rate-acidity plot was due to protonation of the organic substrate required that the pK_{BH}^+ of *p*-toluic acid be shifted from -6.92 in sulfuric acid-water media to about -3.8 in sulfuric acid-acetic acid media. Such a shift seems entirely unlikely and an attempt was made to determine the pK_{BH}^+ of *p*-toluic acid in acetic acid-sulfuric acid media using the acidity function developed by Roček. Such an investi-

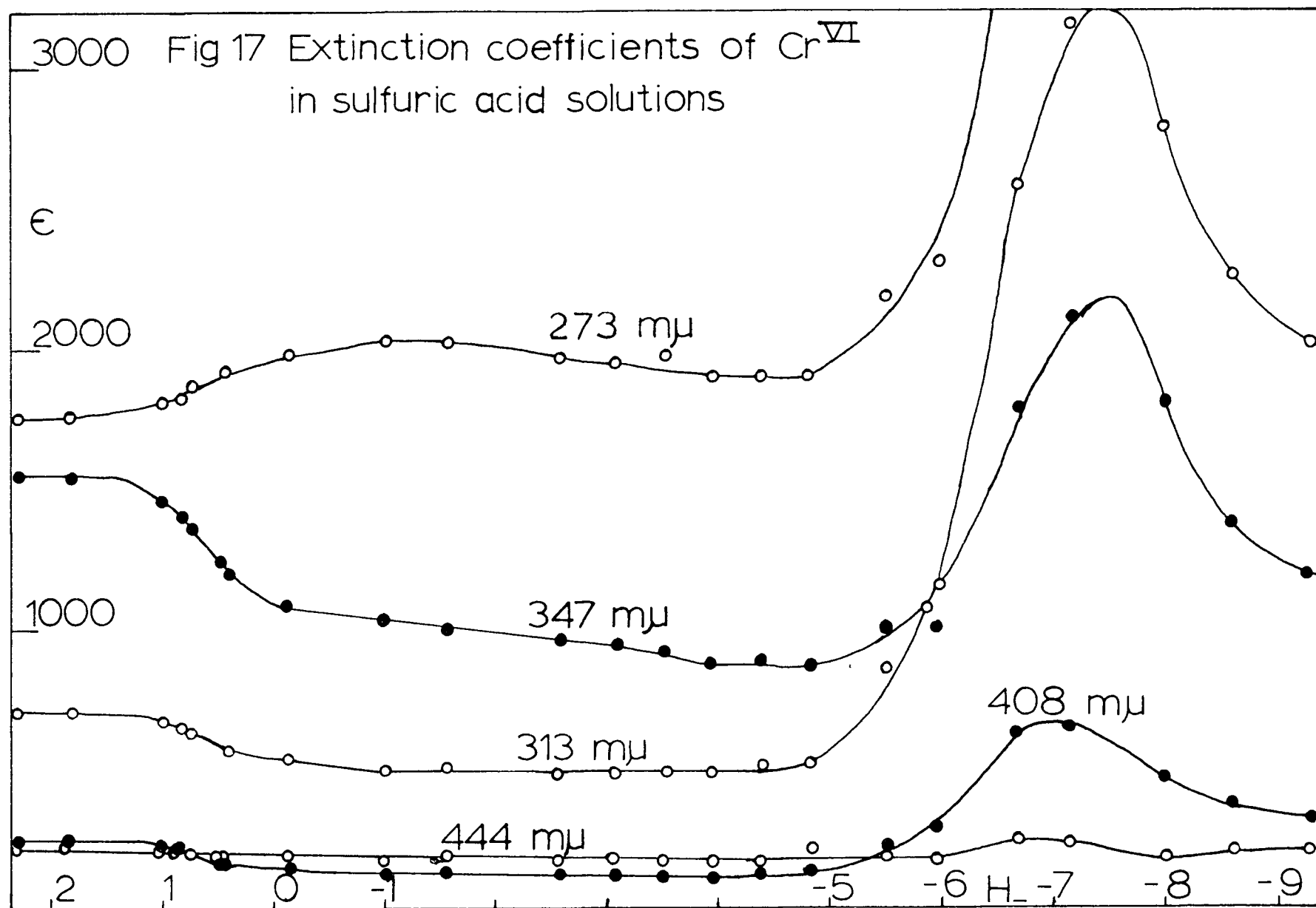
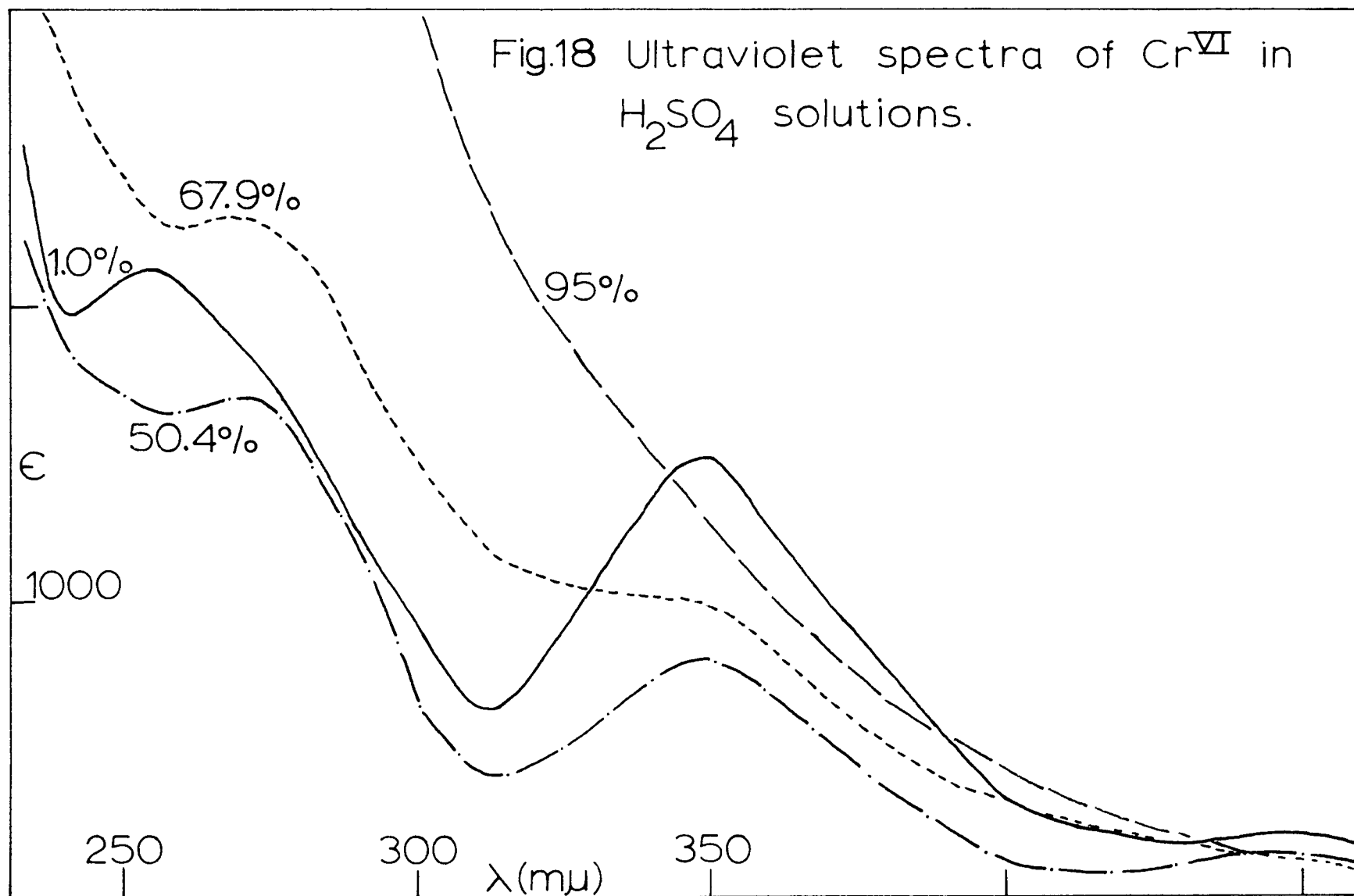


TABLE XII
EXTINCTION COEFFICIENTS OF Cr^{VI} IN
SULFURIC ACID SOLUTIONS

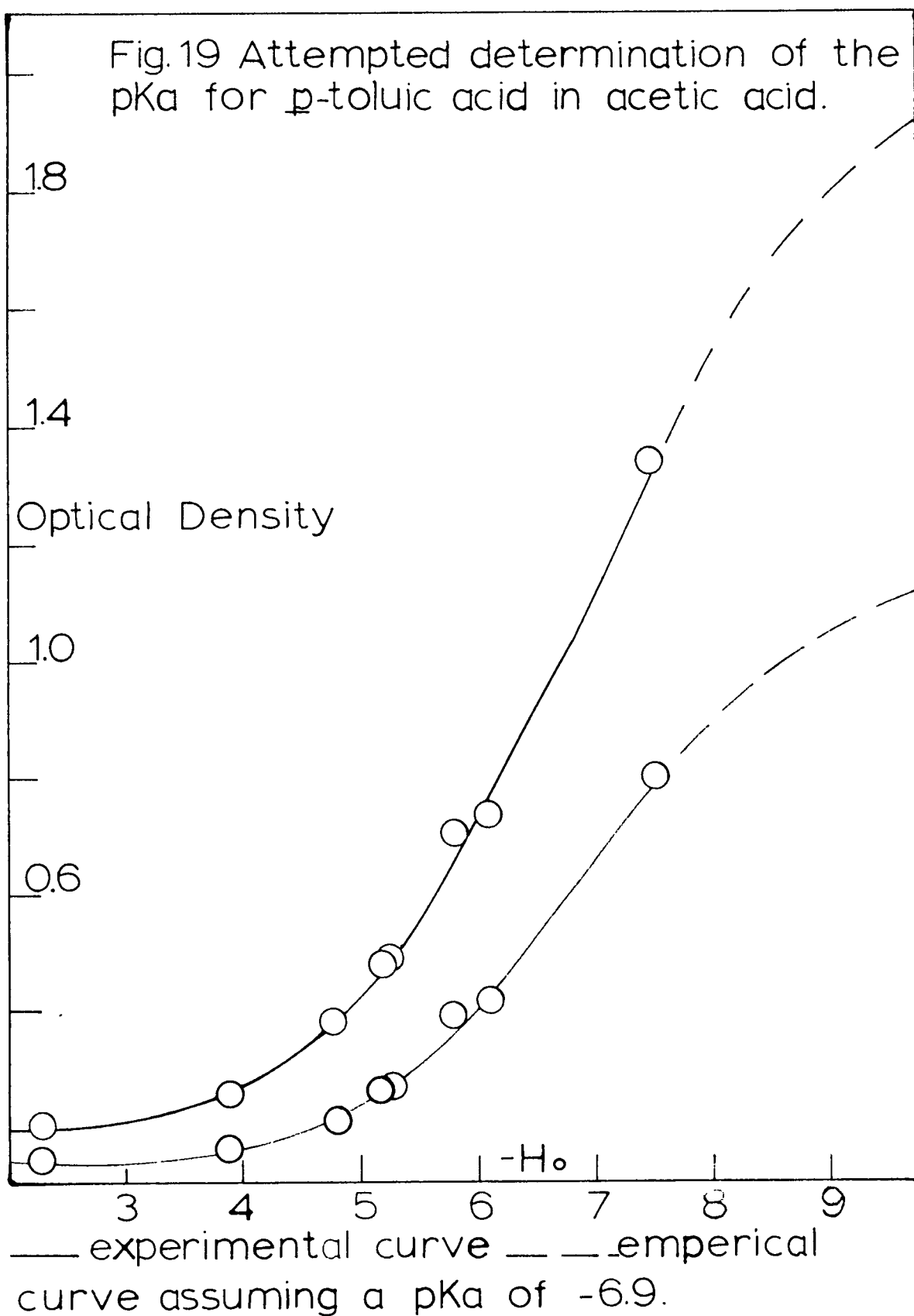
$\% \text{H}_2\text{SO}_4$	H-	ϵ_{445}	ϵ_{408}	ϵ_{313}	ϵ_{347}	ϵ_{273}
	2.95	220	260	709	1540	1750
	2.66	214	257	704	1550	1750
	1.81	213	253	702	1550	1760
1.0	1.00	209	236	671	1460	1810
1.75	0.82	205	226	650	1410	1830
2.40	0.74	199	208	627	1370	1870
4.80	0.44	193	173	581	1250	1920
5.29	0.40	193	173	573	1210	1930
10.6	-0.14	194	155	538	1090	1990
20.2	-1.02	168	129	496	1020	2030
25.8	-1.56	192	140	510	1000	2030
36.4	-2.58	174	118	481	961	1970
41.4	-3.08	178	121	477	938	1960
46.2	-3.54	173	122	491	922	1980
50.4	-3.96	168	118	477	879	1900
54.4	-4.39	173	130	507	890	1900
59.4	-4.84	218	140	521	867	1900
64.6	-5.52	183	229	858	998	2180
67.9	-5.96	180	292	1160	1010	2310
74.0	-6.68	254	613	2580	1790	4380
78.8	-7.16	241	662	3160	2110	5170
84.0	(-8.00)	192	482	2790	1820	5550
88.5	(-8.60)	216	391	2260	1380	4830
95.0	(-9.40)	206	320	2000	1190	4670



gation was a rather difficult undertaking since the ultraviolet peaks usually used for such determinations were obscured because of absorption by the acetic acid medium. However, the spectral shifts were followed at two wavelengths and as the plot in Fig. 19 indicates it is quite probable that the pK_{BH^+} does not shift appreciably in acetic acid-sulfuric acid media.

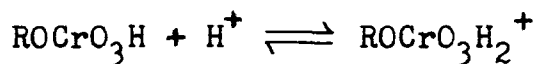
In a final attempt to resolve this problem it was decided to study the rates of oxidation of three alcohols, 2-propanol, 1,1,1-trifluoro-2-propanol and 1,1,1,3,3,3-hexafluoro-2-propanol in solutions of varying sulfuric acid concentrations. While the pK_{BH^+} values for these alcohols are not known it is to be expected that they will vary greatly since it has been found by Haszeldine (97) that the pK_a values for these alcohols vary by factors of greater than four units. The fact that it has recently been found that a good correlation exists between the pK_a and the pK_{BH^+} values of many organic compounds lends weight to this suggestion (98).

A rate-acidity plot for these alcohols is shown in Fig. 20. (The results obtained by Roček (31) from a polarographic investigation of the rates of oxidation of 2-propanol in sulfuric acid solutions of varying strengths are included as closed circles for comparison purposes.) It can be seen that the plots for the



different alcohols do indeed crest at different acidities. However, the distance from crest to crest is not nearly as great as was predicted from the pK_a values of these compounds.

In light of all the results obtained it would seem that the best explanation for the observed crest in the rate versus acidity plots might lie in the prediction of a chromate ester protonation step. The pK_{BH^+} of these esters would be close to that of free chromic acid and it would not vary greatly with changes in the structure of the organic substrate.



Such a suggestion is readily compatible with the previously proposed cyclic mechanism for this reaction. Thus the rate law in 5-70% sulfuric acid is

$$v = k [\text{alcohol}] [H_2CrO_4] h_o$$

indicating that the gross composition of the transition state must include one molecule of alcohol, one molecule of chromic acid and a proton. If it is assumed that a chromate ester is the intermediate, then the species participating in the rate-determining step

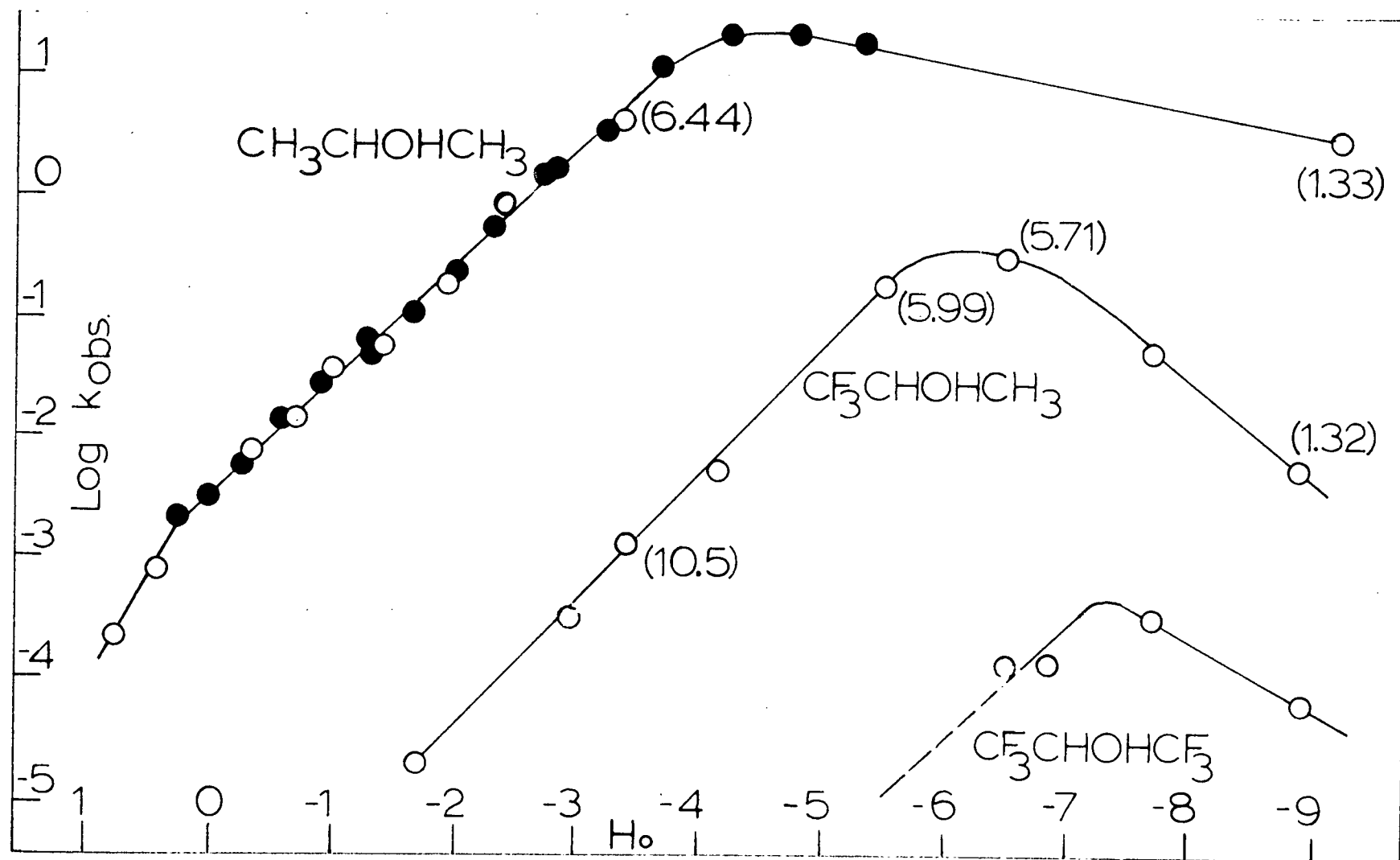


Fig.20 Relationship between H_0 and the rate of oxidation of three 2-propanols in sulphuric acid solutions. Primary deuterium isotope effects indicated in parenthesis.

TABLE XIII
 OXIDATION OF $\text{CF}_3\text{CROHCH}_3$ BY Cr^{VI} IN SULFURIC
 ACID SOLUTIONS AT 25.0°C

No.	R	% H_2SO_4	$[\text{Cr}^{\text{VI}}]$ ($\times 10^4 \text{M}$)	$[\text{alc.}]$ ($\times 10^3 \text{M}$)	k_1 ($\times 10^5 \text{sec}^{-1}$)	k_2 ($\text{Moles}^{-1} \text{sec}^{-1}$)	$k_{\text{H}}/k_{\text{D}}$
475	H	29.4	10.3	36.5	0.0766	.000021	
474	H	45.7	12.4	22.0	0.738	.000335	
495	H	50.1	10.3	74.4	9.07	.00122	
494	H	50.1	10.3	37.2	4.21	.00113	
465	H	50.1	10.3	37.4	4.36	.00116	
485	D	50.1	10.3	36.9	0.370	.000110	10.54
469	D	50.1	10.3	78.0	0.865	.000112	
473	H	57.6	10.3	11.0	5.68	.00515	
471	H	63.6	6.18	22.8	141.0	.0619	
461	H	68.5	6.18	34.4	671.0	.195	
462	H	68.5	6.18	10.8	136.0	.126	
463	H	68.5	6.18	23.2	422.0	.182	
466	D	68.5	6.18	33.5	91.0	.0281	5.99
467	H	76.4	6.18	36.2	1060	.293	
468	D	76.4	6.18	38.3	198.0	.0516	5.71
472	H	85.7	6.18	22.4	116.0	.0518	
455	H	95.3	6.15	17.5	11.1	.00635	
457	H	95.3	6.15	18.2	9.40	.00515	
458	D	95.3	6.15	70.9	38.3	.00540	1.32
459	D	95.3	6.15	37.7	12.5	.00332	

TABLE XIV
OXIDATION OF $\text{CH}_3\text{CROHCH}_3$ IN SULFURIC ACID
SOLUTIONS AT 25°C

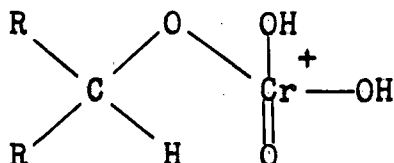
No.	R	% H_2SO_4	$[\text{Cr}^{\text{VI}}]$ ($\times 10^3 \text{M}$)	[alc.] (M)	k_1 ($\times 10^3 \text{sec}^{-1}$)	k_2 ($1 \text{ moles}^{-1} \text{sec}^{-1}$)	$k_{\text{H}}/k_{\text{D}}$
334	H	5.29	4.10	0.129	0.296	0.0023	
338	H	10.6	4.23	0.129	0.821	0.00636	
333	H	16.0	4.13	0.129	1.87	0.0145	
339	H	20.2	4.13	0.129	3.37	0.0261	
332	H	25.8	4.10	0.129	7.66	0.0595	
379	H	33.4	3.42	0.0409	7.35	0.179	
393	H	50.1	1.03	0.0131	55.2	4.21	
394	H	50.1	1.03	0.0131	55.8	4.26	
395	H	50.1	1.03	0.0131	53.1	4.06	
486	D	50.1	1.03	0.0343	23.4	0.683	6.27
487	D	50.1	1.03	0.0214	14.4	0.673	
488	D	50.1	1.03	0.0103	8.09	0.626	
426	H	97.3	0.0515	0.00964	0.0230	2.39	
428	H	97.3	0.0515	0.01326	0.0380	2.86	
429	H	97.3	0.0515	0.01820	0.0484	2.63	
427	D	97.3	0.0515	0.00888	0.0168	1.89	1.33
430	D	97.3	0.0515	0.0169	0.0345	2.04	

TABLE XV

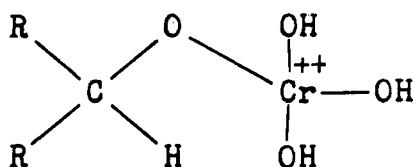
OXIDATION OF 1,1,1,3,3,3-HEXAFLUORO-2-PROPANOL
IN SULFURIC ACID SOLUTIONS AT 25°C

No.	%H ₂ SO ₄	[Cr ^{VI}] (x10 ⁴ M)	[alc.] (x10 ² M)	k ₁ (x10 ⁶ sec ⁻¹)	k ₂ (1 moles ⁻¹ sec ⁻¹)
507	76.4	6.18	3.18	4.46	0.000140
481	79.4	6.18	3.38	4.52	0.000134
493	85.7	4.12	2.96	9.30	0.000314
508	95.3	6.18	3.22	2.02	0.0000628

would be



As long as the reaction was carried out below the pK_{BH^+} of the ester the rate would be first order in h_0 . However at acidities above the pK_{BH^+} the rate would be zero order in h_0 . Further protonation would lead to formation of a diprotonated species,



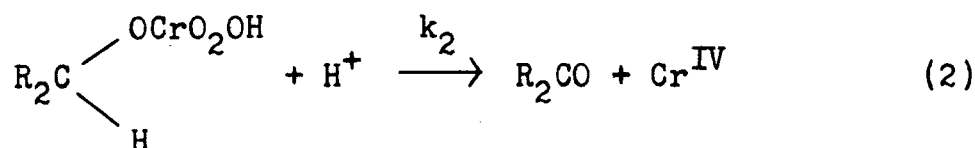
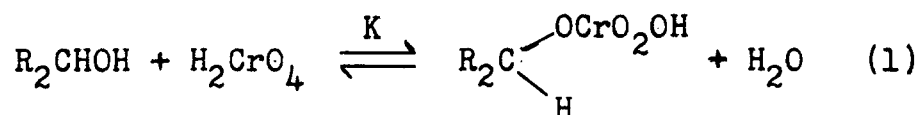
This ion would not contribute to the rate since there are no unprotonated oxygen atoms available for participation in a hydrogen transfer step. Hence one would observe a levelling in the plot of $\log k$ v.s. H_0 at the pK_{BH^+} of the ester. Further, the R groups would be expected to have much less effect on the pK_{BH^+} value of this ester than they would have on the free alcohol. This is in accord with the observation that positions of the change in slope of the plots in Fig. 20 do not differ by as great a magnitude as expected from a consideration of the probable pK_{BH^+} values for the free alcohols.

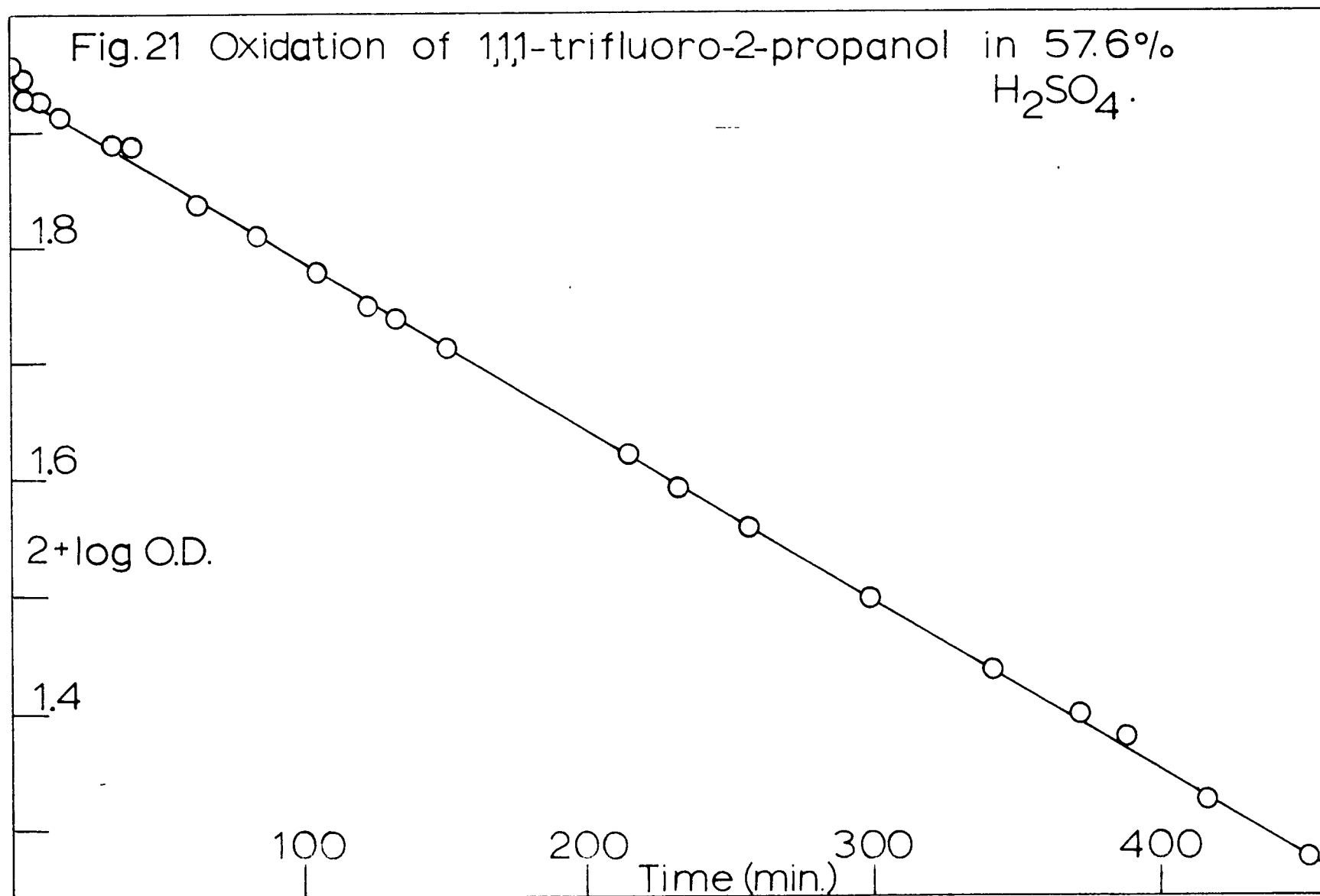
The situation is complicated by the fact that another species of chromium VI appears in about 75% sulfuric acid. Mishra and Symons (99) have suggested that this new species is a disulfate, $\text{CrO}_2(\text{OSO}_3\text{H})_2$. Results which will be presented in section 9 of this thesis indicate that the chromium VI species existing in 20 to 55% H_2SO_4 is a monosulfate, HCrSO_7 . If this species is first protonated, as the curve in Fig. 17 suggests, and then further sulfonated to form a new species in very concentrated acid, the final species would be a protonated disulfate, $\text{HOCr}^+(\text{OSO}_3\text{H})_2$. Also at approximately the same place that the new species of chromium VI is observed to appear the magnitude of the isotope effect obtained in the oxidation of 1,1,1-trifluoro-2-propanol begins to decrease. It is possible, therefore, that this species of chromium VI oxidizes via a different mechanism than H_2CrO_4 does. Or it may be that a different step, such as ester formation, becomes rate-determining. In this connection it is interesting to note that while oxidations in sulfuric acid solutions of less than 63.6% give good straight line plots from the initial point on, above 63.6% sulfuric this is not so as Figures 21 to 26 illustrate. In each of these runs chromium VI of a definite concentration in the various sulfuric acid solutions was first thermostated at 25°C

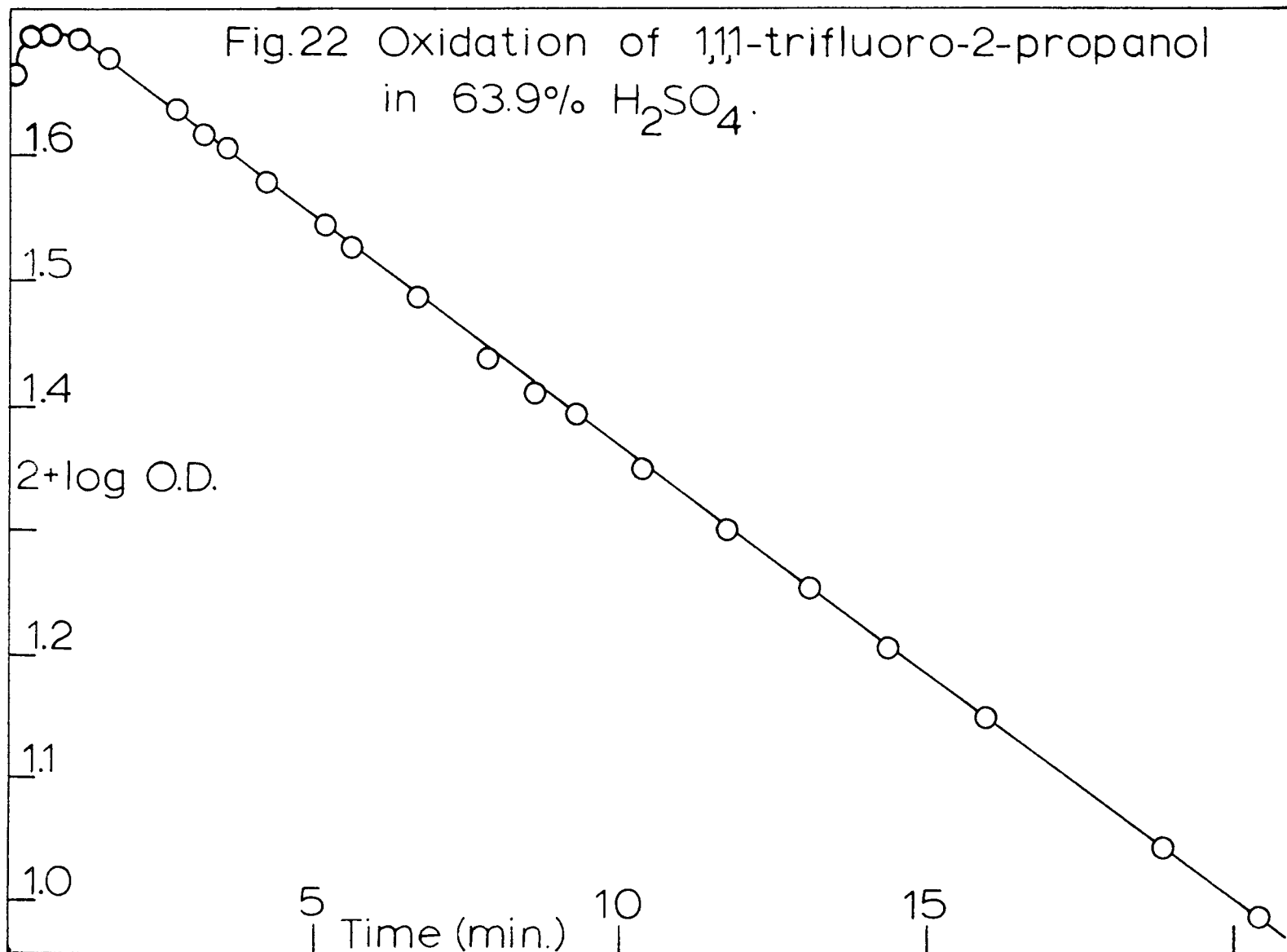
in a 1 cm. cell, alcohol was then added and the optical density at 349 m μ was observed at intervals. It can be seen from the plots that an intermediate (or a species in equilibrium with the intermediate) forms initially and that this entity then decomposes by a first order rate law. In 96.3% sulfuric acid a good straight line from the initial point on is again obtained. Also in 96.3% H_2SO_4 the isotope effect is almost unity. (The difference from unity could be due to a secondary isotope effect.) These two facts taken together seem to indicate that the formation of this intermediate is rate-determining in very concentrated acid. i.e. If the intermediate is an ester, decomposition must occur simultaneously with ester formation.

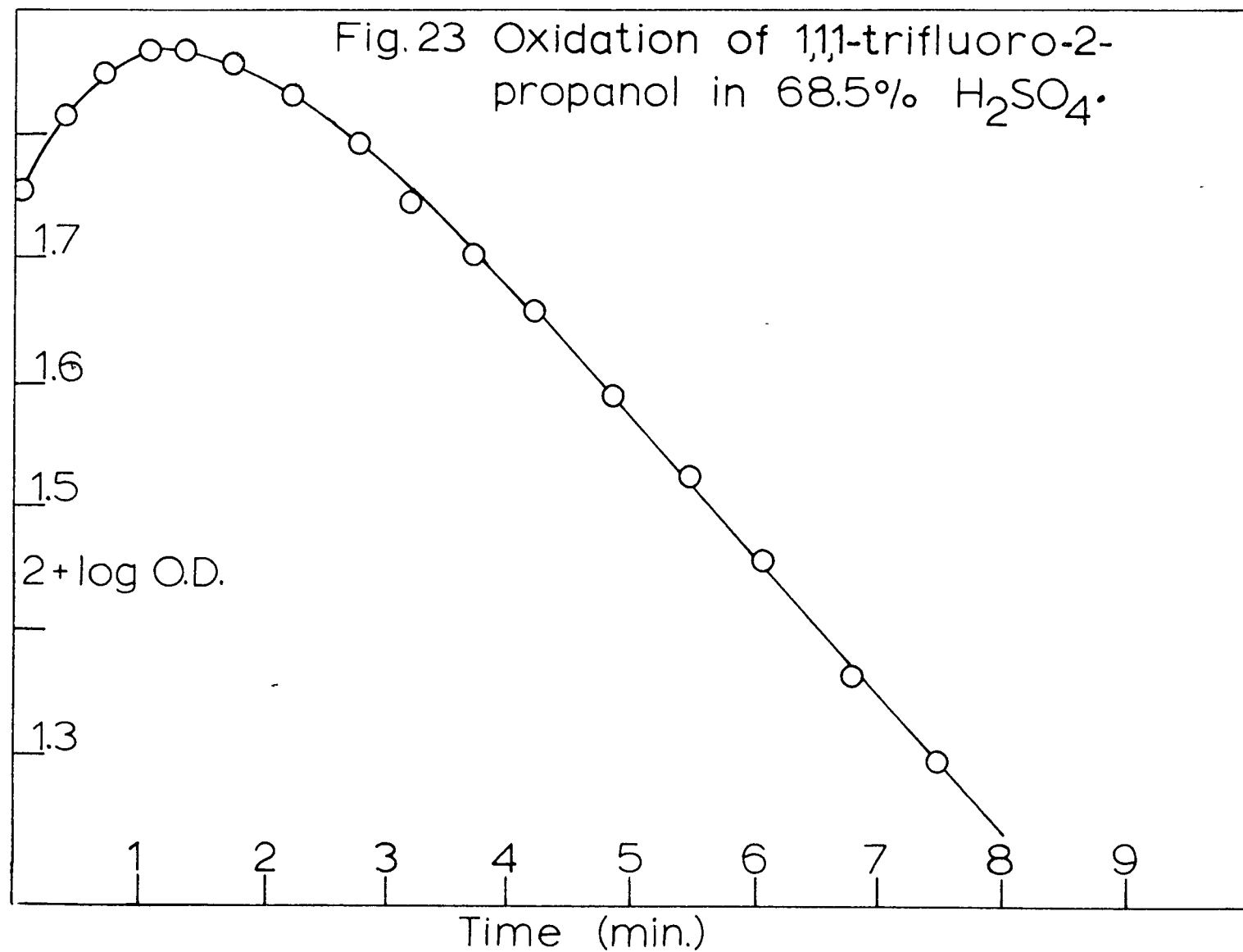
The distinction between the proposed mechanisms in 20 to 60% and in 96% sulfuric acid could then be illustrated as follows.

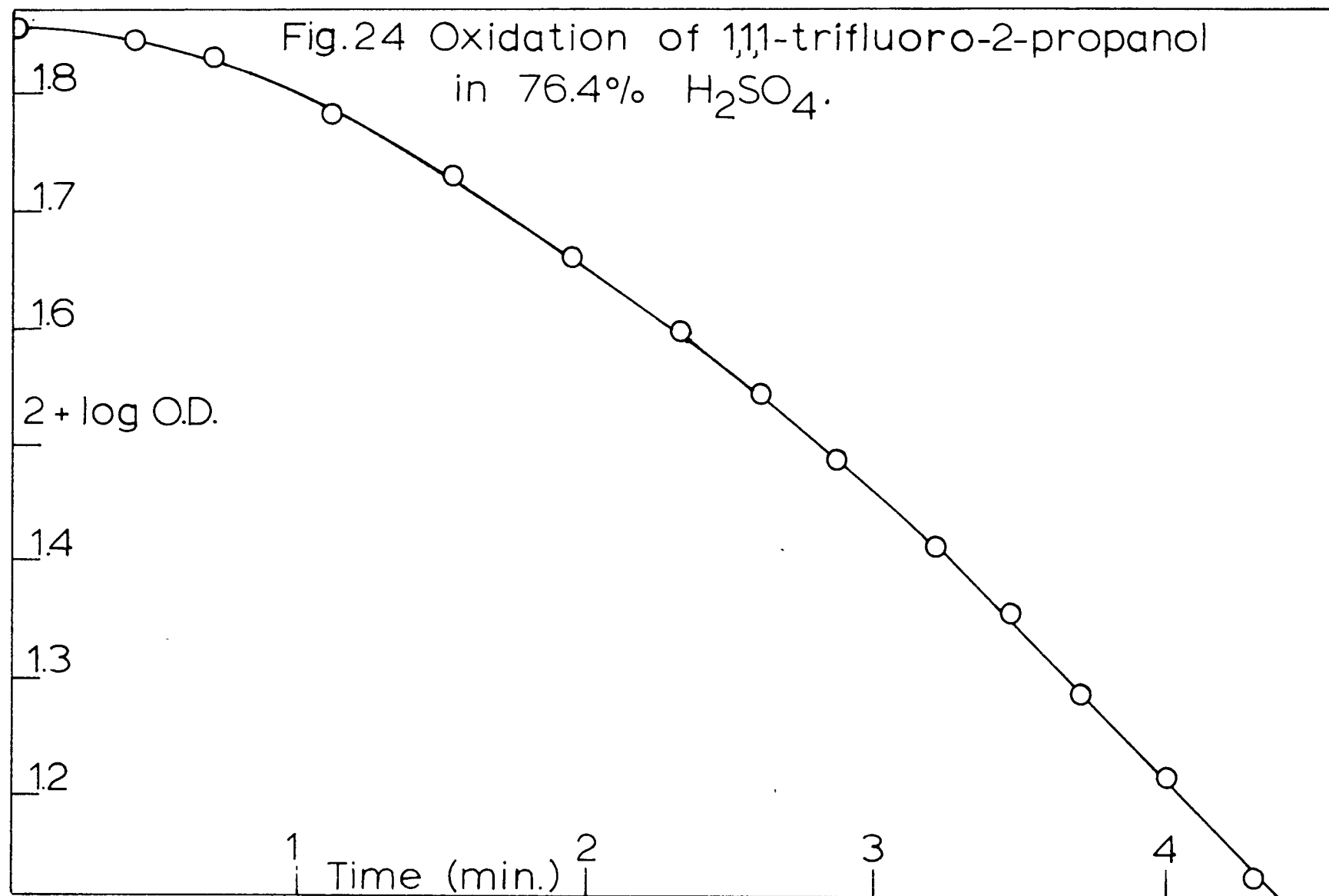
In 20 - 60% H_2SO_4 :

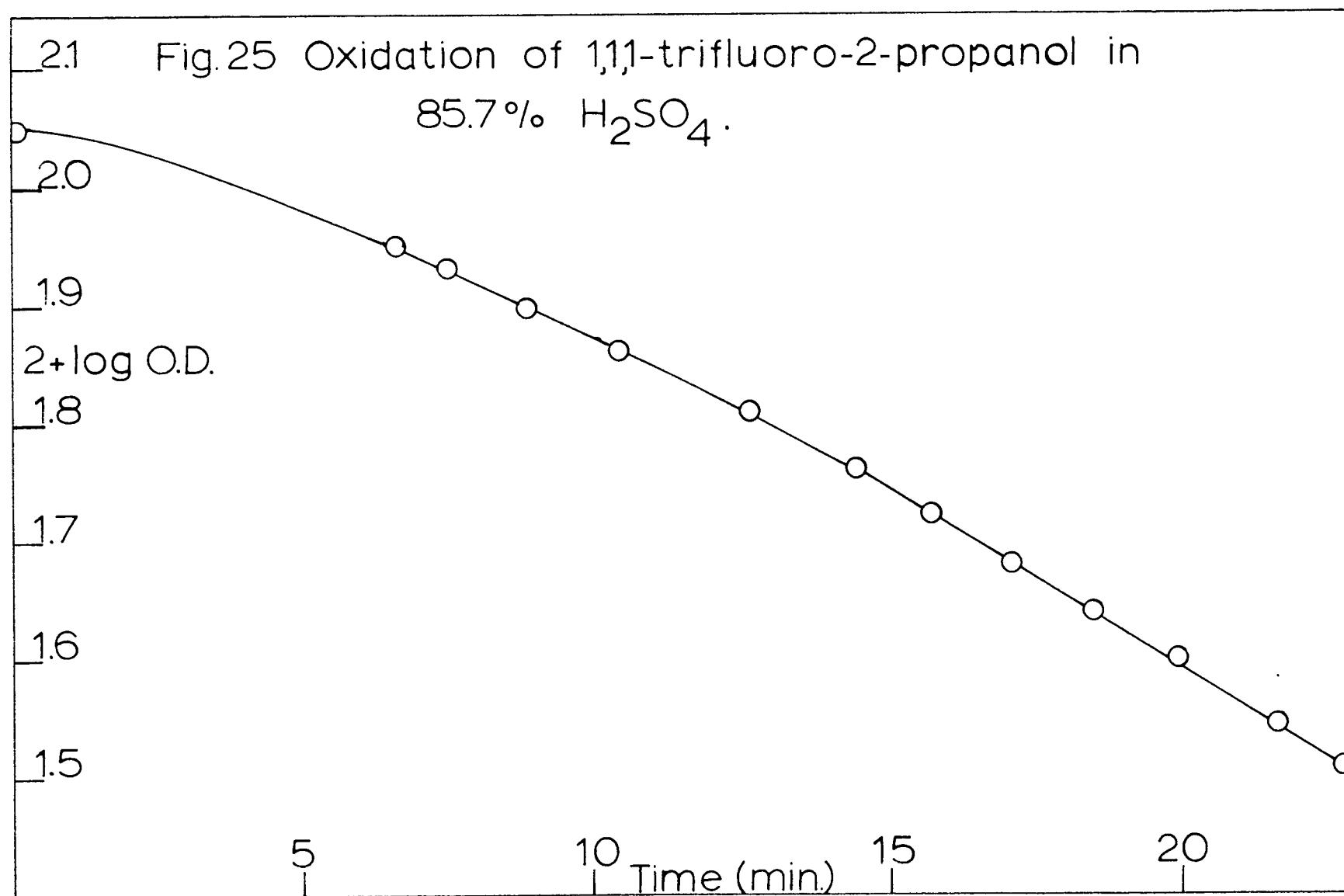


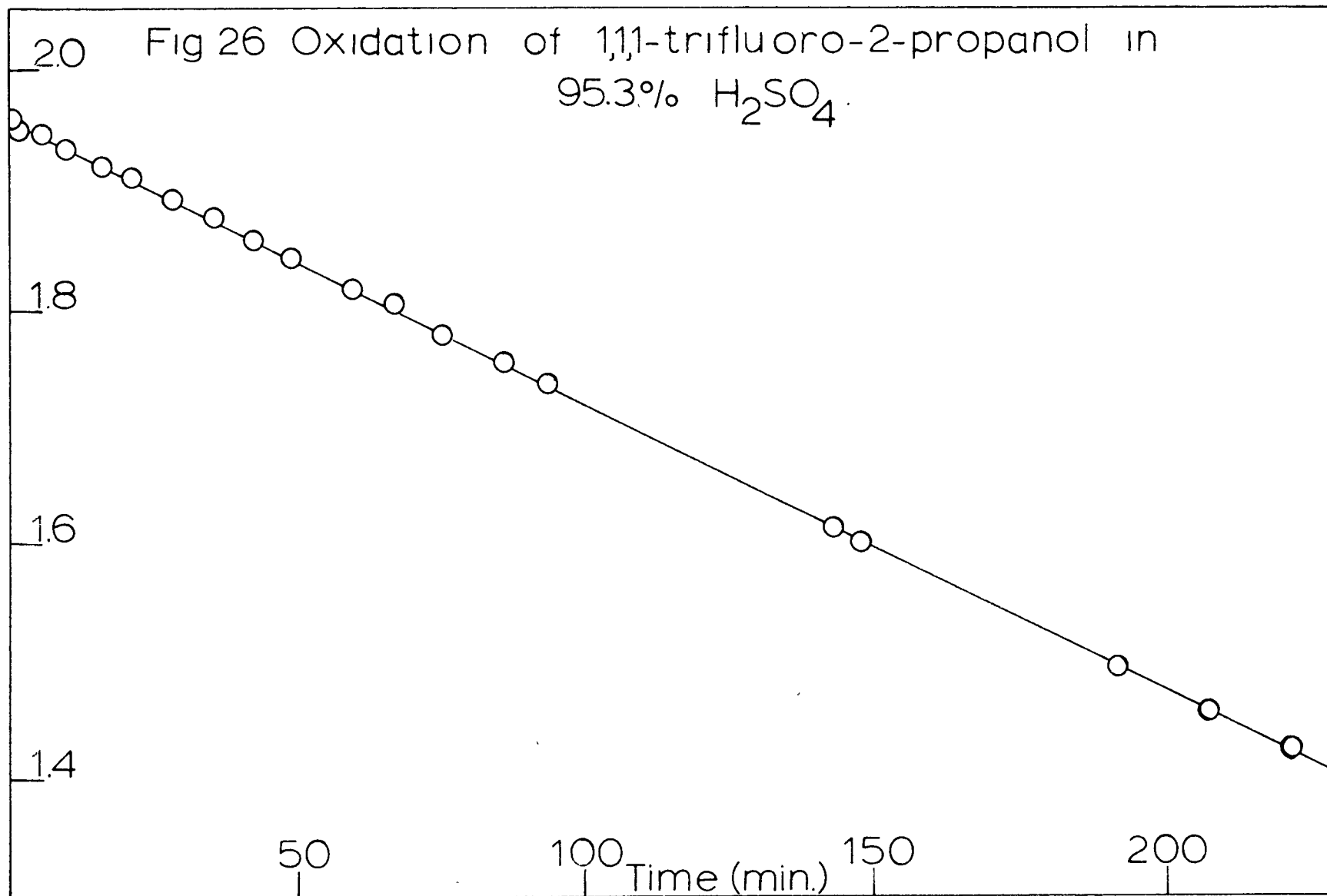






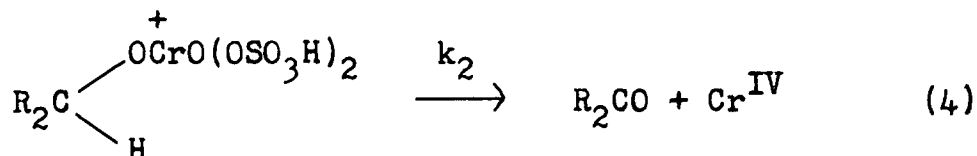
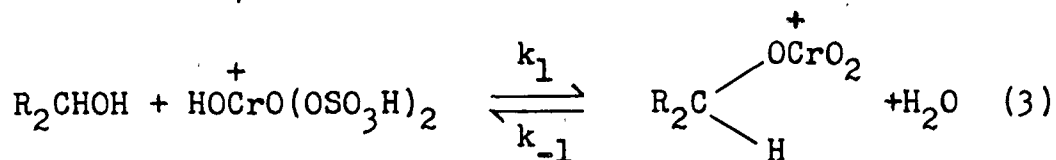






In this case step (1) would be a rapid equilibrium with step (2) being the rate-determining reaction. The rate law would be $V = Kk_2 [R_2CHOH] [H_2CrO_4] h_o$ and the reaction would show a primary deuterium isotope effect. Since the extinction coefficient of the chromate ester is larger than that of chromic acid at 349 m μ (52) the equilibrium concentration of the ester must remain low during the course of the reaction. If the ester concentration did not remain low one would observe a sharp increase in the optical density after introduction of the alcohol into the chromic acid solution and the straight line obtained by plotting $\log [Cr^{VI}]$ against time would not extrapolate back through $\log [Cr^{VI}]_{initial}$ at time zero. This is in accord with the observation made by Kwart and Francis that addition of a tertiary alcohol did not greatly inhibit the rate of oxidation of α -(p-nitrophenyl)-ethanol in acetic acid solutions. If the chromate ester concentration were high much of the total chromium present would have been tied up in the form of an unreactive tertiary ester and a large decrease in the reaction rate would have been observed.

In 96% H_2SO_4 :



In this case step (3) would be a slowly established rate controlling equilibrium, step (4) would be fast and the rate law would be $V = k_1 [\text{R}_2\text{CHOH}] [\text{H}_3\text{CrS}_2\text{O}_{10}^+]$. This mechanism would not lead to a primary deuterium isotope effect when the α -hydrogen atom of the alcohol was substituted with deuterium, but could however, show a secondary deuterium isotope effect associated with the ester forming step. From a consideration of Figures 21 to 26 it is apparent that if this is a correct picture of the mechanism the equilibrium concentration of ester must become greater in very concentrated acid solutions and the rate at which this intermediate is formed must become slower and slower until in 96% H_2SO_4 the rate of decomposition is equal to the rate of ester formation.

6. DETERMINATION OF THE ρ^* VALUE FOR THE CF_3 GROUP

Taft (100) has indicated that the rates of a

wide variety of reactions of aliphatic compounds of the type RY fit with good precision the equation

$$\log k/k_0 = \rho^* e^*$$

where ρ^* is the polar substituent constant for the group R, e^* is a constant giving the susceptibility of a given reaction series to polar substituents, k is the rate constant for the reaction of RY and k_0 is the rate constant for the reaction of CH_3Y . Since it was of some interest in the present investigation to know the value of the polar substituent constant for the CF_3 group, the rates of oxidation of a series of primary alcohols of the type RCH_2OH were determined at 25°C in 3.82 M HClO_4 . (Roček (32) had previously observed that the rates of oxidation of a number of alcohols of this type in 1.0 M HClO_4 at 20°C could be fitted to Taft's equation.)

The results obtained in the present work for the oxidation of *n*-propanol, ethanol, methanol, 2-methoxyethanol, 2-chloroethanol, 2,2,2-trifluoroethanol and isopropyl alcohol are listed in Table XVI. A plot of the log of the rate constant against ρ^* values for the first five alcohols mentioned was then made and the best straight line was extrapolated to $\log k$ for 2,2,2-trifluoroethanol. As the plot in

Figure 27 shows this procedure gives a σ^* value for the CF_3 group of about +3.9. It is of interest to note that a good correlation with the oxidation rates of substituted 2-propanols in 50.1% sulfuric acid is also observed when this value for the CF_3 group is used (See Figure 15).

Figure 27 indicates that the oxidation of methanol is anomalously slow (or that the σ^* value for the H substituent is too low). This has also been observed by Roček in his work (32). He has suggested that this anomaly may be due to the fact that it is a methyl group which is oxidized in methanol while in the other primary alcohols a methylene group forms the point of attack.

7. DETERMINATION OF THE "TRUE RATE CONSTANT", $k_2 = k_{\text{obs.}}/K$ FOR THE CHROMIC ACID OXIDATION OF SOME PRIMARY ALCOHOLS

If a chromate ester is assumed to be an intermediate in the chromic acid oxidation of alcohols the complete rate law for the reaction in moderately concentrated acid is,

$$V = Kk_2 [\text{H}_2\text{CrO}_4] [\text{ROH}] h_o$$

where K is the ester equilibrium constant and k_2 is the rate constant for ester decomposition. Thus the

TABLE XVI

OXIDATION OF SUBSTITUTED METHANOLS IN 3.82 M
 HClO_4 ($H_0 = -1.62$), $[\text{Cr}^{\text{VI}}] = 1.03 \times 10^{-3} \text{M}$, $T = 25.0^\circ\text{C}$.

Alcohol	No.	[alc.] ($\times 10^2$)	$k_1 (\text{sec}^{-1})$	$k_2 (1 \text{ moles}^{-1} \text{sec}^{-1})$
n-Propanol	551	1.34	0.0131	97.7
	552	3.12	0.0285	91.3
Ethanol	554	5.72	0.0435	76.0
	555	4.56	0.0329	72.2
2-Methoxy-ethanol	559	4.24	0.00623	14.7
	560	2.12	0.00322	15.2
2-Chloro-ethanol	547	5.03	0.00311	6.20
	549	4.05	0.00232	5.74
Methanol	556	4.15	0.00175	4.22
	557	8.30	0.00366	4.41
Trifluoro-ethanol	558	68.8	0.000023	0.0033
	561	45.9	0.000018	0.0039
Isopropyl alcohol	367	4.09	0.0268	61.7

bimolecular rate constants ($k_{\text{obs.}}$) which are usually reported for this reaction are actually a product of two constants. The "true rate constant" for the rate-determining ester decomposition would be given by, $k_2 = k_{\text{obs.}}/K$ and could only be evaluated if an independent determination of the ester equilibrium could be made. Fortunately Klaning (52) has developed a method for the determination of this equilibrium constant in dilute acid solutions and Klaning and Symons (43) have listed the values obtained for a large number of alcohols. In the same manner (as described in the experimental section) we have determined the equilibrium constant for 2-methoxyethanol and 2,2,2-trifluoroethanol. By use of these equilibrium constants it was possible to determine the "true rate constants" (k_2) for the oxidation of six primary alcohols. The pertinent data is listed in Table XVII.

A plot of $\log k_2$ against Taft's σ^* values revealed that the ρ^* value for the rate-determining step for this reaction is negative (Figure 27). This is in accord with the suggestion previously made that the rate-determining step involved hydride transfer and casts serious doubts on the explanation originally given by Kwart and Francis (27) for the

TABLE XVII

CALCULATION OF THE "TRUE RATE CONSTANTS",
 $k_2 = k_{\text{obs}}/K$ FOR SOME SUBSTITUTED METHANOLS IN AQUEOUS
 PERCHLORIC ACID SOLUTIONS

Alcohol	$k_2 \times 10^2$ (1 moles ⁻¹ sec ⁻¹)	K	k_2/K	σ^*
n-Propanol	94.5	9.7	9.74	-0.100
Ethanol	74.1	6.9	10.75	0.000
2-Methoxy- ethanol	15.0	8.3	1.81	0.520
2-Chloro- ethanol	5.97	5.9	1.01	1.050
Methanol	4.32	4.7	0.92	0.490
2,2,2-Trifluoro- ethanol	3.6×10^{-3}	1.3	2.77×10^{-3}	3.9
Isopropyl alcohol	61.7			

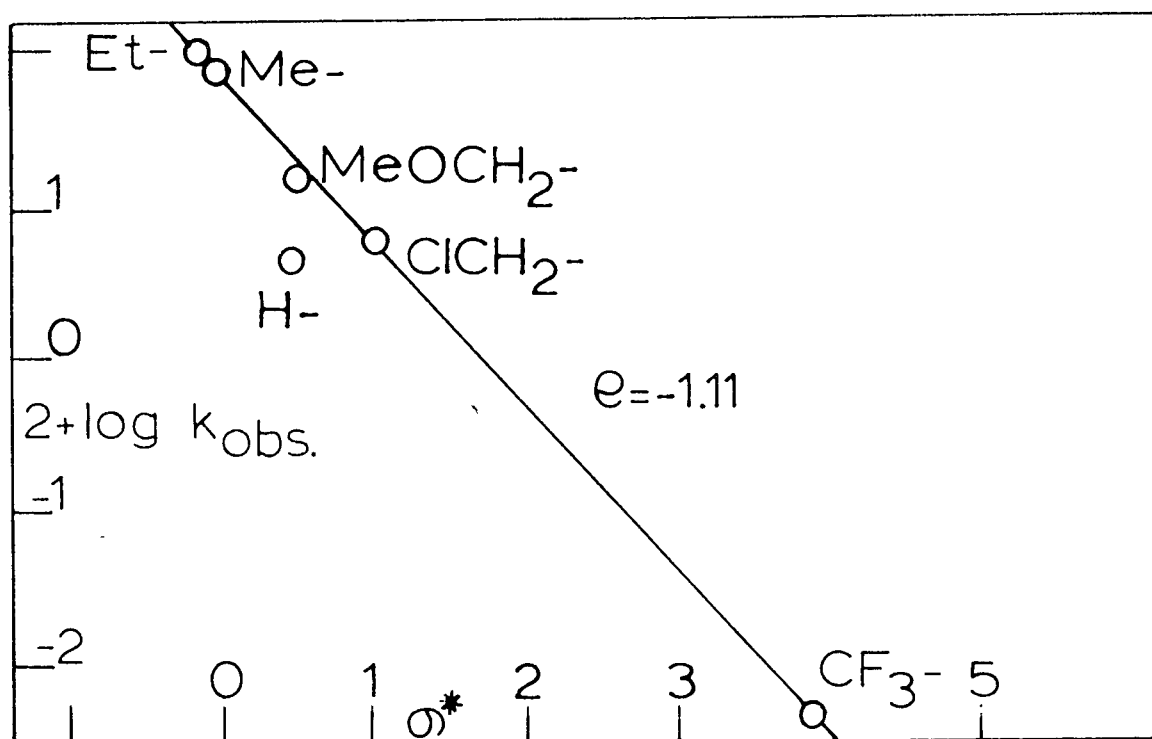


Fig.27 Relationship between $k_{\text{obs.}}$ and σ^* for the oxidation of substituted methanols.

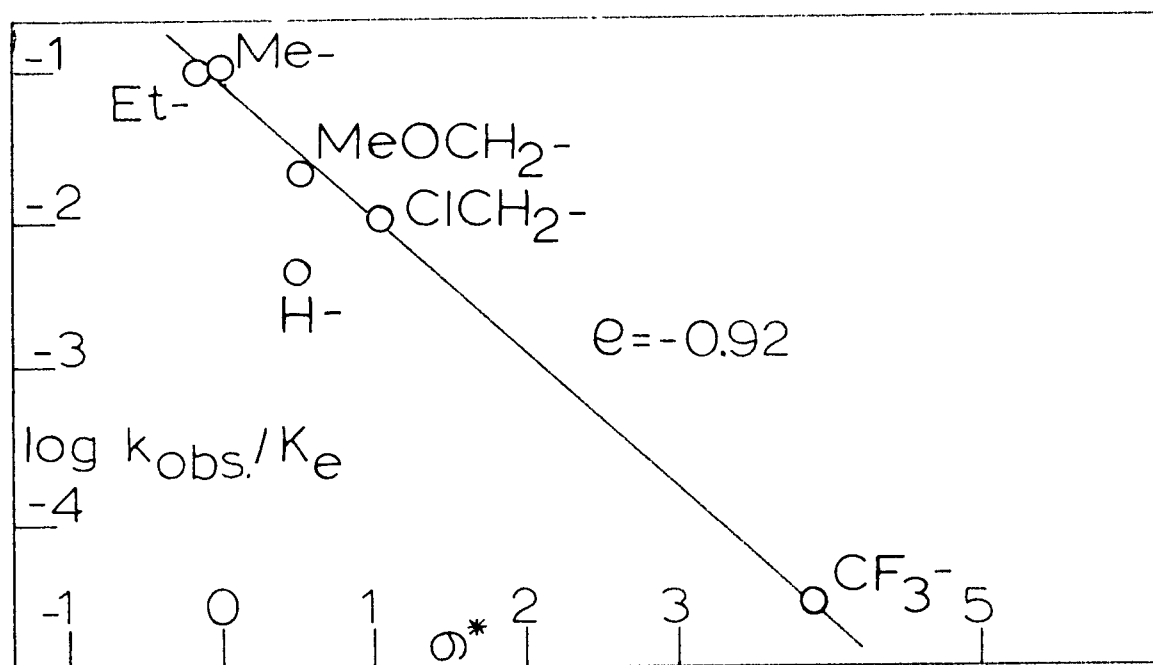


Fig.28 Relationship between the "true rate constant" and σ^* .

negative "rho" value observed in the oxidation of arylmethylcarbinols. Since the ester mechanism had received general acceptance they suggested that the observed negative "rho" is a result of changes caused by the substituents in the position of the ester equilibrium.

It should be noted, however, that while these results to a large extent invalidate the contentions of Kwart and Francis, the suggestion made by Westheimer (22) and by Wiberg (2) that the negative "rho" is merely a consequence of the removal of two electrons as well as a proton still remains as a possibility.

8. ACIDITY FUNCTIONS FOR NITRIC AND PHOSPHORIC ACID SOLUTIONS WITH ADDED SODIUM PERCHLORATE

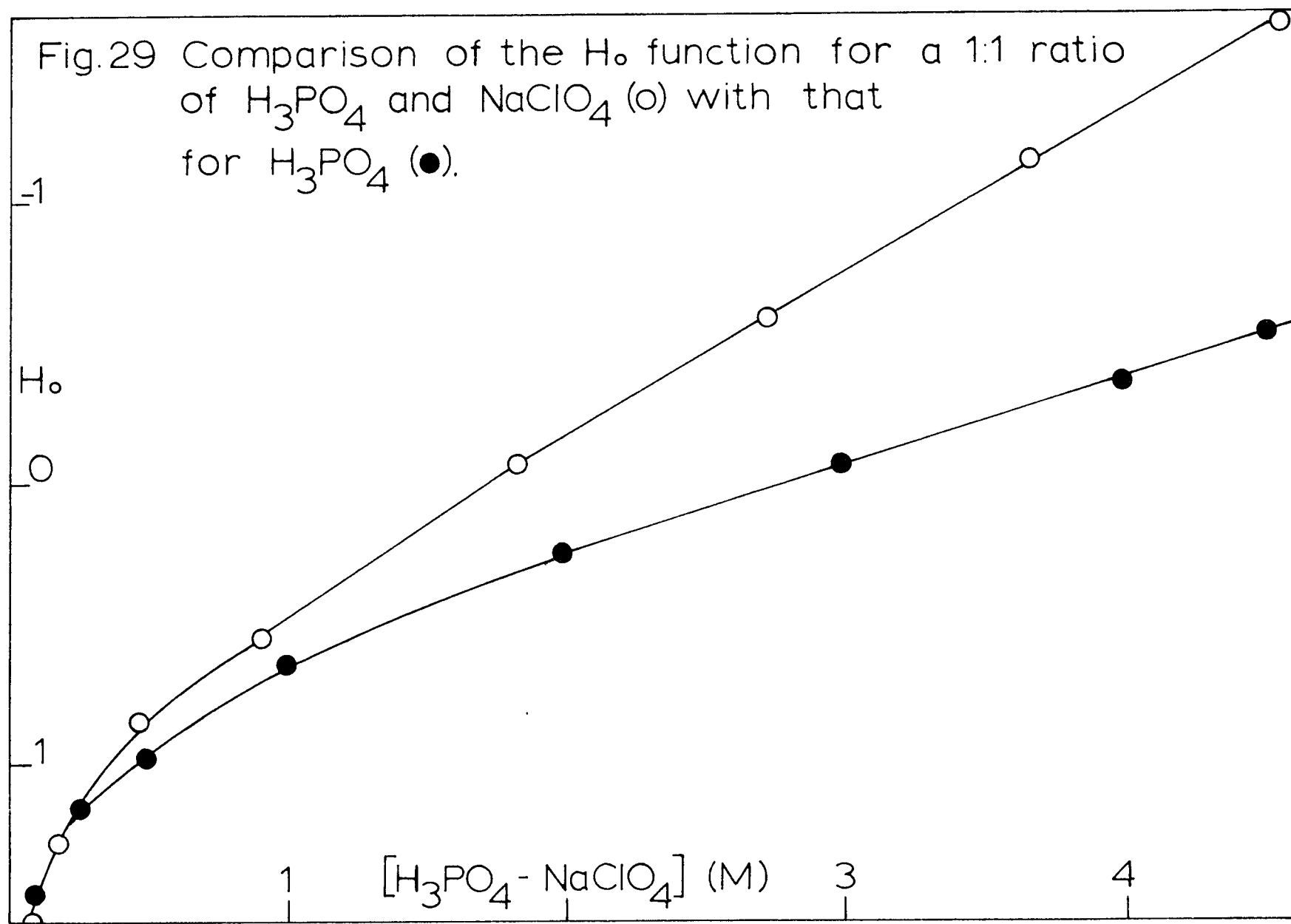
In the course of the investigation of the mechanism of chromic acid oxidations it became necessary to determine the acidity functions for nitric and phosphoric acid solutions containing added sodium perchlorate. In each case a 1:1 molar ratio of acid to salt was used. The functions were determined by use of weak bases for indicators in the manner described by Paul and Long (91). The derived acidities for these solutions are presented in Tables XVIII and XIX and the functions are plotted in Figures 29 and 30. The acidity

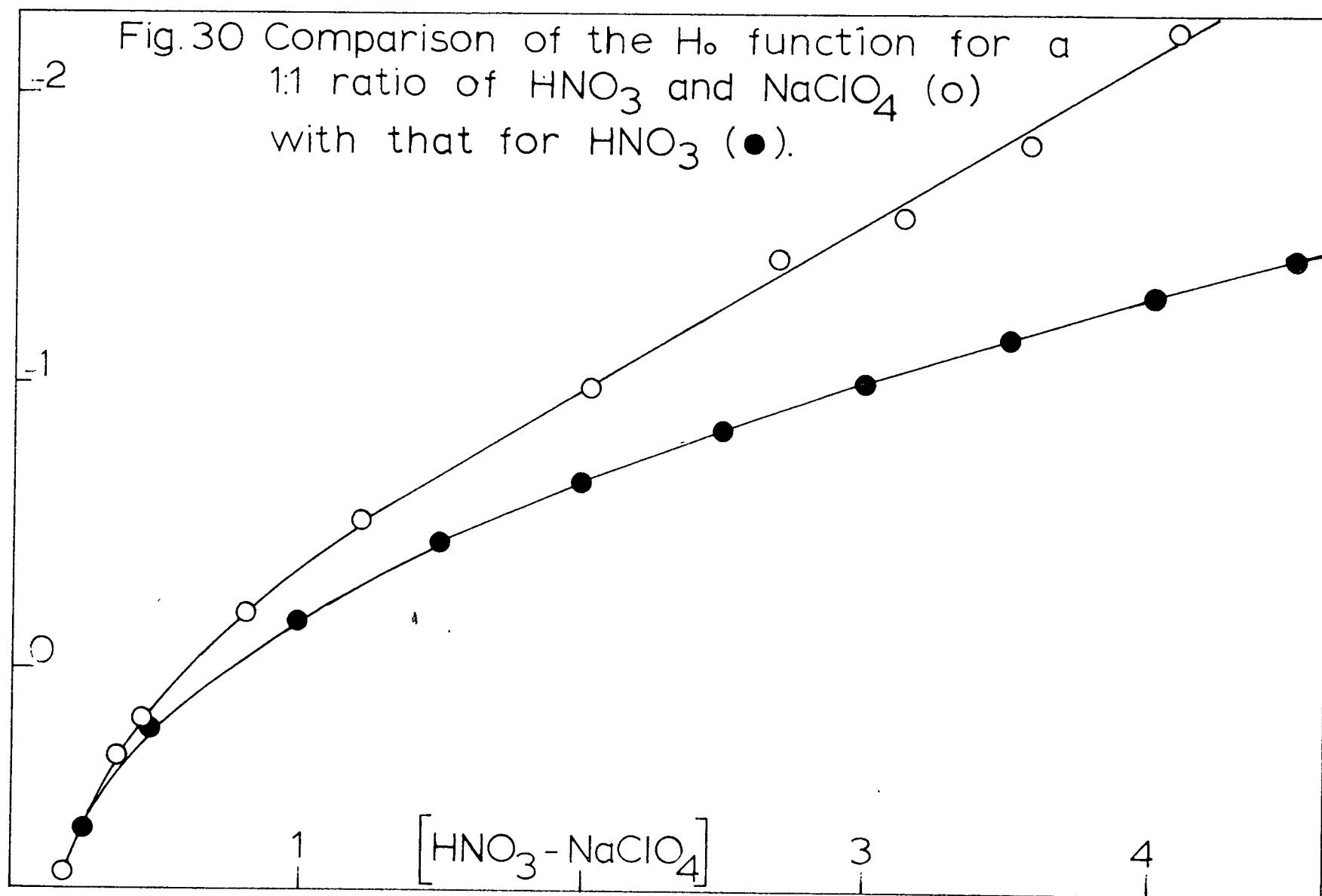
TABLE XVIII
ACIDITIES OF SOLUTIONS CONTAINING A 1:1 MOLAR
RATIO OF PHOSPHORIC ACID AND SODIUM PERCHLORATE

$\text{H}_3\text{PO}_4 - \text{NaClO}_4$ (M)	H_2O
0.25	1.15
0.50	0.81
1.00	0.48
1.50	0.14
2.00	-0.17
2.50	-0.47
3.00	-0.76
3.50	-1.05
4.00	-1.34
4.50	-1.64

TABLE XIX
ACIDITIES OF SOLUTIONS CONTAINING A 1:1 MOLAR
RATIO OF NITRIC ACID AND SODIUM PERCHLORATE

$\text{HNO}_3 - \text{NaClO}_4$ (M)	H_o
0.25	0.55
0.50	0.12
1.00	-0.35
1.50	-0.69
2.00	-0.99
2.50	-1.28
3.00	-1.58
3.50	-1.88
4.00	-2.17





functions for phosphoric and nitric acid solutions containing no added salts are included in these figures for comparison purposes.

While no studies identical to this one have previously been conducted Harbottle (101) and Paul (102) have reported that the addition of varying amounts of sodium perchlorate to perchloric acid and hydrochloric acid solutions results in an increase in the acidity of the medium. Paul and Long (91) have suggested a possible reason for this increase. They point out that $-H_o$ can be defined as,

$$-H_o = \log C_{H^+} + \log \frac{f_{H^+}}{f_{BH^+}} + \log f_B$$

and that while studies of salt effects on nonelectrolytes indicate that the acids hydrochloric, nitric, sulfuric and perchloric have little tendency either to salt in or salt out, the sodium salts of these acids show definite tendencies to do so. From this they deduce that the more rapid increase in $-H_o$ as compared to $\log C_{H^+}$ in acid solutions containing no added salt is due to an effect on the $\log \frac{f_{H^+}}{f_{BH^+}}$ term. This they suggest is plausible since studies have indicated that the influence of electrolyte concentration on the activity coefficient of a small cation can

become very large relative to that of a large cation. The addition of neutral salts would salt out the non-electrolyte causing an increase in the $(\log f_B)$ term and as in the previous case increasing the electrolyte concentration would have an effect on the

$$\log \frac{f_{H^+}}{f_{HB^+}} \text{ term.}$$

The functions obtained in the present investigation are identical with the previously determined functions containing no added salts in dilute regions. This is reasonable since the addition of small amounts of added salts should have very little effect on the acidity of dilute aqueous solutions. In more concentrated solutions, however, the addition of increasing amounts of added salts results in a continual increase in acidity as compared to solutions containing no added salt. This would seem to be consistent with the suggestions previously advanced by Paul and Long.

9. VARIATION IN THE pKa OF CHROMIC ACID WITH CHANGES IN THE IDENTITY OF THE MINERAL ACID SOLVENT

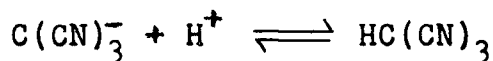
The apparent pKa of chromic acid was determined, as has been described, by plotting

$$\log \frac{\epsilon_{HCrO_4^-} - \epsilon}{\epsilon - \epsilon_{H_2CrO_4}}$$

against H_0 or H_- for a variety of mineral acids. The

results, presented in Table XX, indicate that the value of -1.01 obtained in perchloric acid is in good agreement with the value of -0.98 previously determined by Bailey, Carrington, Lott and Symons (80). The surprising aspect of the results, however, is that the apparent pKa's are not constant from one acid medium to another. The variation in pKa is very large and coupled with the evidence that will be presented in the next section completely rules out the possibility that the variation could be due to experimental error. In this connection it is also noteworthy that the reported pKa of permanganic acid differs from perchloric to sulfuric acid media (72).

The protonation of organic indicators such as the cyanocarbon anions is known to occur by means of a conventional equilibrium step involving a cyanocarbon anion, the corresponding cyanocarbon acid and a proton (92).



However, the results presented in Table XX indicate that in the protonation of an inorganic indicator such as chromate anion or permanganate anion some consideration must also be given to the proton source. i.e. The equilibrium must be established in such a way that there is a direct involvement of the mineral acid which

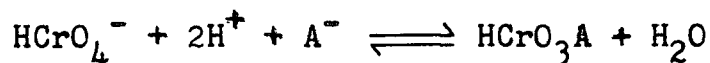
TABLE XX

COMPARISON OF THE pK_a OF H_2CrO_4 IN AQUEOUS SOLUTIONS OF VARIOUS MINERAL ACIDS AND THE POINT OF SLOPE CHANGE IN A PLOT OF $\log K$ v.s. H_o FOR THESE ACIDS

Acid	pK_a H_- scale	H_o scale	Point of slope change
HNO_3		-1.91	-2.45
$HClO_4$	-1.10	-0.83	-1.25
H_2SO_4	+0.51	+0.34	+0.02
HCl	+0.76	+0.52	+0.59
H_3PO_4		+1.74 [*]	+1.10
$H_3PO_4-NaClO_4$ (1:1 molar ratio)		+1.38	+1.35

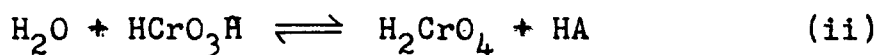
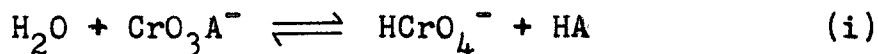
* This value was determined in these laboratories by Miss M. M. Wei.

furnishes the protons.



Further, it has been observed that at acidities below the apparent pKa of chromic acid the spectral character and oxidizing ability of Cr^{VI} solutions are independent of the proton source. However, at acidities greater than the pKa of chromic acid both spectral character and oxidizing ability are found to depend on the identity of the mineral acid present. This is illustrated by the data presented in Tables XXI, XXII and XXIII and by the spectra reproduced in Figures 31-34.

This evidence would seem to indicate that the ion CrO_3A^- is not present in significant concentrations under conditions where the monoanion is the dominant species but that HCrO_3A is the major neutral Cr^{VI} species.



i.e. Equilibrium (i) would seem to be to the right but equilibrium (ii) to the left.

Indications are that the following species are formed in the protonation of HCrO_4^- by the various

TABLE XXI
SPECTRAL DATA FOR THE ACID CHROMATE ION IN
VARIOUS MINERAL ACIDS

Mineral Acid	Concentration (M)	λ_{max}	ϵ
HClO_4	1.74×10^{-2}	430	230
		349	1584
		257	2140
H_2SO_4	pH = 2.95	430	242
		349	1572
		258	2170
HCl	1.0×10^{-3}	430	219
		349	1528
		257	2070
H_3PO_4	1.20×10^{-2}	435	245
		349	1616
		257	2200

TABLE XXII
SPECTRAL DATA FOR CHROMIC ACID IN VARIOUS
MINERAL ACIDS

Mineral Acid	Concentration (M)	λ_{max}	ϵ
HClO_4	3.50 M	440	193
		347	1158
		265	1760
H_2SO_4	3.10 M	445	184
		349	1028
		265	2050
HCl	3.60 M	445	176
		354	1240
		283	1699
		248	2110
H_3PO_4	3.00 M	445	198
		348	1090
		275	1920

TABLE XXIII
RATE OF OXIDATION OF ISOPROPYL ALCOHOL IN MINERAL
ACIDS OF A GIVEN ACIDITY. ($H_o = -2.5$)

Mineral Acid	k_{obs} (1 moles ⁻¹ sec ⁻¹)
HCl	7.1×10^{-3}
H ₃ PO ₄	0.28
H ₂ SO ₄	0.63
HClO ₄	5.0
HNO ₃	18

Fig.31 Ultraviolet spectrum of Cr^{VI} in 3.50 HClO_4 .

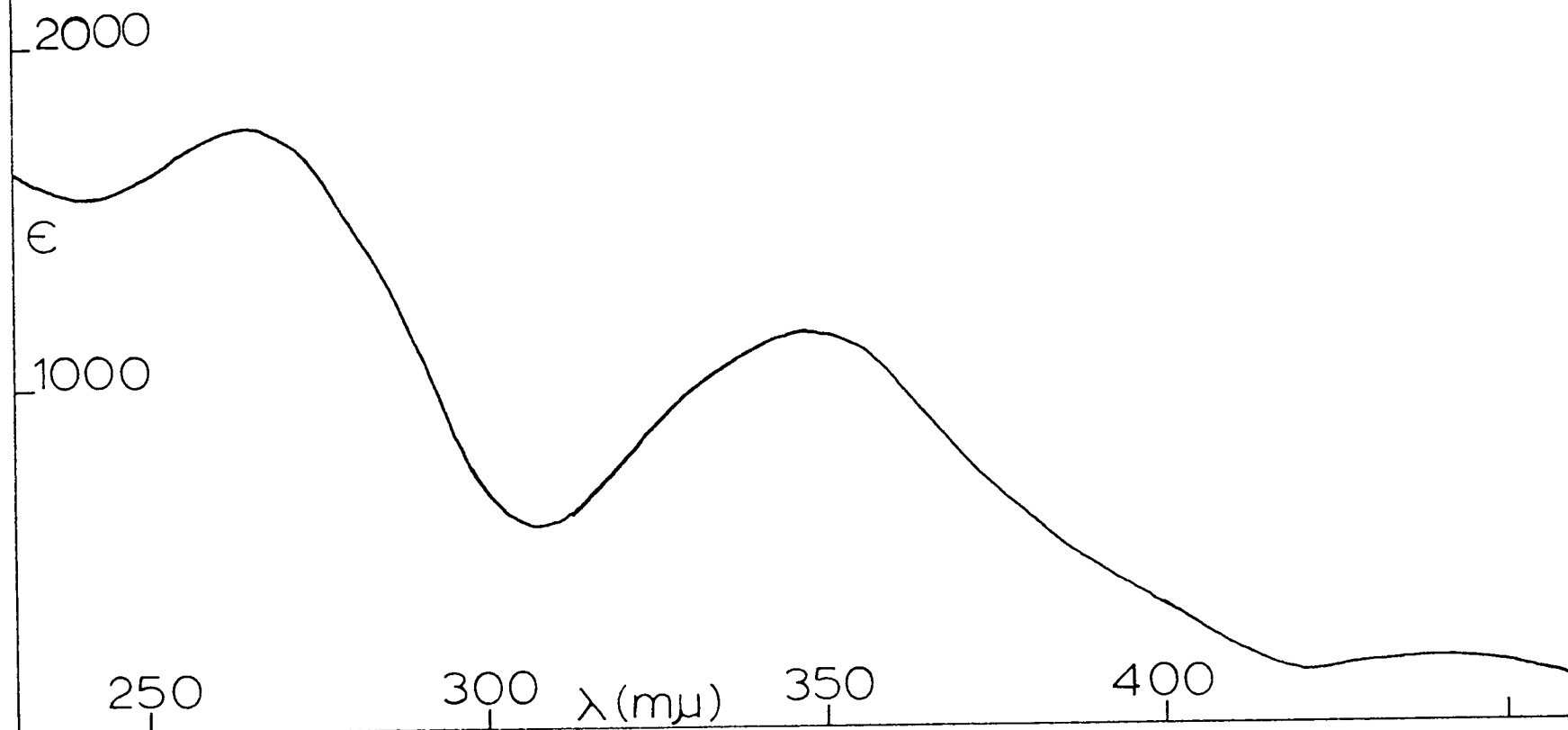


Fig.32 Ultraviolet spectrum of Cr^{VI} in 3.10M H_2SO_4 .

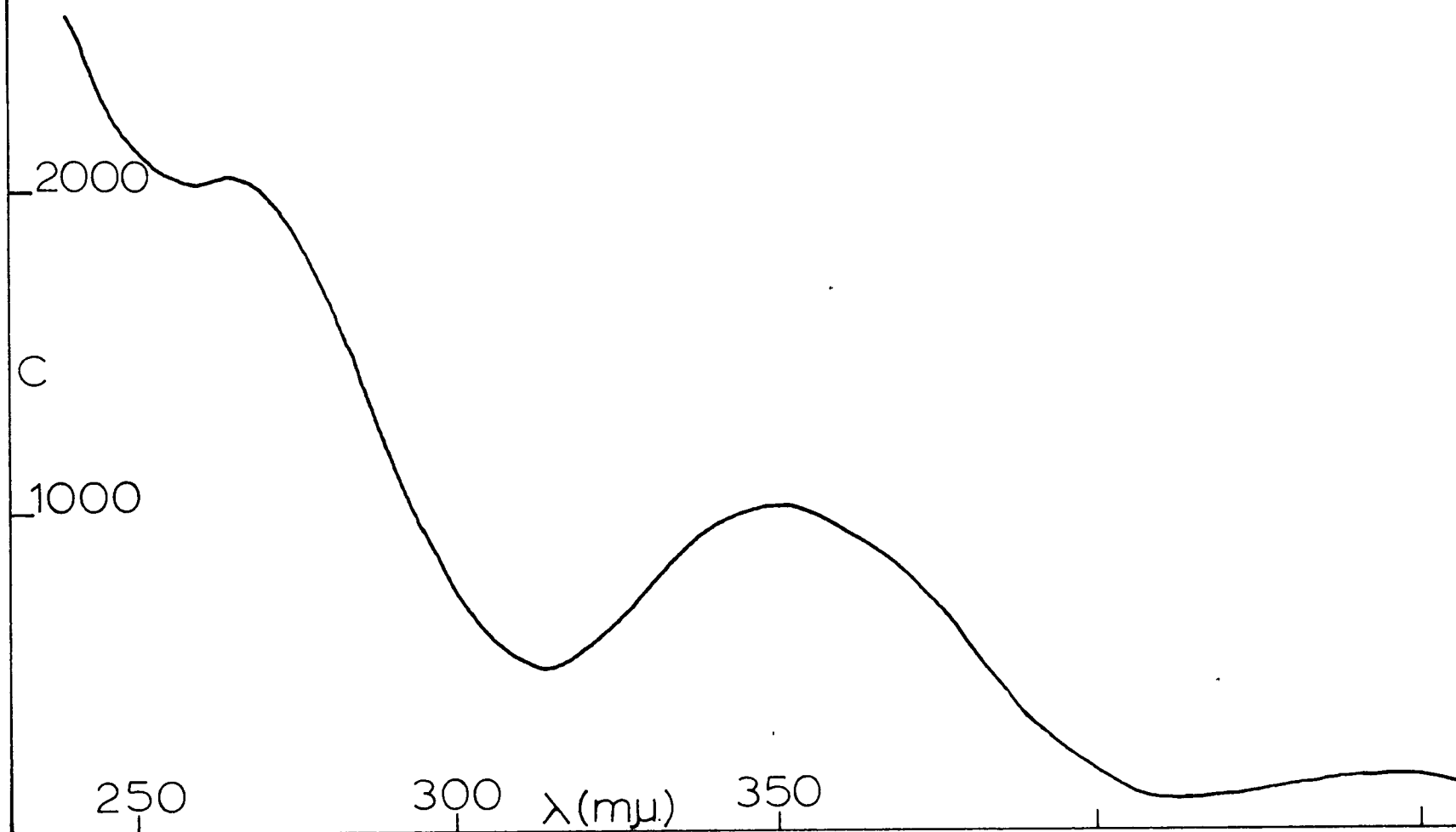


Fig.33 Ultraviolet spectrum of Cr^{VI} in 3.60M HCl.

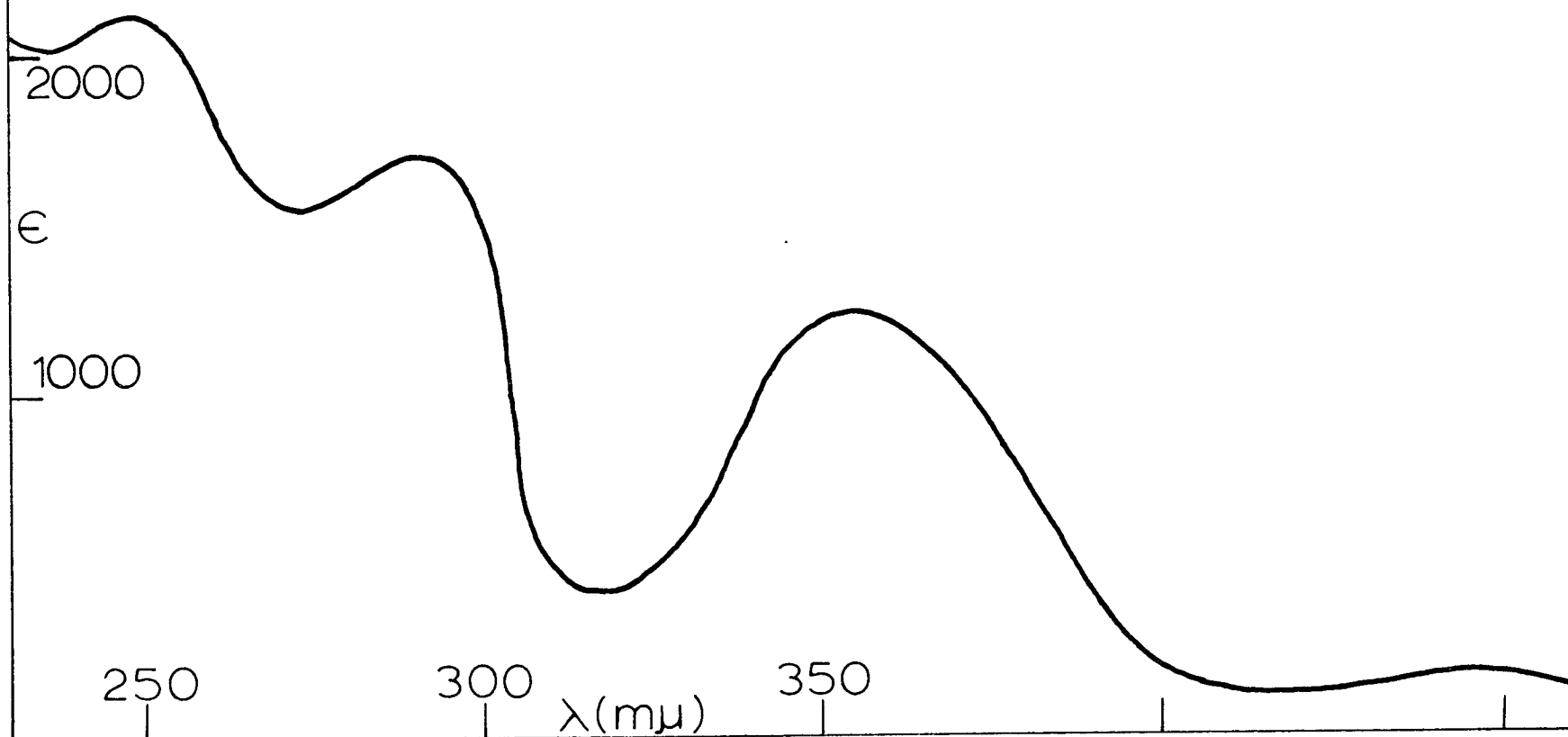
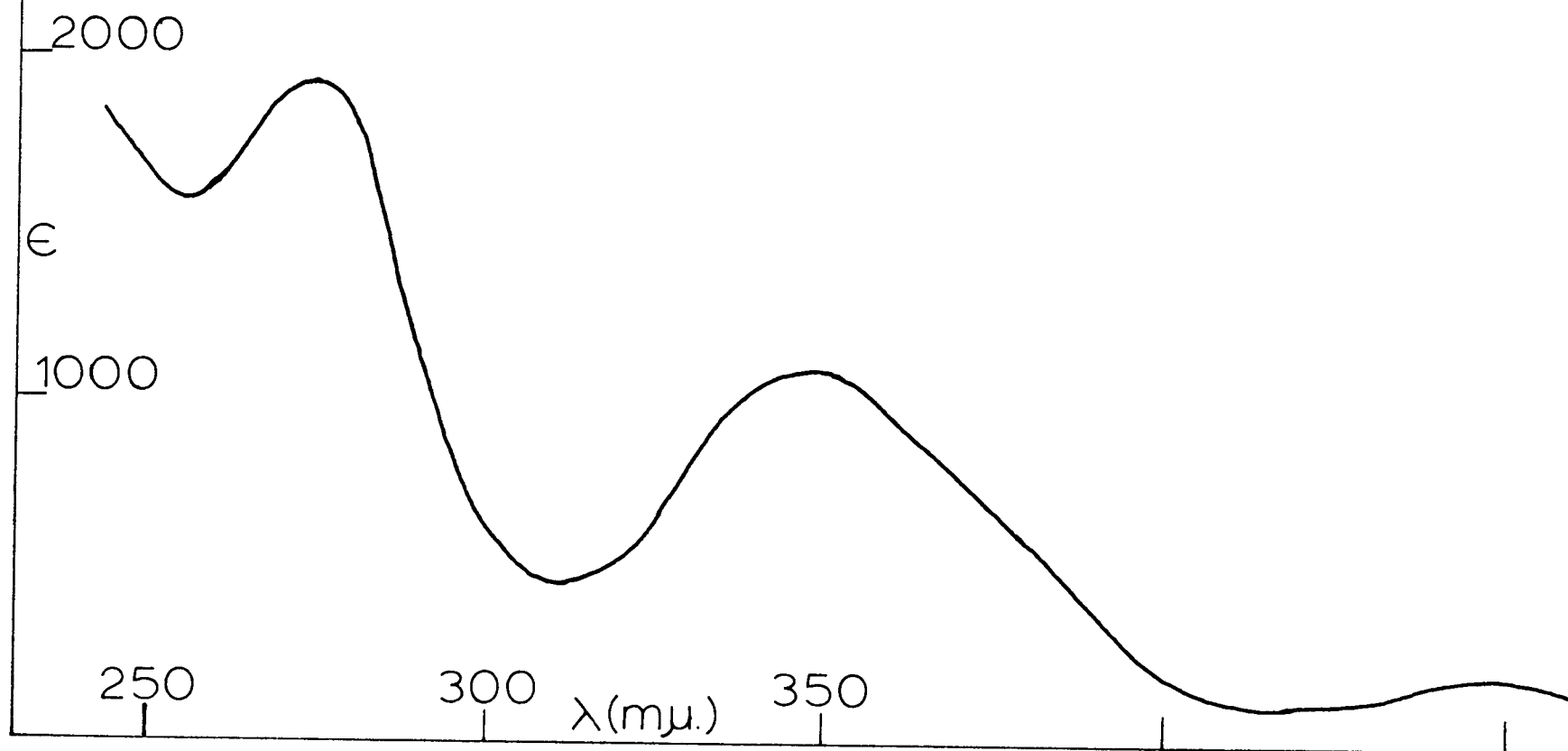
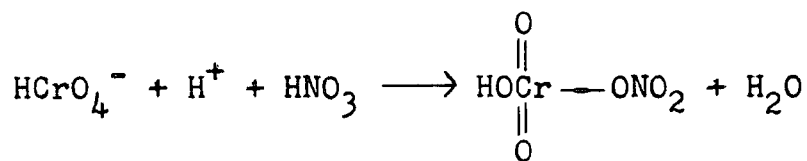
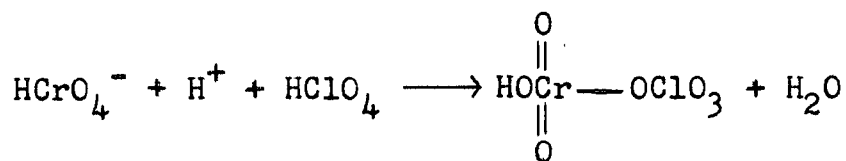
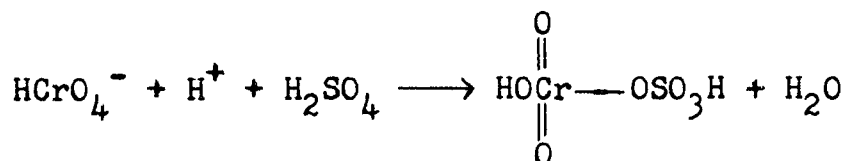
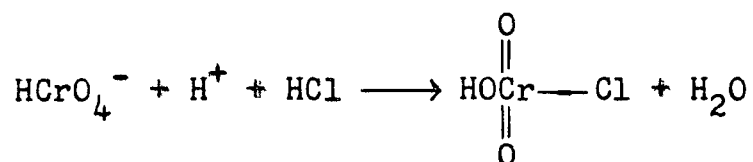
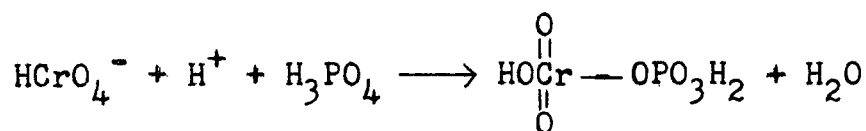


Fig.34 Ultraviolet spectrum of Cr^{VI} in 3.00M H_3PO_4 .

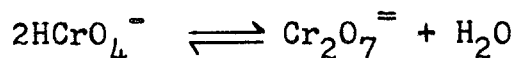


mineral acids.



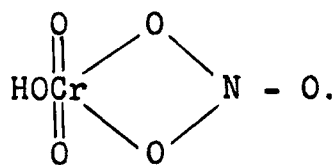
The postulation of the formation of these species is not completely without precedent since in addition to the aforementioned suggested formation of CrO_3Cl^- (34), Holloway (103) has also found spectroscopic evidence for the formation of a complex between chromic and phosphoric acid and Chang (104) has obtained spectroscopic evidence for CrSO_7^- or its protonated analogs. The well known case of complex formation between two acid chromate anions to give a dichromate anion can also

be considered as another example of this general reaction.



Further, if this is a correct picture one would expect the pKa's of these species to increase with decreasing electron withdrawing power of the A groups. For example, since the bisulfate group has greater electron withdrawing power than chloride one would expect the pKa for H_2CrSO_7 to be more negative than the pKa of HCrO_3Cl . i.e. The greater the electron withdrawing power of the A group the less available for protonation will be the electrons associated with the oxygen atom attached to chromium. Since the strengths of the mineral acids, HA, also vary in a similar way with electron withdrawing power of the A groups one would expect that a correlation should exist between the strengths of the mineral acids and the corresponding HCrO_3A species. Such a correlation with acid strengths is seen to exist for all the mineral acids investigated with the exception of HNO_3 . i.e. The strengths of these acids increase in the order $\text{H}_3\text{PO}_4 < \text{HNO}_3 < \text{HCl} < \text{H}_2\text{SO}_4 < \text{HClO}_4$ (91) while the -pKa's increase in the order $\text{H}_3\text{CrPO}_7 < \text{HCrO}_3\text{Cl} < \text{H}_2\text{CrSO}_7 < \text{HCrClO}_7 < \text{HCrNO}_6$.

The apparent anomaly of the HCrNO_6 species in this respect is not as yet completely understood. It is possible however, that the bonding in this species is different from the bonding in the other cases. For example, HCrNO_6 may exist as an oxygen bridged compound



If this is so it would be expected that Cr^{VI} would have a considerably different ultra-violet spectrum in HNO_3 as compared to other mineral acids. However, nitric acid itself has an absorption band at $350 \text{ m } \mu$ blanking out the most interesting part of this spectrum.

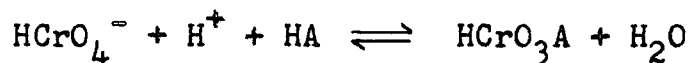
The spectra of chromic acid in H_3PO_4 , H_2SO_4 and HClO_4 are all very similar, as would be expected if all of these species contained chromium-oxygen bonds. The spectrum of chromic acid in HCl , on the other hand, shows considerable variation from the spectra obtained in H_3PO_4 , H_2SO_4 and HClO_4 . (See Figures 31-34). The explanation for this variation being that in the particular case of hydrochloric acid a chromium-chlorine bond is substituted for a chromium-oxygen bond.

The bonding in these species could be considered to be mostly covalent in analogy with the bonding in

chromium compounds such as chromyl chloride (105), chromyl bromide (105), and chromyl acetate (15). While covalent perchlorate compounds are not widely known some have recently been prepared (107, 108) and it is conceivable that even the bonding in HCrClO_7 is covalent in nature to a considerable extent. In this connection it should be noted that addition of sodium perchlorate to solutions of phosphoric and nitric acid did not greatly affect the observed pK_a of chromic acid in these solutions. This indicates that perchlorate will not replace either phosphate or nitrate in these compounds.

In addition to the above considerations it follows that if the protonation equilibrium involves a molecule of mineral acid a plot of $\log \frac{e_{\text{HCrO}_4^-} - e}{e - e_{\text{H}_2\text{CrO}_4}}$ against

either a simple H_0 or H_- function should not necessarily give a straight line of unit slope. The function that should give rise to a linear plot of unit slope can be derived in the following way:



$$K = \frac{(a_{\text{HCrO}_4^-}) (a_{\text{H}^+}) (a_{\text{HA}})}{(a_{\text{HCrO}_3\text{A}}) (a_{\text{H}_2\text{O}})}$$

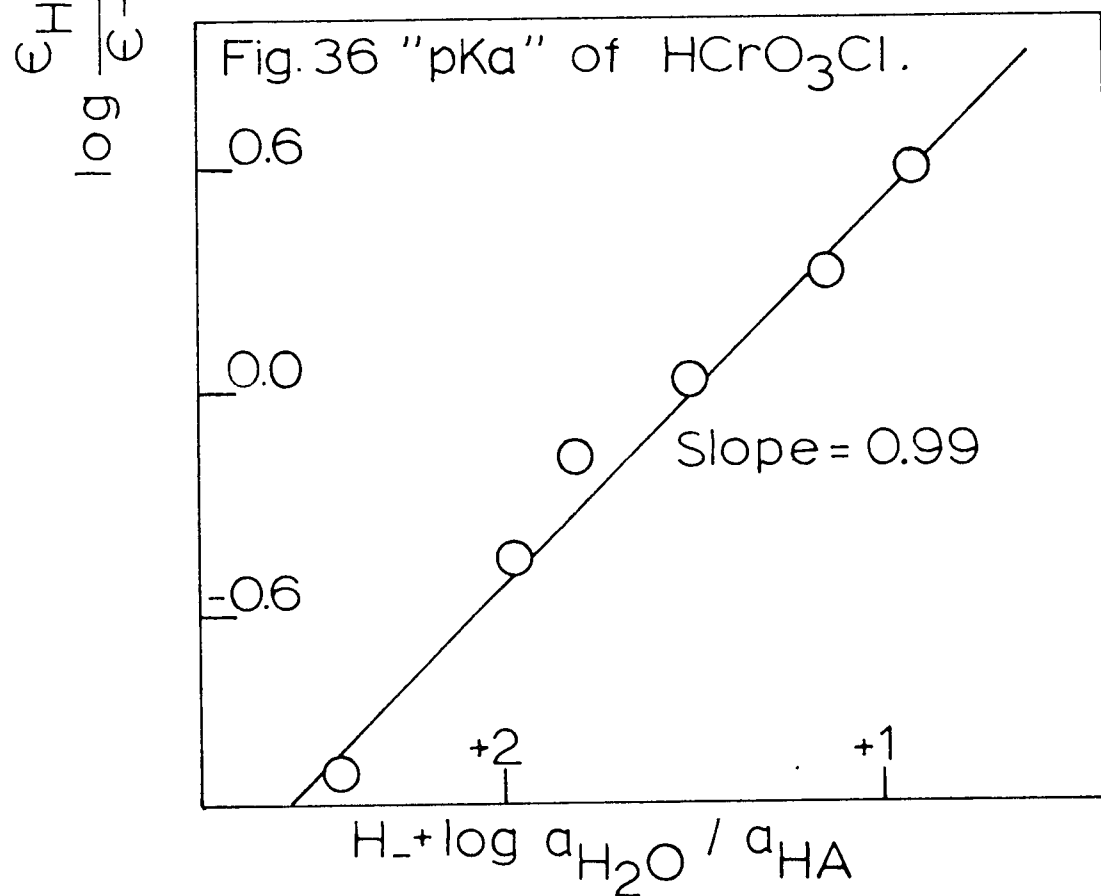
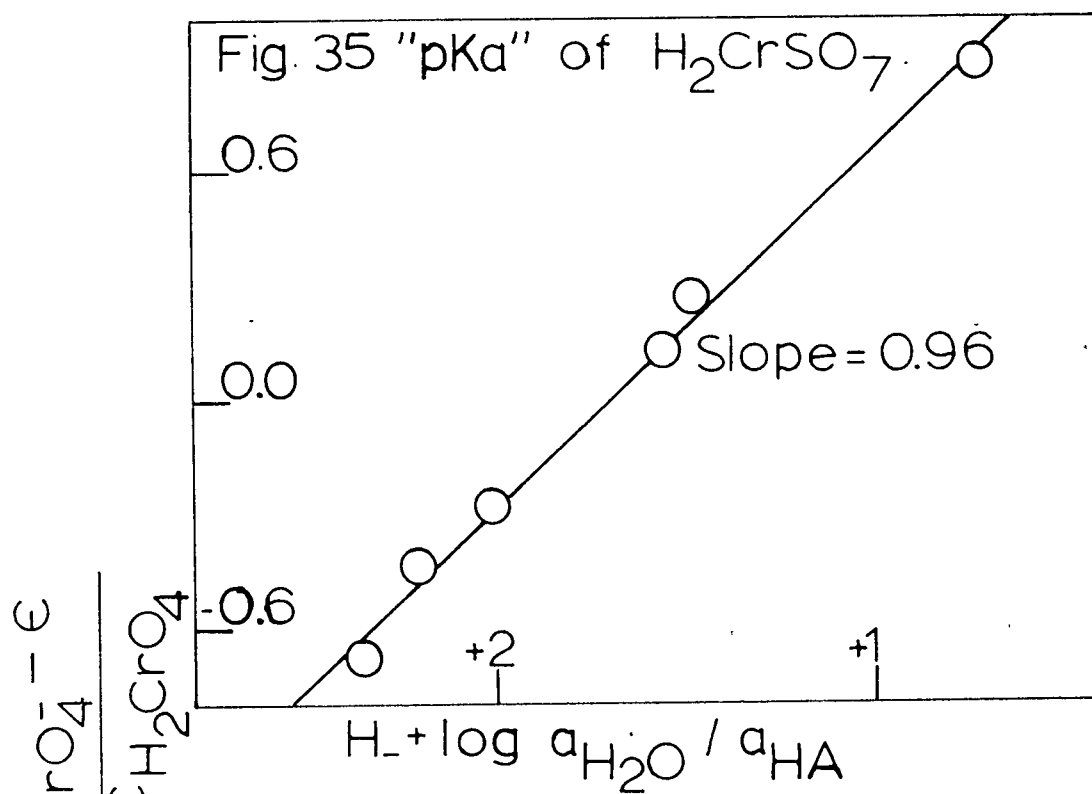
$$pK = \log \frac{C_{HCrO_3A}}{C_{HCrO_4^-}} - \log \frac{a_{H^+} f_{HCrO_4^-}}{f_{HCrO_3A}} - \log \frac{a_{HA}}{a_{H_2O}}$$

$$pK = \log \frac{C_{HCrO_3A}}{C_{HCrO_4^-}} + H_- + \log \frac{a_{H_2O}}{a_{HA}}$$

Hence a plot of $\log \frac{C_{HCrO_3A}}{C_{HCrO_4^-}} + H_-$ against the function,

$\log \frac{a_{H_2O}}{a_{HA}}$, should yield a straight line of unit

slope. Such a function has been calculated for HCl, H_2SO_4 and $HClO_4$ using the value for the logarithm of the activity of water given in ref. (49) and the mean activity coefficients for the electrolytes listed in ref. (109). The plots for HCl and H_2SO_4 illustrated in Figures 35 and 36 indicate that good straight line plots with unit slopes are obtained when this function is used. By comparing these plots with those in Figures 3 and 5 where the simple H_0 and H_- functions are used it is evident that the slopes obtained when this new function is used are much closer to unity. This result serves to further justify the previous assumption that there is a distinct difference between the protonation reaction of organic and inorganic bases of this type. In the latter case a molecule of the proton supplying



mineral acid becomes incorporated into the species when protonation occurs. This has not been observed for the organic bases.

In the case of perchloric acid the slope obtained with the simple H_- function is almost unity (Fig. 4) and application of the new function resulted in no improvement. Unavailability of the required data prevented the calculation of this new function for the nitric and phosphoric acid systems.

10. VARIATION IN RATE OF CHROMIC ACID OXIDATIONS WITH CHANGES IN THE IDENTITY OF THE MINERAL ACID SOLVENT

If the picture of the chromic acid equilibrium presented in the preceding section is correct one would expect that the physical and chemical properties of chromic acid would vary somewhat with the identity of the mineral acid solvent. It has previously been pointed out that while the acid chromate spectrum is identical for all the mineral acids investigated (Table XXI) the spectrum of chromic acid itself varied somewhat from acid to acid (Figures 31-34). Similarly it was found that the rate of oxidation of isopropyl alcohol by the acid chromate anion depended only on the acidity of the medium and not on the nature of the proton supplying mineral acid. On the other hand it

has been observed that the rate of oxidation by chromic acid depends not only on the acidity of the medium, but also on the identity of the mineral acid. These observations are illustrated in Fig. 37 where the logarithm of the rate constant for oxidation of isopropyl alcohol by chromium VI is plotted against H_0 for H_3PO_4 , HCl , H_2SO_4 , $HClO_4$ and HNO_3 . In addition, points are plotted for solutions of H_3PO_4 and HNO_3 containing a 1:1 molar ratio of sodium perchlorate. It can be seen that the addition of sodium perchlorate to these solutions had no effect on the rate of oxidation outside of its effect on the acidity of the medium.

It is interesting to note that a sharp change in slope is observed for each particular mineral acid solution very near to the pK_a of chromic acid in that medium (Table XX). Apparently the rate of oxidation by the protonated species of chromium VI varies with the acidity of the solution in a different manner than does the rate of oxidation by the unprotonated acid chromate anion. The observation that a variation in oxidation rate does not appear until after the pK_a of the Cr^{VI} species supports the suggestion that this equilibrium is such that a molecule of mineral acid does not become incorporated in the monoanion.

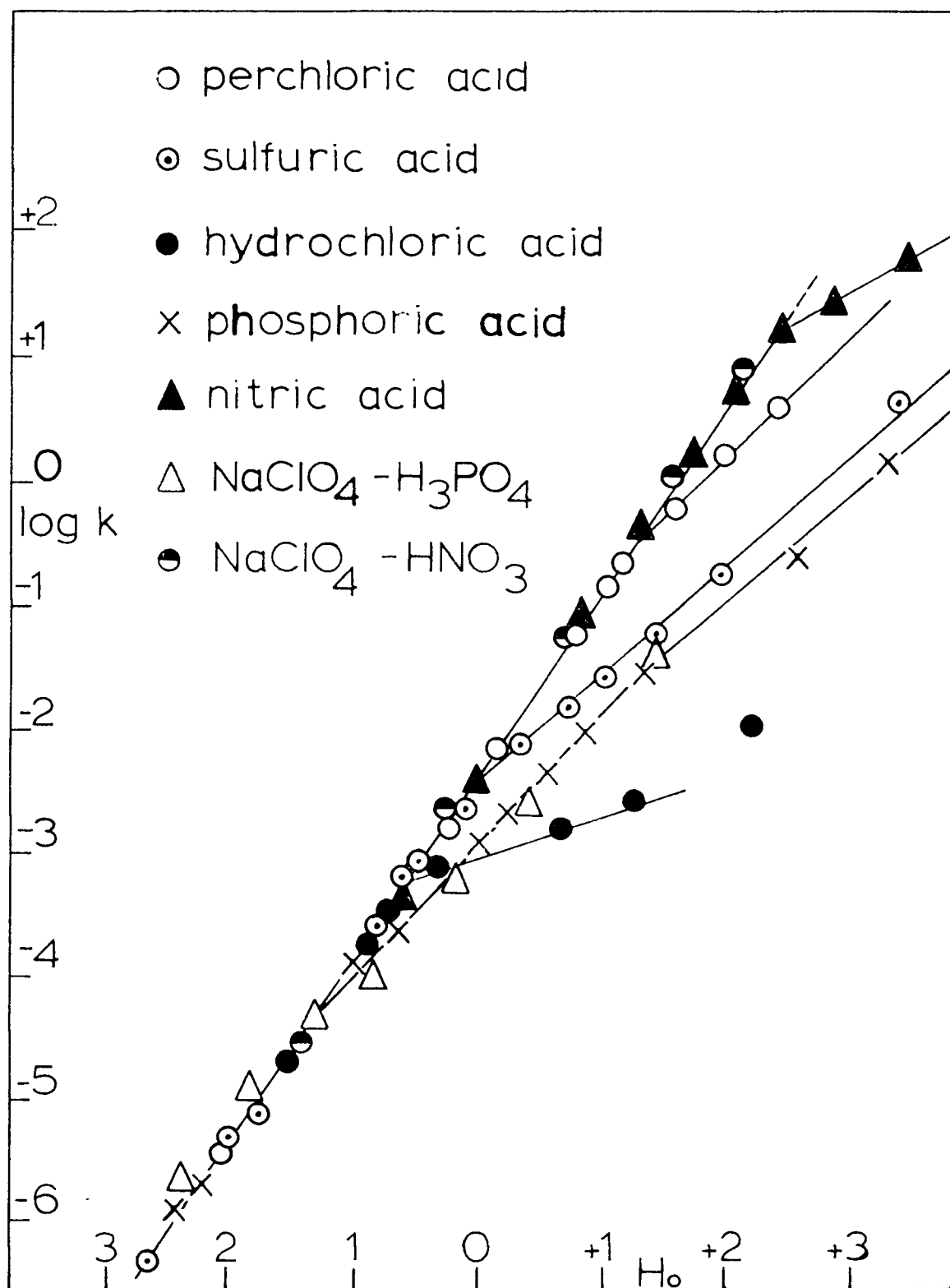


Fig.37 Chromic acid oxidation of isopropyl alcohol in aqueous solutions of mineral acids.

TABLE XXIV
 RATES OF OXIDATION OF ISOPROPYL ALCOHOL IN
 SULFURIC ACID SOLUTIONS AT 25°C.

No.	$[H_2SO_4]$ (M)	H_2O	$[Cr^{VI}]$ ($M \times 10^3$)	[Alc.] (M)	k_1 (sec^{-1})	k_2 (1 moles ⁻¹ sec^{-1})
343		2.62	4.07	0.129	6.48×10^{-8}	5.03×10^{-7}
342	0.0105	1.98	4.10	0.129	6.09×10^{-7}	4.95×10^{-6}
337	0.0214	1.77	4.27	0.129	9.47×10^{-7}	7.34×10^{-6}
341	0.0464		4.17	0.129	3.68×10^{-6}	2.85×10^{-5}
335	0.116	0.78	4.10	0.129	3.14×10^{-5}	2.43×10^{-4}
340	0.24	0.44	4.07	0.129	1.03×10^{-4}	7.98×10^{-4}
334	0.54	0.08	4.10	0.129	2.96×10^{-4}	2.30×10^{-3}
338	1.06	-0.35	4.23	0.129	8.21×10^{-4}	6.36×10^{-3}
333	1.62	-0.72	4.13	0.129	1.87×10^{-3}	1.45×10^{-2}
339	2.26	-1.02	4.13	0.129	3.37×10^{-3}	2.61×10^{-2}
332	3.04	-1.43	4.10	0.129	7.66×10^{-3}	5.95×10^{-2}
379	4.19	-1.95	3.46	0.0409	7.35×10^{-3}	1.79×10^{-1}
393	7.10	-3.37	1.03	0.0131	5.52×10^{-2}	4.21
394	7.10	-3.37	1.03	0.0131	5.58×10^{-2}	4.26
395	7.10	-3.37	1.03	0.0131	5.31×10^{-2}	4.06

TABLE XXV

RATES OF OXIDATION OF ISOPROPYL ALCOHOL
IN PERCHLORIC ACID SOLUTIONS AT 25°C.

No.	$[\text{HClO}_4]$ (M)	H_2O	$[\text{Cr}^{\text{VI}}]$ ($\text{M} \times 10^3$)	$[\text{Alc.}]$ (M)	k_1 (sec^{-1})	k_2 (1 moles $^{-1}$ sec^{-1})
370	0.0301	1.50	3.42	0.129	2.69×10^{-6}	2.08×10^{-5}
365	0.192	0.70	3.42	0.129	4.29×10^{-5}	3.32×10^{-4}
361	0.463	0.20	3.42	0.129	2.13×10^{-4}	1.59×10^{-3}
364	0.93	-0.18	3.42	0.129	9.20×10^{-4}	7.13×10^{-3}
362	2.08	-0.82	3.60	0.129	7.44×10^{-3}	5.76×10^{-2}
363	2.63	-1.05	3.42	0.129	1.82×10^{-2}	1.41×10^{-1}
366	2.98	-1.21	3.42	0.0409	9.81×10^{-3}	2.40×10^{-1}
367	3.82	-1.62	3.42	0.0409	2.68×10^{-2}	6.56×10^{-1}
368	4.53	-1.99	3.42	0.0409	6.57×10^{-2}	1.71
376	5.34	-2.44	0.342	0.00873	3.51×10^{-2}	4.03

TABLE XXVI

RATES OF OXIDATION OF ISOPROPYL ALCOHOL
IN PHOSPHORIC ACID SOLUTIONS AT 25°C

No	$[\text{H}_3\text{PO}_4]$ (M)	H_2O	$[\text{Cr}^{\text{VI}}]$ ($\text{M} \times 10^3$)	$[\text{Alc.}]$ (M)	k_1 (sec^{-1})	k_2 (1 moles $^{-1}$ sec^{-1})
386	Dil.	2.45	3.42	0.129	1.54×10^{-7}	1.19×10^{-6}
385	Dil.	2.22	3.42	0.129	2.43×10^{-7}	1.88×10^{-6}
382	0.504	0.97	3.42	0.129	1.51×10^{-5}	1.17×10^{-4}
392	0.903	0.69	3.42	0.129	2.88×10^{-5}	2.23×10^{-4}

373	3.71	0.01	3.42	0.129	1.39×10^{-4}	1.08×10^{-3}
374	3.61	-0.25	3.42	0.129	2.81×10^{-4}	2.17×10^{-3}
375	4.51	-0.53	3.42	0.129	5.60×10^{-4}	4.34×10^{-3}
371	5.44	-0.82	3.42	0.129	1.16×10^{-3}	9.04×10^{-3}
377	6.70	-1.32	3.42	0.129	3.66×10^{-3}	2.84×10^{-2}
380	10.00	-2.59	3.42	0.0409	9.96×10^{-3}	0.244
383	13.16	-3.30	3.42	0.0384	5.82×10^{-2}	1.52

TABLE XXVII

RATES OF OXIDATION OF ISOPROPYL ALCOHOL
IN HYDROCHLORIC ACID SOLUTIONS AT 25°C.

No.	[HCl] (M)	H _o	[Cr ^{VI}] (M $\times 10^3$)	[Alc.] (M)	k ₁ (sec ⁻¹)	k ₂ (1 moles ⁻¹ sec ⁻¹)
519	0.009	2.06	3.42	0.129	4.65×10^{-7}	3.60×10^{-6}
529	0.15	0.81	3.42	0.129	2.89×10^{-5}	2.24×10^{-4}
513	0.40	0.33	3.42	0.129	9.56×10^{-5}	7.40×10^{-4}
514	2.0	-0.69	3.42	0.129	1.98×10^{-4}	1.53×10^{-3}
512	3.6	-1.26	3.42	0.129	3.58×10^{-4}	2.97×10^{-3}
515	6.1	-2.17	3.42	0.129	1.39×10^{-3}	1.08×10^{-2}

TABLE XXVIII
 RATES OF OXIDATION OF ISOPROPYL ALCOHOL
 IN NITRIC ACID SOLUTIONS AT 25°C.

No.	[HNO ₃]	H ₂ O	[Cr ^{VI}] (Mx10 ³)	[Alc.] (M)	k ₁ (sec ⁻¹)	k ₂ (1 moles ⁻¹ sec. ⁻¹)
523	0.245	0.56	3.42	0.129	6.67x10 ⁻⁵	5.16x10 ⁻⁴
520	0.724	0.00	3.42	0.0436	1.56x10 ⁻⁴	3.80x10 ⁻³
521	2.45	-0.82	3.42	0.129	9.73x10 ⁻³	7.55x10 ⁻²
518	5.71	-1.74	3.42	0.0436	6.45x10 ⁻²	1.61
522	4.08	-1.34	3.42	0.129	6.05x10 ⁻²	4.69x10 ⁻¹
525	7.55	-2.10	3.42	0.00513		6.01
526	9.42	-2.48	3.42	0.00513		17.95
527	11.31	-2.86	3.42	0.00513		27.0
524	14.2	-3.45	3.11	0.00467		63.4

TABLE XXIX

RATES OF OXIDATION OF ISOPROPYL ALCOHOL IN
SOLUTIONS CONTAINING A 1:1 MOLAR RATIO OF H_3PO_4 to NaClO_4

No.	$[\text{H}_3\text{PO}_4\text{-NaClO}_4]$ (M)	H_2O	$[\text{Cr}^{\text{VI}}]$ ($\text{M} \times 10^3$)	[Alc.] (M)	k_1 (sec^{-1})	k_2 (1 moles $^{-1}$ sec^{-1})
542	0.00914	2.30	3.42	0.129	2.81×10^{-7}	2.18×10^{-6}
541	0.0457	1.78	3.42	0.129	1.69×10^{-6}	1.31×10^{-5}
540	0.183	1.27	3.42	0.129	6.12×10^{-6}	4.74×10^{-5}
539	0.457	0.84	3.42	0.129	1.40×10^{-5}	1.085×10^{-4}
535	1.37	0.18	3.42	0.129	8.14×10^{-5}	6.30×10^{-4}
534	2.28	-0.35	3.42	0.129	3.20×10^{-4}	2.48×10^{-3}
533	4.11	-1.40	3.42	0.129	6.18×10^{-3}	4.79×10^{-2}

TABLE XXX

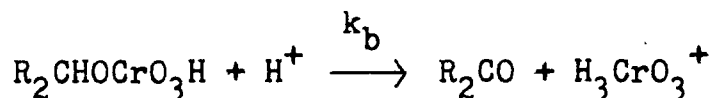
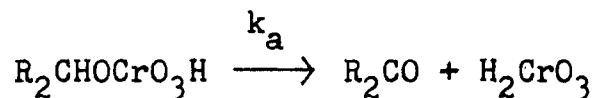
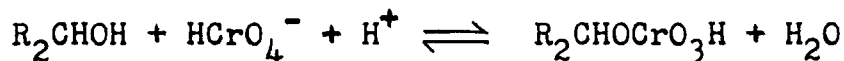
RATES OF OXIDATION OF ISOPROPYL ALCOHOL IN
SOLUTIONS CONTAINING A 1:1 MOLAR RATIO OF HNO_3 to NaClO_4

No.	$[\text{HNO}_3\text{-NaClO}_4]$ (M)	H_2O	$[\text{Cr}^{\text{VI}}]$ ($\text{M} \times 10^3$)	[Alc.] (M)	k_1 (sec^{-1})	k_2 (1 moles $^{-1}$ sec^{-1})
575	0.0417	1.40	3.42	0.129	3.28×10^{-6}	2.55×10^{-5}
574	0.0417	0.22	3.42	0.129	3.15×10^{-4}	2.44×10^{-3}
573	1.54	-0.72	3.42	0.129	7.46×10^{-3}	5.78×10^{-2}
572	3.08	-1.63	3.42	0.129	5.36×10^{-2}	1.23
571	4.02	-2.18	3.42	0.129		8.92

The oxidizing ability of the protonated species, HCrO_3A , increases in the order $\text{H}_2\text{CrPO}_7 < \text{HCrClO}_3 < \text{H}_2\text{CrSO}_7 < \text{HCrClO}_7 < \text{HCrNO}_6$. This is the same order in which the pK_a 's of these species vary. Such a correlation is not unexpected since "A" groups which are electron withdrawing will decrease the ease of protonation of the species, but increase the tendency of the chromium species to accept electrons from a reducing agent. From a consideration of the relative electron withdrawing power of the HPO_4^- , Cl^- , HSO_4^- , ClO_4^- and NO_3^- groups the position of the HCrNO_6 species in the above series is anomalous in that one would not expect the NO_3^- group to be the most strongly withdrawing group in the series. This anomaly was also noted in the case of the relative pK_a 's of these species and is not as yet completely understood.

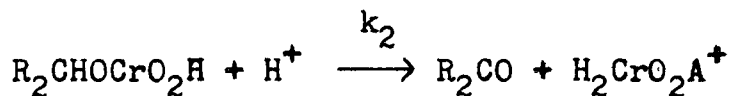
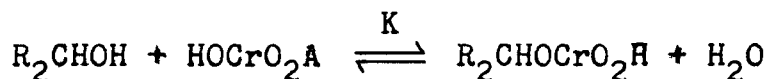
The slopes of the lines in Fig. 37 are also of some interest. The slope of the plot of H_0 against the logarithm of the rate constant for oxidation by chromate ion is about 1.8, while the slopes for oxidation in regions beyond the pK_a for chromic acid in the various media are much lower, being in most cases close to unity. It has previously been suggested by Westheimer (37) that the high slope in dilute acid region arises from the fact that the chromate ester

can decompose either with or without involvement of a proton.



$$v = \frac{K [R_2CHOH] [HCrO_4^-]}{[H_2O]} (k_a [H^+] + k_b [H^+]^2)$$

In the more acidic regions, beyond the pKa of chromic acid, the following mechanism is consistent with the results obtained in this as well as other investigations.



$$v = k_2 K \frac{[R_2CHOH] [HOCrO_2A] [H^+]}{[H_2O]}$$

V. CONCLUSION

The ultimate goal in the study of any chemical reaction is a complete determination of the mechanism of

that reaction. A mechanism simply refers to the path that the molecules follow in going from reactants to products. Complete mechanism elucidation involves determination of the movements and interaction of all particles (atoms, ions and electrons) during the course of the reaction as well as an estimate of the energy and configuration of every intermediate or transition state formed. While such a complete mechanism elucidation has not been obtained for the chromic acid oxidation reaction, many features of the reaction have been investigated and it is possible to estimate on the basis of chemical knowledge what form the unknown features of the reaction will take.

The oxidation of all alcohols used in this investigation showed a very pronounced primary isotope effect when the α -hydrogen was substituted with deuterium. The only case in which such an isotope effect was not observed was for oxidations carried out in 96% sulfuric acid. These observations indicate that the rate-determining step of this reaction involves carbon-hydrogen bond fission except in very concentrated sulfuric acid solutions.

In addition the "rho" value for the rate-determining step of the reaction was found to be negative indicating that considerable positive charge resides on the α -carbon

atom in the transition state. These first two observations taken together lead one to the conclusion that the rate-determining step must involve some form of hydride ion transfer, since only in this way can a carbon-hydrogen bond be broken and leave a residual positive charge on the carbon atom. While these considerations are not as straight forward if one considers the possibility of a cyclic internal hydrogen transfer as the rate-determining step, one is still left with the conclusion that the reaction must occur mainly by hydride transfer.

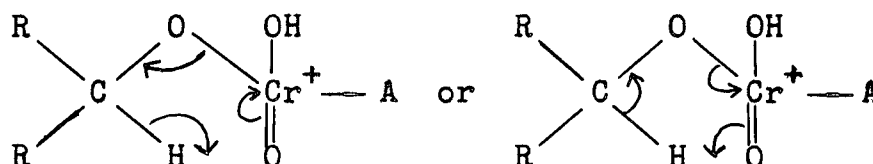
A review of the literature reveals that there is considerable evidence indicating that chromate esters play the role of intermediates in the chromic acid oxidation of secondary alcohols. For example; (i) diisopropyl ether (where no ester formation is possible) is oxidized only about 1/1500 as rapidly as isopropyl alcohol under the same experimental conditions (22), (ii) cis-1,2-diols are oxidized much more readily than trans-1,2-diols (24, 25, 26), (iii) chromate esters have been observed to form at least under some experimental conditions (42) and (iv) in the oxidation of certain highly hindered alcohols the deuterium isotope effect becomes unity indicating that the esterification reaction has become rate

controlling (104). The results of the present investigation are also consistent with the ester mechanism. A study of the rates of oxidation of three substituted 2-propanols in solutions of concentrated sulfuric acid has indicated that the rate maxima found around 70% H_2SO_4 is probably associated with the protonation of the chromate ester at this point. It has further been suggested that the disappearance of an appreciable isotope effect in very concentrated sulfuric acid solutions is due to rate-determining ester formation in this medium.

Assuming that the chromate ester is an intermediate in this reaction another problem concerning the mechanism presents itself. Does the ester decompose in an open form or does it undergo a cyclic decomposition? While there is at present no definitive evidence on which to make a choice between a cyclic and a non-cyclic decomposition it would seem that the cyclic mechanism most adequately explains all the observed features of the reaction. While Richer, Pilato and Eliel (56) have recently challenged this mechanism on the basis of the rates of oxidation of several alkylated cyclohexanols, Kwart (57) has adequately replied to this attack pointing out that the observed rates can be expressed in such a way

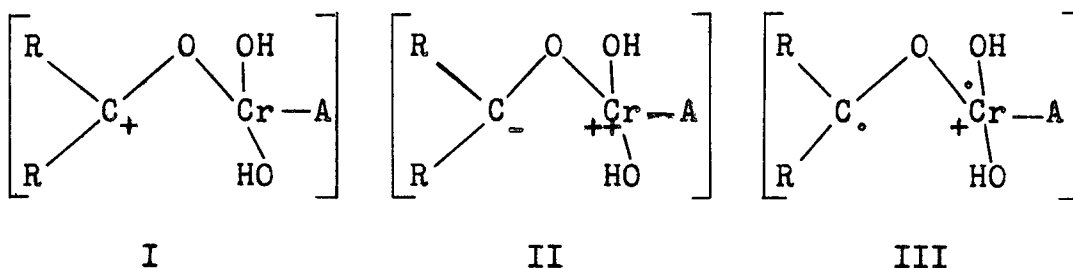
that they actually substantiate the cyclic decomposition mechanism.

If a cyclic decomposition mechanism is operative the significance of a negative "rho" value is not readily apparent since such a mechanism could facilitate electron transfer either through the O-Cr bond or through the developing H-O bond.



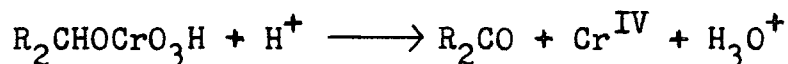
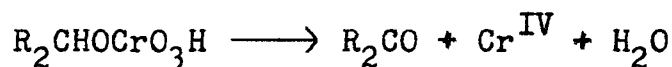
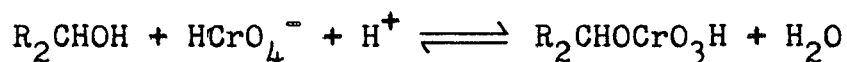
The mode of transfer would depend on the amount of orbital overlap between these atoms in the transition state. Observance of a negative "rho" value for such a mechanism would seem to indicate that the transference of electrons is mostly through the H-O bond.

Another approach to the nature of the transition state would be to consider it as a resonance hybrid of several possible forms as Roček (4) has recently done for the corresponding oxidation of hydrocarbons by chromic acid.



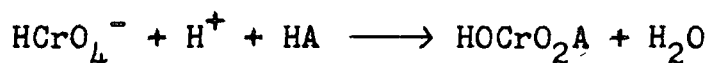
In this instance a negative "rho" value would merely indicate that form I contributed more to the transition state than did form II. This again simply means that the reaction proceeds mainly by hydride transfer.

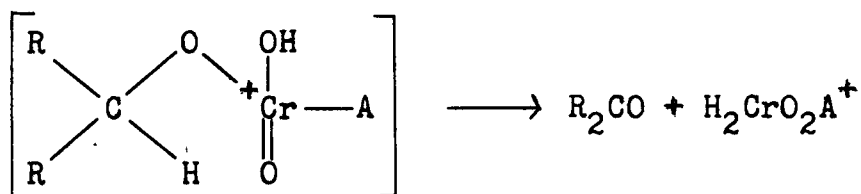
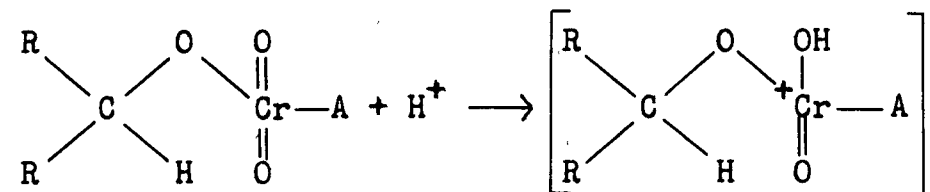
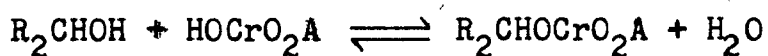
The present study has also indicated that the detailed mechanism of oxidation of alcohols by chromium VI may vary depending on the acidity of the medium used and in some regions upon the identity of the mineral acid used as a proton source. In dilute acid the following mechanism is operative:



Such a mechanism correctly predicts the observed rate law, it allows C-H bond fission to be the rate-determining step and it indicates that the reaction rate should be independent of the nature of the proton source in this region.

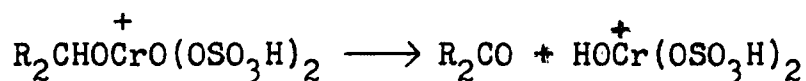
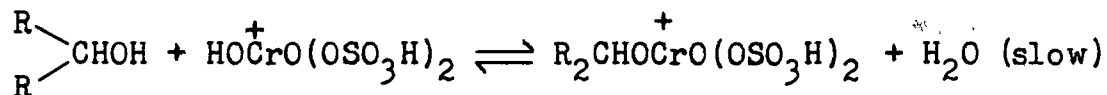
In more acidic solutions, beyond the pKa of chromic acid, this mechanism is modified in the following manner:





This mechanism fits the observed kinetic rate law, it allows C-H bond fission to be the rate-determining step, it suggests that a negative "rho" value should be observed, it incorporates ester rather than alcohol protonation into its framework and it indicates that the rate of reaction should be dependent on the nature of the mineral acid medium in which the reaction is carried out.

Finally, in very concentrated sulfuric acid the mechanism changes in such a way that the deuterium isotope effect closely approaches unity. Such an observation suggests that ester formation may become rate-determining in this medium.



VI SUGGESTIONS FOR FURTHER RESEARCH

During the course of this investigation a very brief study was made of the use of trifluoroacetic acid as a solvent for chromic acid oxidation reactions. This reagent has good solvent properties similar to those of acetic acid and it has the added advantage of possessing no oxidizable carbon hydrogen bonds. By use of this solvent one should then be able to eliminate any possibility of interference in the reaction by solvent oxidation. In order for it to be useful in mechanistic studies one would first have to determine an acidity function for the trifluoroacetic acid-sulfuric acid system similar to the one that Mareš and Roček (6) have developed for the acetic acid-sulfuric acid system.

The brief use made of trifluoroacetic acid in this investigation revealed however that it had one disadvantage - it is difficult to purify. When distilled from chromic acid a volatile red complex, apparently containing chromium VI, distills over at 72°C. It should be interesting to investigate further the exact nature of this complex.

Another possibility for further work would be the use of a series of substituted sulfonic acids as proton sources. It should be possible to test

the ideas concerning mineral acid incorporation beyond the pK_a of H_2CrO_4 by use of these acids. This should be possible since one is able to predict with fair certainty what effect incorporation of these acids would have on the physical and chemical properties of the chromium species. i.e. One should be able to predict from prior knowledge how the properties of $HO-CrO_2OSO_2C_6H_4CH_3$ should differ from those of $HO-CrO_2OSO_2C_6H_4NO_2$.

VII APPENDIX - RATES NOT APPEARING IN THE MAIN BODY
OF THE THESIS

OXIDATION OF ISOPROPYL ALCOHOL IN BUFFERED SOLUTIONS

No.	$[\text{NaH}_2\text{PO}_4]$ (M)	$[\text{HClO}_4]$ (M)	pH	Temp. (°C)	$[\text{Cr}^{\text{IV}}]$ (M)	$[\text{Alc.}]$ (M)	k_2 1 moles ⁻¹ sec ⁻¹
351	1.001	0.416	1.73	97.6	0.00361	0.0436	2.85×10^{-3}
353	1.001	0.208	2.3	97.6	0.00347	0.0654	1.195×10^{-3}
354	1.001	0.104	2.70	97.6	0.00428	0.0654	5.87×10^{-4}
355	1.001	0.0416	3.15	97.6	0.00338	0.0654	2.95×10^{-4}
356	1.001	0.416	1.7	0.0	0.00340	0.131	3.28×10^{-6}
357	1.001	0.208	2.3	0.0	0.00340	0.131	1.00×10^{-6}
358	1.001	0.104	2.9	0.0	0.00340	0.131	3.75×10^{-7}
359	1.001	0.0416	3.3	0.0	0.00340	0.131	1.51×10^{-7}
	NaOAc (M)						
360	1.00	1.01	*	0.0	0.00340	0.131	5.35×10^{-5}

* When this acetate buffer was used the pH gradually increased from an initial value of 2.3 to a value of 3.1 after one quarter of the chromium VI had reacted.

VIII BIBLIOGRAPHY

1. F. H. Westheimer and A. Novick, J. Chem. Phys., 11, 506 (1943)
2. K. B. Wiberg and R. J. Evans, Tetrahedron 8, 313 (1960)
3. K. B. Wiberg and G. Foster, J. Am. Chem. Soc., 83, 423 (1961)
4. J. Roček, Tetrahedron Letters, 135 (1962)
5. F. Mareš, J. Roček and J. Sicher, Coll. Czech. Chem. Comm., 26, 2355 (1961)
6. S. G. Brandenberger, L. W. Maas, I. Dvoretzky, J. Am. Chem. Soc., 83, 2146 (1961)
7. J. Roček and F. Mareš, Coll. Czech. Chem. Comm., 24, 2741 (1959)
8. Y. Ogata and H. Akimoto, J. Org. Chem., 27, 294 (1962)
9. I. Nescoiu and C. D. Nenitzeacu, Chem. and Ind., 377 (1961)
10. R. Slack and W. A. Waters, J. Chem. Soc., 599 (1949)
11. W. F. Sager and A. Bradley, J. Am. Chem. Soc., 78, 1187 (1956)
12. K. B. Wiberg and T. Mill, J. Am. Chem. Soc., 80, 3022 (1958)
13. G. T. E. Graham and F. H. Westheimer, J. Am. Chem. Soc., 80, 3030 (1958)
14. J. Roček, Tetrahedron Letters, 1 (1959)
15. P. Lepse, Ph.D. Thesis, University of Washington (1961)
16. K. B. Wiberg and W. H. Richardson J. Am. Chem. Soc., 84, 3800 (1962)
17. J. Roček, Coll. Czech. Chem. Comm., 22, 1519 (1957)

18. K. Petit, Bull. Soc. Chem. France, 12, 568 (1945)
19. P. A. Best, J. S. Littler and W. A. Waters, J. Chem. Soc., 822 (1962)
20. F. Mareš and J. Roček, Coll. Czech. Chem. Comm., 26, 2389 (1961)
21. H. C. S. Snethloge, Rec. trav. Chem., 60, 877 (1941)
22. R. Brownell, A. Leo, Y. W. Chang and F. H. Westheimer, J. Am. Chem. Soc., 82, 406 (1960)
23. W. A. Mosher, F. W. Steffgen and P. T. Lansbury, 26, 670 (1961) (and references therein)
24. H. Kwart, J. A. Ford Jr. and G. C. Corey, J. Am. Chem. Soc., 84, 1252 (1962)
25. Y. W. Chang and F. H. Westheimer, J. Am. Chem. Soc., 82, 1401 (1960)
26. J. Roček and F. H. Westheimer, J. Am. Chem. Soc., 84, 2241 (1962)
27. H. Kwart and P. S. Francis, J. Am. Chem. Soc., 77, 4907 (1955)
28. J. R. Holum, J. Org. Chem. 26, 4814 (1961)
29. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, J. Chem. Soc., 39 (1946)
30. E. Pungor and J. Trompler, J. Inorg. Nucl. Chem., 5, 123 (1957)
31. J. Roček and J. Krupička, Coll. Czech. Chem. Comm., 23, 2068 (1958)
32. J. Roček, Coll. Czech. Chem. Comm., 25, 1052 (1960)
33. J. Roček, Coll. Czech. Chem. Comm., 22, 1519 (1957)
34. M. Cohen and F. H. Westheimer, J. Am. Chem. Soc., 74, 4387 (1952)
35. S. V. Anantakrishnan and N. Venkatasubramanian, Curr. Sci., 28, 2 (1959)

36. N. Venkatasubramanian, J. Sci. Ind. Res., 20B, 385 (1961)
37. F. H. Westheimer, Chem. Rev., 45, 419 (1949)
38. W. A. Waters, Quat. Rev., 12, 277 (1958)
39. H. Kwart, Suomen Kemistilehti, A34, 173 (1961)
40. W. Walamabe and F. H. Westheimer, J. Chem. Phys., 17, 61 (1949)
41. A. Leo and F. Westheimer, J. Am. Chem. Soc. 74, 4383 (1947)
42. F. Holloway, M. Cohen and F. H. Westheimer, J. Am. Chem. Soc., 73, 65 (1951)
43. U. Klaning and M.C.R. Symons, J. Chem. Soc., 3204 (1961)
44. J. Hampton, A. Leo, and F. H. Westheimer, J. Am. Chem. Soc., 78, 306 (1956)
45. L. Kaplan, J. Am. Chem. Soc., 77, 5469 (1955)
46. J. Scheiber and A. Eschenmosher, Helv. Chem. Acta., 38, 1529 (1955)
47. D. H. R. Barton, Experientia, 6, 316 (1950)
48. L. Zucker and L. P. Hammett, J. Am. Chem. Soc., 61, 6791 (1939)
49. J. F. Bunnett, J. Am. Chem. Soc., 83, 4956, 4968, 4973, 4978 (1961)
50. H. Kwart and P. S. Francis, J. Am. Chem. Soc., 81, 2116 (1959)
51. J. S. Littler, J. Chem. Soc., 2190 (1962)
52. U. Klaning, Acta. Chem. Scand., 11, 1313 (1957); 12, 576 (1958)
53. K. B. Wiberg and R. Stewart, J. Am. Chem. Soc., 80, 3022 (1958)

54. F. H. Westheimer and Y. W. Chang, J. Phys. Chem., 63, 438 (1959)
55. F. Holloway, M. Cohen, and F. H. Westheimer, J. Am. Chem. Soc., 73, 65 (1951)
56. J. C. Richer, L. A. Pilato and E. L. Eliel, Chem. and Ind., 2007 (1961)
57. H. Kwart, Chem. and Ind., 610 (1962)
58. H. Kwart and P. S. Francis, J. Am. Chem. Soc., 81, 2116 (1959)
59. K. Wiberg, Chem. Rev. 55, 713 (1955)
60. H. Eyring and A. Sherman, J. Chem. Phys. 1, 435 (1933)
61. W. A. Mosher and F. C. Whitmore, J. Am. Chem. Soc., 70, 2544 (1948)
62. R. P. Bell, The Proton in Chemistry, Cornell University Press, Ithaca, New York (1959) (a) pp 183, (b) pp 207
63. National Bureau of Standards, Infrared Spectral Data, Serial No 748 (1948)
64. National Bureau of Standards, Infrared Spectral Data, Serial No 1146 (1951)
65. K. J. Laidler, Chemical Kinetics, McGraw-Hill Book Company, Inc. Toronto (1950) (a) pp 68, (b) pp 75
66. L. Melander, Isotope Effects on Reaction Rates, The Ronald Press Company, New York (1960) pp 21-22
67. F. H. Westheimer, Chem. Rev., 61, 265 (1961)
68. E. R. Thornton, J. Org. Chem. 27, 1943 (1962)
69. E. L. Eliel, P. H. Wilken, F. T. Tang and S. H. Wilen., J. Am. Chem. Soc., 80, 3303 (1958)
70. A. Streitwieser Jr., D. E. Van Sickle and L. Reif, J. Am. Chem. Soc., 82, 3303 (1958)

71. R. Stewart and R. Van der Linden, Far. Soc. Disc., 29, 211 (1960)
72. M. Mocek, Ph.D. Thesis, University of British Columbia (1962)
73. W. Kauzmann, Quantum Chemistry, Academic Press Inc., New York (1957) pp 207
74. R. P. Bell, J. A. Fendley, and J. R. Hulett, Proc Roy. Soc. (London), 235A, 152 (1956)
75. J. R. Hulett, J. Chem. Soc., 468 (1960)
76. V. J. Shiner and M. L. Smith, J. Am. Chem. Soc., 83, 593 (1961)
77. C. G. Swain, R. A. Wiles and R. F. W. Bader, J. Am. Chem. Soc. 83, 1945 (1961)
78. K. B. Wiberg and L. H. Slough, J. Am. Chem. Soc., 80, 3033 (1958)
79. C. G. Swain, R. F. W. Bader, R. M. Esteve, Jr. and R. N. Griffin, J. Am. Chem. Soc., 83, 1951 (1961)
80. N. Bailey, A. Carrington, K. A. Lott and M. C. R. Symons, J. Chem. Soc., 290 (1960)
81. R. Van der Linden, Ph.D. Thesis, University of British Columbia (1960)
82. R. Stewart and R. Van der Linden, Can. J. Chem., 38, 399 (1960)
83. E. D. Bergmann and S. Cohen, J. Chem. Soc., 2259 (1958)
84. J. B. Conant and O. R. Quayle, Org. Sym. Coll. Vol. I, 211 (1941)
85. Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., 39th Ed. (1957-58), (a) pp 1126 (b) pp 797, (c) pp 1196
86. F. Swarts, Bull. Soc. Chem. Belg., 38, 99-109 (1929); C. A. 23, 4440 (1929)
87. D. I. Legge, J. Am. Chem. Soc., 81, 502 (1959)

88. H. C. Brown and A. Tsukamoto, J. Am. Chem. Soc., 81, 502 (1959)
89. H. C. Brown and B. C. Subba Rao, J. Am. Chem. Soc., 80, 5377 (1958)
90. L. P. Hammett and A. J. Deyrup, J. Am. Chem. Soc., 54, 2721 (1932)
91. M. A. Paul and F. A. Long, Chem. Rev., 57, 1 (1957)
92. R. H. Boyd, J. Am. Chem. Soc., 83, 4288 (1961)
93. R. H. Boyd, Private Communication.
94. N. C. Deno and W. L. Evans, J. Am. Chem. Soc., 79, 5804 (1957)
95. E. Bunce and A. N. Bourns, Can. J. Chem., 38, 2457 (1960)
96. J. W. Baker and T. G. Heggs, J. Chem. Soc., 616 (1955)
97. R. N. Haszeldine, J. Chem. Soc., 1757 (1953); 3284 (1952)
98. J. P. O'Donnell, Ph.D. Thesis, University of British Columbia (1962).
99. H. C. Mishra and M. C. R. Symons, J. Chem. Soc., 4411 (1962)
100. R. W. Taft, Steric Effects in Organic Chemistry (Edited by M. S. Newman) Wiley, New York (1956) pp. 556
101. G. Harbottle, J. Am. Chem. Soc., 73, 4024 (1951)
102. M. A. Paul, J. Am. Chem. Soc., 76, 3236 (1954)
103. Frank Holloway, J. Am. Chem. Soc., 74, 224 (1952)
104. F. H. Westheimer, Private Communication to Ross Stewart
105. W. H. Hartford and M. Darrin, Chem. Rev., 58, 1 (1958)

106. V. H. L. Krause and K. Stark, Z. Naturforsch.,
176, 1 (1962)
107. B. J. Hathaway and A. E. Underhill, J. Chem. Soc.,
3705 (1960)
108. H. C. Clark, Private communication.
109. C. F. Prutton and S. H. Maron, Fundamental
Principles of Physical Chemistry, The
Macmillan Company, New York (1951),
pp. 478.

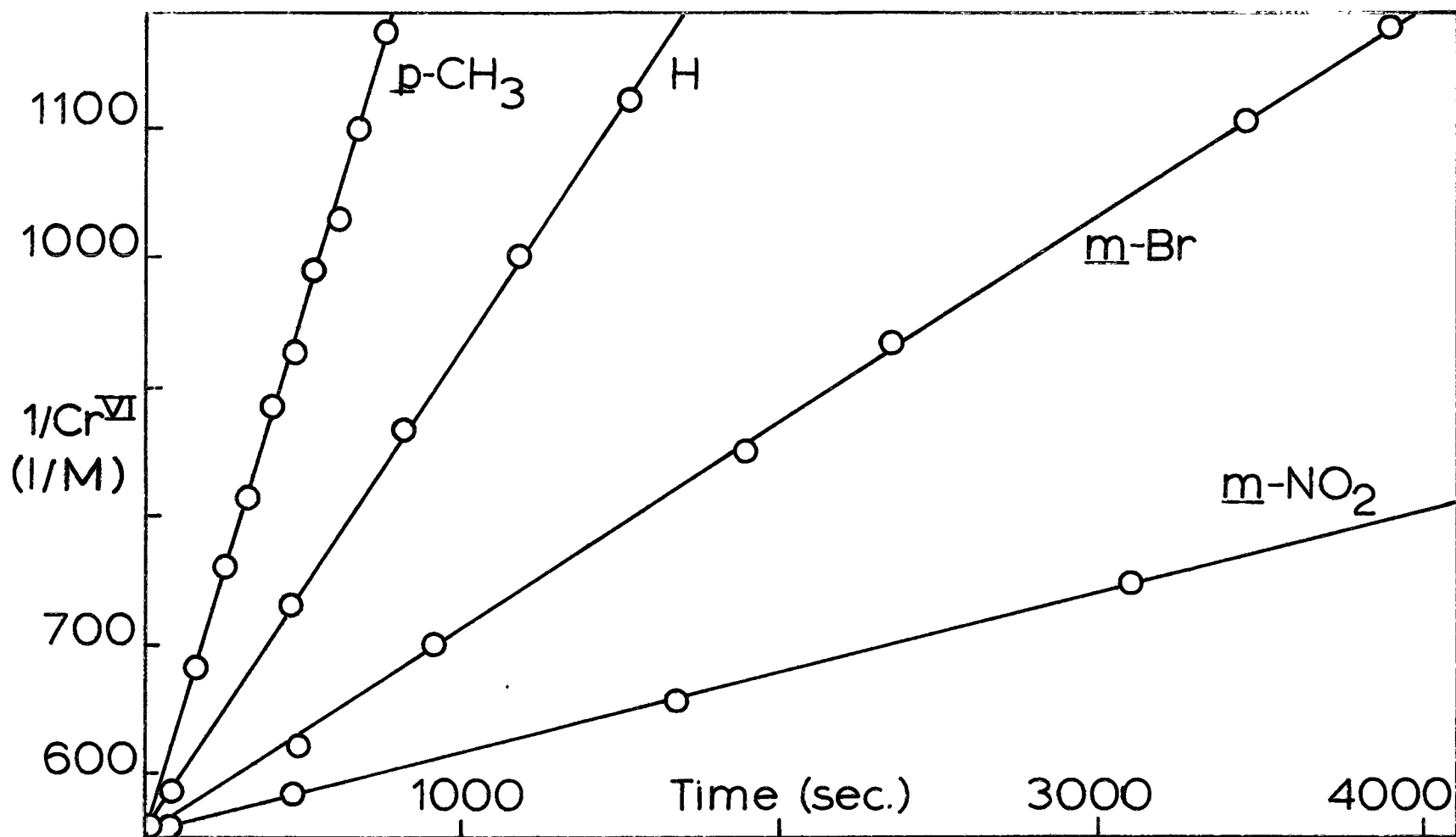


Fig.1 Typical rate plots for the oxidation of aryltrifluoromethylcarbinols in 77.2% acetic acid.

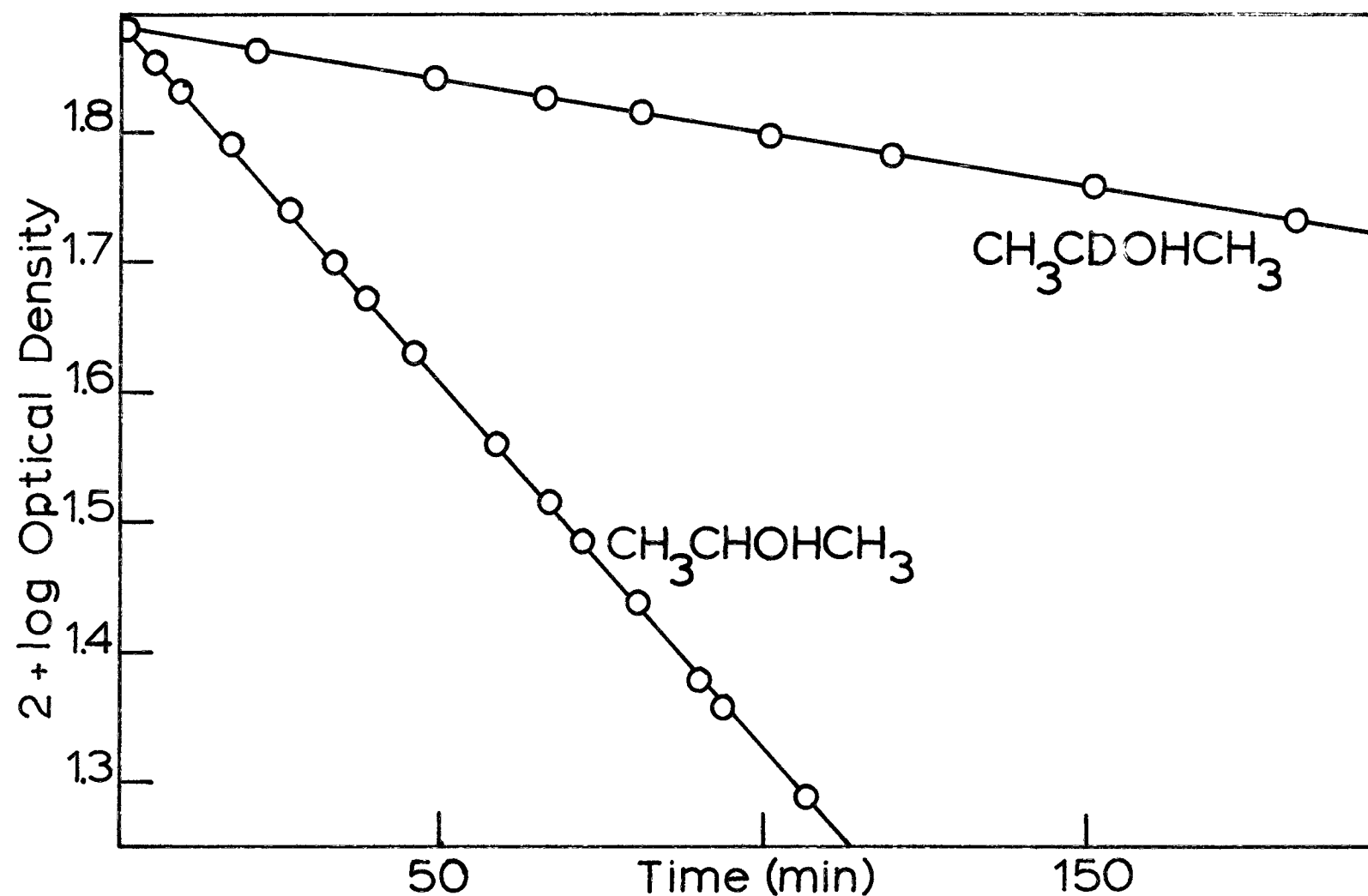
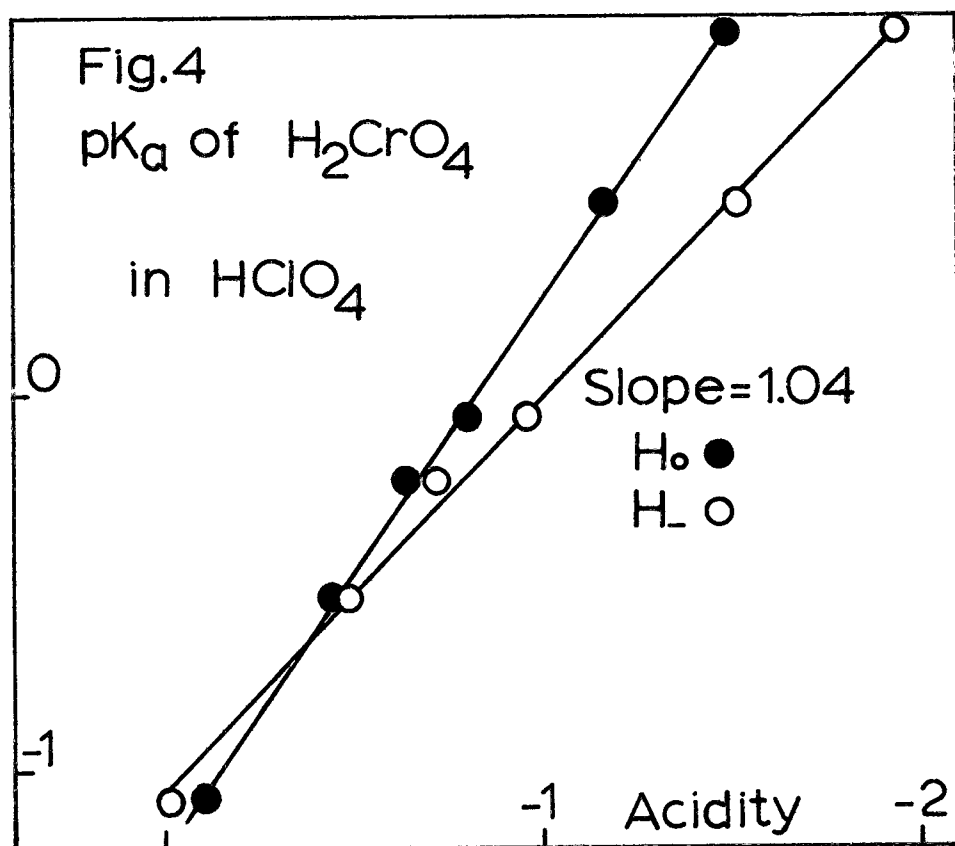
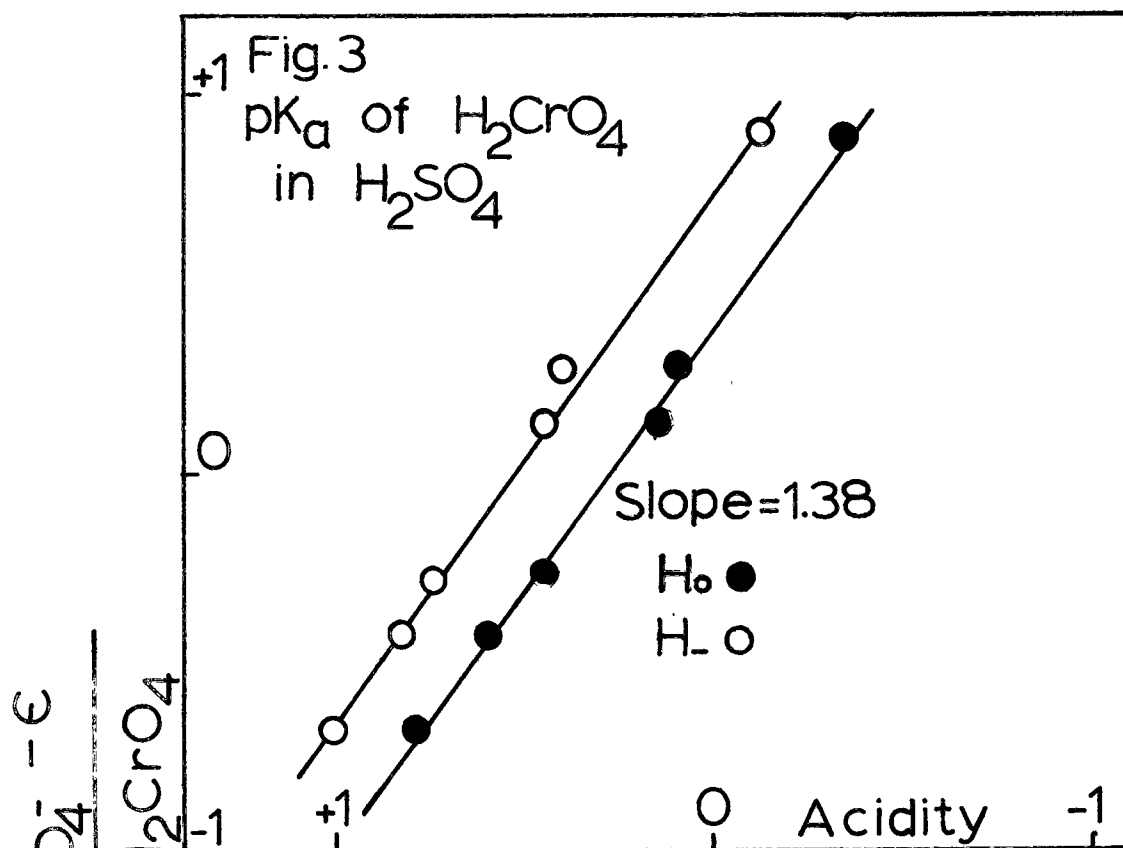
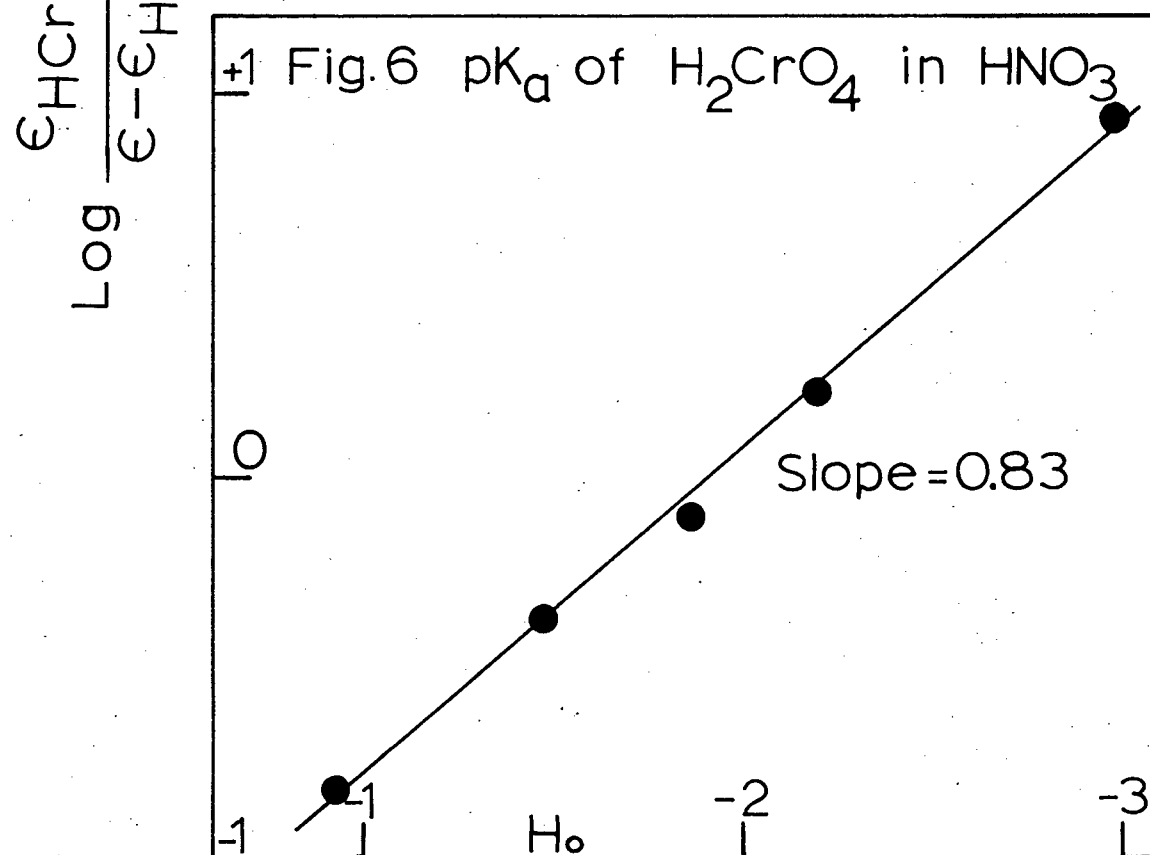
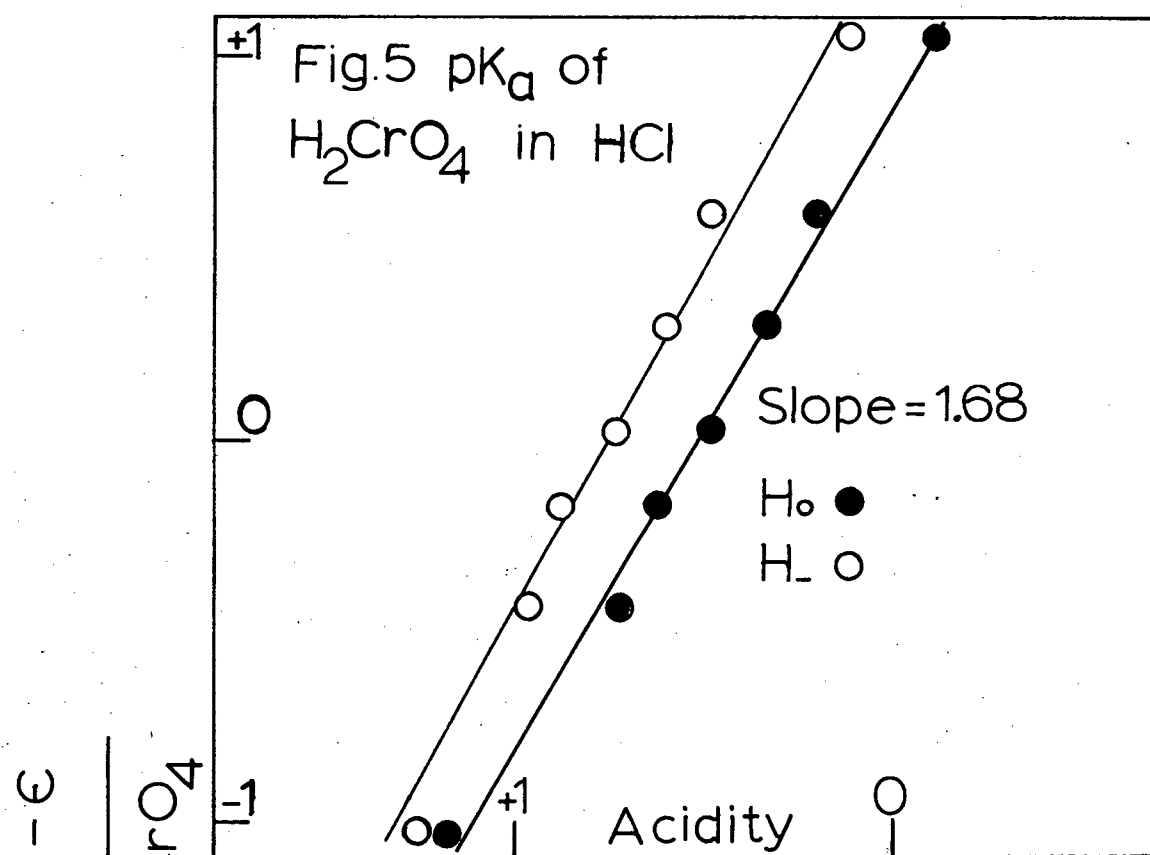
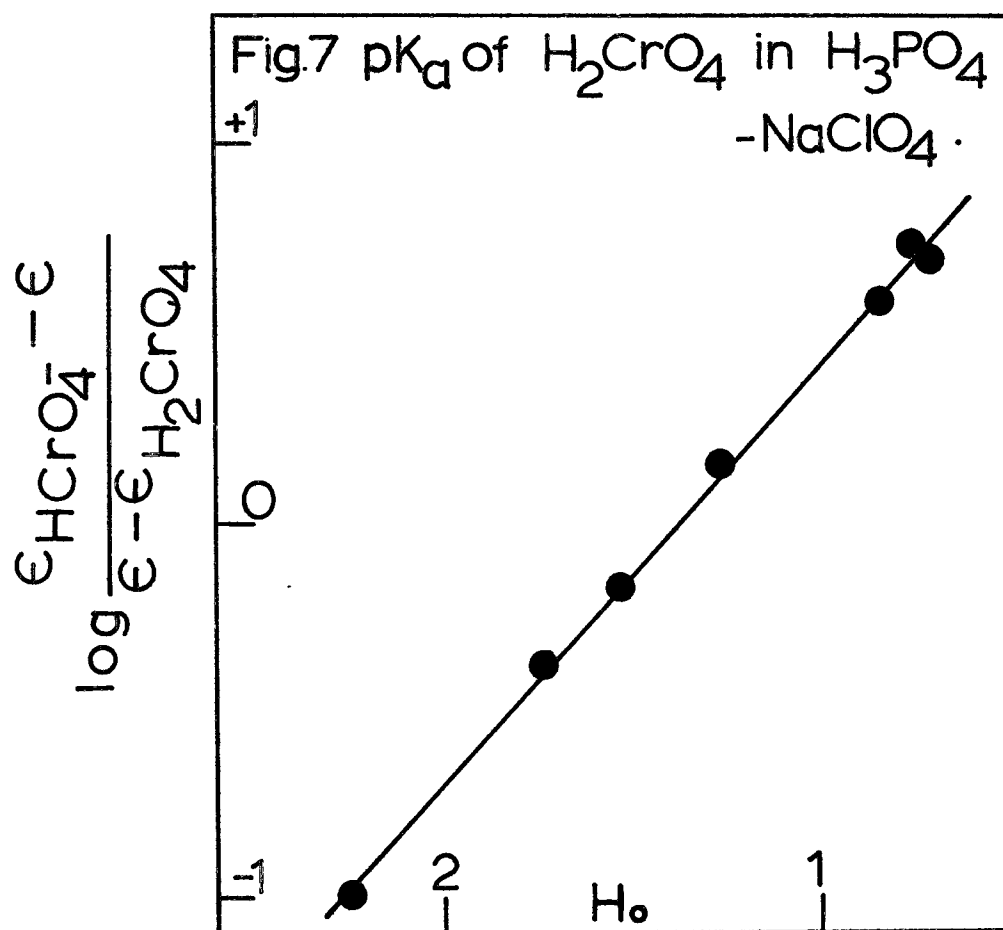


Fig.2 Typical rate plots for the oxidation of isopropyl alcohol in 0.463M HClO_4 .







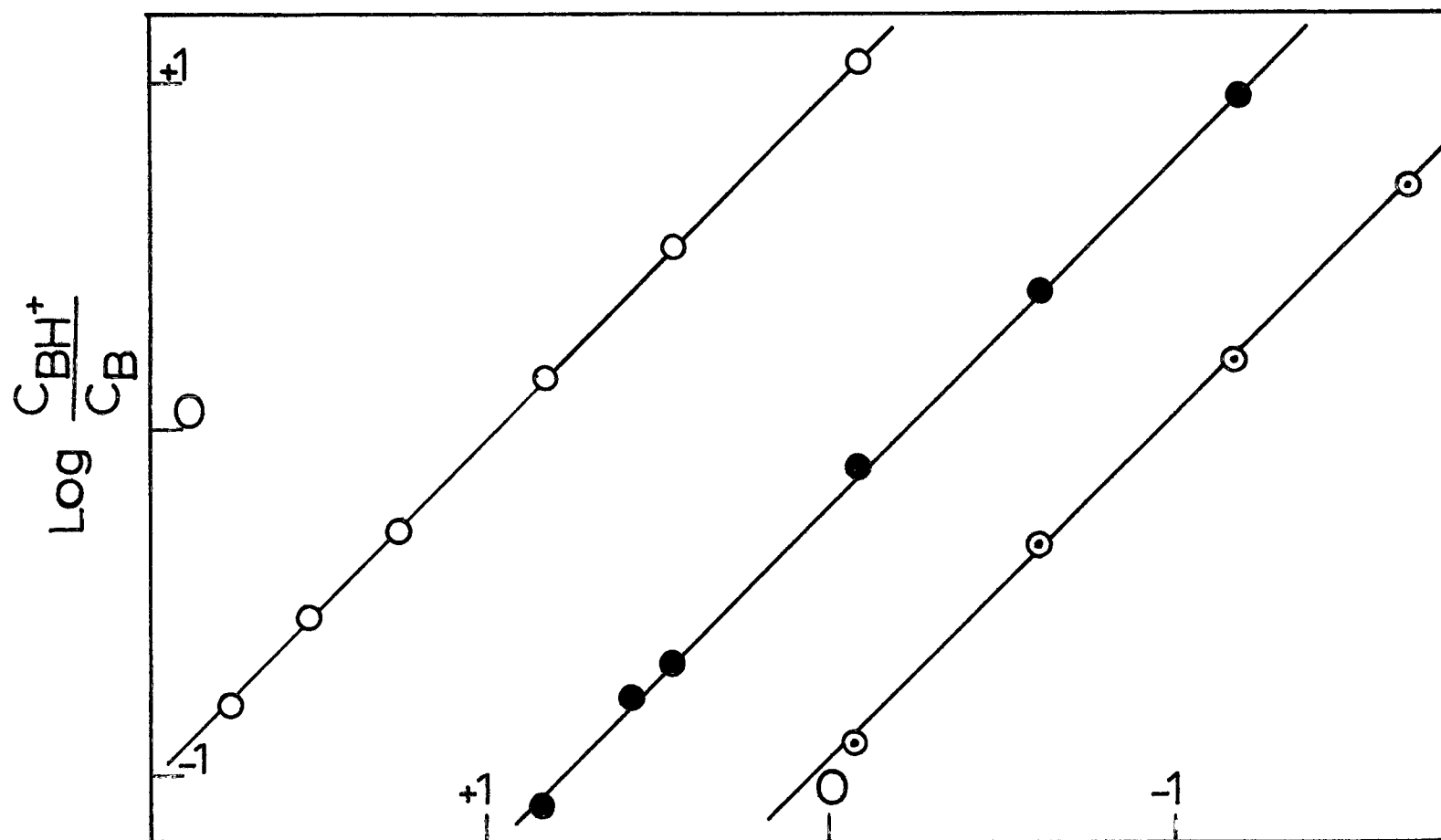


Fig.8 Ionization of indicators in H_3PO_4 - NaClO_4 solutions.
 ○, *o,p*-nitroaniline. ●, *o*-nitroaniline. ⊙, 4-chloro-2-nitroaniline.

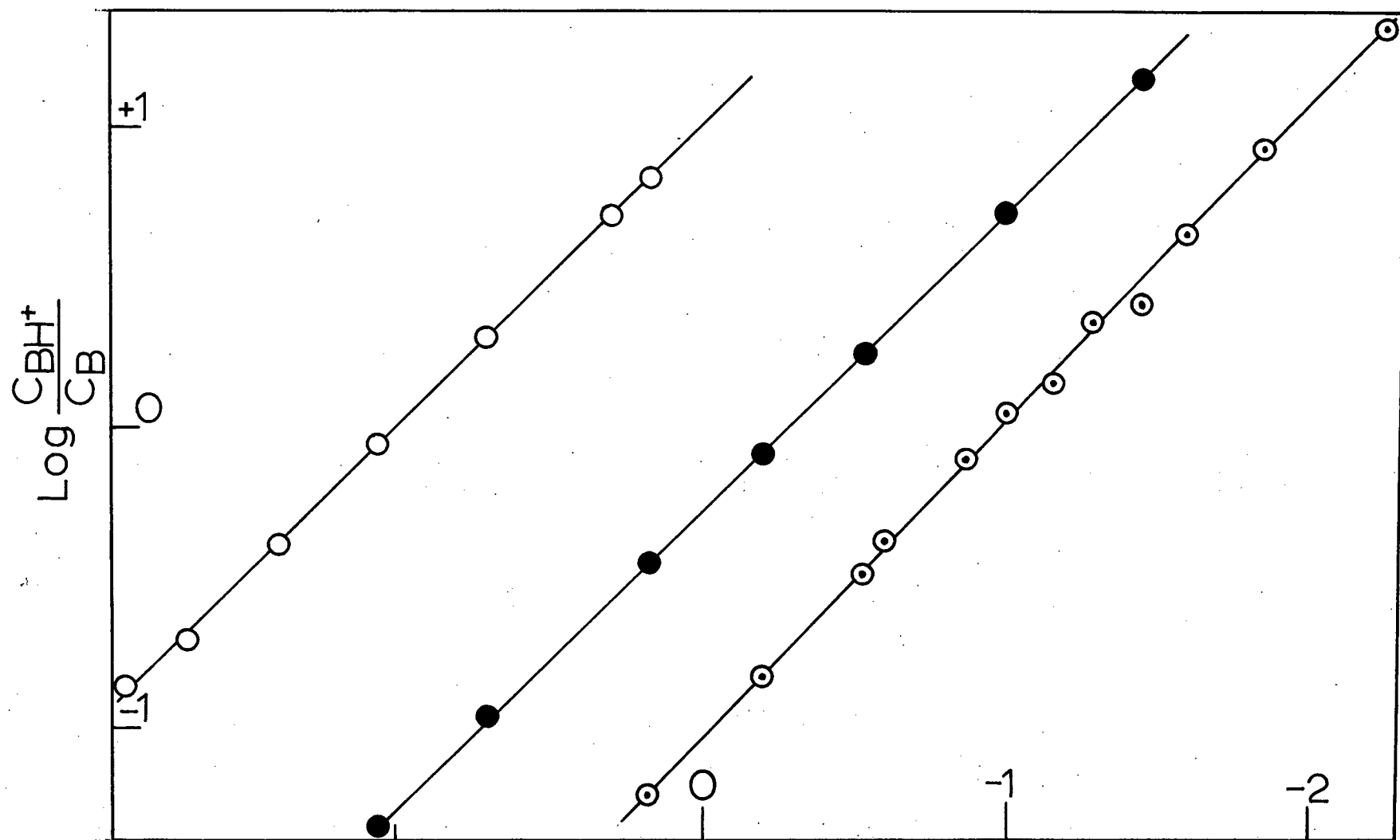


Fig.9 Ionization of indicators in $\text{HNO}_3\text{-NaClO}_4$ solutions. \circ , *o,p*-nitroaniline. \bullet , *o*-nitroaniline. \odot , 4-chloro-2-nitroaniline.

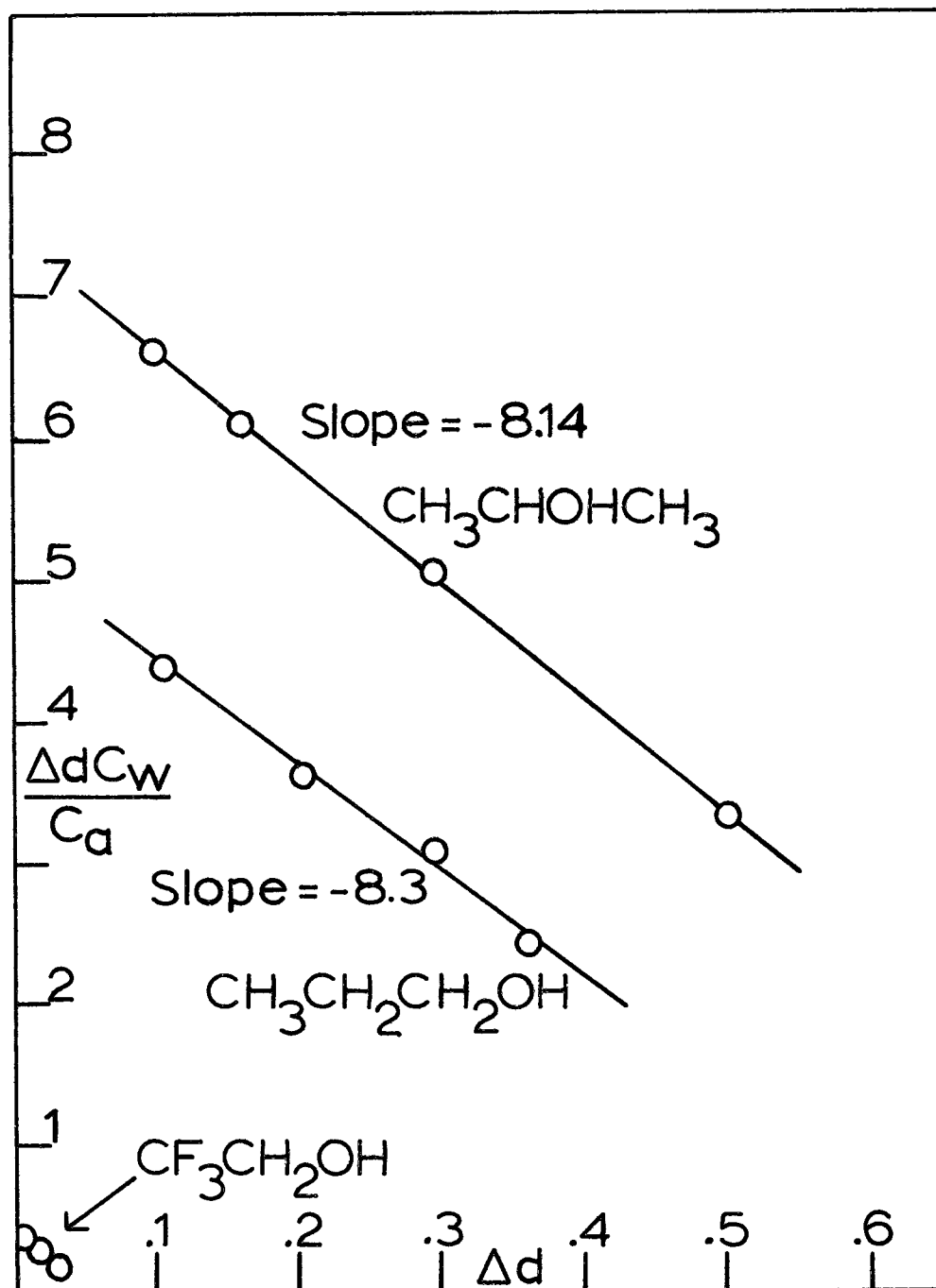
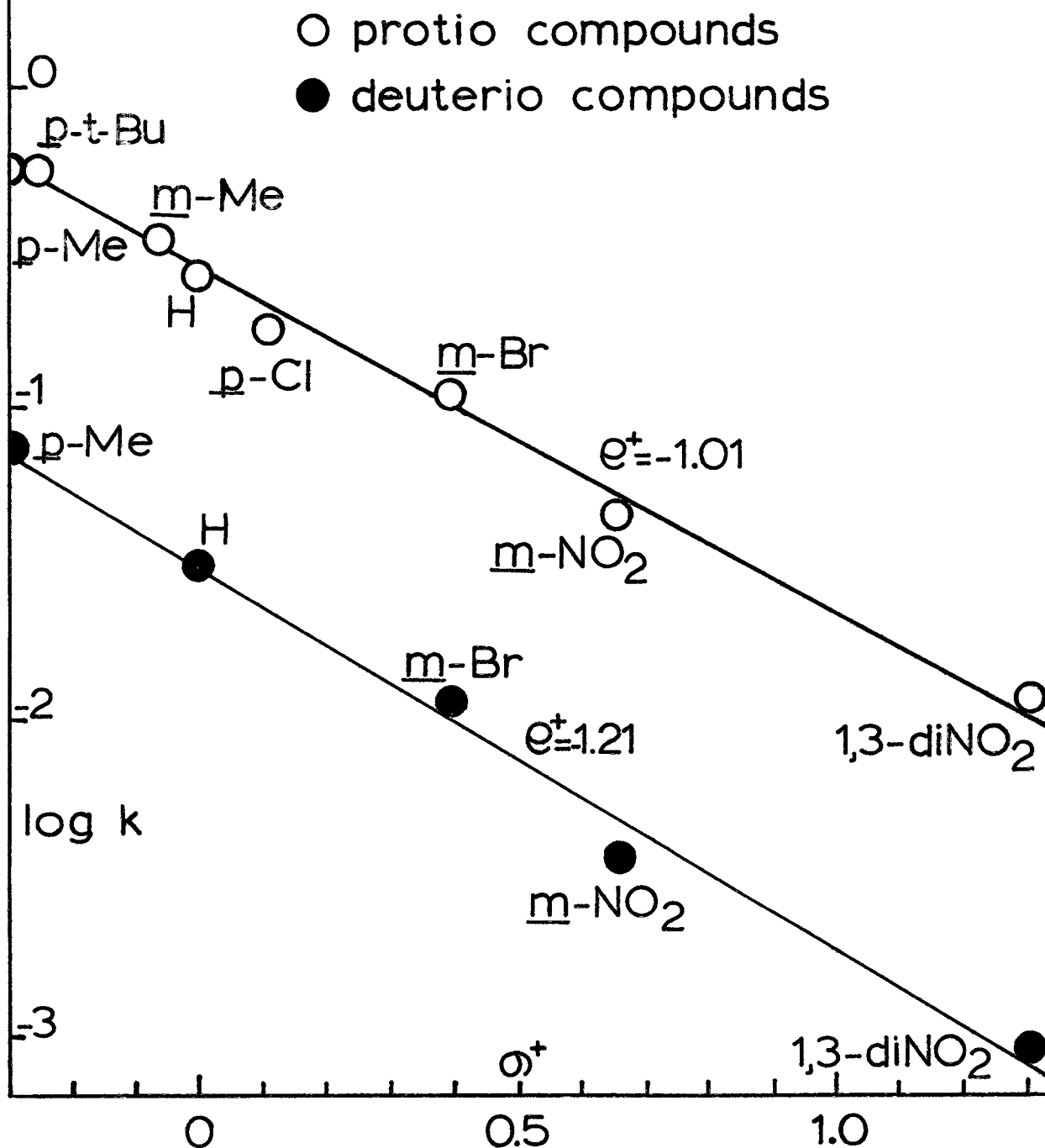
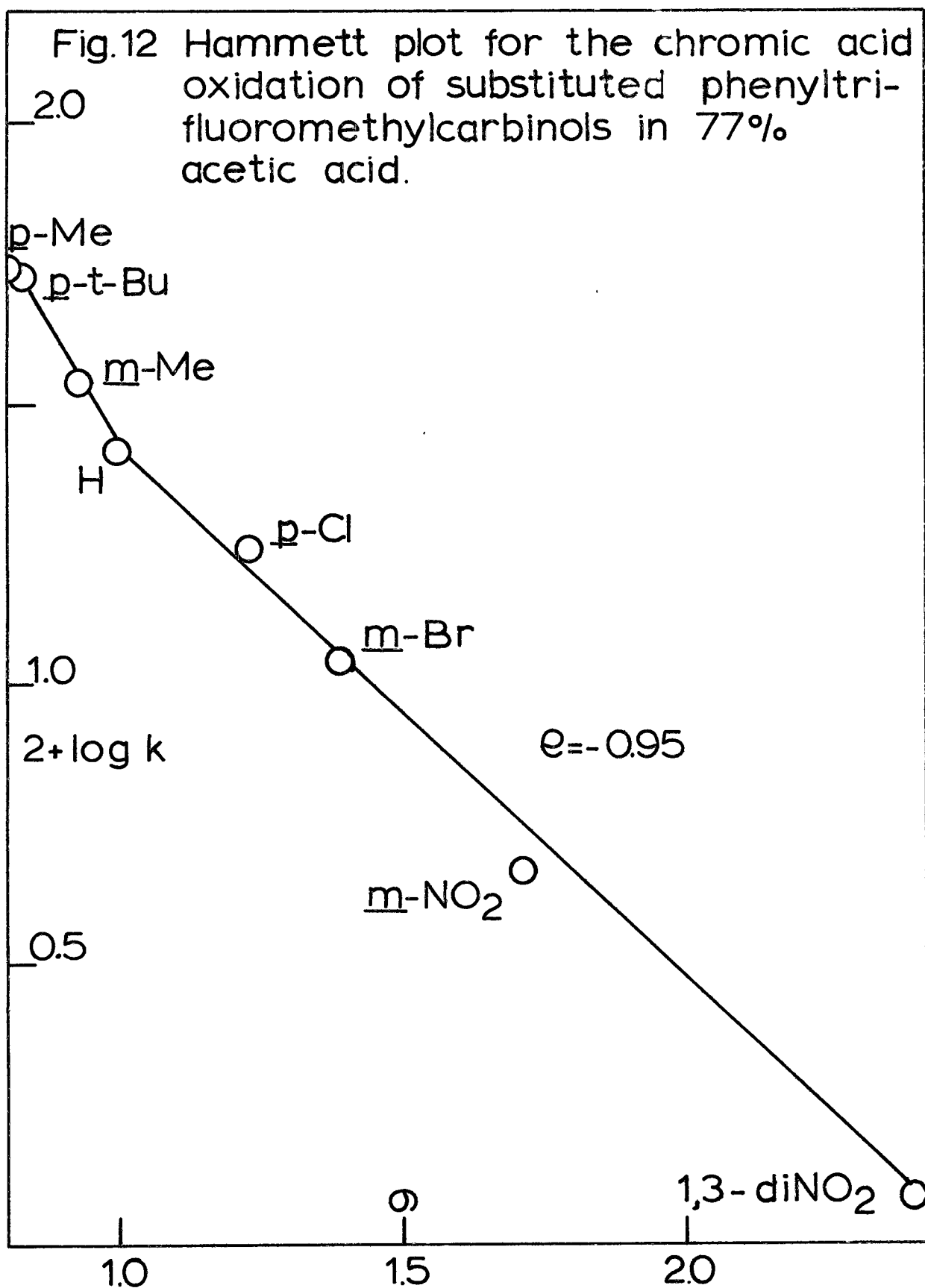


Fig.10 Chromate ester equilibrium Constants.

Fig.11 Hammett plot for the chromic acid oxidation of substituted phenyltrifluoromethylcarbinols in 77% acetic acid.





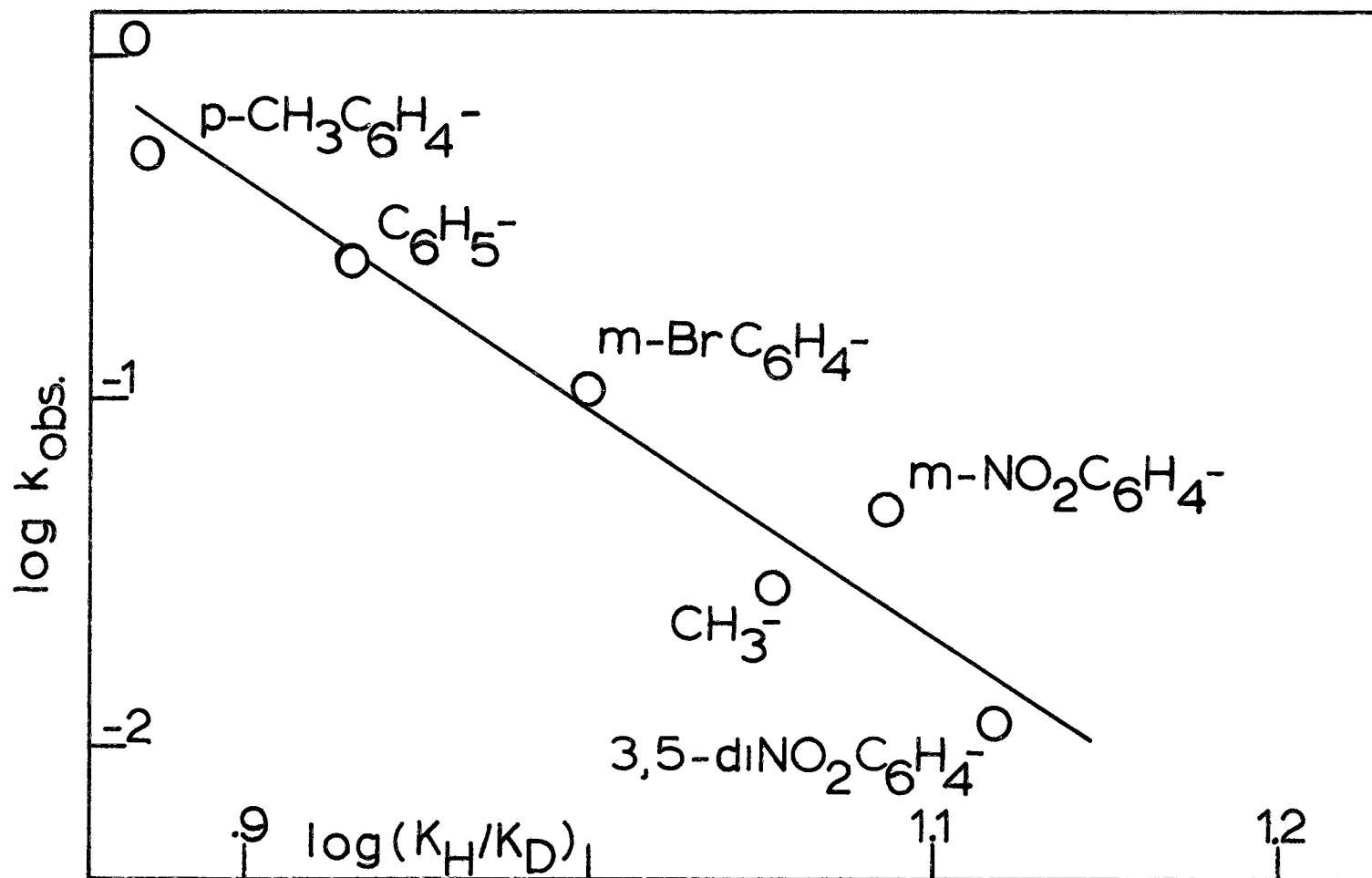


Fig.13 Relationship between the rate of oxidation of trifluoromethylcarbinols in 77.2% acetic acid and the primary deuterium isotope effects.

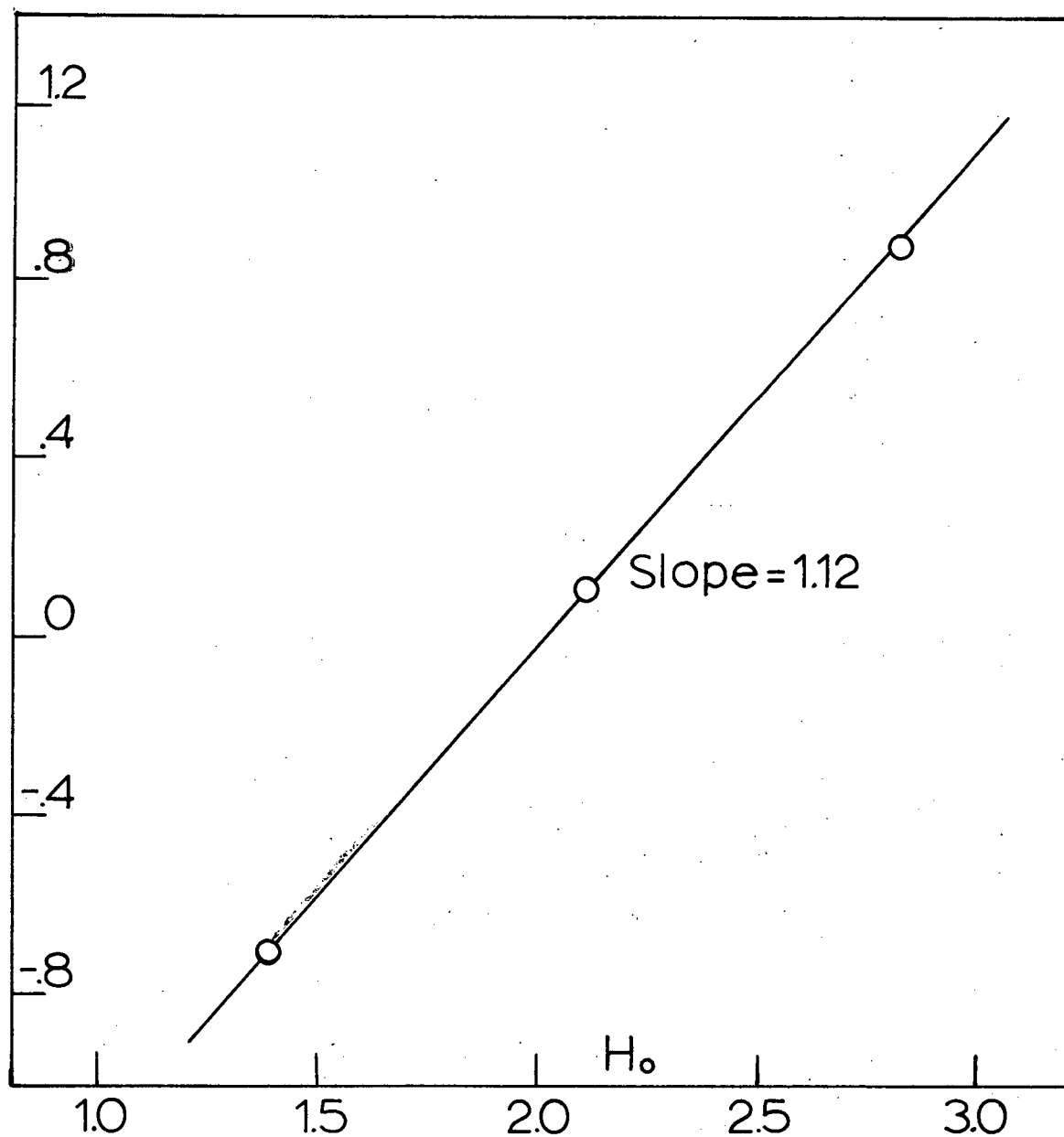


Fig.14 Linear relationship between rate and acidity for the oxidation of phenyl-trifluoromethylcarbinol in 77.2% acetic acid.

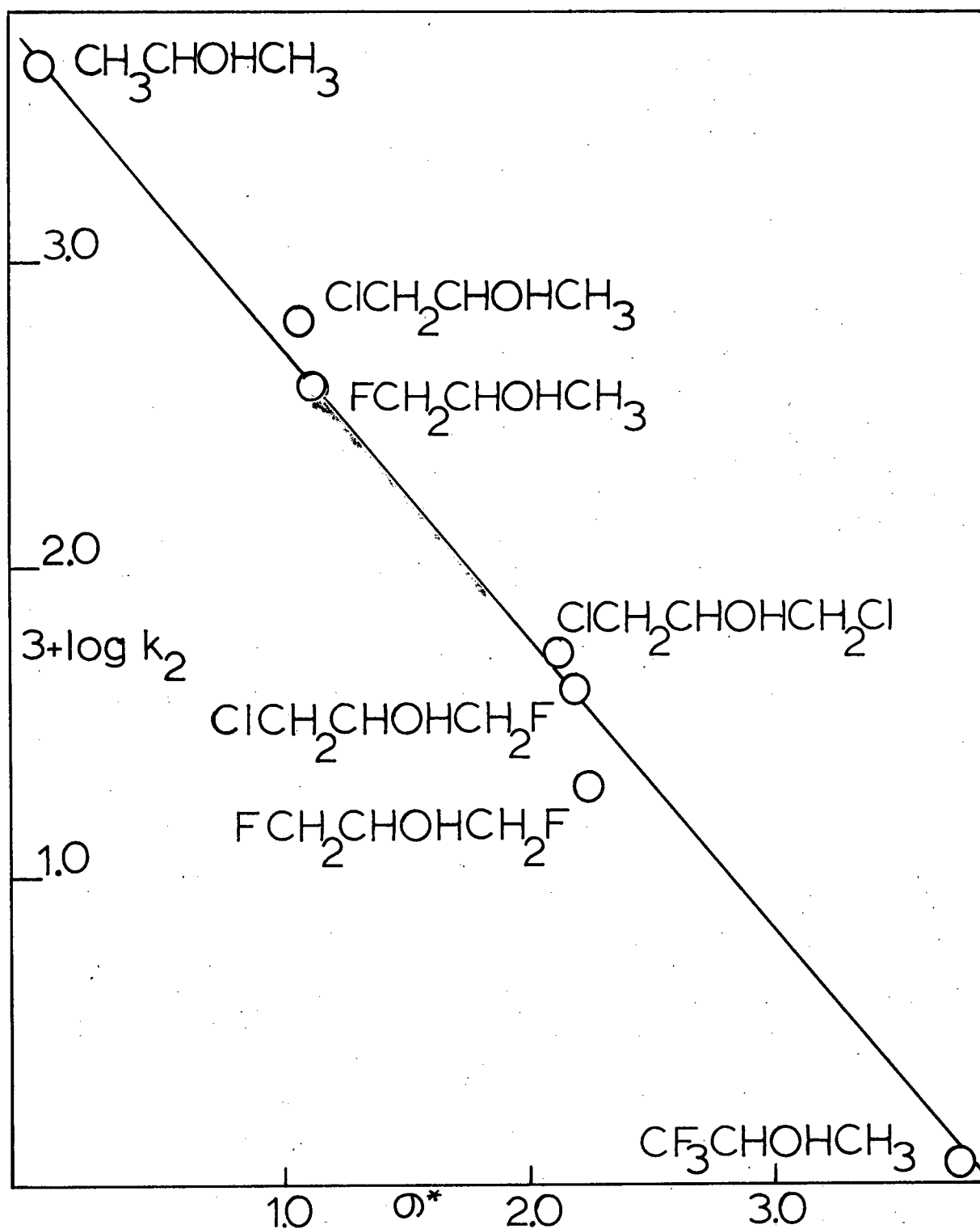
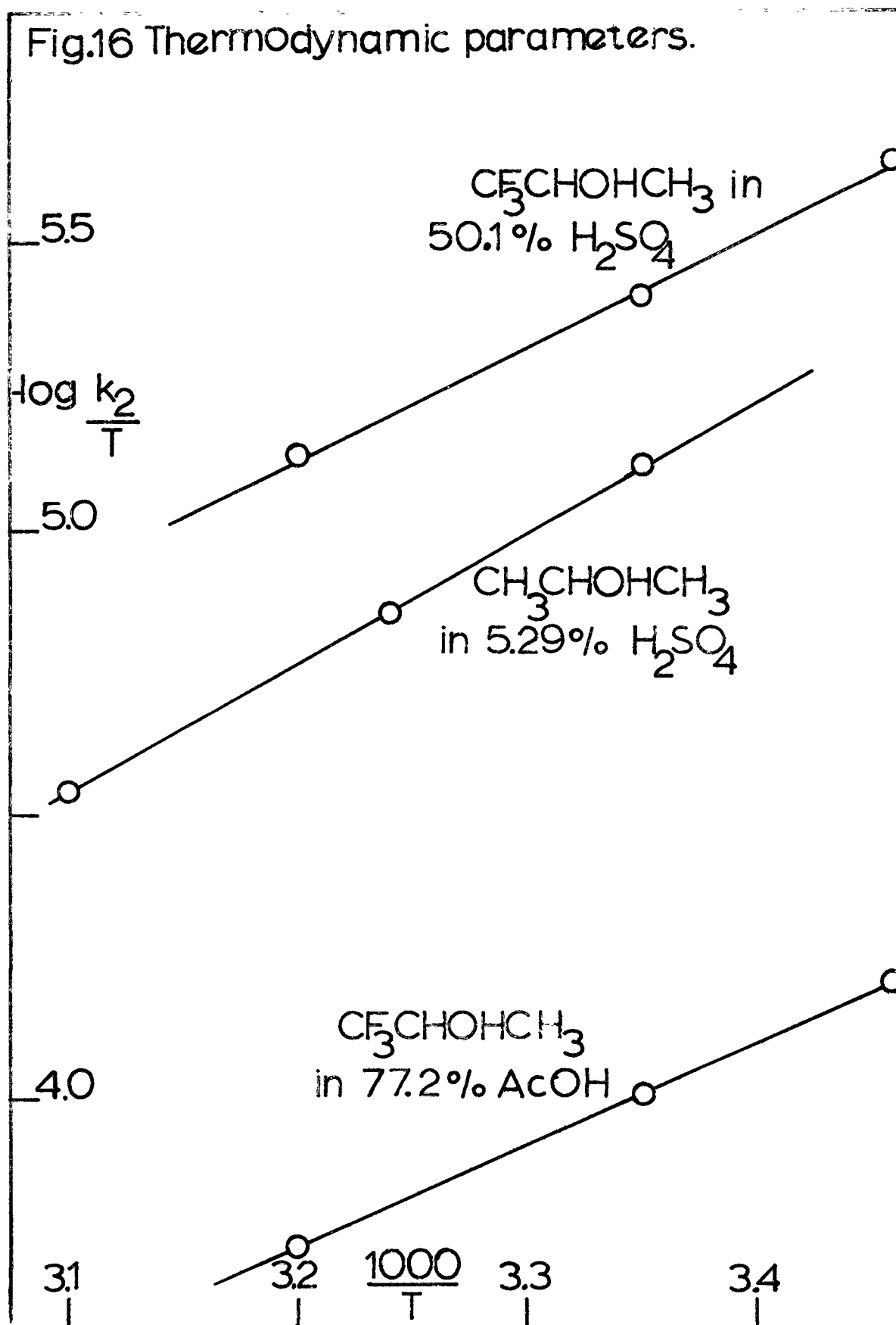
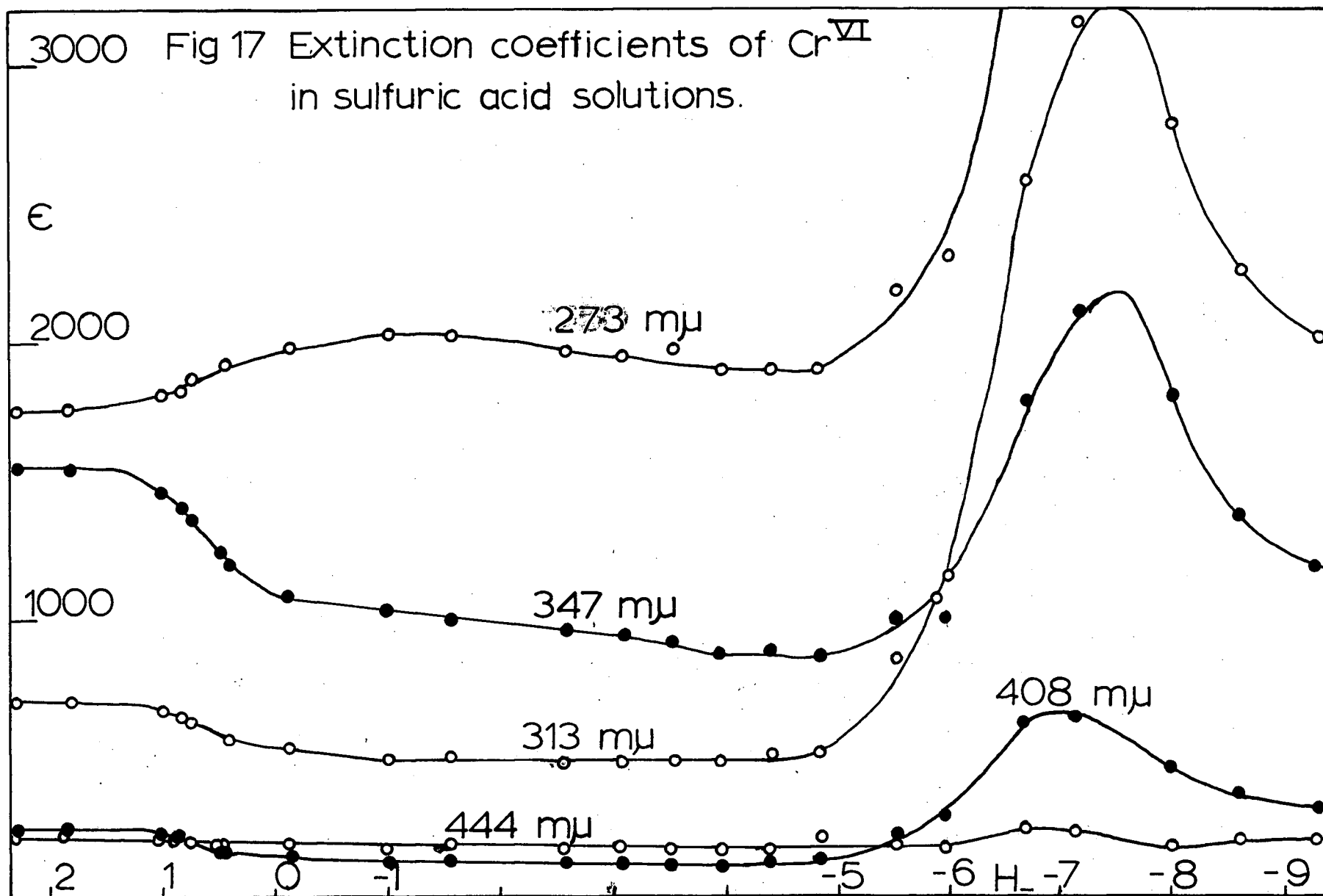
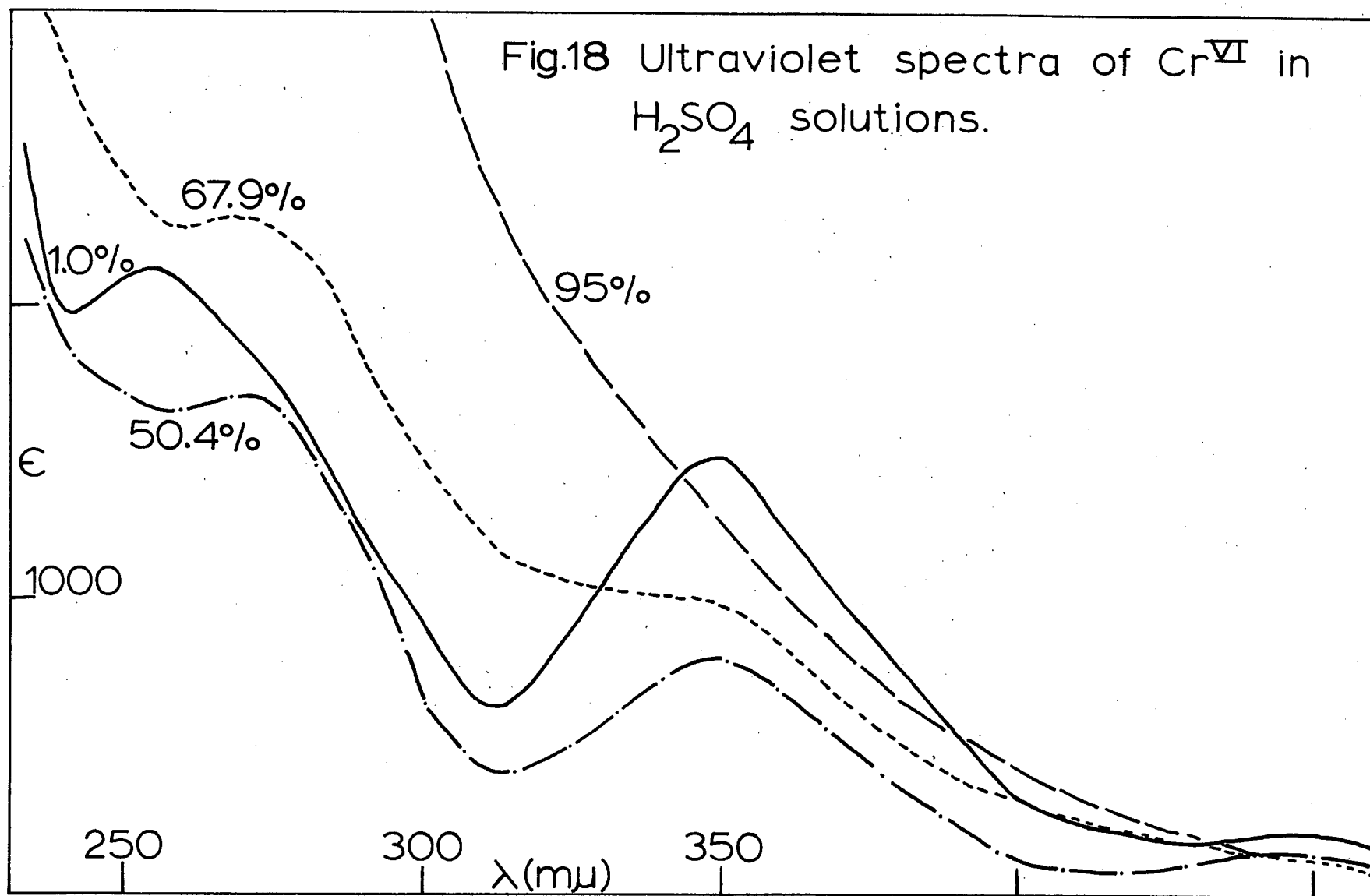


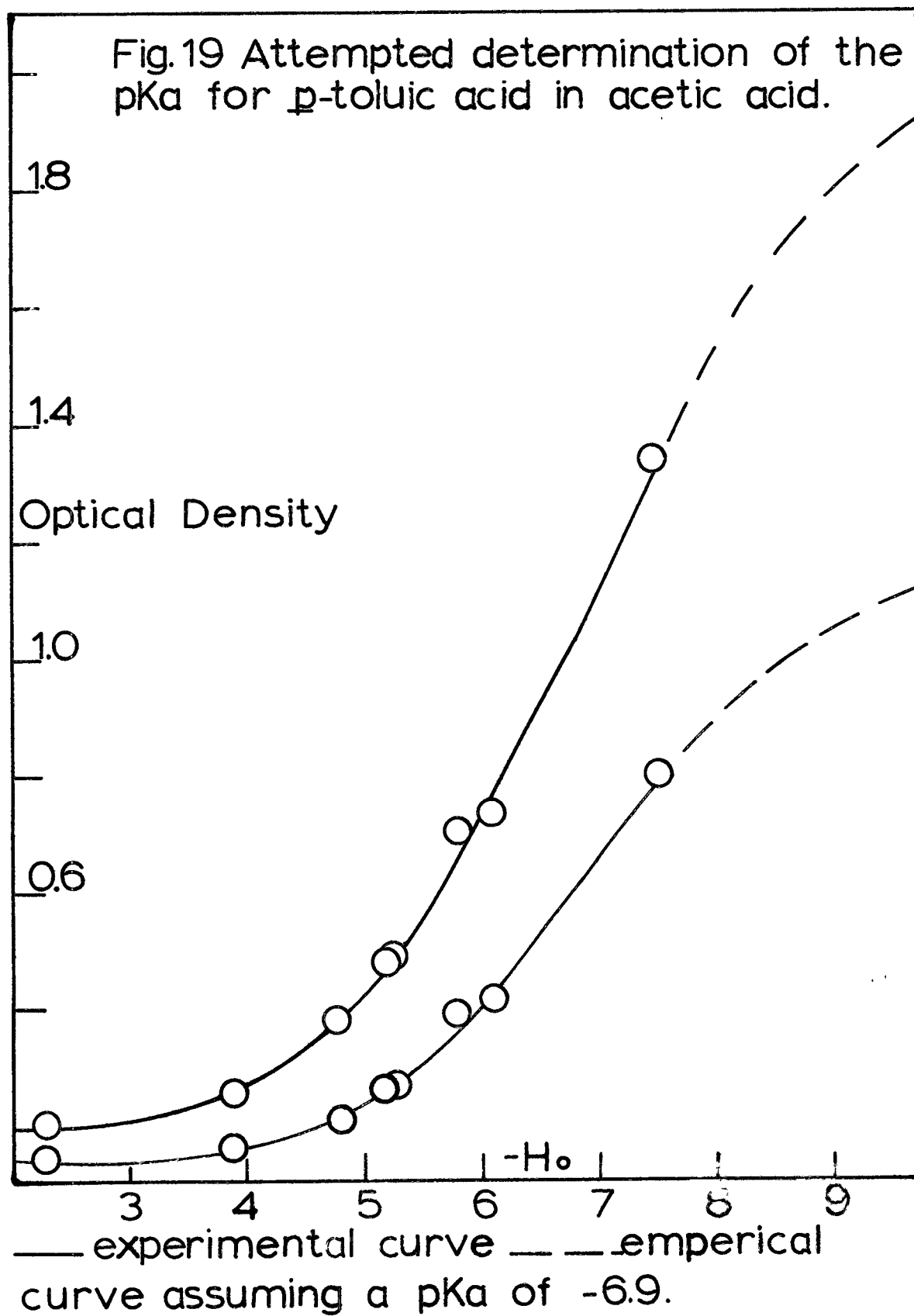
Fig.15 Taft ρ^* - e^* plot for the oxidation of substituted 2-propanols in 50.1% H_2SO_4 .

Fig.16 Thermodynamic parameters.









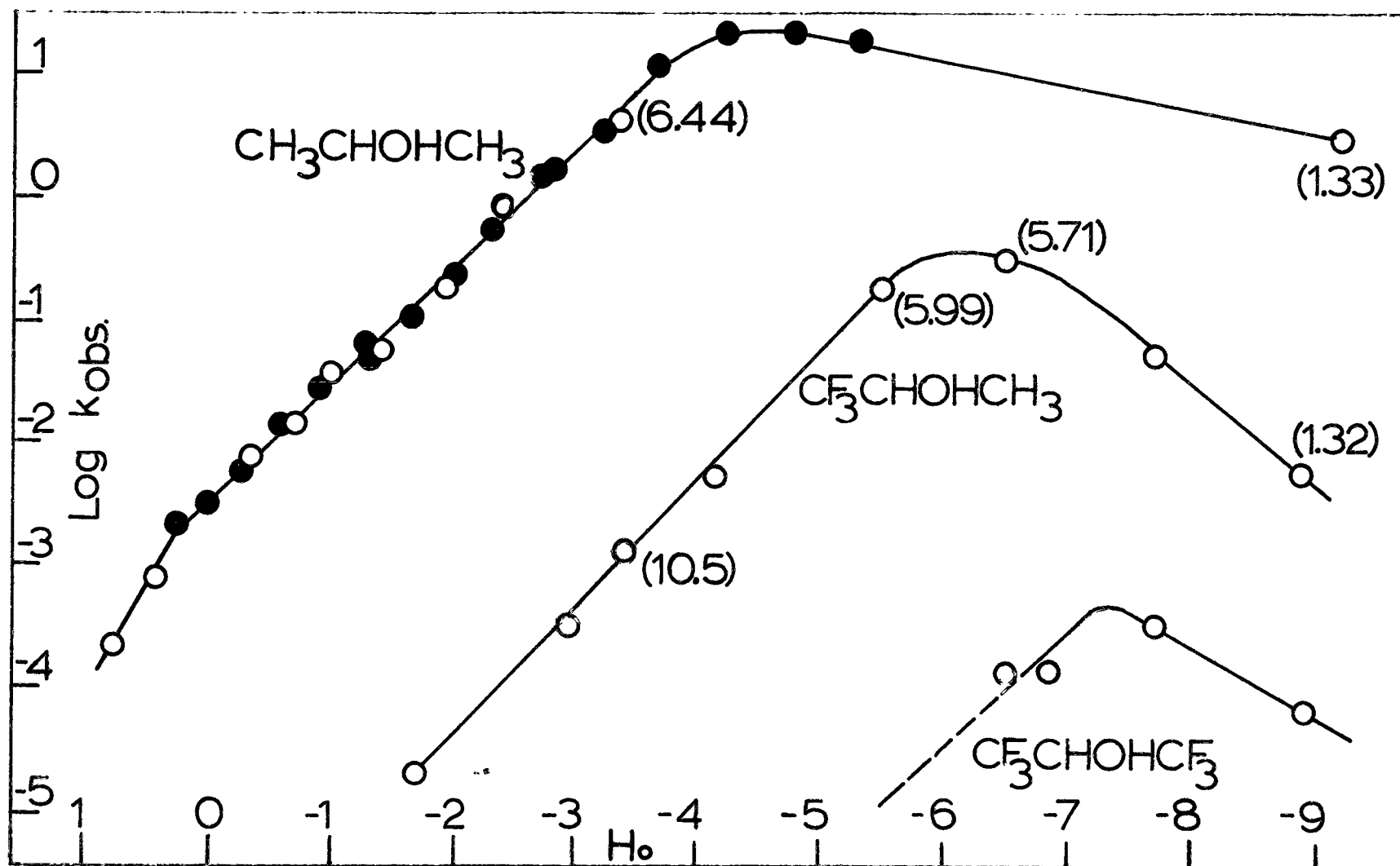
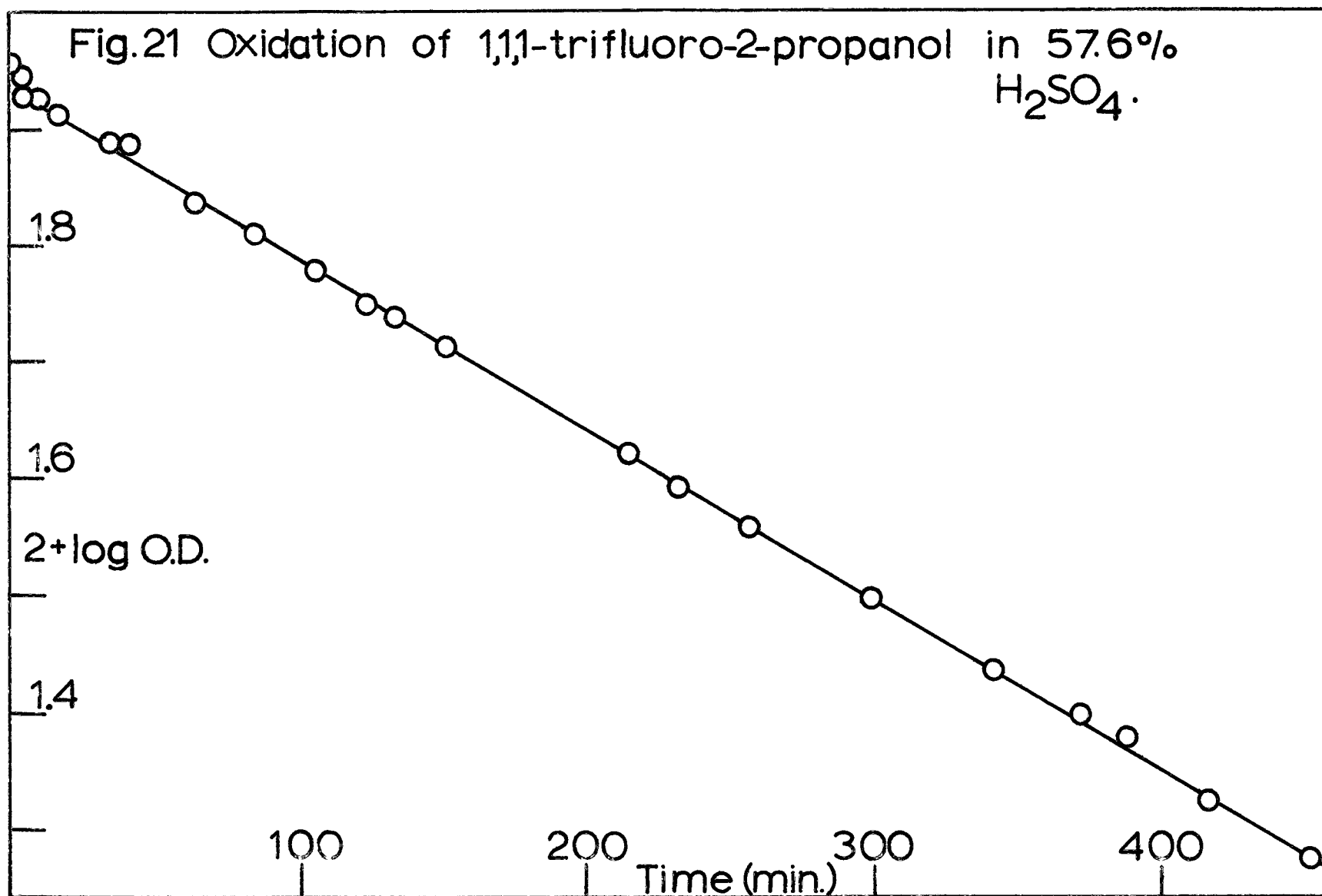
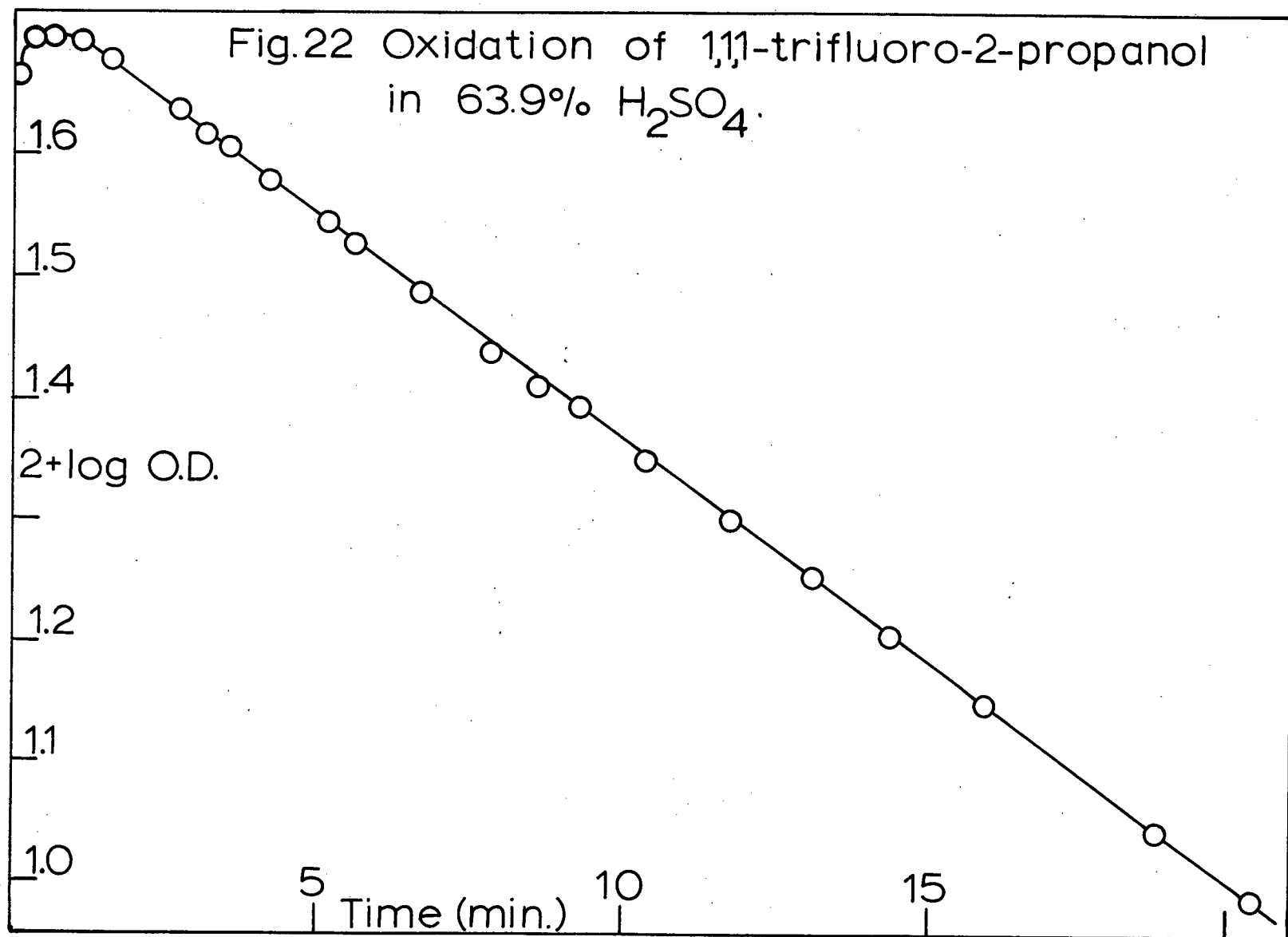
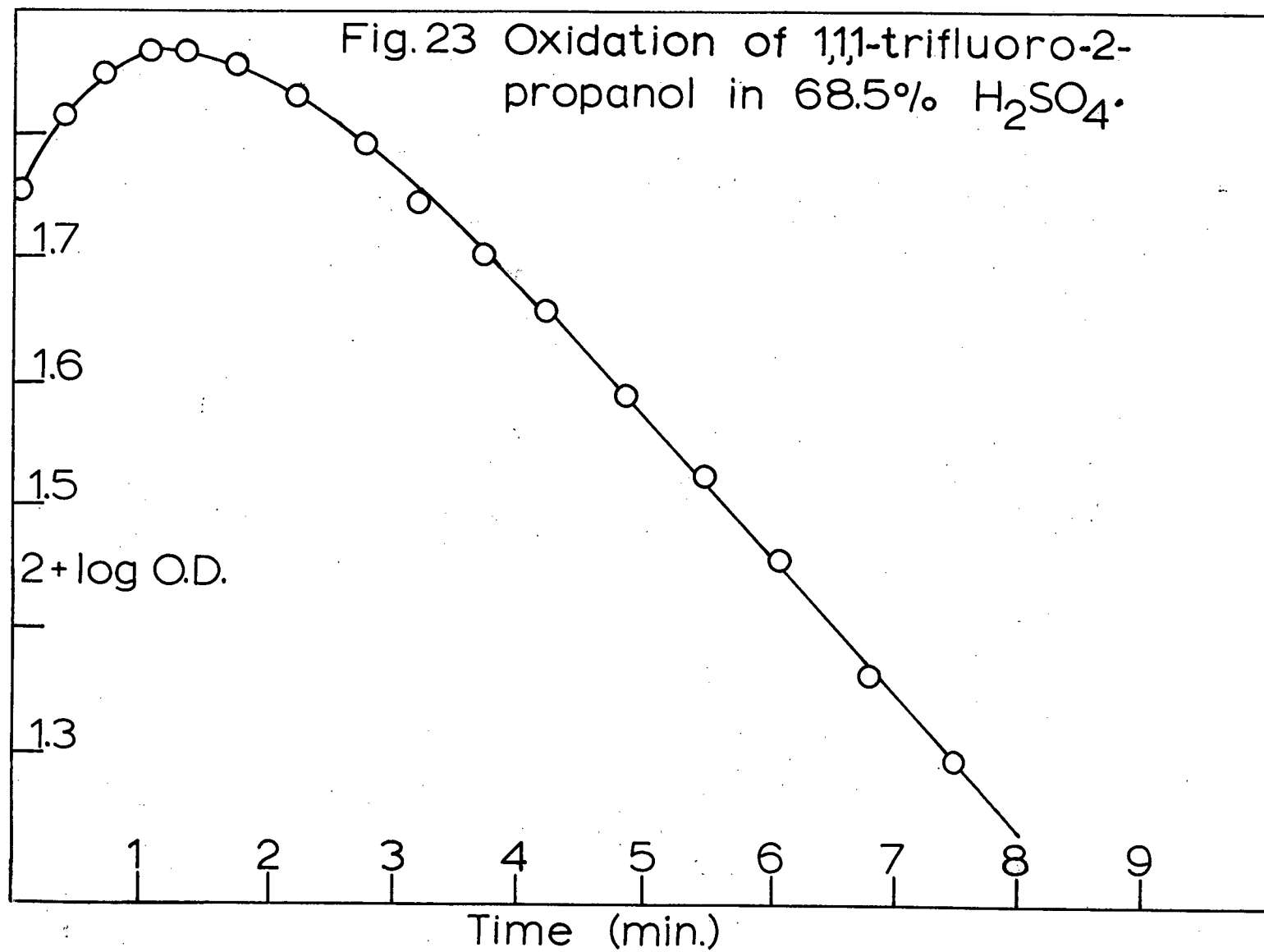
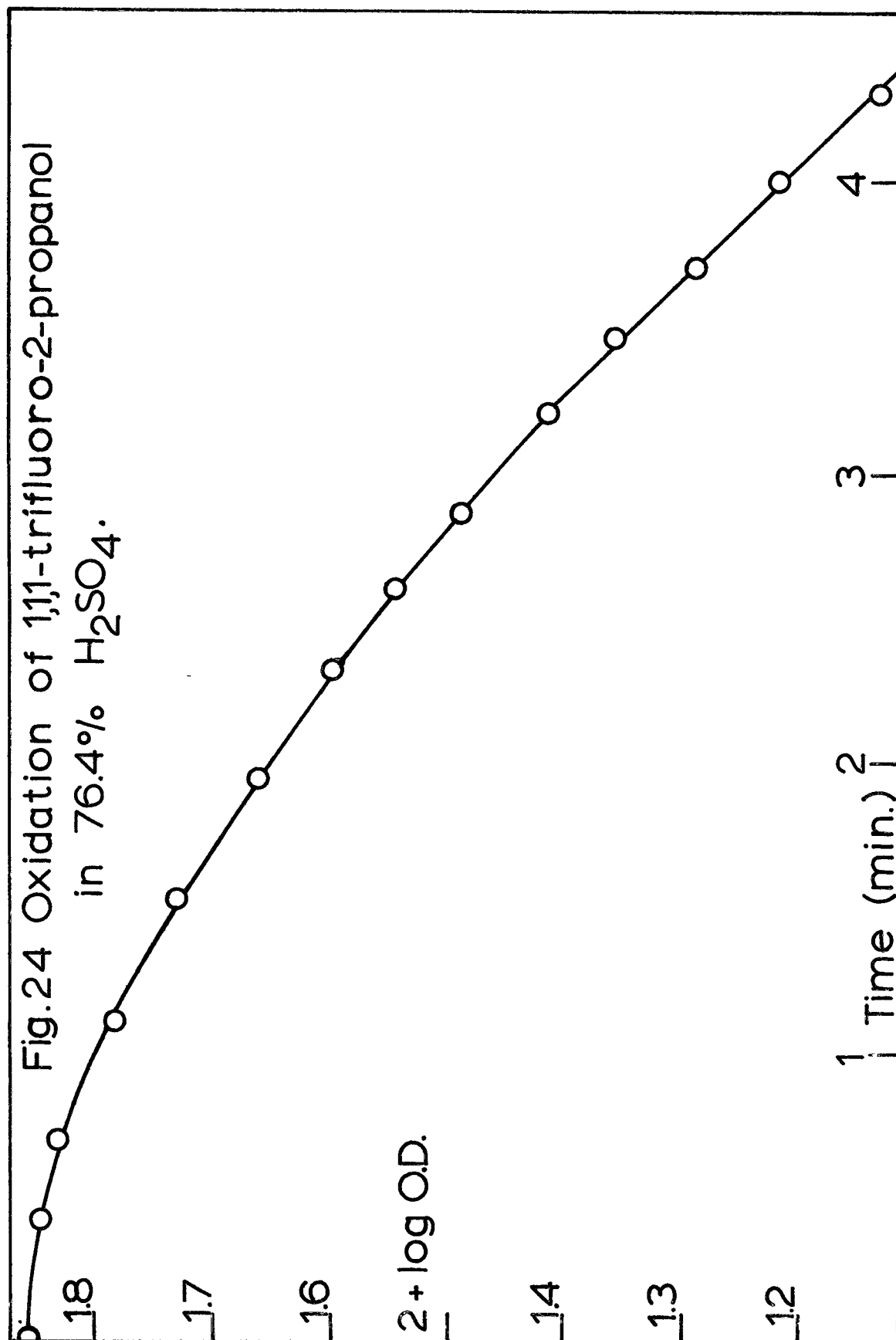


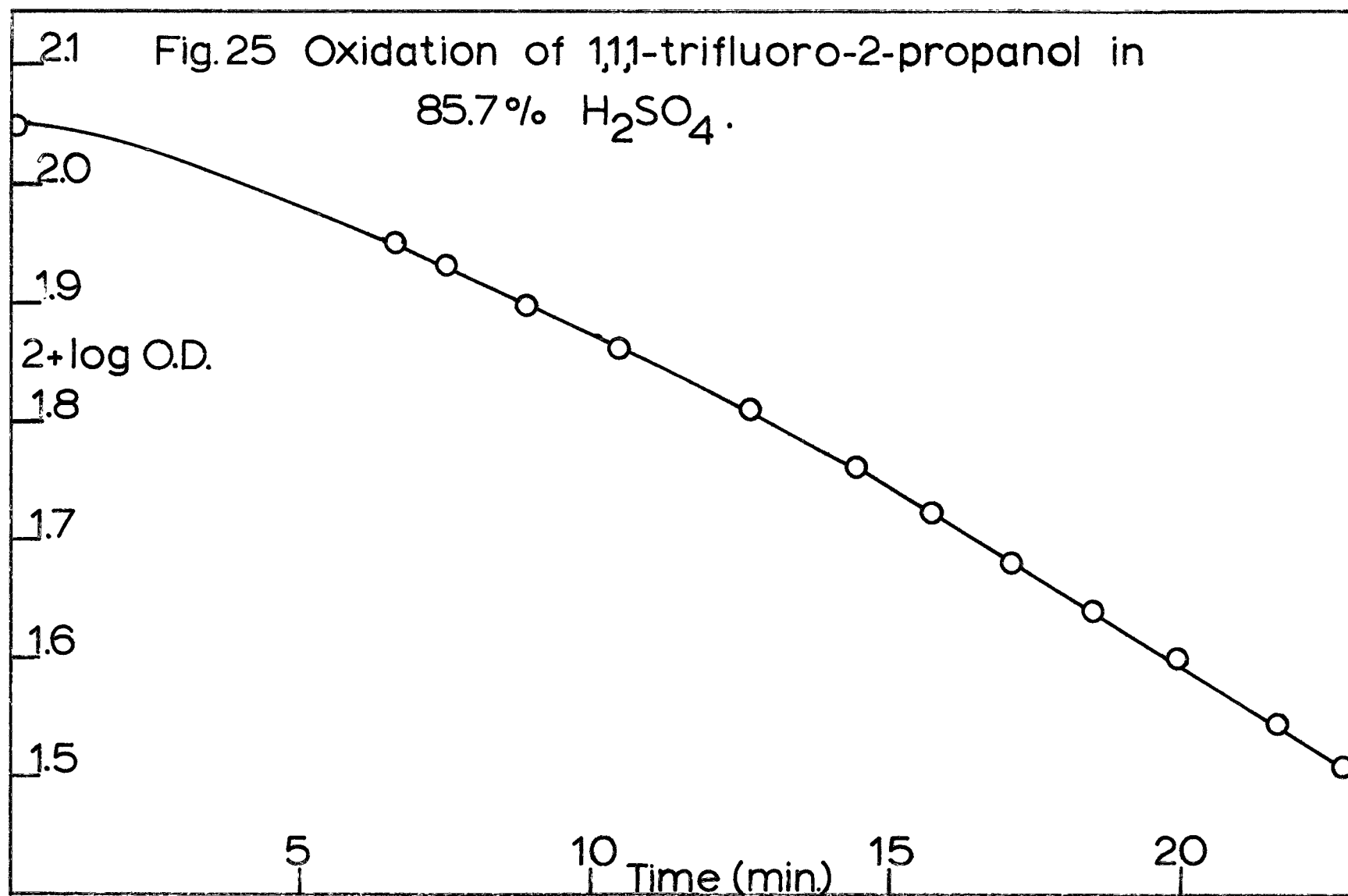
Fig.20 Relationship between H_0 and the rate of oxidation of three 2-propanols in sulphuric acid solutions. Primary deuterium isotope effects indicated in parenthesis.

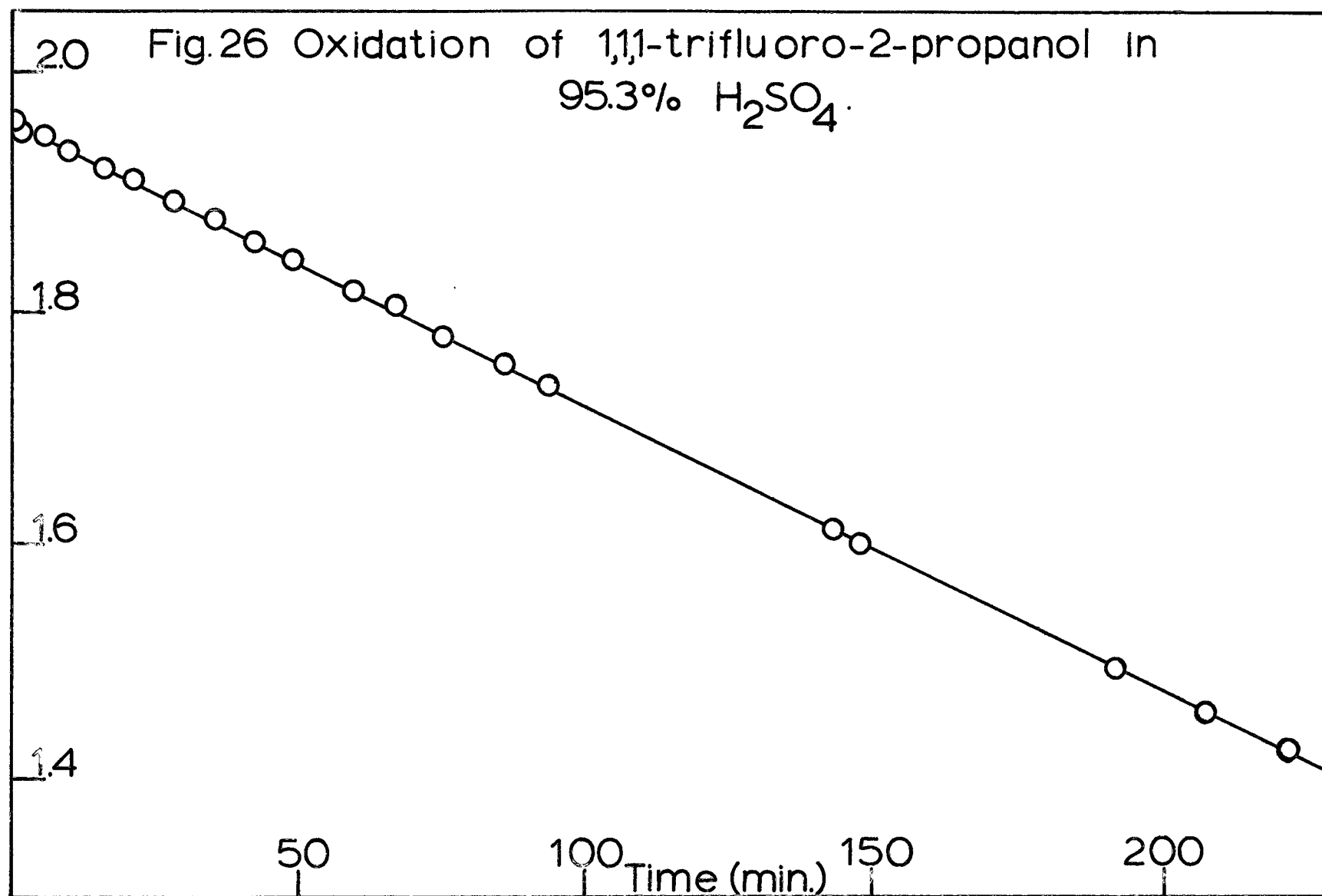












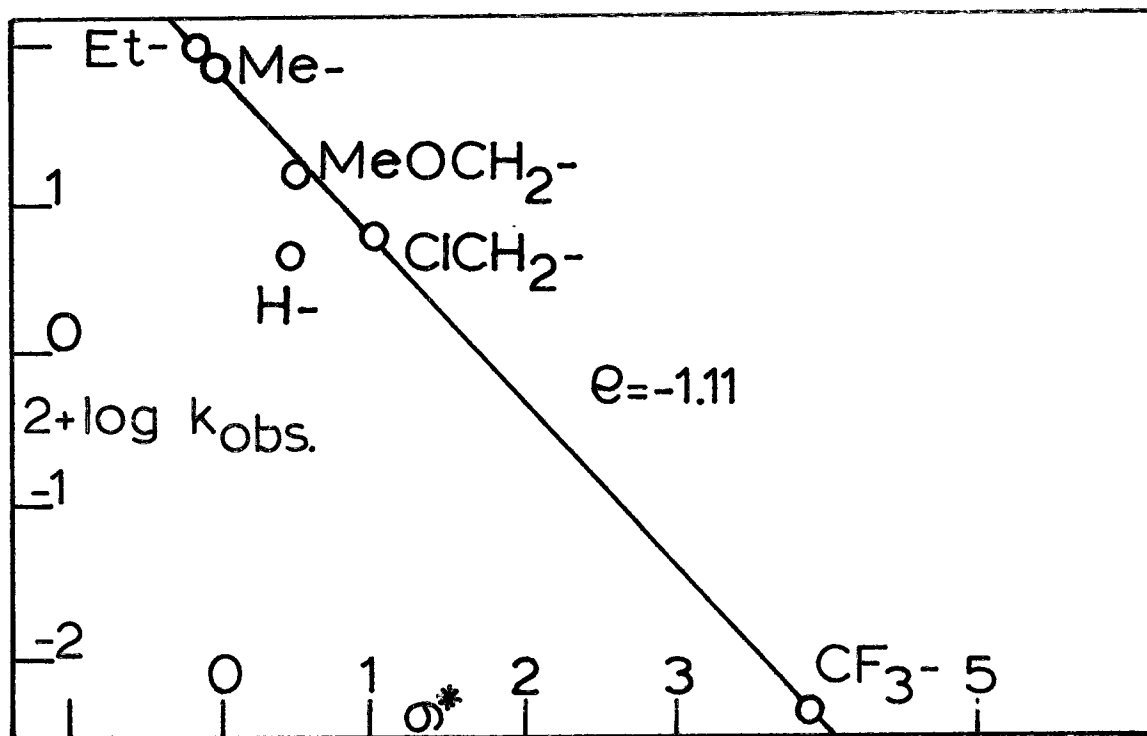


Fig.27 Relationship between k_{obs} and σ^* for the oxidation of substituted methanols.

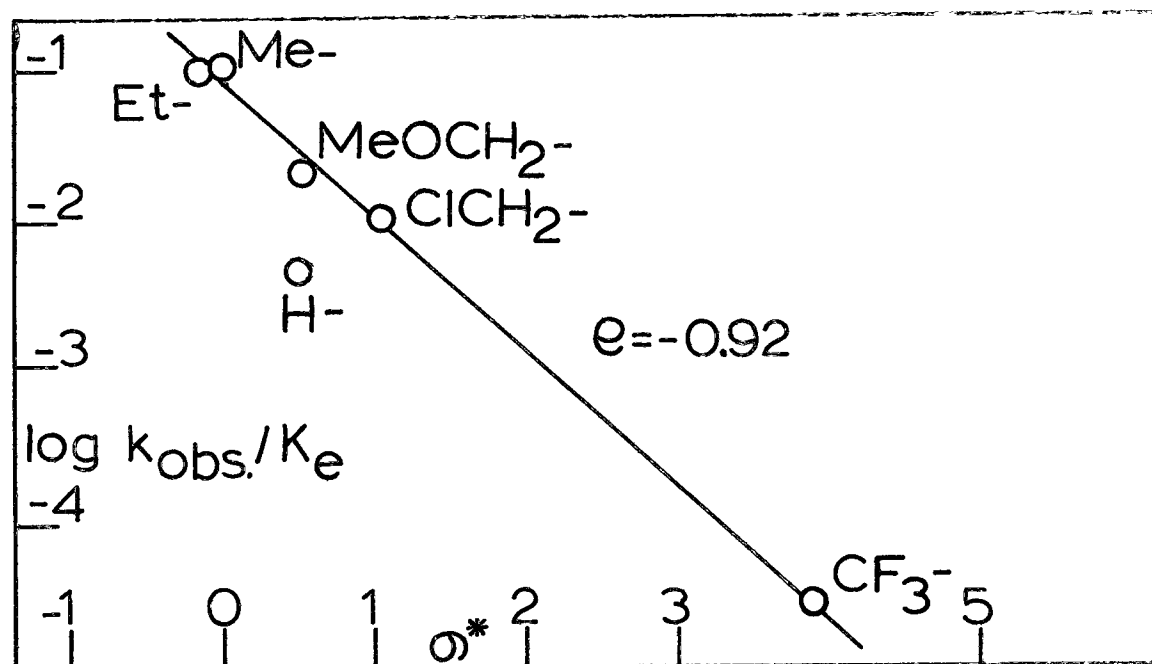
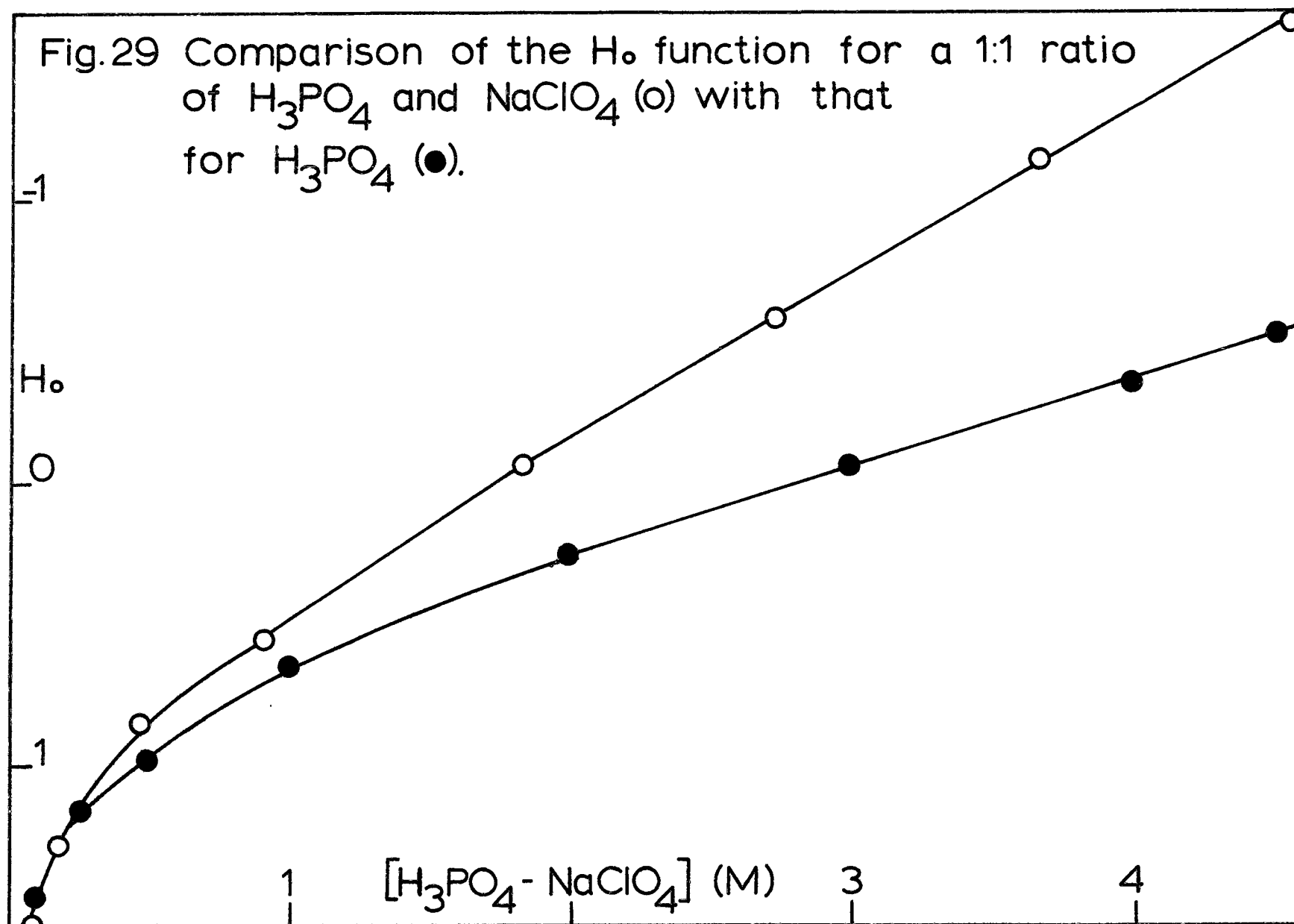


Fig.28 Relationship between the "true rate constant" and σ^* .



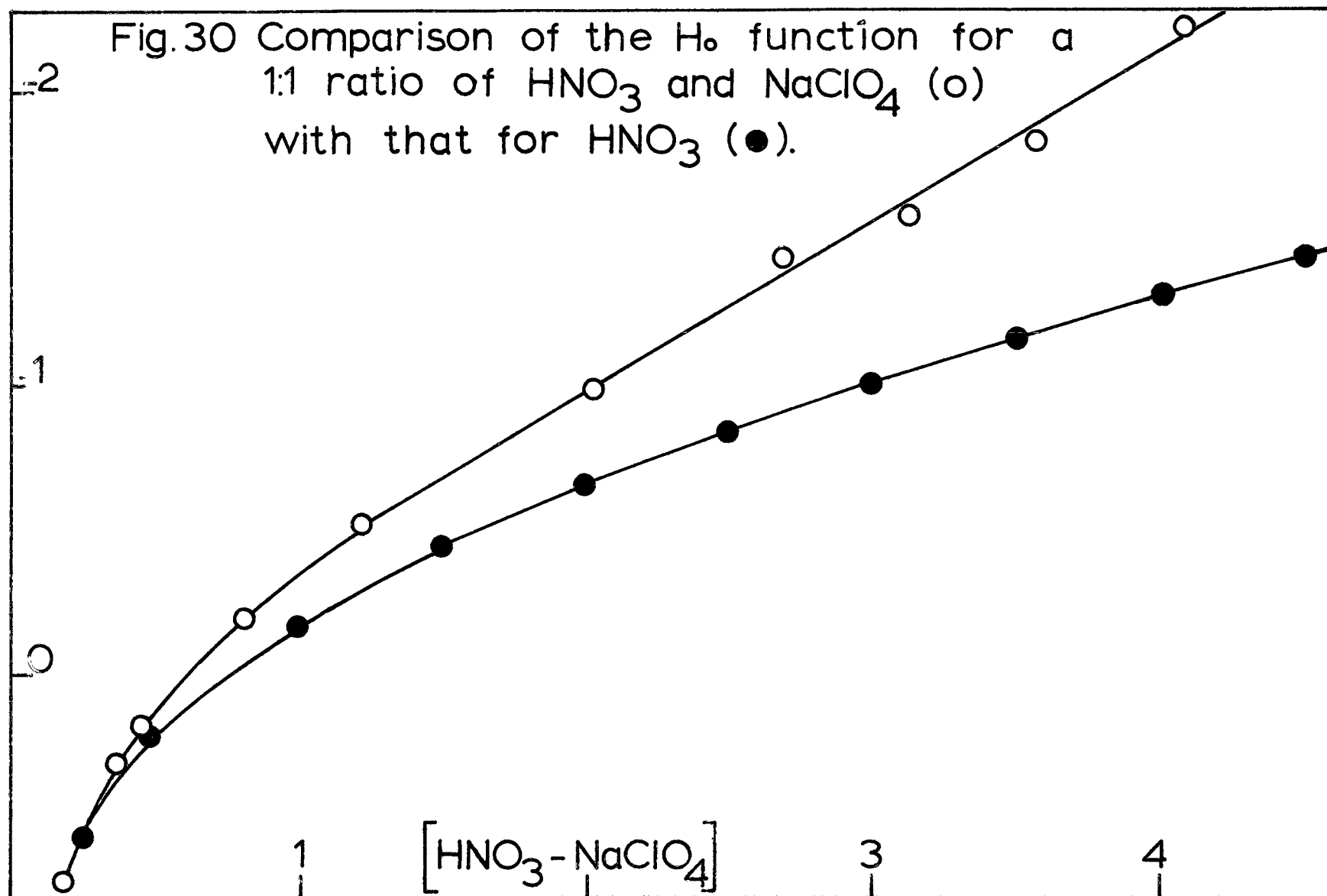


Fig.31 Ultraviolet spectrum of Cr^{VI} in 3.50 HClO_4 .

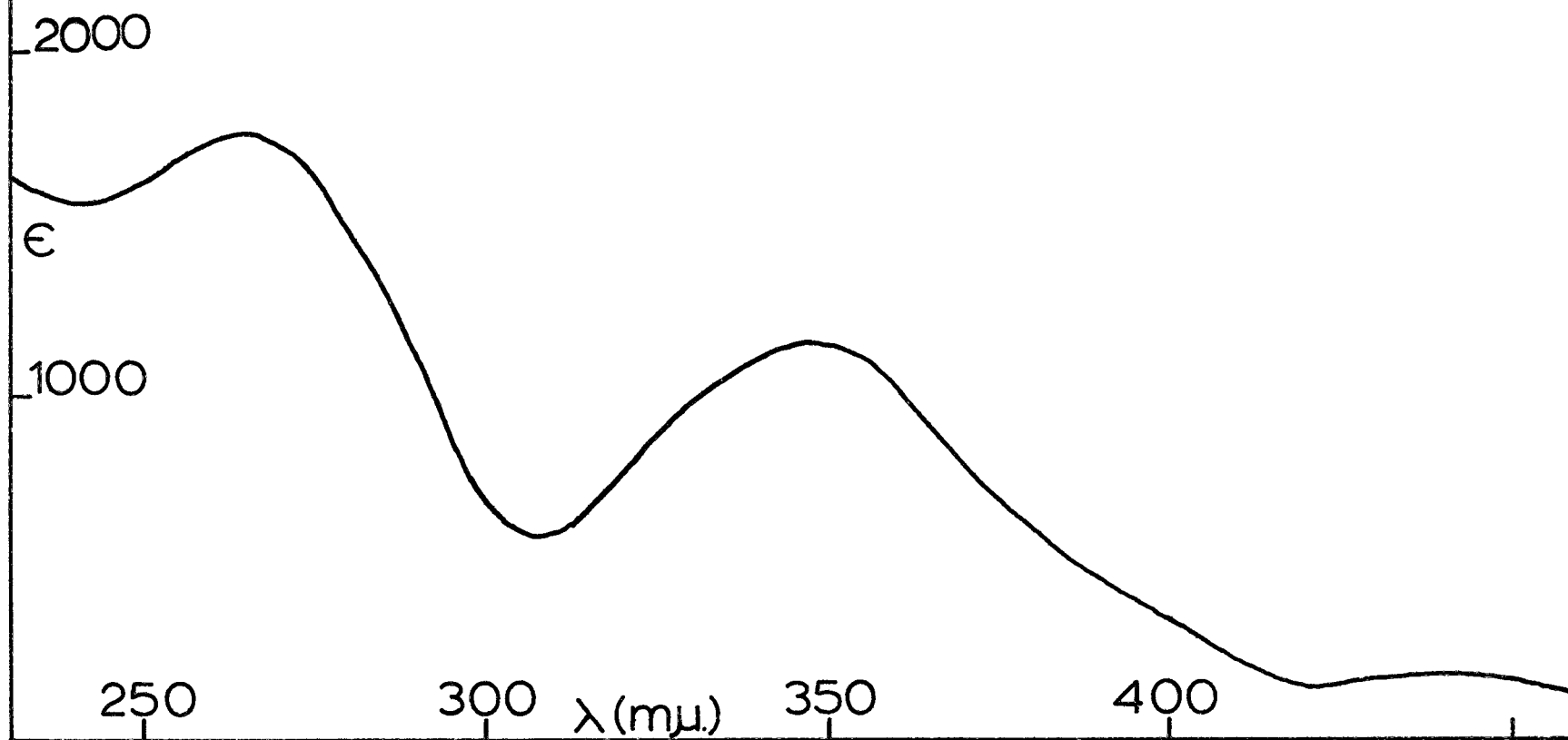


Fig.32 Ultraviolet spectrum of Cr^{VI} in 3.10M H_2SO_4 .

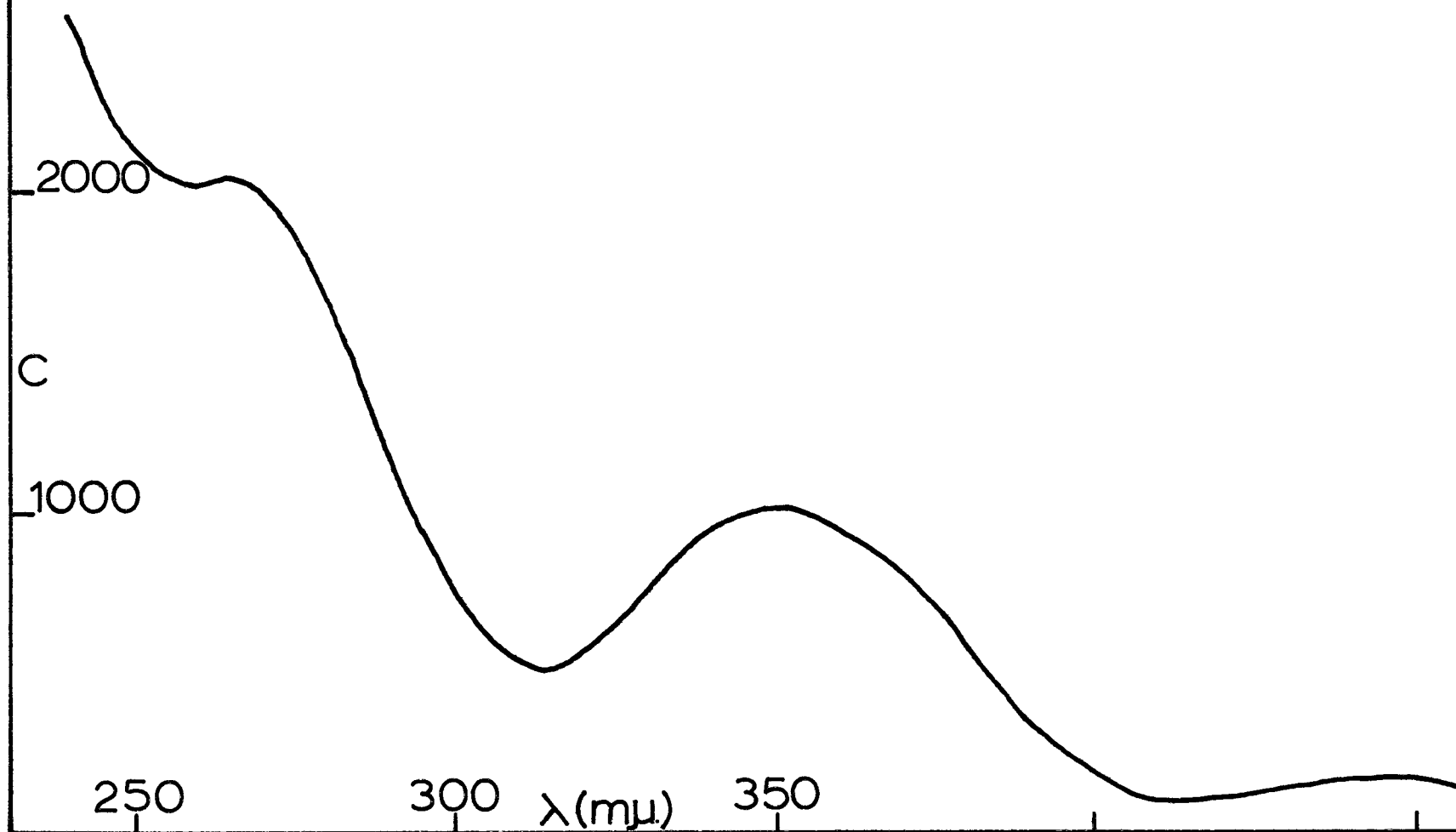


Fig.33 Ultraviolet spectrum of Cr^{VI} in 3.60M HCl.

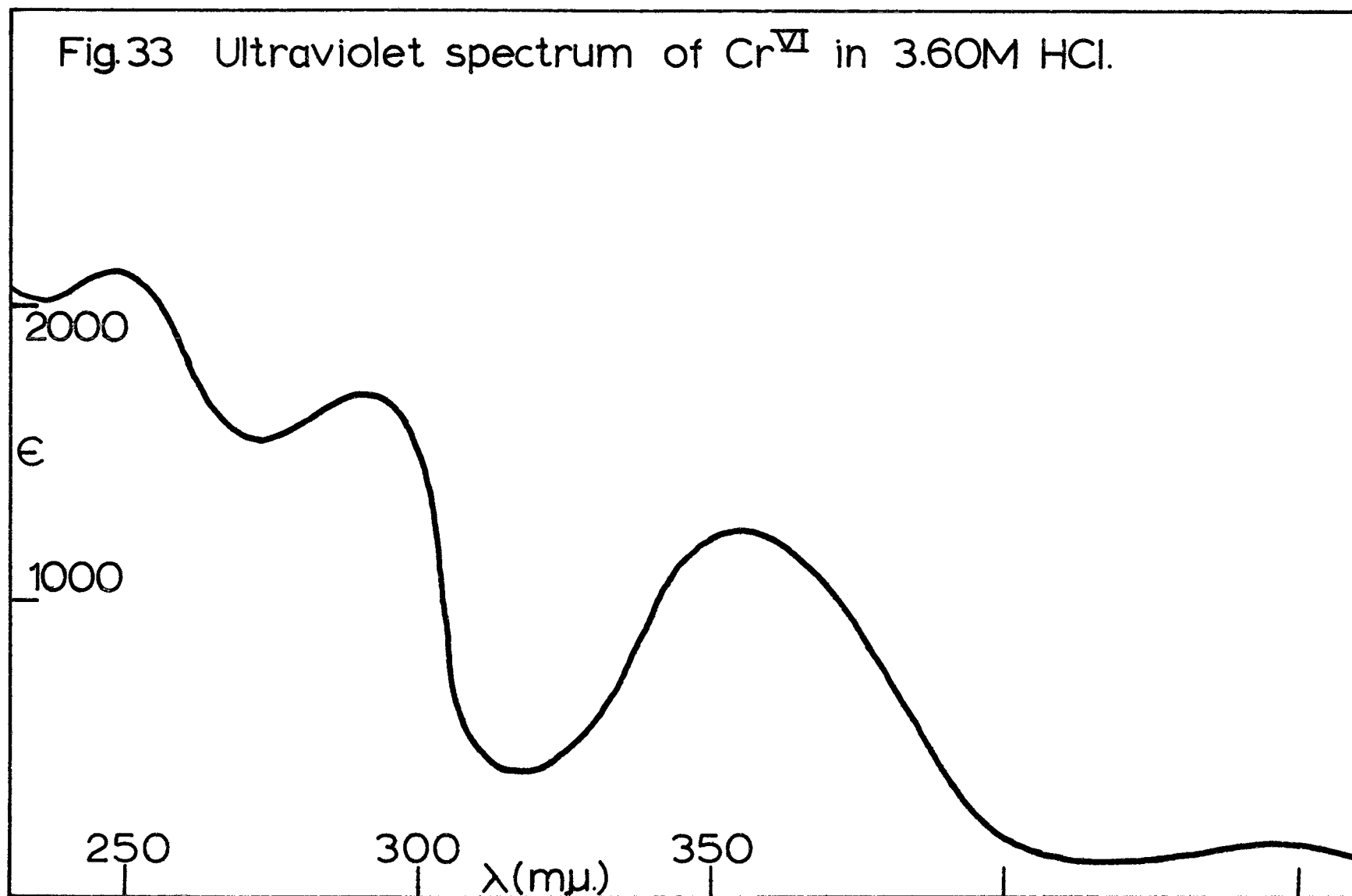
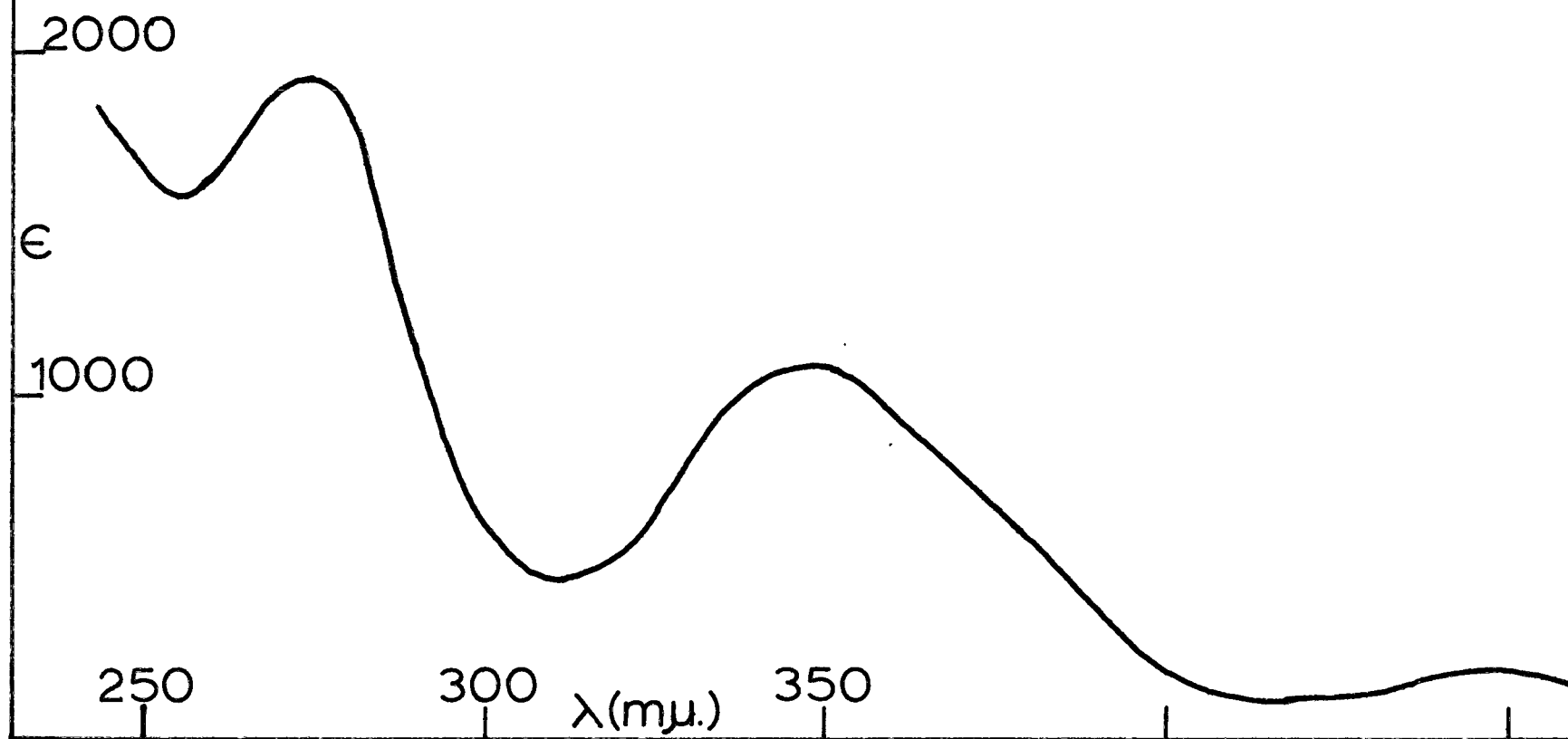
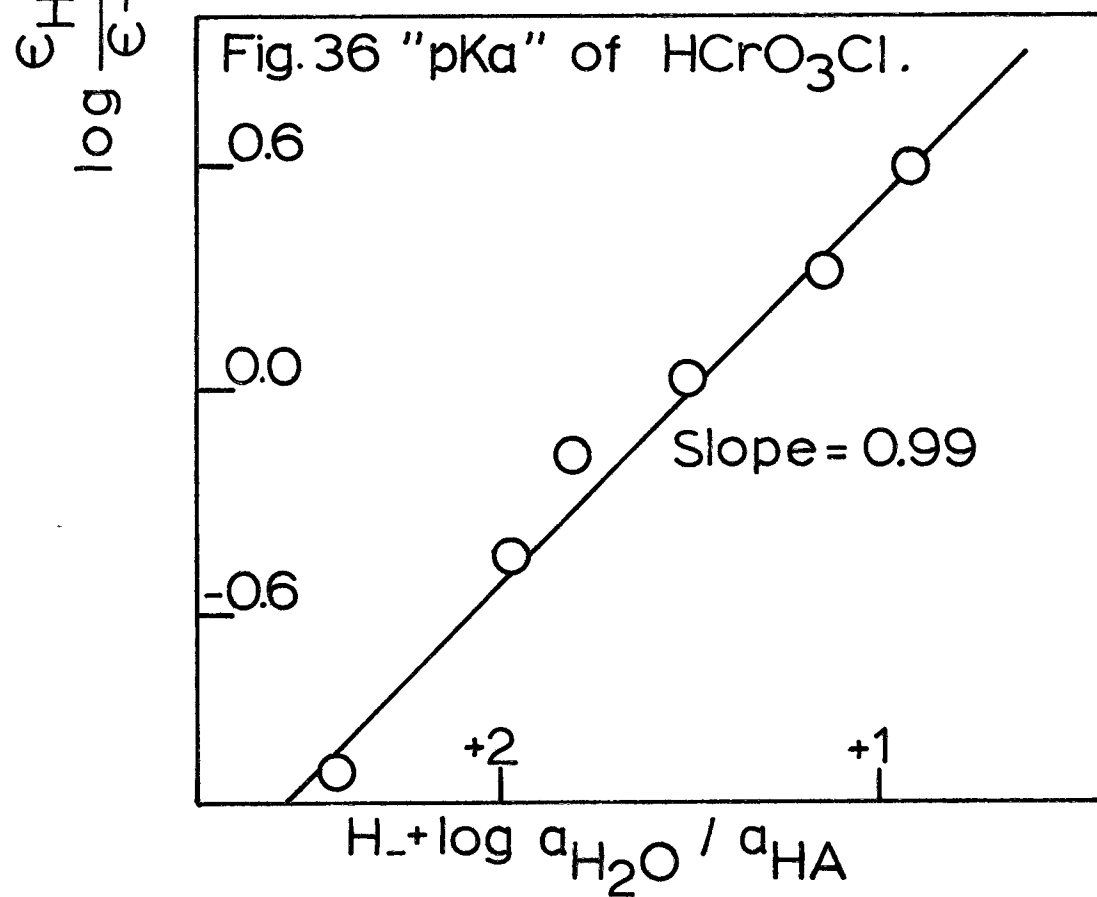
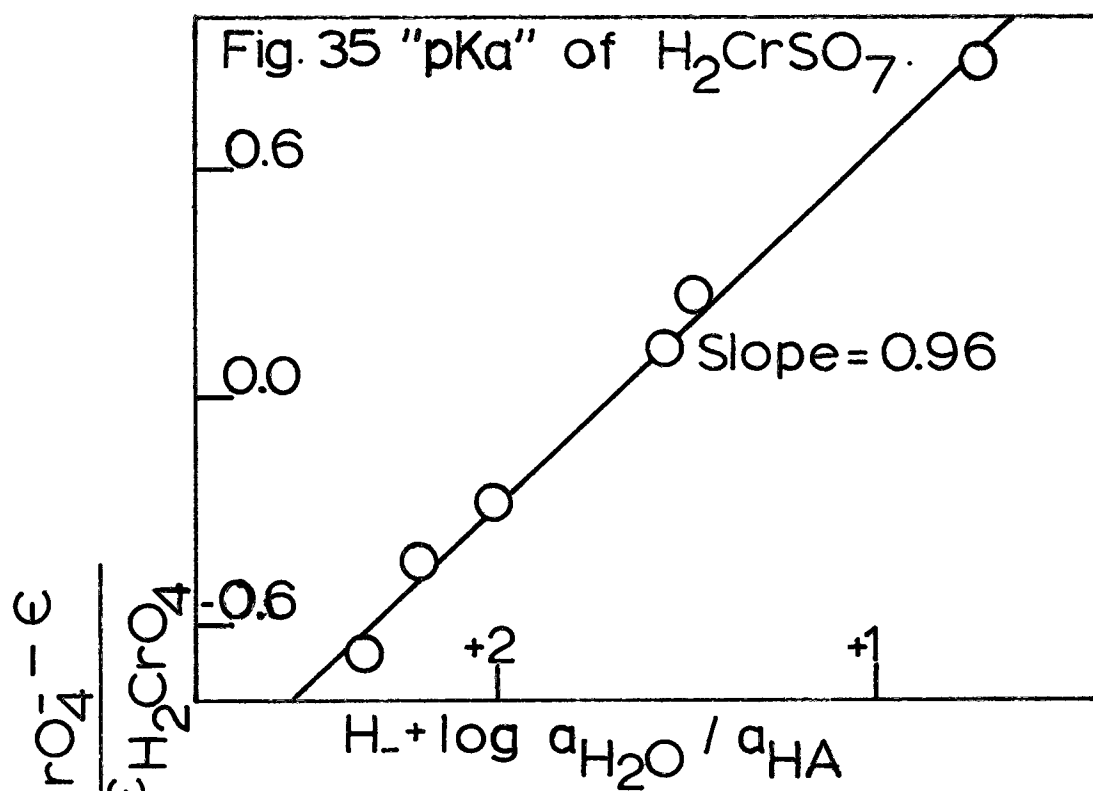


Fig.34 Ultraviolet spectrum of Cr^{VI} in 3.00M H_3PO_4 .





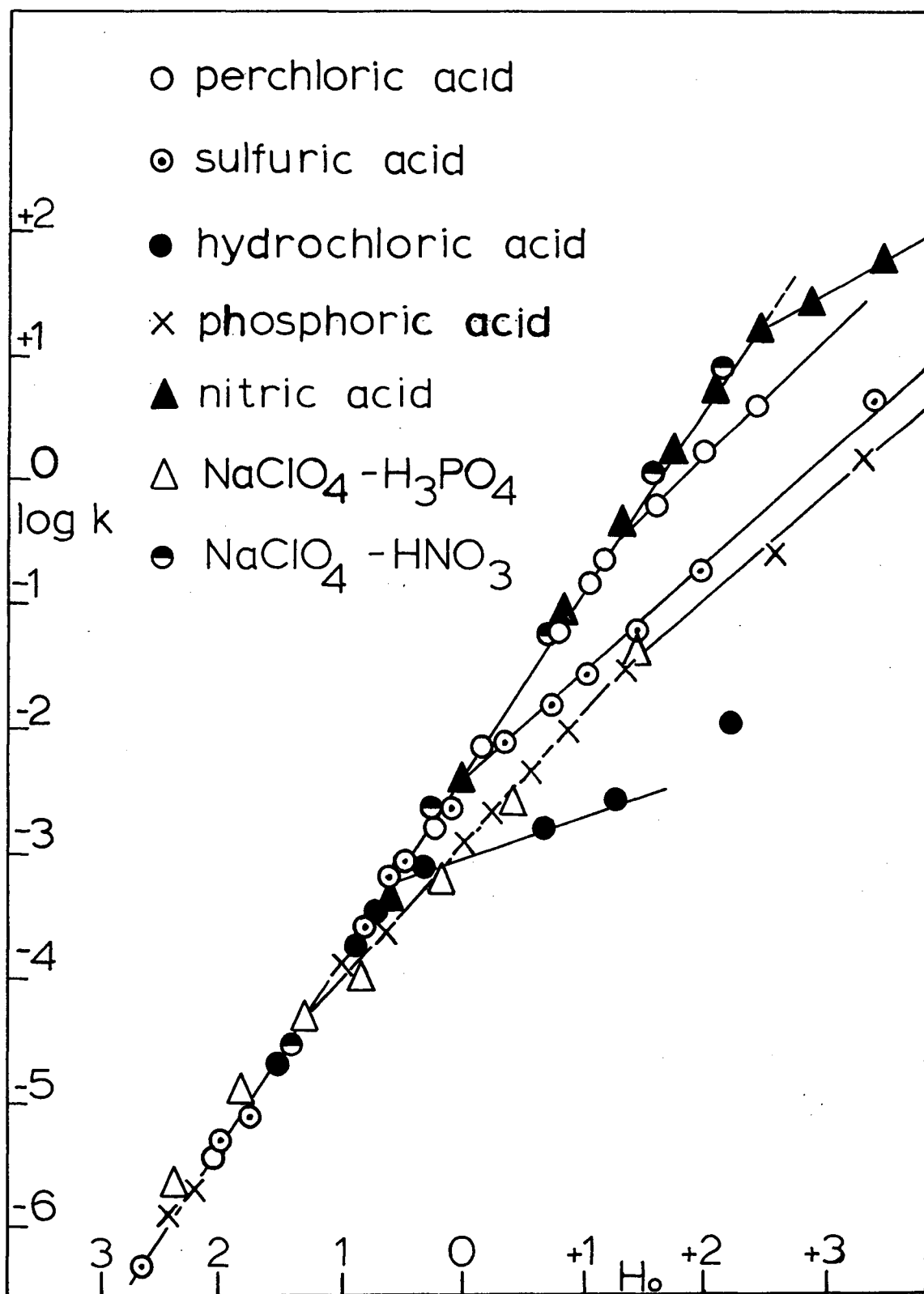


Fig.37 Chromic acid oxidation of isopropyl alcohol in aqueous solutions of mineral acids.