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C. LEWIS

ON OF SECONDARY
BY DIPOTASSIUM
FERRATE (VI) IN
ND DILUTE POTASSIUM
DE SOLUTIONS

W. C.

THE OXIDATION
ALCOHOLS BY
TETRAOXO
CONCENTRATED A
HYDROXIDE

THE OXIDATION OF SECONDARY ALCOHOLS BY DIPOTASSIUM TETRAOXOFERRATE (VI)
IN CONCENTRATED AND DILUTE POTASSIUM HYDROXIDE SOLUTIONS

by

William C. Lewis

March 9, 1965

Thesis presented in partial fulfillment of the requirements
for the M. A. degree, State University of New York at
Binghamton, New York.

Accepted in partial fulfillment of the requirements for the
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TABLE OF CONTENTS

	Page
SUMMARY	1
HISTORICAL	2
EXPERIMENTAL	
Preparation of potassium ferrate	8
Analysis of potassium ferrate	10
Preparation of potassium deuterioxide and deuterium oxide solutions	11
Preparation of 1,1,1,3,3,3-hexafluoro- propanol-2	13
Preparation of 1,1,1-trifluoro- propanol-2	14
Preparation of phenyltrifluoro- methyl carbinols	15
Kinetic solutions	18
Kinetic runs in concentrated potassium hydroxide	19
Kinetic runs in potassium hydroxide- potassium fluoride solutions	20
Rate of acetone production	21
Isolation of products	22
Temperature corrections	25
EXPERIMENTAL DISCUSSION	
Preparation and analysis of potassium ferrate	26
Gas-liquid chromatographic analysis for ketones, carbinols, and alcohols	27
Treatment of data	28
Calculations	30
DISCUSSION	31
TABLES	46
FIGURES	62

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S U M M A R Y

Potassium ferrate of known purity was used to oxidize three alcohols (propanol-2, 1,1,1-trifluoropropanol-2, and 1,1,1,3,3,3-hexafluoropropanol-2) in 8 M potassium hydroxide, and a series of substituted phenyltrifluoromethyl carbinols (m-nitrophenyl-, m-bromophenyl-, p-methylphenyl-, and unsubstituted) in 0.5 M potassium hydroxide and 3.5 M potassium fluoride. The reactions were found to obey pseudo-first order kinetics and shown to be first order in ferrate ion and first order in alkoxy ion (ionized carbinol or alcohol); acetone production from the oxidation of propanol-2 also followed first order kinetics; oxygen evolution was 3/2 order in some reactive intermediate, other than iron-VI. Deuterium isotope effects show that the breaking of the C-H bond on the α -carbon is the rate determining step for the oxidations. The isotope effects also indicate, by applying the Swain Criteria, that a hydride mechanism is likely. The salt effect, isokinetic relationship, and Hammett ρ plot all give confirmation of the suggested hydride mechanism.

HISTORICAL

The heating of a mixture of iron filings, nitre, and potash constituted the first preparation of Potassium ferrate (dipotassium tetraoxoferrate VI) (1). This took place in 1702 but little quantitative

(1) G. E. Stahl, Specimene Becheriano, Franckfurth, 1702, page 247.

work was done on the compound until about 1950. Methods of preparing 25 iron-VI salts were known (2), but yields and purity were low until

(2) J. M. Mellor, Comprehensive Inorganic and Theoretical Chemistry, Longmans, Green, and Co., vol. XIII, 1924, page 935-936.

Thompson, Ockerman, and Schreyer (3) proposed their synthesis, which

(3) G. W. Thompson, L. T. Ockerman, and J. M. Schreyer, J. Am. Chem. Soc., 73, 1379 (1951).

utilizes sodium hypochlorite to oxidize iron-III nitrate to iron-VI. The reaction produces a large quantity of iron-III hydroxide, so that much of the synthesis is devoted to purification of the iron-VI compound.

More recently Gump (4) has reported the preparation, using

-
- (4) J. R. Gump, Diss. Abs., 20, 3502 (1960); UNIV. OF KENTUCKY, 1952
-

essentially the same process as in (3), of high purity iron-VI ferrates of lithium, sodium, potassium, rubidium, cesium, cadmium, zinc, and lanthanum.

Compounds of iron-V and iron-IV have been reported (5, 6, 7, 8).

-
- (5) J. S. McGee, Ph. D. Thesis, The Kinetics of the Decomposition of Potassium Tetraoxoferrate (VI) in Aqueous Solution, University of Delaware, 1961.
- (6) R. v. Scholder, H. v. Bunsen, and W. Zeiss, Z. anorg. u. Allgem. Chemie, 283, 330 (1956) - - - - reference 19 in McGee's thesis (5).
- (7) W. Klemm and K. Wahl, Angew. Chemie, 65, 261 (1953).
- (8) B. Jezowska-Trzebiatowska and M. Wronska, Cong. intern. Chim. pure, et, appl., 16^e, Paris, 1957, 827-835 (Pub. 1958) - - - - reference 17 in McGee's thesis (5).
-

Klemm and Wahl (7) have determined that K_3FeO_4 disproportionates in aqueous solution to give iron-III hydroxide and potassium ferrate while Scholder, Bunsen, and Zeiss (6) have obtained iron-III hydroxide and ferrate ion as the decomposition products of Na_4FeO_4 in dilute sodium hydroxide solution. McGee (5) noted a black precipitate when potassium ferrate was decomposed in strong sodium hydroxide; the precipitate was assumed to be Na_2FeO_3 . Barium ferrate ($BaFeO_3$) has been named (2) as a possible intermediate in the thermal decomposition of barium ferrate (VI).

Cotton and Wilkenson (9) state, however, that "X-ray studies have shown

-
- (9) F. A. Cotton and G. Wilkenson, Advanced Inorganic Chemistry, Interscience Publishers, 1962, pages 718-719.
-

that these (Ba_2FeO_4 and Sr_2FeO_4) do not contain any discrete ferrate (IV) ions, although the compounds are commonly called ferrates (IV), but that they are mixed metal oxides, the barium one having the spinel structure." The spinel structure is a common one for compounds of mixed oxidation states. These authors do salvage some hope for the iron-IV ion since they list the compound $\left[\text{Fe}^{\text{IV}} (\text{diars})_2 \text{Cl}_2 \right] \left[\text{Fe}^{\text{III}} \text{Cl}_4 \right]_2$ as being the only discrete iron-IV complex to be reported. In the cation complex, (diars) is the bidentate of diarsine, o-phenylenebisdimethyl arsine. No quantitative data on the X-ray studies ~~were~~ presented by the authors.

Aqueous species of iron-IV have been suggested in cytochrome oxidation (10) and for some reactions of iron-II and iron-III with hydrogen

-
- (10) R. Stewart, Oxidation Mechanisms, Applications to Organic Chemistry, W. A. Benjamin, Inc., New York, 1964, pages 145 to 149. See also references therein.
-

peroxide (11). McGee (5) has proposed aqueous species of iron-IV and

-
- (11) A. E. Cahill and H. Taube, J. Am. Chem. Soc., 74, 2312 (1952).
-

iron-V as intermediates in the oxidation of water to oxygen by potassium ferrate. Iron-IV is also the proposed intermediate in the oxidation of

propanol-2 (12) which is the subject of this paper.

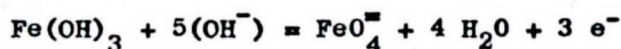
-
- (12) B. E. Norcross and W. C. Lewis, The Oxidation of Propanol-2 and 2-Deuteropropanol-2 with Dipotassium Tetraoxoferrate (VI), Abstract of Papers, 146th Meeting of the American Chemical Society, Denver, Colorado, 1964.
-

Perferric acid, H_2FeO_5 , and a few other iron-VIII compounds have been mentioned in the literature (2) but are not considered herein.

Wood (13) has given the potential of the iron-III-iron-IV

-
- (13) R. H. Wood, J. Am. Chem. Soc., 80, 2038 (1958).
-

half-cell to be 0.71 ± 0.03 v. for the reaction



Values for potassium ferrate's heat of formation (-116 kcal/mole), free energy of formation (-78 ± 2 kcal/mole), entropy of formation (9 ± 4 E.U.), and details of its ultraviolet and visible spectra were given in the same paper with the wavelength of maximum absorbance being 505 mμ.

The ferrate ion is tetrahedral (14), and has been compared

-
- (14) H. Krebs, Z. anorg. u. allgem. Chemie, 263, 175 (1950).
-

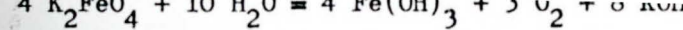
to the chromate ion, $\text{CrO}_4^{=}$, by X-ray studies (15) which have shown the

(15) B. Helferich and K. Lang, ibid., pg. 169.

two ions to be almost identical in cell dimensions. The same types of studies have also been done on barium ferrate by Jellinek (16).

(16) F. Jellinek, J. Inorg. and Nuclear Chem., 13, 329 (1960).

McGee (5) examined the decomposition of potassium ferrate in basic aqueous solutions by measuring the partial pressure of oxygen produced according to the equation



The products of this decomposition had been observed before (17) while

(17) J. M. Schreyer and L. T. Ockerman, Anal. Chem. 23, 1312 (1951).

the stability of potassium ferrate in solutions of electrolytes was being studied. It has been observed (17, 18, 19) that stability of ferrate ion

(18) W. F. Wagner, J. R. Gump, and E. N. Hart, Anal. Chem., 24, 1497 (1952).

(19) W. F. Wagner and J. R. Gump, Trans. Kentucky Acad. Sci., 15, 112-116 (1954); C. A., 49, 2921^D (1955) - - - - reference 16 in McGee's thesis (5).

increases in aqueous solution with increasing size of the alkali metal ion, the strength of base, and decreases with an increase in the iron-VI concentration.

McGee (5), Wood (13), Jezowska-Trzebiatowska and Wronska (8), have all found a first order dependence on ferrate ion for the decomposition of the iron-VI compound in strong base; however, McGee shows reason to doubt the conclusions of the latter investigators. McGee determined the following relationships for the decomposition of ferrate ion in the noted pH regions:

$$\begin{array}{ll} \text{pH } 9.2 \text{ to } 9.6 & \text{rate} = k(\text{FeO}_4^{=})^2 (\text{H}^+) \\ \text{pH } 10 \text{ to } 11.4 & \text{rate} = k(\text{FeO}_4^{=}) (\text{OH}^-)^{3/2} \\ \text{pH } 12 \text{ to } 7 \text{ M KOH} & \text{rate} = k(\text{FeO}_4^{=}) (\text{OH}^-)^{0-1} \end{array}$$

The mechanisms of all these reactions are complex but the last is of particular interest, showing a dependency on base concentration that is not calculable from available activity coefficient data. Further mention of this point is made in the discussion section.

OUTLINE OF THE PROBLEM

The unusual reactivity of potassium ferrate was first noted in this laboratory when crystals of the substance were rapidly decomposed by ethanol during the final steps of a ferrate preparation. The possibility of using potassium ferrate as an oxidant for alcohols was quite attractive and propanol-2 was chosen as the first substrate, since its only oxidation product should be acetone. The high extinction coefficient of potassium ferrate in aqueous solution, at 505 m μ , presented an easy method of following the oxidation reaction by tracing the decay of the ferrate peak at that wavelength. (This was the wavelength used for the kinetic studies discussed in this paper.)

Preliminary experiments with propanol-2 were promising enough to warrant a full-scale investigation. Basic solutions were used to achieve ferrate stability and also to ionize the alcohol. Problems were encountered due to incomplete ionization of propanol-2, even in very concentrated potassium hydroxide; therefore, trifluoro- and hexafluoropropanol-2 were prepared and used for kinetic studies, since they are completely ionized in the basicity range used for these experiments (0.5 M to 8.0 M). Potassium fluoride had to be added to the less concentrated potassium hydroxide solutions to prevent iron-III from precipitating as the hydroxide.

α -Deuteropropanol-2 gave a slower rate of reaction with potassium ferrate than did propanol-2 by a factor of 9.6, thus indicating that the rate determining step in the oxidation is the breaking of the C-H bond at the α position.

The information gathered from the foregoing experiments was not

sufficient to allow a firm distinction between a proton or hydride transfer mechanism in the rate determining step. This situation led to the synthesis of a series of aryltrifluoroalcohols, herein referred most frequently to as "carbinols," which are completely ionized in one-tenth molar alkali (28). The kinetic data obtained from this series of carbinols, using the interpretation given in the "Discussion Section," is consistent with a hydride mechanism.

EXPERIMENTAL

PREPARATION OF POTASSIUM FERRATE

Potassium ferrate [dipotassium tetroxoferrate(VI)] was synthesized (3) in low yields of varying purity by the following modified procedure. Chlorine was added to a well stirred solution of 30 grams sodium hydroxide in 75 ml. water, while the temperature was maintained at or below 30° (20), until a weight gain of at least 20 grams was observed.

(20) All temperatures are given in degrees centigrade unless otherwise noted.

The hypochlorite solution thus obtained, maintained below 30°, was saturated with sodium hydroxide, cooled to below 10° and filtered on a coarse, fritted-glass funnel. The filtrate was placed in a 250-ml. beaker equipped with a magnetic stirrer; with vigorous stirring and while keeping the temperature between 25° and 30°, small portions of pulverized iron(III) nitrate nonahydrate were added over a period of one hour until a total of 25 grams had been added. As the oxidation took place, the solution turned from a brown to a very deep red. The resulting deep red solution was saturated with sodium hydroxide, while maintaining the temperature below 30°, and then centrifuged (21) for

(21) Inorganic Synthesis, vol. IV, J. C. Bailar, Jr., editor, McGraw-Hill Book Co., Inc., 1953, pages 164-167.

30 minutes. After centrifugation, the solution was immediately filtered on a coarse, fritted-glass funnel of large surface area equipped with a pad of glass wool (3), which greatly enhanced the speed of filtration. The filtrate was added to 100 ml. chilled, saturated potassium hydroxide in a 400-ml. beaker. This mixture was stirred for 10 minutes, and then rapidly cooled to 10° and filtered on a coarse, fritted-glass funnel. The residue on the funnel was a mixture of a brown sludge and purple crystals. The purple crystals of potassium ferrate were separated from the brown impurities by dissolving the crystals with four or five 10-ml. rinses of 3 M potassium hydroxide. All these portions were collected in a single flask containing 50 ml. of chilled, saturated potassium hydroxide, which was then added to the collected washings. Crystals of potassium ferrate were observed on the sides of the vessel after the solution was further chilled and stirred. Filtration of this solution on a fritted-glass funnel of medium porosity gave purple-red crystals; these crystals were then washed with 10 ml. of benzene followed by three 20-ml. portions of 100% ethanol. The product, which was greater than 90% pure, was washed with ether and then stored under vacuum for twenty-four hours.

ANALYSIS OF POTASSIUM FERRATE

The analysis (22) of five different potassium ferrate samples

-
- (22) J. M. Schreyer, G. W. Thompson, and L. T. Ockerman, Anal. Chem., 22, 1426 (1950).
-

gave purities ranging from 40% to 96%. In this method of analysis, the sample of potassium ferrate to be tested is used to oxidize a basic solution of Cr-III to CrO_4^{2-} ; the resulting chromate solution is then acidified and titrated with standard Fe-II using sodium diphenylaminesulfonate indicator. The procedure outlined in (22) was used with two modifications: the indicator was added near the end point to prevent indicator oxidation; and a light was placed behind the titration vessel for better detection of the subtle purple to green end-point. The solution in the titration flask was stirred magnetically and care was taken to insure that the ferrate sample was completely dissolved.

Another method of analyzing potassium ferrate was also developed (12) which utilized the oxidative powers of ferrate to produce acetone from propanol-2. The acetone produced was then condensed with salicylaldehyde in basic solution (23). The resulting solution, after heating,

-
- (23) G. B. Ginther and R. C. Finch, Anal. Chem., 32, 1894 (1960).
-

was red-orange in color and possessed an absorption peak at 500 m μ (12). The optical density at this wavelength was then read on the Cary 14 recording spectrophotometer and corrected by subtracting the optical

density of a blank that had been treated in exactly the same manner. Five solutions of known acetone concentration were run simultaneously with the ferrate analysis under identical conditions. The optical density at 500 m μ was read and the blank reading subtracted. Values of this corrected optical density, plotted versus the acetone concentration, produced a standard curve from which the acetone concentration for the ferrate analysis could be interpolated; that is, the corrected optical density for the analysis could then be used to interpolate the quantity of acetone produced from the reaction with ferrate. The purity of the sample could then be calculated from these data.

PREPARATION OF POTASSIUM DEUTEROXIDE AND DEUTERIUM OXIDE SOLUTIONS

Potassium deuteroxide was prepared with a few modifications of the usual technique (24). Potassium metal (0.5 mole), prepared by

(24) Inorganic Isotopic Synthesis, R. Herber, editor, W. A. Benjamin Co., New York, 1962, pages 27-29.

scraping the surface clean in a dry nitrogen atmosphere, was added to a previously dried, three-necked, standard taper flask equipped with a dropping funnel, a vacuum source and a nitrogen inlet. The flask was flushed with dry nitrogen before and during the addition of the potassium metal. The apparatus was then sealed, the nitrogen turned off, and the whole system evacuated. The vacuum was turned off and dry nitrogen allowed to flow in. The evacuation and nitrogen flushing was repeated three times. A vacuum was then drawn and the potassium melted; while cooling, the flask was swirled, depositing a thin coat of the metal on the sides of the flask. After cooling was complete, 15 g. of deuterium oxide (the deuterium oxide in excess of the stoichiometric amount was intended to keep the potassium deuteroxide in solution) was added dropwise with periodic application of vacuum to draw out the deuterium gas produced. The reaction was exothermic and very vigorous so that it was important to draw off the deuterium gas before a sufficient quantity accumulated to combust. The resulting solution contained some oxidizable organic impurities, which would interfere with kinetic determinations. The solution was purified by adding a small amount of potassium ferrate and allowing the mixture to react for twenty-four hours. By this time, the impurities were oxidized and the excess ferrate

decomposed. The precipitated Fe(OD)_3 was filtered out of the solution on a fine porosity fritted-glass funnel while the whole filtering apparatus was under a nitrogen atmosphere. An aliquot of the filtered solution was then titrated with standard hydrochloric acid. After the concentration was known, an aliquot, large enough to make 100 ml. of 7.5 M potassium deuterioxide, was placed in a 100-ml. volumetric flask and diluted to the mark with deuterium oxide. An aliquot of this new solution was then titrated with dilute hydrochloric acid to find the exact concentration.

A comparison of the proton NMR (Nuclear Magnetic Resonance) spectrum for potassium deuterioxide in deuterium oxide with the spectrum for potassium hydroxide in water showed the isotopic purity of the product to be greater than 95%.

PREPARATION OF 1,1,1,3,3,3-HEXAFLUOROPROPANOL-2

A 1000-ml., three-necked, standard taper flask was equipped with a gas delivery tube, a stirrer, and an 18-cm. cold finger condenser cooled with dry ice and acetone. Two hundred and fifty ml. of dry ether were added to the flask along with 0.024 mole (0.90 g.) of lithium aluminum hydride. The stirrer was started and hexafluoroacetone* bubbled into the contents of the flask while the temperature was maintained at 0°. After 25 to 30 minutes, the rate of bubbling was observed to increase significantly; this was taken as evidence that the reaction was essentially complete.

Any remaining reducing agent was destroyed by addition of 6 M hydrochloric acid; the resulting two layers were separated, and the ether layer dried and then fractionally distilled on a spinning band column. The fraction boiling at 76-77° was collected and analyzed by gas-liquid chromatography using a column of 15% Ucon Polar on chromabsorb W (50-60 mesh); flow rate = 60 cc./min.; oven temperature = 75°. This fraction was found to contain hexafluoropropanol-2 and ether, apparently an azeotrope. Using the same column and conditions as above, the two components were separated and collected. GLC analysis of the collected alcohol showed no impurities; NMR gave a heptuplet with peaks at 4.09, 4.19, 4.30, 4.39, 4.49, 4.61, and 4.69 parts per million (δ) and an OH peak at 4.56 δ . The refractive index was found to be 1.2751 at 25° compared to the literature value (26) of 1.2750 at 22°.

(26) C. A., 57, 12306b (1963); I. L. KUNYANTS, ET AL.

* OBTAINED FROM COLUMBIA ORGANIC CHEMICAL CO.

-14-

PREPARATION OF 1,1,1-TRIFLUOROPROPANOL-2

A quantity of 1,1,1-trifluoroacetone was obtained from Columbia Organic Chemical Company and separated from its impurities on a Nester-Faust Prepkromatic GLC (Gas-Liquid Chromatograph) using a column of 10% polypropylene glycol on chromabsorb W (45-60 mesh); flow rate = 600 cc./min.; and column temperature = 40°.

The purified 1,1,1-trifluoroacetone (13.1 g., 0.129 mole) was then reduced with 1.3 g. (0.0343 mole) lithium aluminum hydride using the method presented for the preparation of the hexafluoropropanol-2. The dry ether solution containing the 1,1,1-trifluoropropanol-2 was chromatographed on the preparative GLC (same column and flow rate as before; column temperature = 85°) to separate the alcohol from ether. The yield was 6.5 g. (49%), based on 1,1,1-trifluoroacetone (25).

(25) McBee and Truchan, J. Am. Chem. Soc., 70, 2910 (1948).

PREPARATION OF PHENYLTRIFLUOROMETHYL CARBINOLS (27)

- (27) These compounds (28) have been sufficiently well characterized that no further proof of identity was needed other than refractive index, melting point, and/or boiling point.

p-Methylphenyltrifluoromethyl carbinol was prepared in 85% yield (28):

- (28) R. Stewart and R. Van der Linden, Can. J. Chem. 38, (1960).

b.p. 94.5 (pressure = 12 mm. Hg); $n_D^{18} = 1.4640$, reported (28)
 $n_D^{24} = 1.4650$.

Phenyltrifluoromethyl carbinol was prepared (28) in 69% yield.

Purification by preparative GLC (column of 10% polypropylene glycol on chromabsorb W, 45-60 mesh; flow rate of 600 cc./min.; column temperature = 175°) produced a clear, colorless oil; $n_D^{25} = 1.4588$, reported (28) $n_D^{25} = 1.4590$.

α -Deuterophenyltrifluoromethyl carbinol was prepared in 90% yield from 1.00 g. (0.0275 mole) of lithium aluminum deuteride and 5.22 g. (0.030 mole) of α, α, α -trifluoroacetophenone (28). Purification by GLC (column of 10% polypropylene glycol on chromabsorb W, 45-60 mesh; flow rate of 60 cc./min.; column temperature = 175°) gave a clear, colorless liquid; $n_D^{24} = 1.4586$.

m-Bromophenyltrifluoromethyl Carbinol - m-Bromo- α, α, α -trifluoroacetophenone was prepared by the method given in (28) with the

exception that 0.2 g. of anhydrous ferric chloride (29) was used

(29) Anhydrous ferric chloride was prepared as in Inorganic Synthesis, vol. III, L. F. Audrieth, editor, McGraw-Hill Book Co., 1953, pages 191-194.

instead of 0.1 g. The 16% yield obtained using the additional ferric chloride was considerably higher than with the smaller amount.

The m-bromo ketone was then reduced to the carbinol with lithium aluminum hydride. The products were fractionally distilled and the fraction boiling at 115° and 12 mm. Hg was collected; GLC analysis (a column of 10% polypropylene glycol on chromabsorb W, 45-60 mesh; flow rate = 60 cc./min.; and oven temperature = 200°) revealed that the product was a mixture of the ketone and the carbinol. The product was then purified on the analytical GLC using the conditions just given. The two liquids collected in the purification were then subjected to NMR analysis. The liquid having the shortest retention time gave an NMR spectra consisting only of aromatic peaks; the liquid of longest retention time gave the same aromatic peaks but also had a quartet at 4.72, 4.80, 4.90, and 5.01 δ and an OH peak at 3.27 δ . The first spectra is that of the ketone while the second is that of the carbinol. The carbinol gave $n_D^{29} = 1.5028$ compared to the expected $n_D^{27} = 1.5005$ (28). Upon standing, the carbinol crystallized into a pure-white solid with m.p. = $27-29^{\circ}$, it previously has been reported (28) only as the oil. The yield of purified carbinol was 89% based on m-bromo ketone.

m-Nitrophenyltrifluoromethyl Carbinol - m-Nitro- α, α, α -trifluoro-acetophenone was prepared (28) in good yield (53.5%) and then reduced to the carbinol with potassium borohydride. A methanol solution of 10 g. (0.045 mole) of m-nitro- α, α, α -trifluoro-acetophenone was added dropwise to a well stirred solution of 2.7 g. (0.05 mole) potassium borohydride in 100 ml. of methanol. After addition of the ketone, the solution was stirred for two hours, acidified with hydrochloric acid, and extracted three times with ether; the ether extract was dried over anhydrous magnesium sulfate. Distillation of the dry ether extract gave a very viscous, yellow-brown oil boiling at 104-106° and 2 mm. Hg. The oil crystallized slowly giving pale yellow crystals, m.p. = 45-52°. Upon recrystallization from benzene and petroleum ether, the m.p. was 48-51° compared to the literature value of 47-48° (28). The yield of purified material was 69%, based on ketone.

α -Deutero-m-nitrophenyltrifluoromethyl carbinol was prepared by the method just described except that ether was the solvent and sodium borodeuteride was the reductant. The m-nitro ketone (6.24 g. 0.0285 mole) was added to an ether solution of 1.00 g. (0.0239 mole) sodium borodeuteride to yield 3.8 g. (61%) of unpurified crystals. Upon recrystallization from benzene and petroleum ether, pale-yellow crystals were obtained with m.p. = 48-51°; reported for protium compound, 47-48°.

KINETIC SOLUTIONS

All potassium hydroxide solutions were made by direct weighing of Fisher Reagent Grade pellets into a volumetric flask. When an alcohol solution was prepared, the alcohol was weighed and transferred quantitatively into a volumetric flask and then the potassium hydroxide pellets were added; the solution was then made up to volume.

In the case of 0.5 M potassium hydroxide and 3.5 M potassium fluoride, a stock solution containing the two was prepared, by direct weighing of the reagents, and stored in a polyethylene container until used. The alcohol or carbinol was then weighed directly into a volumetric flask and the hydroxide-fluoride stock solution added to the mark. The very small concentration error due to the carbinol dilution (0.2-0.5%) was well within experimental error (1-5%).

Care had to be taken in preparing the carbinol solutions to avoid cleavage of the trifluoromethyl group. In fact, the reason for the hydroxide-fluoride solvent was to limit this cleavage by lowering base strength, while maintaining sufficient hydroxide concentration to retain a slow iron-VI decay rate in the absence of substrate. The fluoride complexed the iron-III produced in the oxidations, thus preventing precipitation of ferric hydroxide, which would interfere with absorption measurements. In general, a new solution of carbinol was used for each temperature, and only that portion needed for a particular kinetic run was heated to the reaction temperature; the rest of the solution remained at room temperature.

KINETIC RUNS IN CONCENTRATED POTASSIUM HYDROXIDE

The disappearance of the purple colored iron-VI ion was followed under pseudo-first order conditions by dissolving a small amount of solid potassium ferrate in a measured quantity (1.00 to 3.50 ml.) of 8 M potassium hydroxide in a 4 ml. Beckman pyrex cuvette, which was then placed in the cell compartment of a Cary Model 14 recording spectrophotometer, operated at a fixed wavelength. This solution was mixed until homogeneous with a medicine dropper, and then the Cary was turned on, recording a plot of time versus optical density. This gave the rate of ferrate decomposition in base alone. A volume of solution of known alcohol concentration, sufficient to bring the volume to 4.00 ml., was then added. The solution was mixed as before and the drive of the Cary again activated to give a plot of optical density versus time for the reaction of ferrate with alcohol. All solutions and measuring pipetts were equilibrated at the reaction temperature for each run.

The above method was also used for solutions of propanol-2 in 7, 6, and 5 M potassium hydroxide.

KINETIC RUNS IN POTASSIUM HYDROXIDE-POTASSIUM FLUORIDE SOLUTIONS

The following method applies to all runs involving fluoride ion, and to runs in 4 and 3 M potassium hydroxide.

The 0.0-0.2 slide wire was placed in the Cary and 10-cm. quartz cells were used. Alcohol or carbinol solution was placed in the 10-cm. cell and then equilibrated at the reaction temperature. A small amount of potassium ferrate was added, dissolved, mixed by shaking and the cell placed in the thermostated cell compartment of the Cary. The time drive was activated giving a plot of optical density versus time.

A decomposition rate of ferrate in solvent alone was determined in a similar fashion. See tables 17 and 18.

RATE OF ACETONE PRODUCTION IN 8 M POTASSIUM HYDROXIDE

An arbitrary amount of potassium ferrate was added to 50 ml. of 8 M potassium hydroxide in a 250-ml. volumetric flask and then the solution was thermostated at 25.1° . A five ml. aliquot was taken, treated as in (12) and called zero acetone concentration. Enough 8 M potassium hydroxide-propanol-2 solution, of known alcohol concentration, was added to the flask to bring the liquid up to the mark. This solution was mixed well and thermostated at 25.1° . At intervals of about 90 seconds, a five ml. aliquot was withdrawn and treated as in (12). (See figure 9 for standard acetone curve and figure 10 for a typical kinetic determination for acetone).

ISOLATION OF PRODUCTS

Propanol-2 oxidation

Ferric ion was identified as an oxidation product by its blood-red complex formed with thiocyanate ion.

Acetone was isolated and identified (12) as its derivative of 2,4-dinitrophenylhydrazine in a ratio of one mole derivative to one mole of potassium ferrate. The melting point of the derivative was 124-125°; reported (30), 126°.

(30) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, The Systematic Identification of Organic Compounds, John Wiley and Sons, Inc., New York, 1956, page 316.

Acetone has also been isolated in a ratio of one mole ferrate to one mole acetone (12), as shown in Table 15, by use of basic condensation of acetone with salicylaldehyde (23).

Carbinol Oxidations

m-Nitro- α, α, α -trifluoroacetophenone was quantitatively isolated and identified after a 0.0536 g. (0.232×10^{-3} mole) sample of potassium ferrate, shown by analysis (22) to be 85.7% pure, was added to 25 ml. potassium hydroxide-potassium fluoride solvent containing 0.0821 g. (0.372×10^{-3} mole) m-nitrophenyltrifluoromethyl carbinol. This solution was mixed well and allowed to react for one hour. The basic solution was then acidified and extracted three times with ether. The ether extract was dried over anhydrous magnesium

sulfate and chromatographed on a 3" x 3/8" column of Woelm activity V alumina using ether as the eluent. All the eluent was collected in a single weighed flask, the ether evaporated, and the flask reweighed to give 0.0547 g. (0.250×10^{-3} mole) of m-nitro- α, α, α -trifluoroacetophenone. The unreacted carbinol was not recovered. The ratio of iron-VI reacted to ketone product isolated was 0.93.

m-Bromo- α, α, α -trifluoroacetophenone was quantitatively identified from a reaction solution containing 0.0606 g. (0.262×10^{-3} mole) potassium ferrate (85.7% pure) and 0.113 g. (0.450×10^{-3} mole) m-bromophenyltrifluoromethyl carbinol in 25 ml. of potassium hydroxide-potassium fluoride solvent.

This solution of carbinol and ferrate was mixed well, allowed to react for one hour, and then acidified. The acid solution was then extracted three times with ether and the ether dried over anhydrous magnesium sulfate. Using a spinning band column, most of the ether was distilled off and the residue was then analyzed on the F&M GLC equipped with a column of 10% polypropylene glycol on chromabsorb W (45-60 mesh); the flow rate was 60 cc./min. and the oven temperature was 200°. Only three peaks showed up, the first was ether, the second was the m-bromo ketone, and the third was the m-bromo carbinol. The ratio of ketone to carbinol was 1.34 compared to the expected 1.39 (see "Experimental Discussion" section for an analysis of the product data).

α, α, α -Trifluoroacetophenone was quantitatively identified using the same procedure as for the m-bromo ketone; a 0.966×10^{-3}

mole sample of 85.7% potassium ferrate was added to a 4.74×10^{-3} mole (0.8105 g.) sample of phenyltrifluoromethyl carbinol. Using the same column and flow rate as for the m-bromo ketone, the GLC was set at an oven temperature of 175° ; GLC analysis of the oxidation products gave a ratio of 0.223 mole of ketone to one mole of carbinol. The expected ratio was 0.257.

p-Methyl- α, α, α -trifluoroacetophenone was quantitatively identified using the same procedure as outlined for the m-bromo ketone; a 0.0768 g. (0.332×10^{-3} mole) sample of 85.7% potassium ferrate was used to oxidize a 0.237 g. (1.26×10^{-3} mole) sample of p-methylphenyltrifluoromethyl carbinol. GLC analysis (conditions and column the same as for the m-bromo compound) gave the ketone to carbinol ratio as 0.357 compared to the expected 0.376.

TEMPERATURE CORRECTIONS

A ten junction copper-constantan thermocouple (calibrated against a previously standardized mercury thermometer) was constructed and used to measure the temperature of the cell compartment of the Cary, which was thermostated by water circulated by a Haake circulator. One end of the thermocouple was placed in the cell compartment and the other end in an ice-water mixture (the ice was made from triply distilled water; the water used was also triply distilled). The leads were connected to a potentiometer (Leeds and Northrup Co.) capable of a tenth of a millivolt accuracy. The temperature control on the Haake circulator was adjusted and the temperature of the Cary allowed to come to equilibrium. The temperature of the water circulated by the Haake was then recorded as was the potential of the thermocouple; this process was repeated every two degrees from 15° to 48°. The potential was interpolated (31)

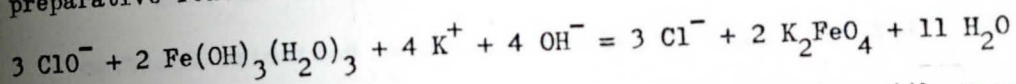
(31) National Bureau of Standards, Circular 561.

to degrees centigrade (see Table 1a) and considered to be the reaction temperature. Table 1a lists the temperature given by the circulating pump versus the real temperature, which is that given by the thermocouple; all temperatures are accurate to $\pm 0.1^\circ$.

EXPERIMENTAL DISCUSSION

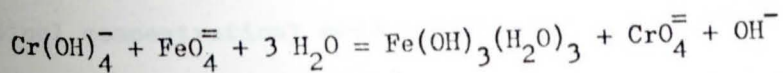
Preparation (3) and Analysis (22) of Potassium Ferrate

Along with the potassium ferrate, a large quantity of iron-III hydroxide is formed requiring that much of the long synthesis be devoted to the purification of the iron-VI compound. The stoichiometry of the preparative reaction is as follows:



It was determined by McGee (5) that purity of the sample, with respect to the ferric hydroxide, had little effect on the rate of decay; the work in this laboratory showed no noticeable effect of ferric hydroxide on the rate of propanol-2 oxidation. Any easily oxidizable impurities, however, led to large rate deviations. This difficulty was avoided by adding a few crystals of potassium ferrate to the solution suspected of containing the impurities. The solution was allowed to stand until the excess ferrate had decomposed, after which the solution could be employed for kinetic purposes, since iron-III hydroxide is non-reactive.

The analysis of potassium ferrate takes advantage of its strong oxidizing powers to oxidize Cr-III to $\text{CrO}_4^{=}$.



The solution of chromate and ferric ions is then acidified, and the dichromate ion produced is titrated with a standard solution of Fe-II (27).

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS FOR KETONES, CARBINOLS, AND ALCOHOLS

GLC was used whenever possible for both analysis of mixtures and the preparation of very pure samples of alcohols and carbinols. All analyses were done on two columns (polypropylene glycol and Ucon Polar, see "Experimental" for details) of differing polarity, while purification was done on whichever column produced the best separation of impurities. All carbinols, except the m-nitro carbinol, and all alcohols, except propanol-2, were purified in this manner.

With the exception of the m-nitro compound, the products of carbinol oxidation were analyzed on the GLC. The ratio of ketone (the oxidation product) to unreacted carbinol was calculated by the following relationship:

$$\frac{\text{mmoles ketone}}{\text{mmoles carbinol unreacted}} = \frac{\text{mmoles ferrate}}{\text{mmoles carbinol - mmoles ferrate added}}$$

This ratio was then compared to the experimental value obtained by dividing the area under the ketone peak, on the GLC graph, by the area under the carbinol peak.

$$\frac{\text{mmoles ketone}}{\text{mmoles carbinol unreacted}} = \frac{\text{area of ketone peak}}{\text{area of carbinol peak}}$$

For the columns and conditions listed under "Isolation of Products," the latter relationship was shown to be accurate ($\pm 10\%$ at the lowest carbinol concentration) over a wide range of known ketone-carbinol ratios. The known mixtures were made by direct weightings and then the analysis run on the appropriate column.

TREATMENT OF DATA

The disappearance of the purple ferrate color was treated as a pseudo-first order process for both the decomposition in base alone and for its reaction with alcohol. The slope of a plot of log optical density versus time for the slow decomposition gave the rate constant for the decomposition process (Figure 1); this was usually about ten times slower than the reaction with alcohol. The reaction with alcohol was generally over in twenty to thirty minutes, and had an infinity point of 0.02-0.05 optical density units (this was due to iron-III complexes). A semi-log plot of $(O.D._t - O.D._\infty)$ versus time, the slope of which gives k_{obs} , was generally linear over two to four half-lives for propanol-2 oxidations (Figure 1a). To obtain the rate due to alcohol reaction alone, the rate of decomposition, k_{FeO_4} , was subtracted from the rate of iron-VI disappearance in the presence of alcohol (k_{obs}). The resulting constant, k_I , when divided by the alcohol concentration in moles per liter, gives the bimolecular rate constant, k_{II} , in liters mole⁻¹ second⁻¹.

The decomposition of ferrate in 0.5 M potassium hydroxide and 3.5 M potassium fluoride was not first order over 100% decomposition; however, the reaction of ferrate with the carbinols was rapid enough to occur within the time corresponding to the decomposition of only a few percent of the initial iron-VI concentration in solvent alone. This was true if only the first two to three half-lives of reaction were considered, since in this region the decomposition was slow and approximated first order. Beyond three half-lives, much variation in rate was observed.

Plots of $\log (OD_t - OD_\infty)$ versus time (where $OD_\infty = 0$ in all cases, owing to the very low Fe-III concentration) were used to determine rate constants for the carbinols (Figure 2). Initial iron-VI concentrations, in the 10-cm. cells used for these kinetic determinations, were on the order of 5×10^{-8} M.

For the rate of acetone production, a calibration curve (Figure 9) was established (12, 23) of optical density of the solution of acetone condensed with salicylaldehyde versus concentration of acetone. The acetone was sufficiently dilute so that the plot followed Beer's law; also, the curve was reproducible over three trials. Semi-log plots of acetone concentration at time = infinity, C_∞ , minus the concentration at any time, C_t , versus time were linear over several ferrate half-lives. These acetone concentrations plotted had been interpolated off the standard curve (Figure 9) for each aliquot of the reaction solution taken. See Figure 10 for a typical kinetic plot of this type and Table 16 for data.

CALCULATIONS

Individual rate constants were determined by graphic means, while ΔH^\ddagger (Table 14), slopes of the isokinetic plots (Figure 7 and 7a), the slope of the Hammett plot (Figure 8), and the rates of acetone production (Table 16) were calculated by the method of least squares (32):

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- (32) F. Daniels, J. H. Mathews, J. W. Williams, P. Bender, and R. A. Alberty, Experimental Physical Chemistry, McGraw-Hill Book Co., New York, 1956, page 339.
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$$\text{SLOPE} = \frac{N \sum xy - \sum x \sum y}{N \sum x^2 - (\sum x)^2}$$

N is the number of points; for isokinetic plots, $x = \Delta S^\ddagger$, $y = \Delta H^\ddagger$; for Hammett plot, $x = \sigma$, $y = \log (k_{II})$; and for the rate of acetone production, $x = \text{time in seconds}$, $y = \log (C_\infty - C_t)$.

DISCUSSION

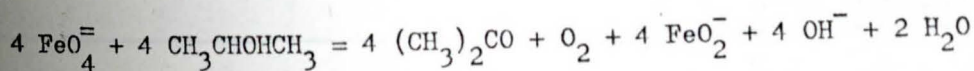
The oxidation of alcohols and carbinols by potassium ferrate was found to be first order in ferrate ion and in alkoxy ion of alcohol or carbinol. It could not be determined what dependency the reaction has on hydroxide ion, but the indications were that it did enter into the rate equation, as was shown for ferrate decomposition (5). The overall rate equation can be written as:

$$\text{rate} = k (\text{FeO}_4^-)^1 (\text{alkoxy ion})^1 (\text{OH}^-)^?$$

However, the alkalinity was kept constant for a series of reactions thus incorporating (OH^-) into the specific rate constant:

$$\text{rate} = k_{\text{II}} (\text{FeO}_4^-) (\text{alkoxy ion})$$

The stoichiometry of the reaction of propanol-2 and ferrate in 8 M potassium hydroxide indicates the following relationship:



< The rate of acetone production was found to be equal (within experimental error) to the rate of ferrate disappearance (see Table 1 and 16), showing that no stable ferrate-propanol-2 intermediate is formed. This also requires that the reaction forming acetone be essentially complete in one step, which is akin to postulating a two electron transfer. > This would reduce the oxidation state of iron from VI to IV (5, 6, 7, 8) and, since an aqueous species of iron-IV has, to date, never been characterized, this state of iron can be assumed to be very reactive. > Support for such a

reactive intermediate is derived from the results of oxygen production (12). Oxygen starts to be evolved as soon as the ferrate and alcohol solution are mixed, and continues for several half-lives after complete consumption of the purple color. Oxygen evolution, then, is not directly related to iron-VI but to some unknown, reactive intermediate, here postulated to be an iron-IV oxyanion decomposing into iron-III and other oxy or peroxy species which then undergoes iron-III catalyzed decomposition, to form oxygen (11). These results lead to some question of the validity of McGee's work (5), wherein he measured the decomposition of ferrate by the rate of oxygen evolution. Was he really measuring the decomposition of iron-VI or was it some reactive intermediate? It should be stated that the decomposition of ferrate may be very much different *FROM* its reaction with organic compounds. If potassium ferrate reacts in a manner similar to permanganate in alkaline solution (33), oxygen evolution would indeed be

(33) M. C. R. Symons, J. Chem. Soc., 1953, 3956; 1954, 3676.

a direct measure of its decomposition.

The stoichiometry of the oxidation of carbinols is not completely known, since the amount of oxygen produced has not been measured, but an approximate one to one mole ratio of ferrate to ketone has been found in all cases (Table 15). The reaction has also been shown to be first order in three of the carbinols (the fourth was not determined), propanol-2, and 1,1,1-trifluoropropanol-2, Table 13, Figure 6. Products of the fluoropropanols were not determined; however, other data point to the likelihood that they react in the same proportions as the carbinols and propanol-2.

The deuterium isotope effect for 2-deuteropropanol-2 gave k_h/k_d of 9.6, indicating that the rate determining step is the breaking of the C-H bond on the α -carbon. Arrhenius plots of the deuterium compound in potassium hydroxide and water solutions were non-linear (Figure 3) as were the plots of the protium alcohol in deuterium oxide-potassium deuterioxide solutions (Figure 3). The Arrhenius plot for the 2-deutero alcohol, however, was linear for the solvent deuterium oxide-potassium deuterioxide (Figure 3). The curved Arrhenius plots might be caused from any of a number of reasons, of which two are most probable: a change in mechanism; or the reaction does not have a linear inverse temperature dependence. Whatever the precise cause of the anomalous Arrhenius curves, it is clear that the C-H bond is being broken in the rate-controlling step.

The deuterium isotope effect on two aryltrifluoromethyl carbinols which are completely ionized, revealed that the rate determining step for their oxidation is also the breaking of the C-H bond on the α -carbon. An Arrhenius plot for α -deuterophenyltrifluoromethyl carbinol was linear, with ΔH^\ddagger and ΔS^\ddagger fitting the isokinetic plot for the carbinols (Figure 7).

For phenyltrifluoromethyl carbinol, k_h/k_d is 5.5 ± 0.3 while for m-nitrophenyltrifluoromethyl carbinol, k_h/k_d is 6.5 ± 0.7 . These values are nearly equal when the limits of experimental error are considered, but there does seem to be a small difference between them.

According to Swain (10, 34a) proton and hydride transfers may be

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- (34) a. C. G. Swain, R. A. Wiles, and R. F. W. Bader, J. Am. Chem. Soc., 83, 1945 (1961).
 b. K. B. Wiberg, Chem. Revs., 55, 723 (1955).
 c. K. B. Wiberg, J. Am. Chem. Soc., 76, 3371 (1954).
-

distinguished by examining the isotope effect when different substituents are placed in the reacting molecule. He points out that known examples of proton transfers (34b) show a sensitivity of isotope effect to addition of substituents or a change in structure, whereas there is little change for a hydride transfer (34a, c). The proton transfers (34b, page 723) have k_h/k_d values as low as 0.84 (neutralization of 1-butyilmagnesium bromide in neutral water-deuterium oxide mixtures) to as high as 12 (racemization and deuterium exchange of (-) 2-butyl phenyl ketone in water and deuterium oxide]. Intermediate k_h/k_d values (34b, page 727) vary from 1.8 to 10, for various oxidation reactions of compounds with differing structure, in solvents that include aqueous acid, methanol, ethanol, aqueous alcohol, water at pH 7, and water at pH 13. A few examples of hydride transfer reactions have been studied (34a, c) and show a range for the isotope effect of only 1.8 (34c) to 2.94 (34a). The latter example is for the bromine oxidation of propanol-2 in water, while the ratio for the oxidation of 1-fluoropropanol-2 by bromine is 2.83. This is a small change for addition of a fluorine atom, which is strongly electron withdrawing. Swain postulates, from these data, that hydride shifts are less responsive to electronic changes than are proton shifts.

The isotope effects for the aryltrifluoromethyl carbinols used in this investigation, according to the Swain Criteria, indicate a hydride

transfer, because of their relative insensitivity to a change in the electronic environment. There are valid objections to the Swain Criteria when the general mechanism or steric character of a reaction changes with substituent, but in the case of ferrate oxidation of carbinols, both factors are constant; the only variation is electron density at the reaction center. The basis for Swain's conclusions is that "The electron pair required for proton transfer would normally occupy a nonbonding level in the three-atom molecular orbital in the transition state, but, because of the short distances involved in bonds to hydrogen, there will be considerable Pauli repulsion between the orbitals of R (the group bonded to the reacting H) and N (the attacking nucleophile), resulting in some anti-bonding character being conferred on the orbital." (35). These repulsions

(35) R. Stewart, Oxidation Mechanisms, Applications to Organic Chemistry, W. A. Benjamin, Inc., New York, 1964, page 24.

cause the transition state for a proton transfer to be more ionic and more polarizable than the transition state of the hydride transfer, thus making the reaction more susceptible to electronic changes. It has been suggested that the hydride transfer is a compact transition state, since the attacking electrophile usually has a low energy, unfilled orbital available for bonding.

Because of the greater polarizability and ionic character of the proton transition state, there should be a significant salt effect for a proton transfer, whereas there should be little change in rate for the hydride mechanism. The latter is found to be the case (Table 9) for the ferrate oxidation of phenyltrifluoromethyl carbinol; the rate in 0.5 M

potassium hydroxide and 3.5 M potassium fluoride is 0.776 liters mole⁻¹ second⁻¹ and in 0.5 M potassium hydroxide and 4.5 M potassium fluoride it is 0.788 liters mole⁻¹ second⁻¹. This is a very small change in rate for a 25% change in salt concentration, and once again points toward a hydride mechanism. The experimental precision in the latter solvent indicates much greater stability of the ferrate ion in the more concentrated solution than in the former, which was the solvent used for most carbinol reactions. This effect is apparently due to complexing of the aqueous iron species by the fluoride ion, which bears a striking resemblance to the hydroxide ion in physical properties. The entropies of the aqueous ions, ΔS° at 298.1° K, are (36): OH⁻, -2.49; F⁻, -2.3.

(36) W. M. Latimer, V. S. Pitzer, and W. V. Smith, J. Am. Chem. Soc., 60, 1829 (1938).

The salting out factors of sodium fluoride and sodium hydroxide are 0.254 and 0.256 respectively (37).

(37) W. F. McDevit and F. A. Long, ibid., 74, 1773 (1952).

The concentration of potassium hydroxide was varied from 8 M to 3 M in one molar steps for the oxidation of propanol-2 (Table 17). Attempts to correlate these data using known measures of basicity (38)

(38) a. G. Yagil and M. Anbar, J. Am. Chem. Soc., 85, 2376 (1963).
 b. M. Anbar, M. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, ibid., page 2380

gave no clear idea of the base dependency of the reaction. Plots of the type suggested in (38b) show a degree of linearity with the slope equal to $\frac{1}{2}$. As admitted by the authors in (38a), "Nevertheless, the conclusions reached here should not be regarded as final until better experimental values of H_- are available." All the graphs presented in these two articles have slopes close to unity, leaving the question of how a slope of $\frac{1}{2}$ should be interpreted. There are two important difficulties to elucidation of the results of propanol-2 oxidation in concentrated potassium hydroxide: the ionization constant of propanol-2 in 8 M base is not known, nor is it known for any solution of concentrated alkali; and little precise data for activity coefficients of concentrated base solutions ARE known (38, 39).

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- (39) a. G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Act.*, 27, 348 (1948).
 b. R. A. Robinson and R. H. Stokes, *Trans. Far. Soc.*, 45, 612 (1949).
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A comparison of the activation parameters and isotope effects of ferrate oxidations (Table 14) with those of other postulated hydride transfers (Table 14a) shows a striking similarity. (It is also of interest to note that there is a likelihood of H^- ion existing in concentrated base solution (40). Fluornoy and Wilmarth present some excellent data

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- (40) J. M. Fluornoy and W. K. Wilmarth, *J. Am. Chem. Soc.*, 83, 2257 (1961).
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in studying base-catalyzed exchange between water and dissolved molecular

hydrogen, leaving little doubt that hydride ions can and do exist in concentrated alkali).

The information, as presented thus far, is consistent with a hydride mechanism, but examination of the rate data in Tables 7-10 reveals that *m*-nitrophenyltrifluoromethyl carbinol reacts fastest of all carbinols and that *p*-methylphenyltrifluoromethyl carbinol reacts slowest. Since a hydride transfer requires removal of H^- , a proton plus two electrons, the *m*-nitro carbinol would be expected to react slowest because of the electron withdrawing properties of the nitro group, and the *p*-methyl carbinol would be expected to react fastest because of its electron donating properties. These data produce a Hammett $\sigma\rho$ plot (Figure 8) with a positive slope of 0.72. "A hydride expulsion should be favored by electron-donating groups and should result in a large negative Hammett rho value." (10, page 65). The rho value for hydride addition to substituted fluorenones (41) has been given as + 2.65. Therefore, it

(41) G. G. Smith and R. P. Boyer, *Tetrahedron*, 18, 323 (1962) - - - - reference 27 in Stewart (10), page 65.

would be expected that hydride expulsion would lead to a rho value of the same size but opposite in sign. Before the material just presented is considered to be at variance with the postulated hydride transfer for ferrate oxidation, the effects of the experimental temperature must be considered.

Richie and Sager (42) state that "Caution - - - (is) - - -

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- (42) Progress in Physical Organic Chemistry, vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, editors, Interscience Publishers, New York, 1964, page 354.
-

urged in the interpretation of rho values as criteria of mechanisms, since even the sign of ρ would depend on the experimental temperature relative to the isokinetic temperature." The isokinetic temperature, β , is given by the slope of the line resulting from a plot of ΔH^\ddagger versus ΔS^\ddagger for a series of variously substituted reactants, in this case a series of para and meta substituted phenyltrifluoromethyl carbinols (43). This (β)

- (43) The isokinetic temperature will be referred to as β and the experimental temperature as T; both are in degrees Kelvin.
-

would be the temperature at which the rates of reaction of all the substituted reactants would be equal. As the experimental temperature goes from below β to above β , the ρ value (of a Hammett ρ plot) will theoretically change signs as β is passed (38, pages 353-354) (44). It

- (44) J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, John Wiley and Sons, Inc., New York, 1963, pages 374-387.
-

has been observed (38, pages 356-365) that, in general, simultaneously linear isokinetic plots and Hammett plots occur only infrequently, and that most of those that do occur can be dismissed as fortuitous for one reason or another. However, there are those that cannot be explained

away (45); Leffler and Grunwald (44) also list several cases that would be

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- (45) a. R. Cross and P. Fugassi, J. Am. Chem. Soc., 71, 223 (1949).
 b. A. I. Biggs, J. Chem. Soc., 1961, 2572.
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difficult to explain without the aid of both the isokinetic and Hammett relationships.

The main objection to simultaneously linear Hammett and isokinetic plots lies in the relationship between the two functions. If both plots are to be linear, then ρ must be proportional to the quantity $(1 - \frac{T}{\beta})$ as shown below (42):

For Hammett,

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = -2.3 RT \sigma \rho \quad (1)$$

For isokinetic

$$\Delta H^\ddagger = \beta \Delta S^\ddagger \quad (2)$$

Substituting (2) into (1)

$$\Delta F^\ddagger = \Delta H^\ddagger - \frac{T\Delta H^\ddagger}{\beta} = -2.3 RT \sigma \rho \quad (3)$$

$$-2.3 RT \sigma \rho = \Delta H^\ddagger \left(1 - \frac{T}{\beta}\right) \quad (4)$$

Instead of the derived proportionality, it has been shown empirically that ρ is inversely proportional to the absolute temperature for a great many cases (46), but in most of these β is very close to the

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- (46) a. P. R. Wells, Chem. Revs., 63, 171 (1963).
 b. R. W. Taft, Jr., and I. C. Lewis, J. Am. Chem. Soc., 81, 5343 (1959).
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experimental temperature. This proximity of temperatures often causes a scattering on the isokinetic plot, possibly because ΔC_p^\ddagger is not constant over the experimental temperature range (47). It also appears that the

(47) J. W. Cobble, *ibid.*, 86, 5394 (1964).

inverse relationship of ρ with T is not in conflict with rho's proportionality to the quantity given in equation 4, since equation 4 can be rearranged to give equation 6:

$$\sigma\rho = \frac{-\Delta H^\ddagger}{2.3R} \frac{1}{T} \left(1 - \frac{T}{\beta}\right) \quad (5)$$

$$\sigma\rho = K \frac{1}{T} \left(\frac{T}{\beta} - 1\right) \quad (6)$$

K is a constant including ΔH^\ddagger and $2.3R$.

When β and T are quite close then the quantity $\left(\frac{T}{\beta} - 1\right)$ can change from negative to positive with only a small change in either T or β ; this is the same as saying that ρ is proportional to $\pm \frac{1}{T}$ that is, experimental error in determining β or a small change in T (as for an Arrhenius plot) can change the slope of the Hammett plot, just as Richie and Sager have stated (42). Examples of the proportionality to $\pm \frac{1}{T}$ can be found in Wells, page 185 (46a). When $\beta \gg T$, then ρ would be proportional to $-\frac{1}{T}$ and would not change much with a small change in T; when $\beta \ll T$, would be proportional to $+\frac{1}{T}$ and would change only slowly with small changes in T. This latter condition, $\beta \ll T$, applies for the case of ferrate oxidation of carbinols and alcohols, where β is 218° K for carbinols and 263° K for the alcohols. An examination of the data revealed that ρ does increase slowly

with small temperature changes and approaches 1.0 at the upper temperature limits used in these investigations. For the particular example of the carbinols, this behavior is predicted by equation 6 by introducing experimental values for β and T:

$$\sigma\rho = K \frac{1}{T} \left(\frac{308}{218} - 1 \right) \quad (6)$$

$$\sigma\rho = + K \frac{1}{T} (0.41) \quad (7)$$

Experimentally, ρ was found to have a positive value of 0.72, just as is predicted by equation 7. The slowness of the increase of ρ with T, can also be attributed to the powerful electron withdrawing effect of the trifluoromethyl group, which is adjacent to the reaction site. This effect is so large as to impart an insensitivity to the electronic effect of adding substituents to the phenyl ring.

The Hammett $\sigma\rho$ relationship is derived from the relative ionization constants, in aqueous media at 25°, of meta and para substituted benzoic acids; this defines a line *with* $\rho = 1.0$. Proton expulsion mechanisms, such as the ionization of substituted anilines (48), where $\rho = 2.889$ and $\beta = 4T$, give positive values of ρ

(48) A. I. Biggs, J. Chem., 1961, 2572.

($\beta > T$). If the isokinetic relationship is true, then a proton mechanism, with $\beta \ll T$, should show a negative ρ value. (This cannot be tested for the substituted anilines, since β is well above the experimental temperatures usually attainable). By the same reasoning, a hydride abstraction

mechanism should have a large negative rho when $\beta \gg T$, but should have a positive rho when $\beta \ll T$. The latter is the situation for the ferrate oxidation of carbinols. No example has been found in the literature of a hydride transfer reaction with a well-defined β greater than the reaction temperature.

Petersen (49) states that many isokinetic plots are just

(49) R. C. Petersen, J. Org. Chem., 29, 3133 (1964).

accidents. He discusses two sets of hypothetical data and shows that a linear $\Delta H^\ddagger - \Delta S^\ddagger$ plot can be obtained even when no true isokinetic relationship exists. As he states, "In no case can the linear $\Delta H^\ddagger - \Delta S^\ddagger$ plot be taken by itself to be an adequate demonstration of the existence of an isokinetic relationship." This is true, but in the case under discussion, a linear Hammett plot also exists. This fact, in the light of the foregoing discussion, puts the apparent isokinetic plot on much firmer footing.

It is also possible to get a linear isokinetic plot due to compensating experimental error (50), but if that were true for the

(50) R. C. Petersen, J. Markgraf, and S. Ross, J. Am. Chem. Soc., 83, 3819 (1961).

instance under consideration, it would have to be considered extremely fortuitous to obtain a linear Hammett plot with the same data. The largest

error in ΔH^\ddagger is ± 0.8 kcal/mole (51), assuming a 5% error in the

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- (51) K. B. Wiberg, Physical Organic Chemistry, John Wiley and Sons, Inc., New York, 1964, page 378.
-

individual rate constants (the error was usually nearer 2%). The total range of ΔH^\ddagger is 4 kcal/mole for the reaction series, which is $2\frac{1}{2}$ times the largest error limits, 2δ (as defined by Wiberg). The values of the entropy of activation show a range of 19 entropy units. This is four times greater than the limits of error (51), ± 4 entropy units.

It appears unlikely that the isokinetic plot is due to either accident or experimental error.

A large amount of corroborative evidence has been presented in support of a hydride transfer mechanism for the previously unexplored area of secondary alcohol oxidation by potassium ferrate. It has also been indicated that the isokinetic relationship and Hammett σ_p plot have a more general interrelation than previously discussed. The hydride mechanism depends upon the validity of this isokinetic relationship, and also upon the inference that a negative ion mechanism should have a positive ρ value when β is much less than T.

The experimental data, using the interpretation given in the preceeding discussion, indicate the most likely mechanism to be the following:

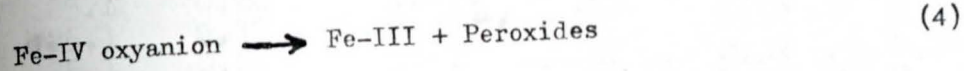
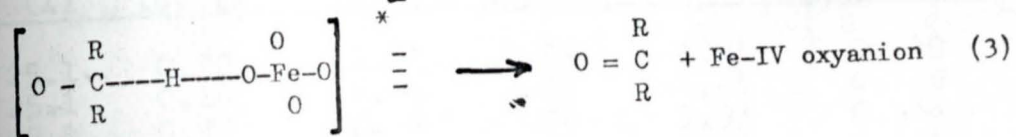
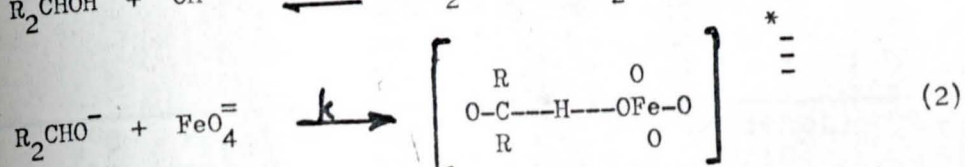
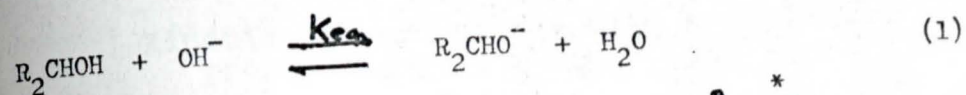


TABLE 1

Kinetic determinations with
propanol-2 in 8 M KOH

Run #	t°C (1)	$k_{\text{FeO}_4} \times 10^3$ (2)	$k_{\text{obs}} \times 10^3$ (3)	$k_I \times 10^3$ (4)	(alcohol) $\times 10^2$	k_{II} (5)
II-27	25.1	0.22	2.91	2.68	1.91	0.140
II-28	25.1	0.18	2.65	2.47	1.91	0.129
II-29	25.1	0.20	2.94	2.74	1.91	0.144
II-30	25.1	0.20	2.89	2.69	1.91	0.141
II-31	25.1	0.17	3.35	3.18	2.18	0.146
II-32	25.1	0.21	3.42	3.21	2.18	0.147
II-33	25.1	0.15	2.79	2.64	1.91	0.138
II-34	31.8	0.18	3.91	3.73	1.91	0.195
II-35	31.8	0.17	4.22	4.05	1.91	0.212
II-36	31.8	0.15	3.98	3.83	1.91	0.200
II-37	31.8	0.13	4.15	4.03	1.91	0.211
II-38	38.5	0.18	5.74	5.56	1.91	0.291
II-39	38.5	0.24	5.35	5.11	1.91	0.268
II-40	38.5	0.25	5.76	5.51	1.91	0.289
II-41	45.2	0.43	7.69	7.26	1.91	0.381
II-42	45.2	0.26	8.23	7.97	1.91	0.416
II-43	45.2	0.33	8.14	7.81	1.91	0.409
II-44	45.2	0.61	7.67	7.06	1.91	0.370
V-1	25.1	0.14	2.84	2.70	2.23	0.121
V-2	25.1	0.15	3.37	3.22	2.23	0.144
V-3	25.1	0.15	5.71	5.56	4.46	0.125
V-4	25.1	0.15	5.90	5.75	4.46	0.129
V-5	25.1	0.15	5.82	5.67	4.46	0.127
V-6	25.1	0.15	3.21	3.06	2.23	0.137
V-7	25.1	0.11	3.24	3.13	2.23	0.140
V-8	25.1	0.12	5.35	5.23	4.46	0.117
V-9	25.1	0.13	6.01	5.88	4.46	0.131
V-10	25.1	0.13	6.16	6.03	4.46	0.135
V-11	25.1	0.13	8.44	8.31	5.95	0.140
V-12	25.1	0.13	8.27	8.14	5.95	0.137
V-13	25.1	0.13	12.8	12.7	8.92	0.142

FOOTNOTES:

- (1) Temperature correction applied, see table 1a.
 (2) k_{FeO_4} = rate of disappearance of ferrate in KOH alone
 (3) k_{obs} = pseudo-first order rate constant for ferrate reaction with propanol-2
 (4) $k_I = k_{\text{obs}} - k_{\text{FeO}_4}$
 (5) k_{II} = second order rate constant = $k_I \times \frac{1}{(\text{alcohol})}$

T A B L E 1a
Temperature Corrections

temperature of machine*	temperature from thermocouple**	temperature of machine*	temperature from thermocouple**
15.5	15.7	31.5	31.3
16.0	16.2	32.0	31.8
16.5	16.7	32.5	32.3
17.0	17.2	33.0	32.7
17.5	17.6	33.5	33.1
18.0	18.1	34.0	33.6
18.5	18.6	34.5	34.1
19.0	19.1	35.0	34.6
19.5	19.6	35.5	35.1
20.0	20.1	36.0	35.6
20.5	20.6	36.5	36.0
21.0	21.1	37.0	36.5
21.5	21.6	37.5	37.0
22.0	22.1	38.0	37.5
22.5	22.6	38.5	38.0
23.0	23.1	39.0	38.5
23.5	23.6	39.5	39.0
24.0	24.1	40.0	39.5
24.5	24.6	40.5	40.0
25.0	25.1	41.0	40.5
25.5	25.6	41.5	40.9
26.0	26.0	42.0	41.4
26.5	26.5	42.5	41.9
27.0	27.0	43.0	42.4
27.5	27.5	43.5	42.9
28.0	28.0	44.0	43.3
28.5	28.5	44.5	43.8
29.0	28.9	45.0	44.3
29.5	29.4	45.5	44.8
30.0	29.9	46.0	45.2
30.5	30.4	46.5	45.7
31.0	30.9	47.0	46.1

* Temperature of machine given by water circulated with a Haake circulator.

** Potential of a ten junction copper-constantan thermocouple was read and interpolated to degrees centigrade by use of National Bureau of Standard's Circular 561

TABLE 2

Kinetic determinations with
propanol-2 in 7.49 M KOD and D₂O

Run #	t°C (1)	k _{FeO₄⁼} 10 ³ (2)	k _{obs} x 10 ³ (3)	k _I x 10 ³ (4)	(alcohol) x 10 ²	k _{II} (5)
II-45	25.1	0.19	4.33	4.14	2.38	0.174
II-46	25.1	0.33	4.67	4.34	2.38	0.182
II-47	25.1	0.16	4.66	4.50	2.38	0.188
II-48	31.8	0.18	5.78	5.60	2.38	0.235
II-49	31.8	0.18	5.96	5.78	2.38	0.242
II-50	31.8	0.21	5.50	5.29	2.38	0.222
II-51	38.5	0.32	9.58	9.26	2.38	0.389
II-52	38.5	0.33	9.17	8.84	2.38	0.371
II-53	38.5	0.28	8.70	8.42	2.38	0.353
II-54	45.2	0.27	10.3	10.0	2.38	0.421
II-55	45.2	1.09	11.3	10.2	2.38	0.426
II-56	45.2	1.93	11.6	9.69	2.38	0.406
II-57*	25.1	0.14	3.06	2.92	2.38	0.122

* Run after kinetic solution had been heated to 45.2°.

FOOTNOTES: see table 1

TABLE 3

Kinetic determinations with
2-deuteropropanol-2 in 7.71 M KOD and D₂O

Run #	t°C (1)	k _{FeO₄⁼} x 10 ³ (2)	k _{obs} x 10 ³ (3)	k _I x 10 ³ (4)	(alcohol) x 10 ²	k _{II} (5)
II-71	25.1	0.10	1.40	1.30	2.10	0.0619
II-72	25.1	0.14	1.30	1.16	2.10	0.0552
II-73	25.1	0.08	1.35	1.27	2.10	0.0605
II-74	31.8	0.17	1.55	1.38	2.10	0.0656
II-75	31.8	0.21	1.63	1.42	2.10	0.0676
II-76	31.8	0.19	1.62	1.43	2.10	0.0672
II-77	38.5	0.18	1.94	1.76	2.10	0.0838
II-78	38.5	0.16	1.97	1.81	2.10	0.0862
II-79	38.5	0.22	2.14	1.92	2.10	0.0915
II-80	45.2	0.32	2.40	2.08	2.10	0.0991
II-81	45.2	0.32	2.68	2.36	2.10	0.112
II-82	45.2	0.30	2.48	2.18	2.10	0.104
II-83*	25.1	0.17	1.27	1.10	2.10	0.0524

* Run after kinetic solution had been heated to 45.2°.

FOOTNOTES: see table 1

TABLE 4

Kinetic determinations with
2-deuteropropanol-2 in 8 M KOH

Run #	t°C (1)	k _{FeO4} ⁼ 10 ³ (2)	k _{obs} x 10 ³ (3)	k _I x 10 ³ (4)	(alcohol) x 10 ²	k _{II} (5)
VI-200	25.1	0.16	0.78	0.62	4.16	0.0149
VI-205	31.8	0.21	1.70	1.49	8.32	0.0179
VI-206	31.8	0.21	1.57	1.36	8.32	0.0164
VI-209	38.5	0.39	2.76	2.37	8.32	0.0285
VI-211	38.5	0.39	2.51	2.12	8.32	0.0255
VI-214	44.5	0.43	4.50	4.07	8.32	0.0489
VI-215	44.5	0.43	4.17	3.74	8.32	0.0449
VI-216	44.5	0.43	4.55	4.12	8.32	0.0496
VI-217*	25.1	0.15	1.03	0.88	8.32	0.0106
VI-218*	25.1	0.15	1.10	0.95	8.32	0.0115
VI-219*	25.1	0.15	1.36	1.21	8.32	0.0145
VI-220*	25.1	0.15	1.40	1.25	8.32	0.0150

At 25.1°, $k_h/k_d = 9.6$

* The kinetic solution for runs VI-217 and VI-218 had been heated the same length of time and to the same temperatures as the kinetic solution for runs VI-200 to VI-216. The kinetic solution for runs VI-219 and VI-220 was thermostated at 25.0° until used; the alcohol was in solution for the same length of time as for the other runs.

FOOTNOTES: see table 1

TABLE 5

Kinetic determinations with
1,1,1-trifluoropropanol-2 in 8 M KOH

Run #	t°C (1)	$k_{FeO_4} \times$ 10^3 (2)	$k_{obs} \times$ 10^3 (3)	$k_I \times$ 10^3 (4)	(alcohol) $\times 10^2$	k_{II} (5)
VI-166	25.1	0.14	4.88	4.74	2.39	0.198
VI-167	25.1	0.17	4.79	4.62	2.39	0.193
VI-168	25.1	0.14	2.34	2.20	1.02	0.216
VI-169	25.1	0.13	2.27	2.14	1.02	0.210
VI-170	25.1	0.20	7.76	7.56	3.58	0.211
VI-171	25.1	0.20	8.06	7.86	3.58	0.220
VI-172	18.1	0.07	5.16	5.09	3.58	0.142
VI-173	18.1	0.10	5.13	5.03	3.58	0.140
VI-174	18.1	0.11	5.00	4.89	3.58	0.136
VI-181	25.1	0.18	4.18	4.00	1.65	0.242
VI-182	25.1	0.11	4.11	4.00	1.65	0.242
VI-183	39.9	0.43	6.80	6.37	1.24	0.514
VI-186	15.7	0.08	2.28	2.20	1.78	0.124
VI-187	15.7	0.06	3.11	3.05	2.66	0.115
VI-188	15.7	0.07	3.20	3.13	2.66	0.118
VI-189	30.0	0.29	5.86	5.57	1.78	0.313

FOOTNOTES: see table 1

TABLE 6

Kinetic determinations with
1,1,1,3,3,3-hexafluoropropanol-2 in 8 M KOH

Run #	t°C (1)	$k_{FeO_4} \times$ 10^3 (2)	$k_{obs} \times$ 10^3 (3)	$k_I \times$ 10^3 (4)	(alcohol) $\times 10^2$	k_{II} (5)
V-24	25.1	0.12	4.59	4.47	2.00	0.224
V-25	25.1	0.15	4.58	4.43	2.00	0.223
V-26	25.1	0.09	4.40	4.31	2.00	0.216
V-27	31.8	0.15	6.45	6.30	2.00	0.315
V-28	31.8	0.18	6.09	5.91	2.00	0.296
V-29	31.8	0.17	6.80	6.72	2.00	0.336
V-30	39.9	0.26	10.9	10.6	2.00	0.532
V-31	39.9	0.51	11.2	10.7	2.00	0.536
V-32	39.9	0.30	11.2	10.9	2.00	0.544
V-33	25.1	0.31	4.38	4.07	2.00	0.302
V-34	21.3	0.17	3.48	3.31	2.00	0.165
V-35	21.3	0.12	3.53	3.41	2.00	0.170
V-36	21.3	0.10	3.62	3.52	2.00	0.176

FOOTNOTES: see table 1

TABLE 7

Kinetic determinations with
 m-nitrophenyltrifluoromethyl carbinol
 in 0.5 M KOH and 3.5 M KF

Run #	t°C (1)	k _{obs} x 10 ³ (2)	((alcohol) x 10 ³	k _{II} (3)
VI-73	25.1	25.4	10.00	2.54
VI-74	25.1	23.0	10.00	2.30
VI-114	25.1	8.18	3.52	2.32
VI-115	25.1	8.45	3.52	2.40
VI-116	25.1	9.50	3.52	2.70
VI-135	15.7	3.77	3.62	1.04
VI-136	15.7	3.96	3.62	1.09
VI-137	15.7	4.28	3.62	1.18
VI-138	20.1	5.11	3.31	1.55
VI-139	20.1	5.40	3.31	1.63
VI-140	20.1	5.09	3.31	1.54
VI-146	31.9	11.9	3.06	3.90
VI-147	31.9	10.2	3.06	3.34
VI-148	31.9	11.9	3.06	3.88

FOOTNOTES:

- (1) Corrected value of the temperature
- (2) Pseudo-first-order rate constant for the reaction of potassium ferrate with the carbinol in question.
- (3) Second order rate constant $k_{\text{obs}} \times \frac{1}{(\text{alcohol})}$

T A B L E 8

Kinetic determinations with
 m-bromophenyltrifluoromethyl carbinol
 in 0.5 M KOH and 3.5 M KF

Run #	t°C (1)	k _{obs} x 10 ³ (2)	(alcohol) x 10 ³	k _{II} (3)
VI-124	25.1	6.70	5.04	1.33
VI-125	25.1	7.05	5.04	1.40
VI-126	25.1	8.09	5.04	1.61
VI-127	25.1	6.18	5.04	1.23
VI-128	25.1	8.01	5.04	1.59
VI-129	25.1	7.87	5.04	1.56
VI-130	25.1	2.59	2.07	1.25
VI-131	25.1	2.68	2.07	1.29
VI-132	25.1	3.19	2.07	1.54
VI-133	15.7	1.78	2.98	0.597
VI-134	15.7	1.83	2.98	0.614
VI-141	20.1	2.83	2.98	0.948
VI-142	20.1	2.40	2.98	0.805
VI-221	15.7	3.12	4.23	0.739
VI-222	15.7	3.14	4.23	0.743
VI-223	15.7	3.72	4.23	0.880
VI-224	30.3	5.43	2.92	1.86
VI-225	30.3	6.95	2.92	2.38
VI-226	30.3	7.02	2.92	2.40

FOOTNOTES: see table 7

T A B L E 9

Kinetic determinations with
phenyltrifluoromethyl carbinol
in 0.5 M KOH and 3.5 M KF

Run 3	t°C (1)	k _{obs} x 10 ³ (2)	(alcohol) x 10 ²	k _{II} (3)
VI-39	25.1	8.42	1.13	0.745
VI-41	25.1	9.16	1.13	0.811
VI-49	30.1	11.1	1.13	0.982
VI-51	30.1	13.0	1.13	1.15
VI-53	34.7	14.4	1.13	1.27
VI-56	34.7	19.2	1.13	1.70
VI-85	25.1	15.0	2.00	0.750
VI-86	25.1	14.6	2.00	0.729
VI-87	25.1	16.2	2.00	0.810

Kinetic determinations with
phenyltrifluoromethyl carbinol
in 0.5 M KOH and 4.5 M KF

VI-155	25.1	18.4	2.35	0.785
VI-156	25.1	18.6	2.35	0.790
VI-157	25.1	18.6	2.35	0.790

Kinetic determinations with
phenyltrifluoromethyl carbinol
in 1.0 M KOH and 3.0 M KF

VI-158	25.1	9.20	1.52	0.605
VI-159	25.1	9.99	1.52	0.656
VI-160	25.1	11.0	1.52	0.721

FOOTNOTES: see table 7

TABLE 10

Kinetic determinations with
p-methylphenyltrifluoromethyl carbinol
in 0.5 M KOH and 3.5 M KF

Run #	t ^o C (1)	k _{obs} x 10 ³ (2)	(alcohol) x 10 ²	k _{II} (3)
VI-63	20.4	4.60	1.18	0.391
VI-64	20.4	4.63	1.18	0.394
VI-65	25.1	5.99	1.18	0.509
VI-66	25.1	6.14	1.18	0.521
VI-67	30.0	8.58	1.18	0.730
VI-68	30.0	8.69	1.18	0.739
VI-69	34.7	11.6	1.18	0.987
VI-70	34.7	10.9	1.18	0.928

T A B L E 11

Kinetic determinations with
 α -deuterophenyltrifluoromethyl carbinol
 in 0.5 M KOH and 3.5 M KF

Run #	t°C (1)	k _{obs} x 10 ³ (2)	(alcohol) x 10 ²	k _{II} (3)
VI-149	25.1	3.09	1.98	0.156
VI-150	25.1	2.66	1.98	0.134
VI-151	25.1	2.78	1.98	0.140
VI-152	25.1	2.60	1.74	0.149
VI-153	25.1	2.54	1.74	0.146
VI-154	25.1	2.50	1.74	0.144
VI-192	16.5	1.26	1.64	0.0769
VI-193	16.5	1.45	1.64	0.0885
VI-194	16.5	1.45	1.64	0.0885
VI-195	30.8	2.93	1.64	0.179
VI-196	30.8	2.98	1.64	0.182
VI-197	30.8	3.37	1.64	0.205
VI-198	37.0	7.84	1.64	0.476
VI-199	37.0	7.71	1.64	0.470

at 25.1°, k_h/k_d = 5.5

FOOTNOTES: for both table 11 and table 12 see table 7

T A B L E 12

Kinetic determinations with
 α -deutero-m-nitrophenyltrifluoromethyl carbinol
 in 0.5 M KOH and 3.5 M KF

Run #	t°C (1)	k _{obs} x 10 ³ (2)	(alcohol) x 10 ³	k _{II} (3)
VI-230	25.1	1.36	4.46	0.304
VI-231	25.1	1.45	4.46	0.325
VI-232	25.1	1.83	4.46	0.410
VI-233	25.1	2.01	5.21	0.385
VI-234	25.1	1.95	5.21	0.374
VI-235	25.1	2.32	5.21	0.444

at 25.1°, k_h/k_d = 6.5

TABLE 13
Determination of order
in alcohol

alcohol	concentration $\times 10^2$	k_I or k_{obs} $\times 10^3$ (1)	order in alcohol (2)
propanol-2	1.91	2.64	1
	2.18	3.19	
	2.23	3.03	
	2.98	3.95	
	4.46	5.61	
	5.95	8.23	
	8.93	12.7	
	0.992	1.40	
1,1,1-trifluoro- propanol-2	2.39	4.68	1
	1.02	2.17	
	3.58	7.71	
	1.65	4.00	
phenyltrifluoro- methyl carbinol	2.00	15.3	1
	1.13	8.79	
m-bromophenyl- trifluoromethyl carbinol	0.207	2.82	1
	0.504	7.32	
m-nitrophenyl- trifluoromethyl carbinol	1.00	24.2	1
	0.352	8.71	

(1) k_I for propanol-2 and 1,1,1-trifluoropropanol-2 and k_{obs} for all carbinols.

(2) See figure 6

T A B L E 14
Activation Parameters

alcohol	ΔH^\ddagger , kcal/mole	ΔS^\ddagger , E.U./mole	k_{II} at 25.0°	solvent
α -deutero propanol-2	7.46	-41.6	0.0149	7.71 M KOD and D ₂ O
propanol-2	8.05	-35.4	0.140	8 M KOH
1,1,1-trifluoro- propanol-2	10.6	-25.9	0.217	8 M KOH
1,1,1,3,3,3- hexafluoro- propanol-2	10.2	-27.3	0.216	8 M KOH
p-methylphenyl- trifluoromethyl carbinol	10.4	-25.8	0.516	0.5 M KOH and 3.5 M KF
phenyltrifluoro- methyl carbinol	11.2	-21.6	0.778	0.5 M KOH and 3.5 M KF
α -deuterophenyl- trifluoromethyl carbinol	9.04	-32.0	0.145	0.5 M KOH and 3.5 M KF
m-bromophenyl- trifluoromethyl carbinol	12.6	-15.5	1.42	0.5 M KOH and 3.5 M KF
m-nitrophenyl- trifluoromethyl carbinol	13.1	-12.8	2.44	0.5 M KOH and 3.5 M KF
α -deutero- m-nitrophenyl- trifluoromethyl carbinol	----	-----	0.374	0.5 M KOH and 3.5 M KF

T A B L E 14a
Other anion oxidations

substrate	oxidant	(OH ⁻)	ΔH^\ddagger	ΔS^\ddagger	k_h/k_d
CF ₃ CH(OH)O ⁻ (1)	MnO ₄ ⁼	0.001	12.4	-18.4	10.1
ArCH(O ⁻)CF ₃ (2)	MnO ₄ ⁼	0.1	9.1	-24.3	16.1
HCO ₂ ⁻ (3)	MnO ₄ ⁼	-----	12	-14	7.0

FOOTNOTES:

- (1) R. Stewart and M. M. Mocek, Can. J. Chem., 41, 1160(1963)
 (2) R. Stewart and R. van der Linden, Disc. Far. Soc., 29, 211(1960)
 (3) J. Halpern and S. M. Taylor, ibid., 29, 174(1960)

T A B L E 15
Isolation of products

reactant	moles K_2FeO_4 added $\times 10^3$ (1)	moles alcohol added $\times 10^3$	moles ketone found $\times 10^3$ (2)	mole ratio K_2FeO_4 to alcohol
m-nitro carbinol	0.232	0.372	0.250 (3)	0.93
m-bromo carbinol	0.262	0.450	-----	1.04
H-carbinol	0.996	4.74	-----	1.15
p-methyl carbinol	0.332	1.26	-----	1.05
propanol-2 (4)	0.0413 0.0440 0.0442	----- ----- -----	0.0389 0.0416 0.0465	1.06 1.06 0.95

FOOTNOTES:

- (1) Corrected for 85.7% potassium ferrate.
- (2) Products analyzed by gas-liquid chromatograph for all carbinols except the m-nitro
- (3) Isolated in a weighed flask after chromatographing a dry ether solution of the products on Woelm activity V alumina using ether as the eluent.
- (4) See reference 12

T A B L E 16
Rate of acetone production
in 8 M KOH

Run #	t°C	$k_{obs} \times 10^3$ (1)	(alcohol) $\times 10^2$	k_{II} (2)
III-5	25.1	3.32	2.18	0.152
III-6	25.1	3.22	2.18	0.148
III-7	25.1	3.75	2.18	0.172

(1) k_{obs} = pseudo-first order rate constant for production of acetone.

(2) $k_{II} = k_{obs} \times \frac{1}{(\text{alcohol})}$

T A B L E 17

Effect of KOH concentration on the
potassium ferrate oxidation of
propanol-2 at 25.1° (1)

Run #	(OH ⁻)	$k_{\text{FeO}_4^-} \times 10^3$ (2)	$k_{\text{obs}} \times 10^3$ (3)	$k_I \times 10^3$ (4)	(alcohol) $\times 10^2$	k_{II} (5)
IV-1	7 <u>M</u>	0.24	2.13	1.89	2.11	0.0896
IV-2	7 <u>M</u>	0.25	2.34	2.09	2.11	0.0991
IV-3	7 <u>M</u>	0.33	2.62	2.29	2.11	0.109
IV-4	6 <u>M</u>	0.20	1.71	1.51	2.13	0.0709
IV-5	6 <u>M</u>	0.24	1.75	1.51	2.13	0.0709
IV-6	6 <u>M</u>	0.19	1.74	1.55	2.13	0.0728
IV-8	5 <u>M</u>	0.41	1.45	1.04	1.91	0.0545
IV-9	5 <u>M</u>	0.34	1.44	1.10	1.91	0.0576
IV-10	5 <u>M</u>	0.27	1.32	1.05	1.91	0.0550
IV-11	4 <u>M</u>	0.31	0.976	0.666	1.97	0.0338
IV-12	4 <u>M</u>	0.50	1.79	1.29	3.17	0.0408
IV-13	4 <u>M</u>	0.49	1.80	1.32	3.17	0.0416
IV-14	3 <u>M</u>	0.35	1.51	1.16	3.98	0.0292
	8 <u>M</u>	see table 1				0.140

FOOTNOTES: see table 1

T A B L E 18

Kinetic determinations with propanol-2
using a constant salt concentration
of 6 M at 25.1°

Run #	A	B	C	D	E	F	G
IV-4	6 M	0	0.20	1.71	1.51	2.13	0.0709
IV-5	6 M	0	0.24	1.75	1.51	2.13	0.0709
IV-6	6 M	0	0.19	1.74	1.55	2.13	0.0728
IV-40	5 M	1 M	0.38	5.55	5.18	7.15	0.0724
IV-41	5 M	1 M	0.38	5.49	5.12	7.15	0.0716
IV-42	5 M	1 M	0.38	5.63	5.26	7.15	0.0736
IV-43	5 M	1 M	0.38	5.44	5.07	7.15	0.0710
IV-27	3 M	3 M	0.16	3.80	3.64	7.26	0.0501
IV-28	3 M	3 M	0.16	3.62	3.48	7.26	0.0479
IV-29	3 M	3 M	0.16	3.69	3.53	7.26	0.0486
IV-31	1 M	5 M	0.54	2.20	1.66	7.37	0.0225
IV-35	1 M	5 M	0.54	2.15	1.61	7.37	0.0219
IV-36	1 M	5 M	0.54	1.85	1.31	7.37	0.0178

A-----molarity of KOH

B-----molarity of KF

C-----rate of disappearance of ferrate in solution alone $\times 10^3$

D-----pseudo-first order rate constant for ferrate reaction
with propanol-2 $\times 10^3$

E-----the result of subtracting column C from column D. The
value shown in column E is multiplied by 10^3

F-----molar concentration of propanol-2 $\times 10^2$

G-----second order rate constant; values of column E divided
by the values of column F

Also see footnotes on table 1

FIGURE I

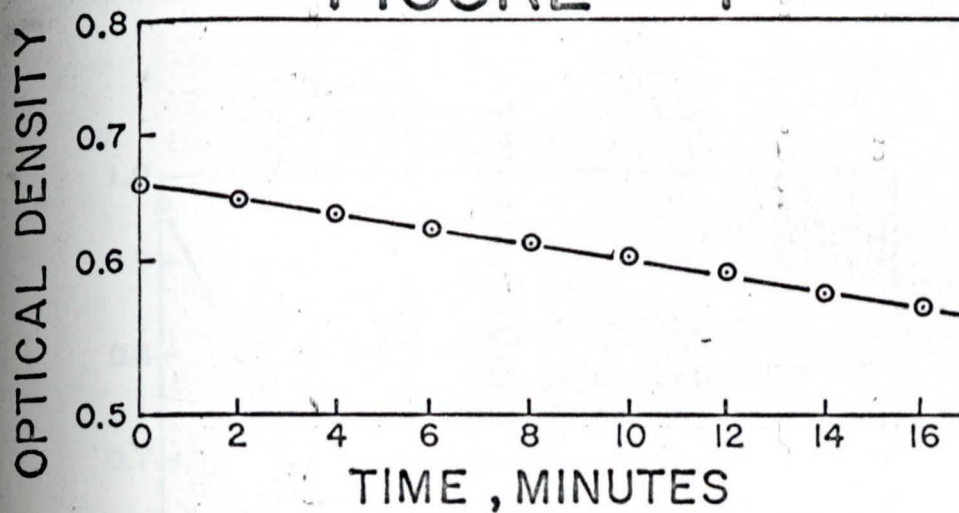


FIGURE Ia

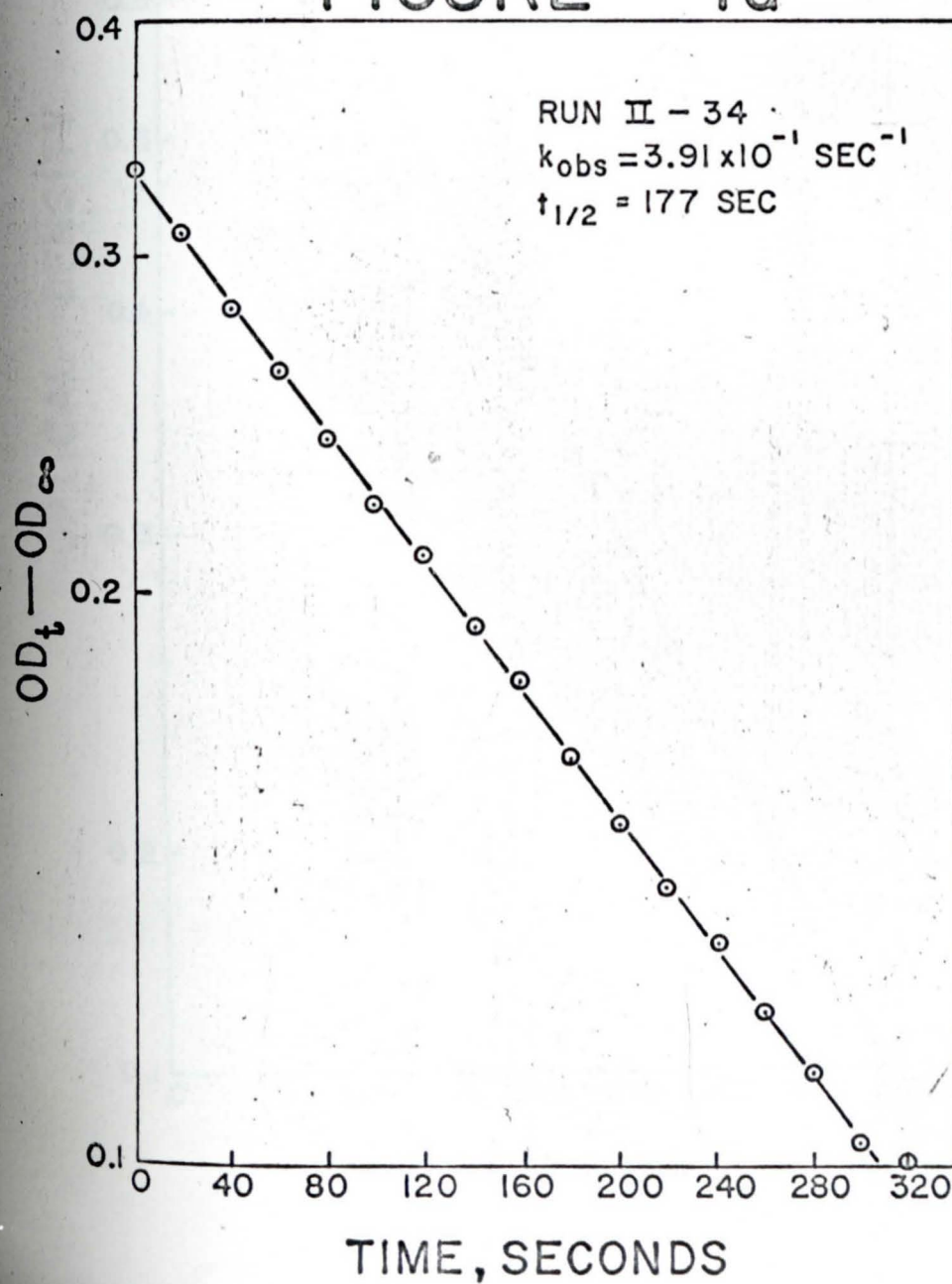


FIGURE 2

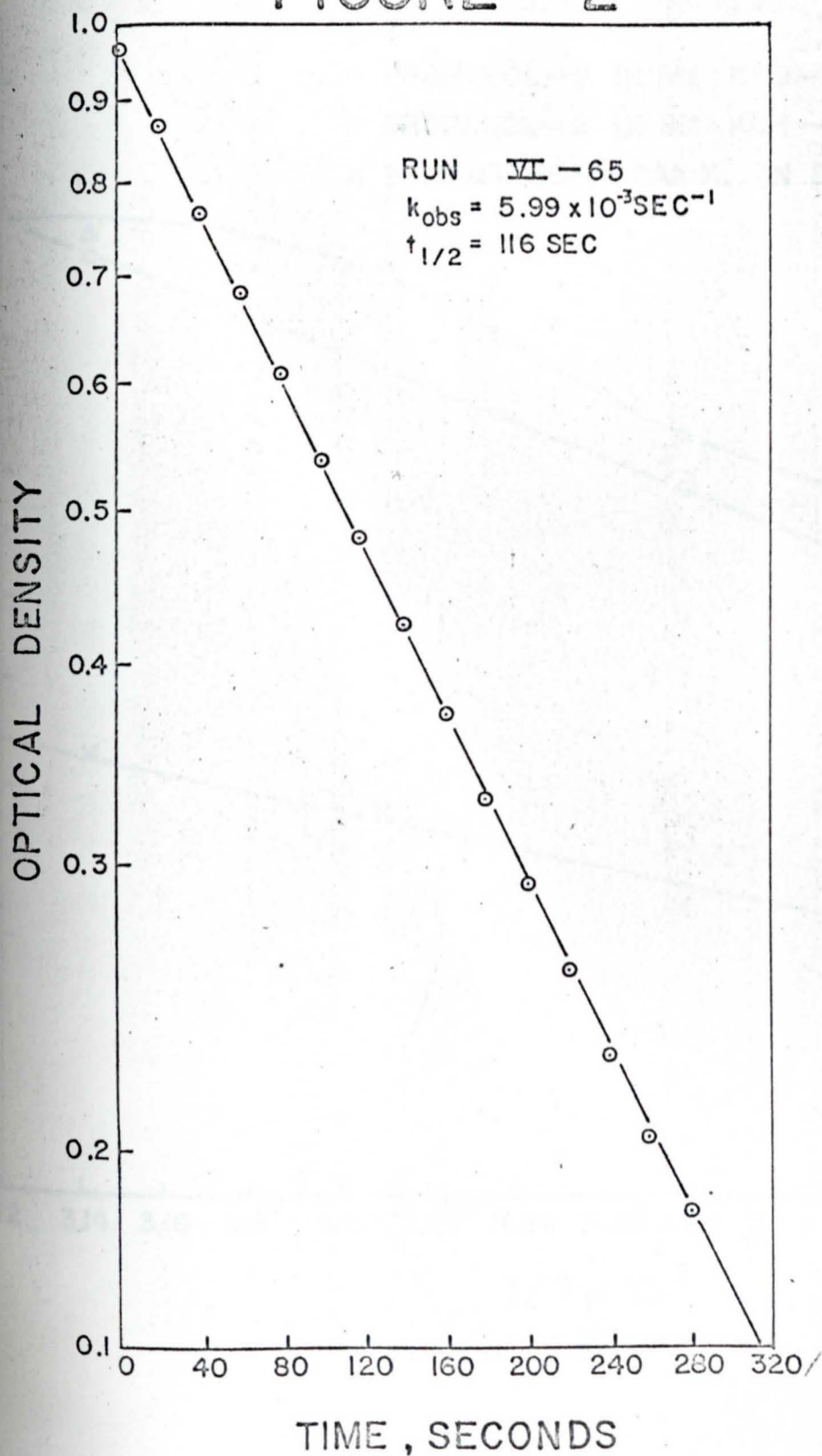


FIGURE 3

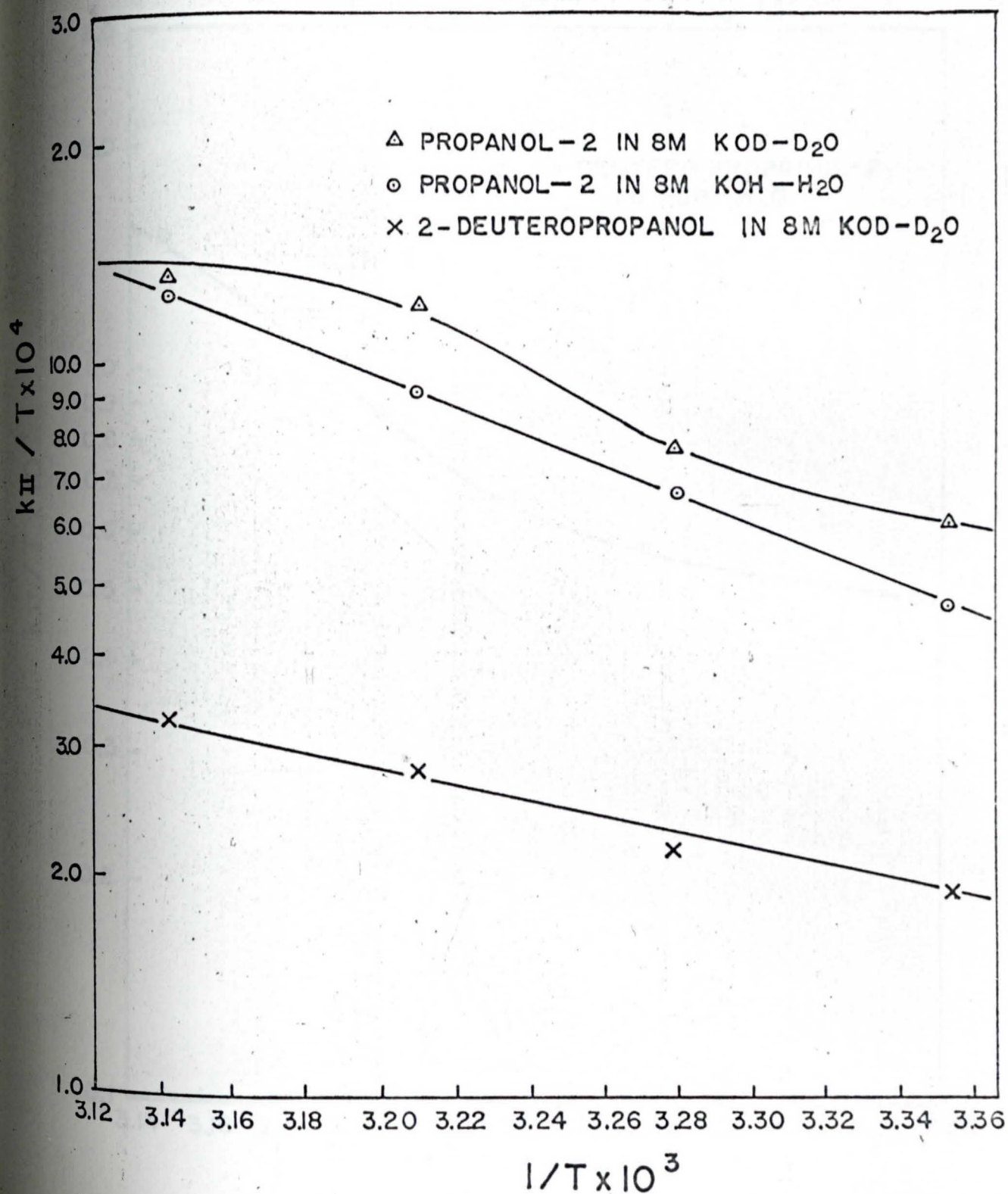


FIGURE 3a

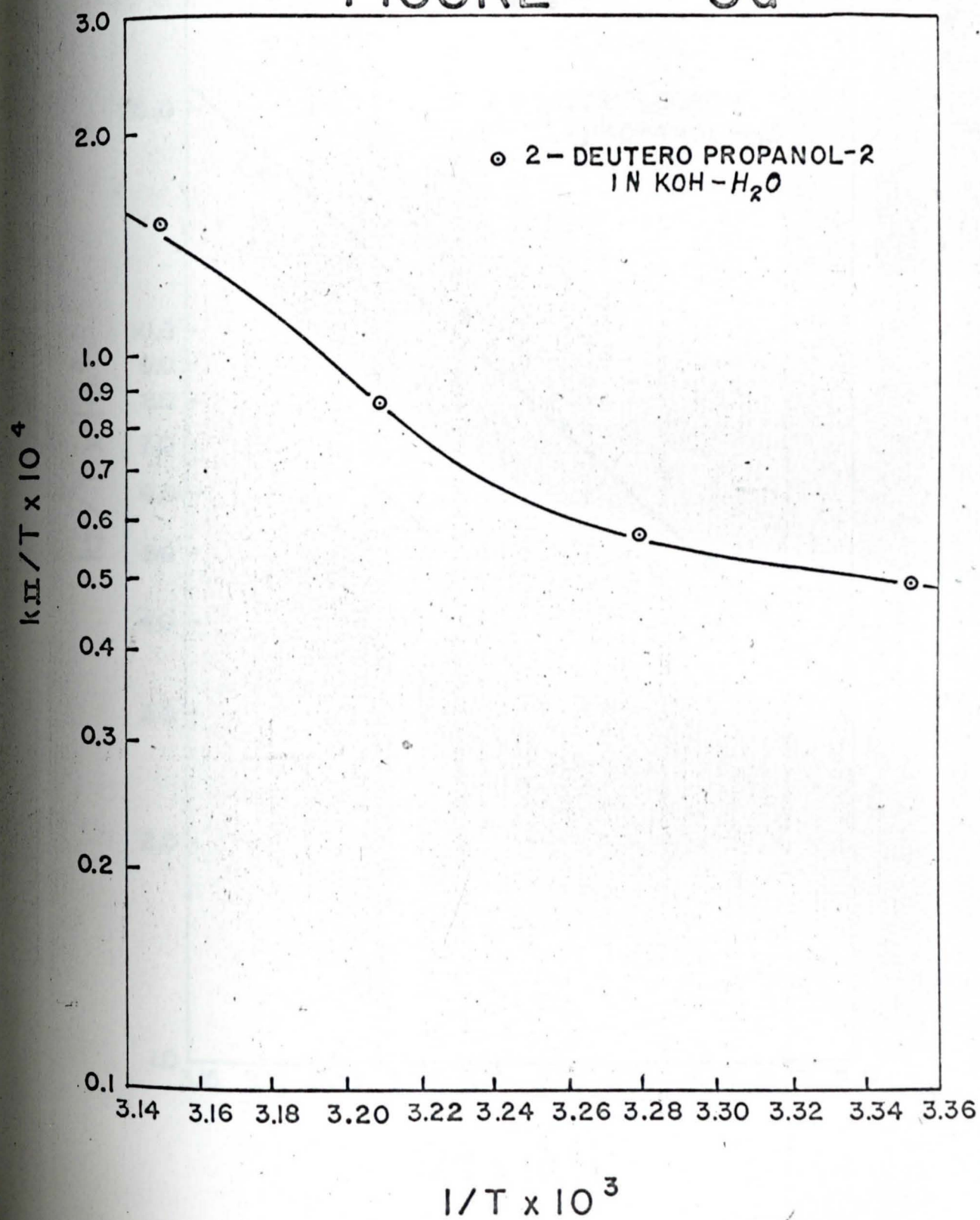


FIGURE 4

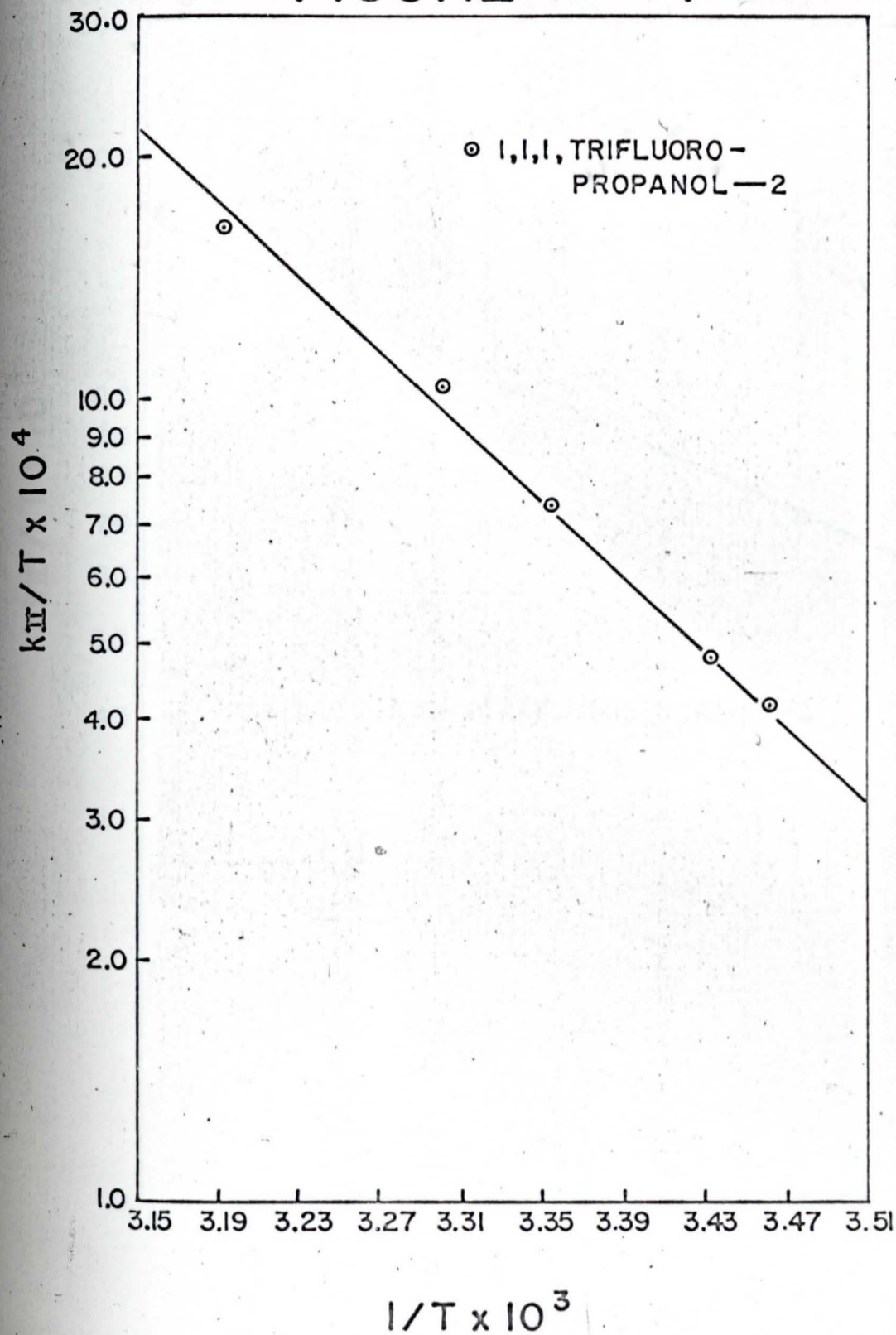
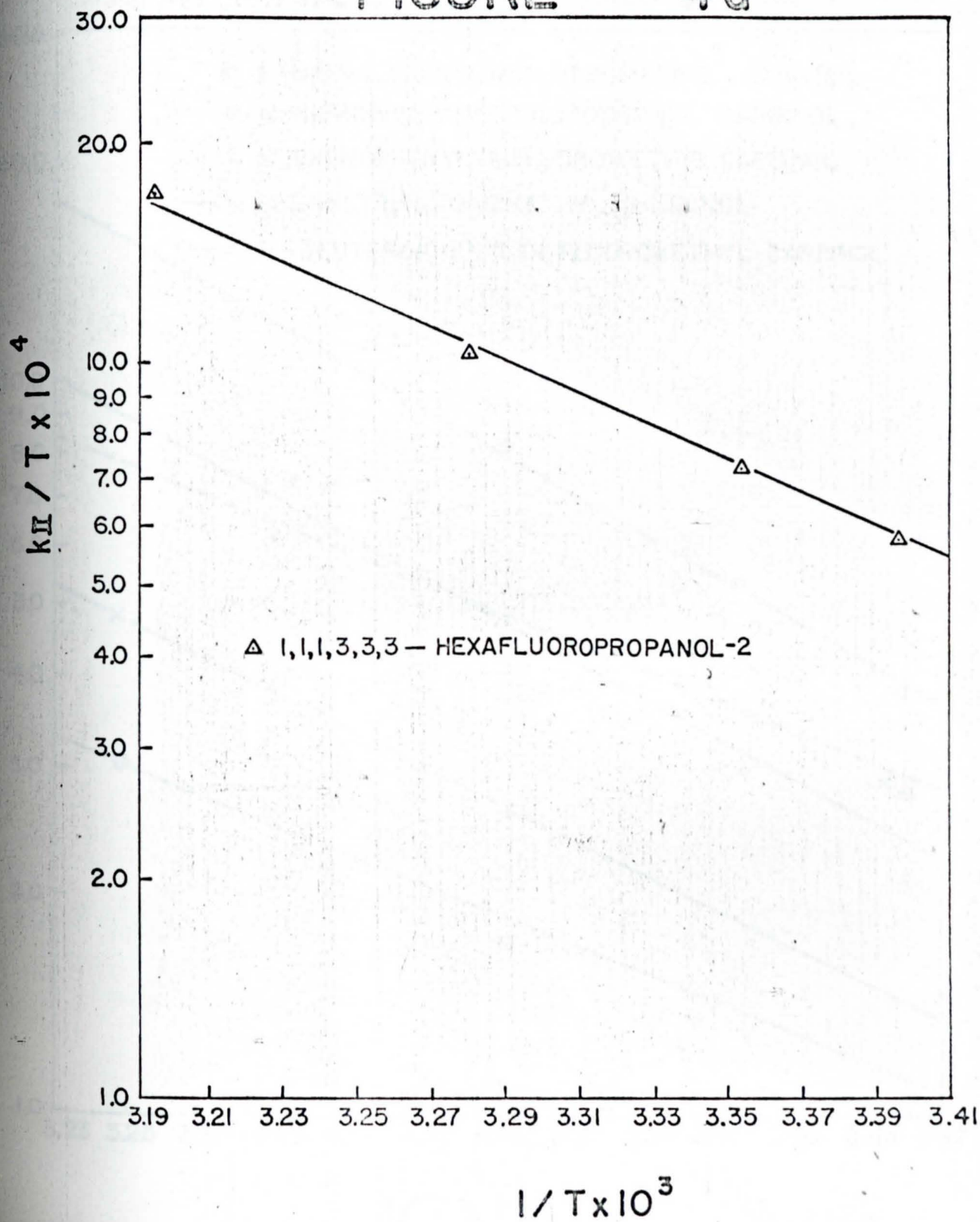
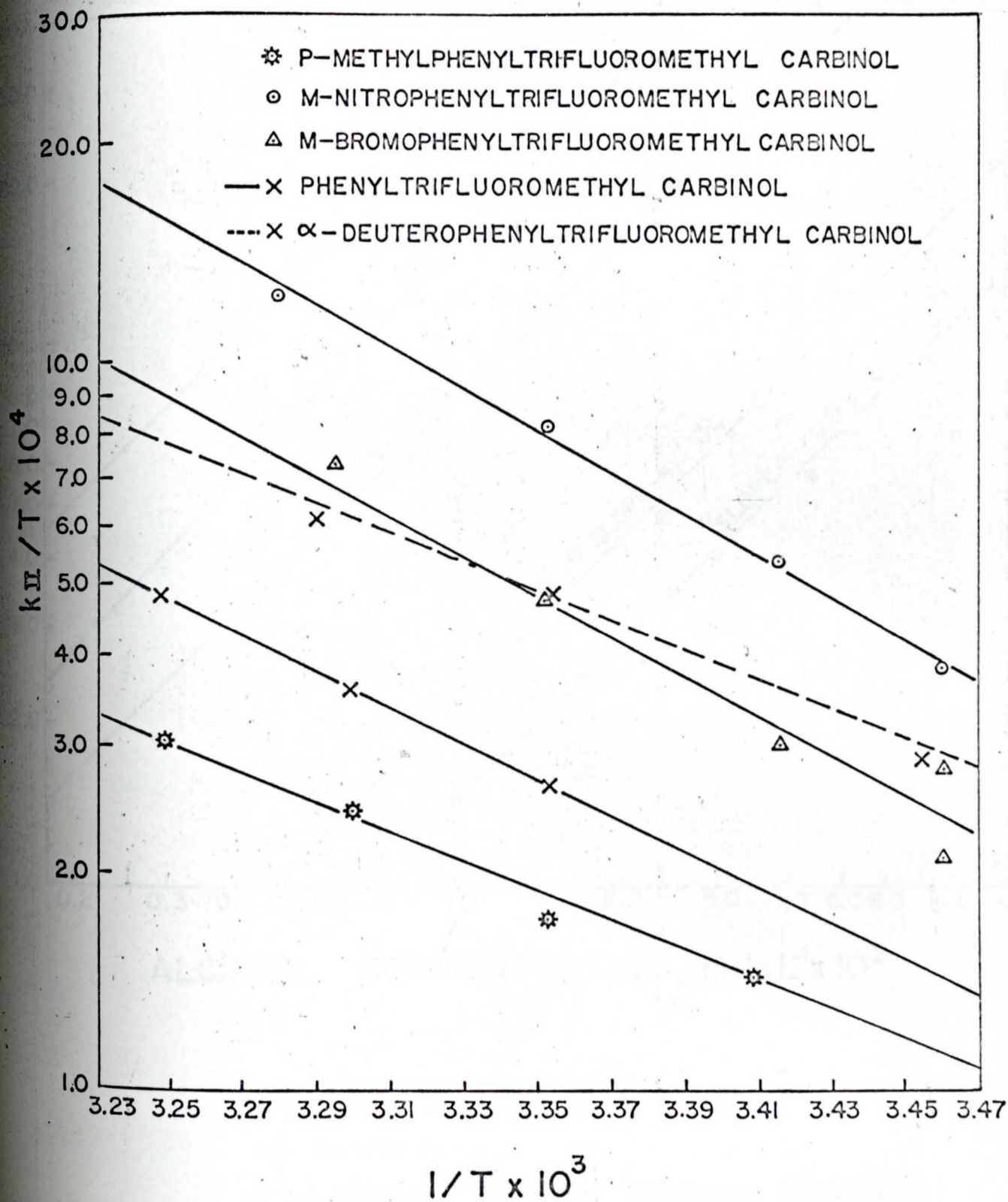


FIGURE 4a



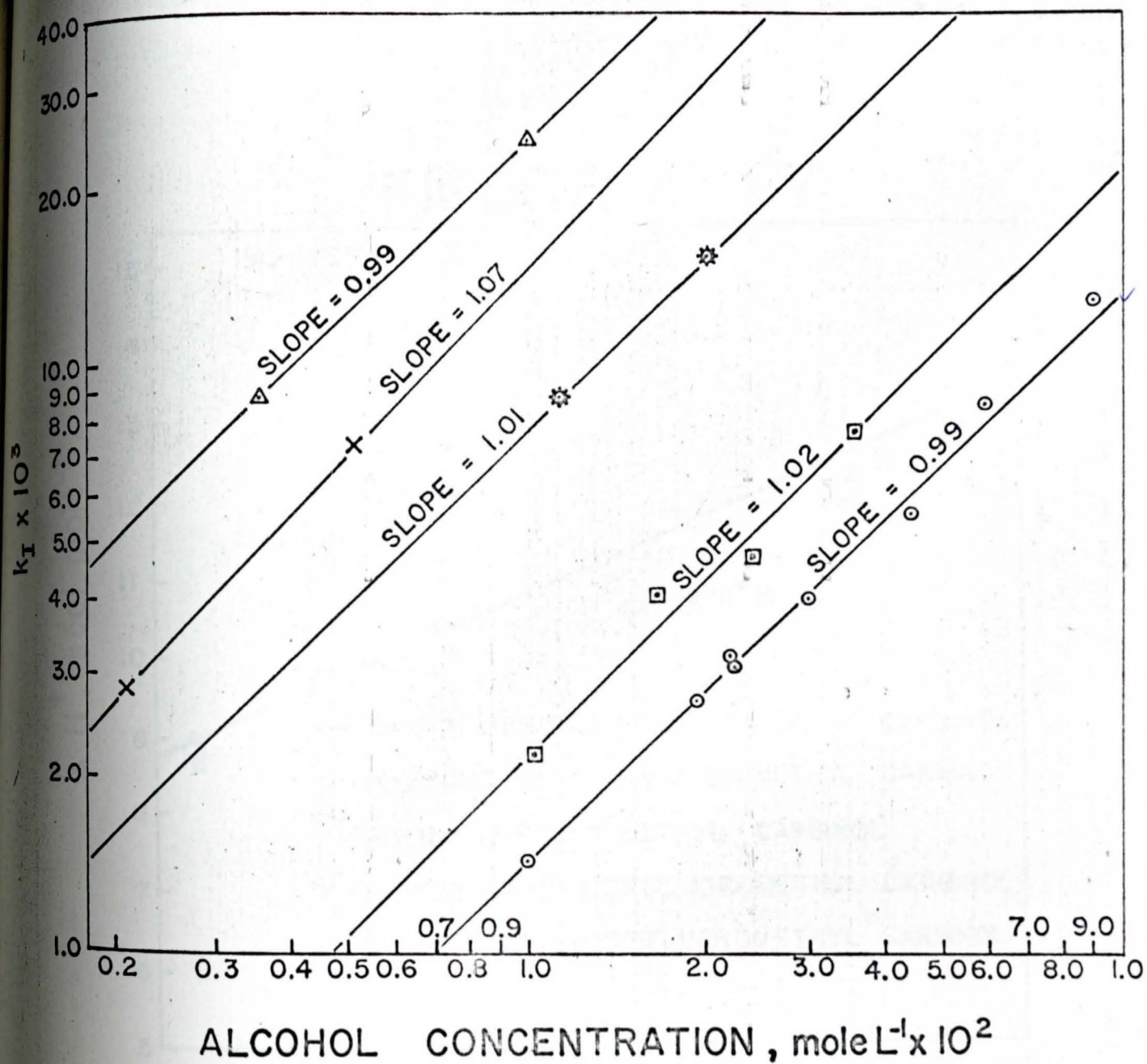
FIGURE

5



FIGURE

6



FIGURE

7

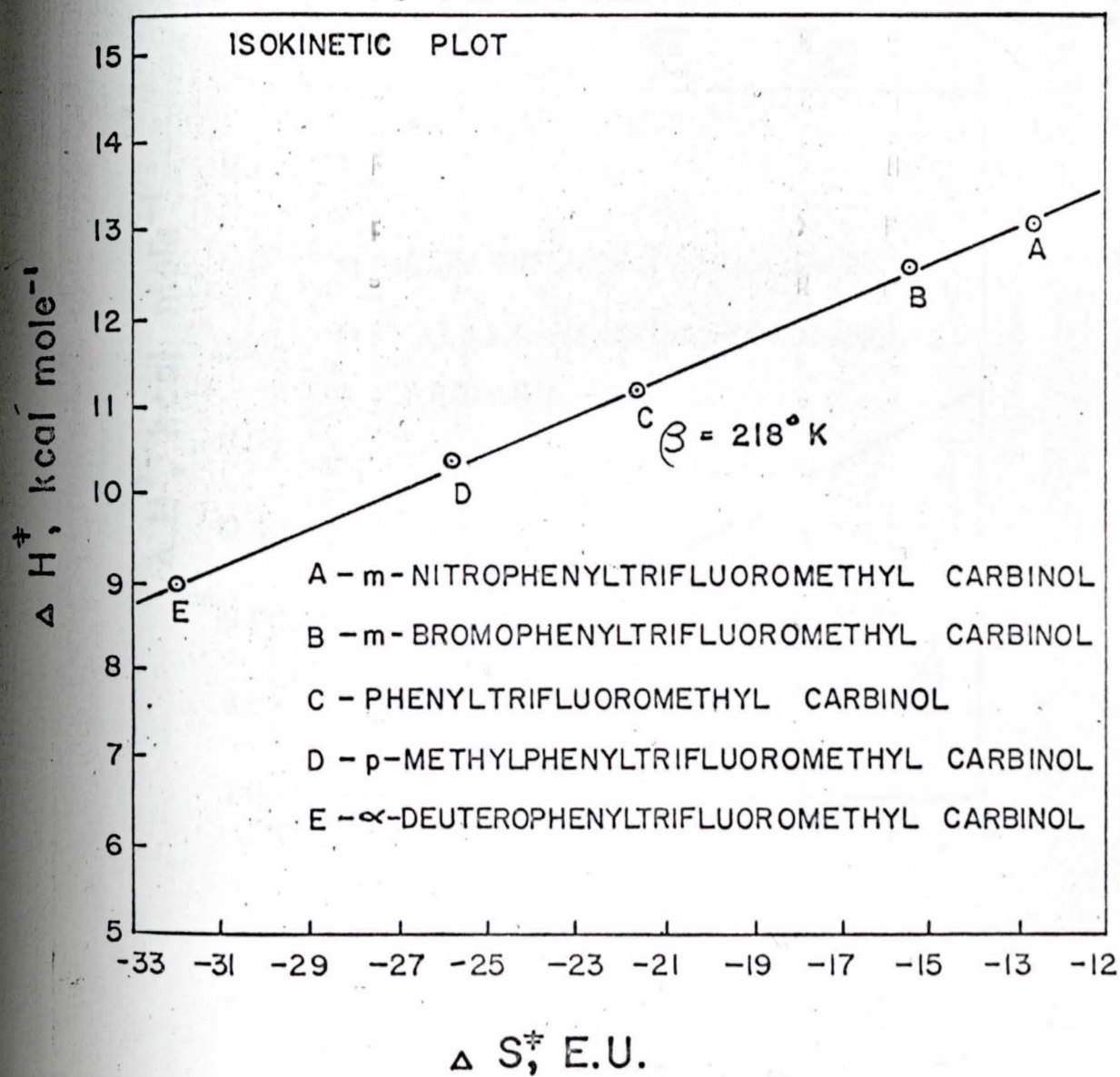
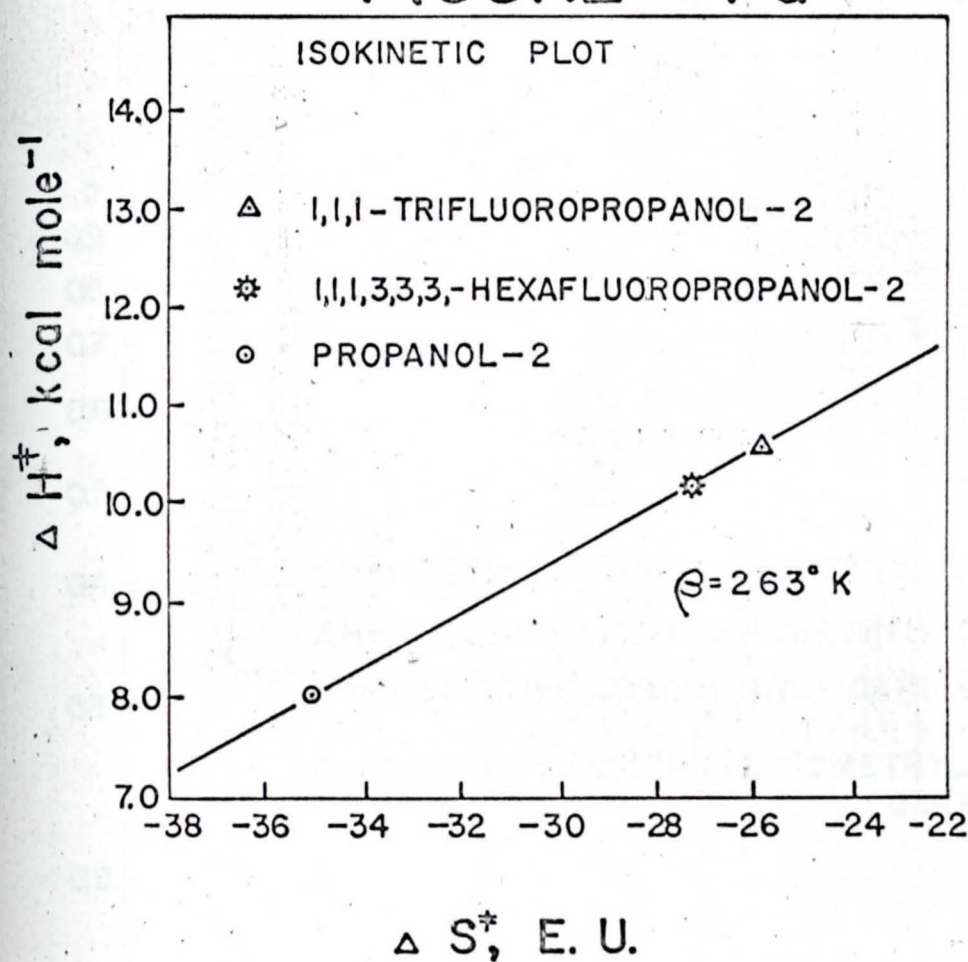
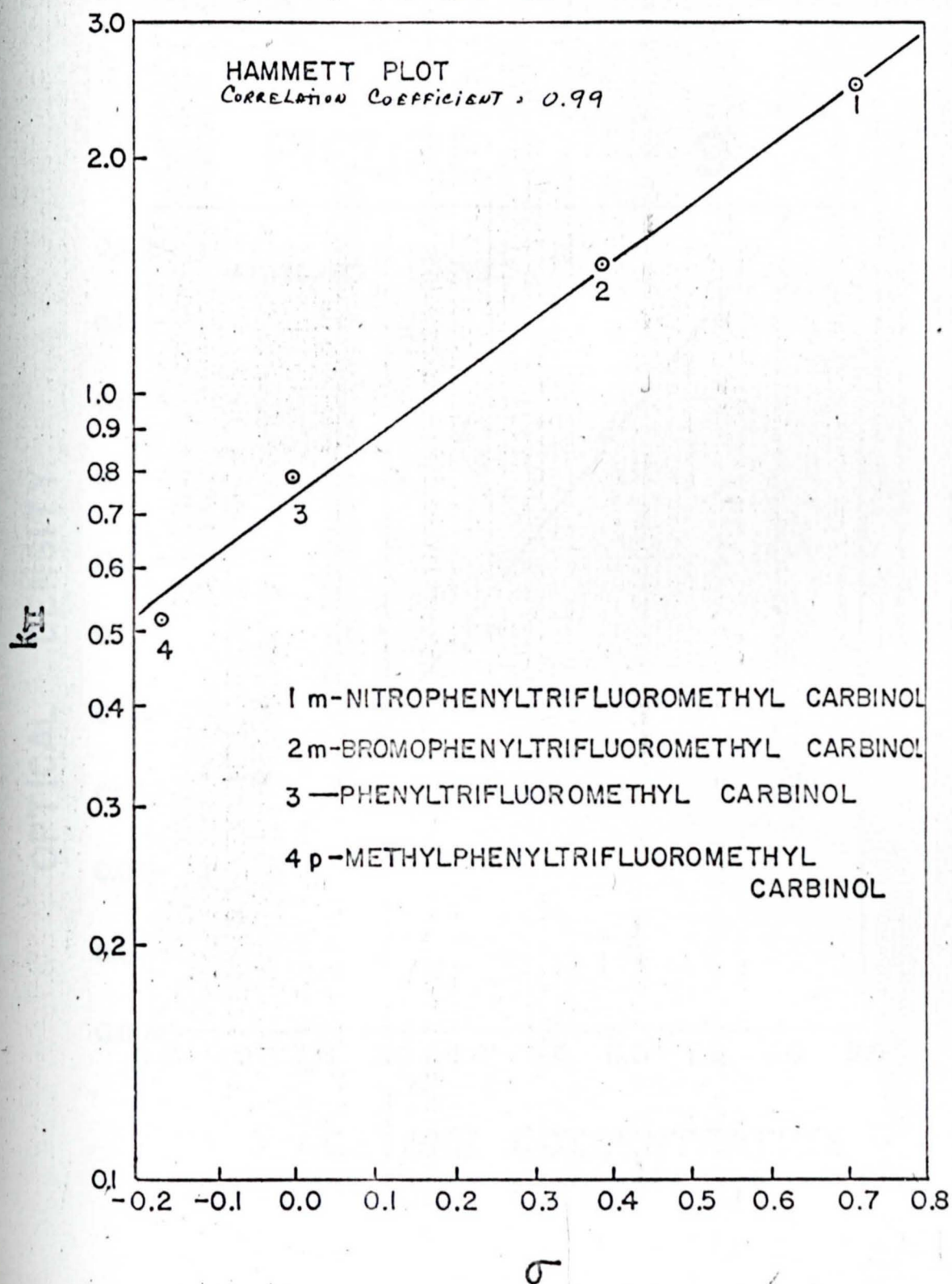


FIGURE 7a



FIGURE

8



FIGURE

9

