UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

A DONOR FUNCTION FOR METHANOLIC SODIUM METHOXIDE SOLUTIONS

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

by Edgar William Knaub, Jr. MS 1966

By Edgar W. Knaub

Approved by Kevork V. Nahabedian
Thesis advisor

Approved by
Committee on Graduate Studies

Date April 22, 1966

Q
402
K67d
1966
c.2

DEDICATION

This thesis is dedicated to my family and father.

To

ACKNOWLEDGMENTS

I am deeply indebted to Dr. K. V. Nahabedian of Union College and University for his interest and help. Also, I must thank people in the Silicone Products Department of the General Electric Company for their assistance in this work: Dr. R. N. Meals for permission to use company facilities; Mr. P. Launer for assistance with infrared measurements; Mr. J. Hatheway for use of the Beckman DK 2 Spectrophotometer; Mr. J. Magnuson for use of a potentiometric titration apparatus; and Mr. A. Sangil for making special ampoules. I am also indebted to my wife, Carol, for typing the finished thesis.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

A directly measured donor function was determined in .1 to 5 molar methanolic sodium methoxide solutions at 25°C using three of the substituted benzaldehyde indicators that were used by MacGregor to develop a donor function for aqueous alkali hydroxide solutions. The donor function, D_0, is based on the following reaction. A contrived H_- scale was also determined using the experimental D_0 scale and the activity of methanol.

$$C_6H_5CHO + CH_3O^- \rightleftharpoons C_6H_5\overset{O^-}{\overset{|}{C}}HOCH_3$$

The theories of Bascombe and Bell, and Perrin were used to explain hyperbasicity and deduce solvation numbers for the methoxide ion in methanol solution. These theories indicate that the methoxide ion may exist as a tri- or tetra-solvated species.

The dependence of reaction rate on basicity parameters in this medium was evaluated for the methanolyses of chloroform, 1-chloropropane, 1-chloro-3,3-dimethylbutane and phenylethyl chloride. A nearly ideal dependence of rate of methanolysis of chloroform on the contrived H_- function implies that this function is an accurate measure of basicity in the Bronsted

sense. The donor function, however, does not appear to be an accurate measure of basicity or nucleophilicity in E2 and S_N2 reactions, respectively, occuring in methanol.

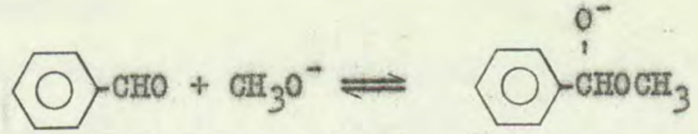
SECTION I

HISTORICAL INTRODUCTION

While for the past thirty years substantial work has been done in the development of acidity functions for acidic media, little attention has been paid to the development of indicator functions for basic media. The same general class of Hammett bases used to develop the H_0 function (1) for acidic media have also been used to develop the H_- function (1) for a variety of basic media. Some of the solvent-base systems that have been studied are water-sodium hydroxide (2,3), water-potassium hydroxide (2), water-hydrazine (4), tetramethylene sulfone-water-aryltrialkylammonium hydroxide (5), pyridine-water-tetraalkylammonium hydroxide (6), dimethylsulfoxide-water-tetraalkylammonium hydroxide (6), and dimethylsulfoxide-methanol-sodium methoxide (7). Studies of basicity in moderately concentrated methanolic sodium methoxide solution have only appeared during the last four years. In this medium, the H_- function scales for equation (I) were based on the ionization of nitrated anilines (8,9,10) and substituted phenols (11).

$$BH + CH_3O^- \rightleftharpoons B^- + CH_3OH \qquad (I)$$

Recently a directly measured donor function (12), D_0, for aqueous alkali hydroxide solutions has been developed using substituted benzaldehyde indicators. The purpose of this project was to determine a donor function scale at 25°C for .1 to 5 molar methanolic sodium methoxide solutions. In this medium, the donor function is described by equation (II).



(II)

The equilibrium on which the D_0 function is based (equation II) differs from that for the H_- function (equation I) by a molecule of solvent. Accordingly, a "contrived H_- function" can be determined using experimental D_0 values, solvent activity and the solvent dissociation constant. The contrived H_- function, in addition to being another fundamental basicity parameter, should allow a comparison with experimental H_- function scales obtained with nitrated anilines and phenols.

It is well known that H^+, OH^-, or CH_3O^- is strongly associated with solvent molecules. Values of the H_0 function for acidic media were accounted for by Bascombe and Bell (13) on the basis of a decrease in free water concentration due to strong hydration of the hydrogen ion. It was recently shown that the experimental H_- (14) and D_0 (12) function scales for aqueous alkali hydroxide solutions could also be explained using the Bascombe and Bell theory if the hydroxide ion is assumed to be associated with three molecules of water. Another purpose of this project was to develop a solvation model for the methoxide ion that would account for the experimental D_0 function using the Bascombe and Bell, and Perrin (15) theories. The Perrin treatment is an expansion of the Bascombe and Bell treatment that allows for variable solvation numbers.

Acidity function parameters have been used to determine the base strengths of weak bases (16), and in mechanistic studies of acid-catalyzed reactions (17,18). While hundreds of kinetic studies have been made with acid-catalyzed reactions, only a few have been reported in aqueous alkali hydroxide or methanolic sodium methoxide solutions over a reasonable range of base strength. Kinetic studies of reactions in sodium methoxide solution include methanolyses of the following substrates: chloroform (19) by an E1CB mechanism, phenylethyl chloride (19) by the E2 mechanism, 1-chloro-3,3-dimethylbutane (19) by mixed E2 and S_N2 mechanisms and 1-chloropropane (this study) by the S_N2 mechanism. A further purpose of this project was to interpret the rate data for the above reactions using the donor function, contrived H_- function, and methoxide ion concentration as parameters for base strength. Also, sufficient data is now available so that a comparison can be made of the nature of the rate dependence on basicity parameters for S_N2 reactions in aqueous (20) and methanolic solutions.

SECTION II

THEORY

Previous studies on the basicity of moderately concentrated methanolic sodium methoxide solutions (8,9,10,11) have employed the ionization of nitrated anilines (8,9,10) and substituted phenols (11) to develop H_- acidity function scales (1). In this medium, the H_- function is described by equation (III).

$$BH + CH_3O^- \rightleftharpoons B^- + CH_3OH \qquad \text{(III)}$$

$$K = \frac{a_{B^-} a_{CH_3OH}}{a_{BH} a_{CH_3O^-}} \qquad \text{(IV)}$$

By rearranging the equilibrium expression so that measurable properties of the indicator appear on the left, and taking logs, the following expression is obtained.

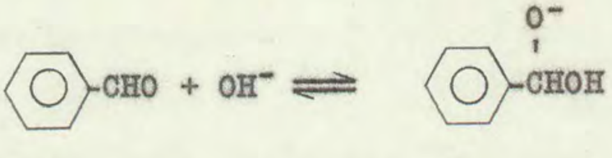
$$pK + \log \frac{C_{B^-}}{C_{BH}} = \log \frac{a_{CH_3O^-}\ f_{BH}}{a_{CH_3OH}\ f_{B^-}} \qquad \text{(V)}$$

The H_- acidity function is therefore defined by equation (VI),

$$H_- \equiv pK_{BH} + \log \frac{C_{B^-}}{C_{BH}} = \log \frac{a_{CH_3O^-}\ f_{BH}}{a_{CH_3OH}\ f_{B^-}} + pK_{CH_3OH} \qquad \text{(VI)}$$

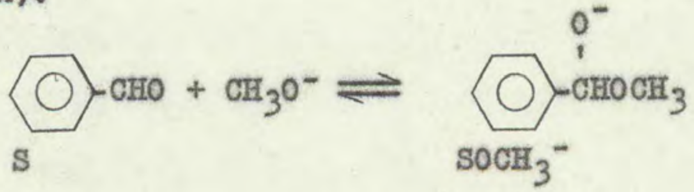
since the last term is equivalent to $\log f_{BH}/a_{H^+} f_{B^-}$. (Throughout this discussion, a = thermodynamic activity, f = activity coefficient, and c = concentration in moles per liter.)

The donor function, D_O, was initially developed for aqueous alkali hydroxide solutions (12) using substituted benzaldehyde indicators. In this medium the benzaldehyde indicators react as Lewis acids according to equation (VII).



(VII)

In methanolic sodium methoxide solution, the reaction is shown by equation (VIII), and the D_0 function is defined by equation (X).



(VIII)

$$K_{SOCH_3^-} = \frac{a_S \, a_{CH_3O^-}}{a_{SOCH_3^-}} \qquad (IX)$$

$$D_0 \equiv pK_{SOCH_3^-} + \log \frac{C_S}{C_{SOCH_3^-}} = -\log \frac{a_{CH_3O^-} \, f_S}{f_{SOCH_3^-}} \qquad (X)$$

If the ratio of the activity coefficients is constant for each indicator, the last term in equation (X) is dependent only on the medium. The quantity, $\log a_{CH_3O^-} f_S/f_{SOCH_3^-}$, becomes a property of the solution in the same sense as $\log a_{CH_3O^-}$, but D_0 is measurable while $\log a_{CH_3O^-}$ is not. In dilute solutions where the activity coefficient ratio approaches unity, D_0 becomes identical with $-\log C_{CH_3O^-}$ ($pOCH_3$).

In order to develop an experimental D_0 scale for methanolic sodium methoxide solutions using equation (X), it is necessary to measure the dissociation constant for the complex, $SOCH_3^-$, and the indicator ratio, $C_{SOCH_3^-}/C_S$. Both quantities can be determined by ultraviolet spectroscopy using methods described by Paul and Long (1).

The indicator ratio is determined using equation (XI),

$$R \equiv \frac{C_{SOCH_3^-}}{C_S} = \frac{\epsilon_S - \epsilon_t}{\epsilon_t - \epsilon_{SOCH_3^-}} \qquad (XI)$$

where ϵ_S is the molar absorptivity for the aldehyde in methanol, ϵ_t is the molar absorptivity for the basic solution containing both forms of the indicator, and $\epsilon_{SOCH_3^-}$ is the molar absorptivity for the methoxylated form of the indicator. All measurements are made at the wavelength of maximum absorption ($\lambda_{max.}$) for each indicator.

The definition of $pK_{SOCH_3^-}$ is given by equation (XII).

$$pK_{SOCH_3^-} = \log \frac{C_{SOCH_3^-}}{C_S C_{CH_3O^-}} + \log \frac{f_{SOCH_3^-}}{f_S f_{CH_3O^-}} \qquad (XII)$$

Since the ratio of the activity coefficients approaches unity in dilute solutions, $pK_{SOCH_3^-}$ may be evaluated using equation (XIII). By plotting $C_{CH_3O^-}$ against the right hand side of equation (XIII) and extrapolating to zero concentration, $pK_{SOCH_3^-}$ is obtained. If the above plot is curved or the

$$pK_{SOCH_3^-} = \lim_{C_{CH_3O^-} \rightarrow 0} \left(\log \frac{C_{SOCH_3^-}}{C_S} - \log C_{CH_3O^-}\right) \qquad (XIII)$$

indicator is not converted to the $SOCH_3^-$ form in dilute methoxide solution, the pK values can be evaluated by the method of direct comparison (1) as shown by equation (XIV).

$$pK_1 - pK_2 = \log R_1 - \log R_2 \qquad \text{(XIV)}$$

Use of the latter method requires a series of indicators whose plots of log R against $C_{CH_3O^-}$ are parallel and overlapping.

Once the D_0 function is measured, it should be possible to develop a "contrived H_- function" based on the difference between the equilibrium expressions for D_0 and H_-. Equation (XV) defines the contrived H_- function which is obtained by solving equation (X) for $a_{CH_3O^-}$, and substituting into equation (VI). By assuming a ratio of unity for the

$$-(D_0 + \log a_{CH_3OH} - pK_{CH_3OH}) = H_- + \log \frac{f_{B^-}\ f_S}{f_{BH}\ f_{SOCH_3^-}} \qquad \text{(XV)}$$

activity coefficient term, the left hand side of the equation becomes a measure of the H_- function.

Bascombe and Bell (13) have shown that the rapid increase in acidity ($H^+ > 1$ molar) can be accounted for if the equilibrium expression (XVI) resulted in the release of four water

$$B + H^+(H_2O)_n \rightleftharpoons BH^+ + nH_2O \qquad \text{(XVI)}$$

molecules for each act of protonation. Water on the right side of the equilibrium represents free water (not bound to protons) and affects the equilibrium to the fourth power. The concentration of free water diminishes rapidly with increasing acid concentration and consequently there is a large increase in the BH^+/B ratio, which determines the H_0 function. By using acid and free water concentrations corresponding to $H^+(H_2O)_4$, Bascombe and Bell calculated H_0 values which agreed up to about 8 molar with experimental H_0 values.

The Bascombe and Bell theory has been applied to aqueous alkali hydroxide solutions and a model of $OH^-(H_2O)_3$ for hydroxide ion was found to correlate with the experimental H_- function (14). It was recently reported that values of the D_0 function (12) are almost exactly accounted for by the $OH^-(H_2O)_3$ model in 1-10 molar aqueous sodium and potassium hydroxide solutions.

The Bascombe and Bell theory can also be applied to methanolic sodium methoxide solutions if the equilibrium expression for the D_0 function is defined by equation (XVII).

$$S + CH_3O^-(CH_3OH)_n \rightleftharpoons SOCH_3^- + nCH_3OH \qquad \text{(XVII)}$$

The equilibrium expression is written on the assumption that S is no more solvated than $SOCH_3^-$.

$$K_{SOCH_3^-} = \frac{a_S \, a_{CH_3O^-}}{a_{SOCH_3^-} \, a^n_{CH_3OH}} \qquad \text{(XVIII)}$$

Since the D_0 function is defined by equation (XIX),

$$D_0 = -\log \frac{a_{CH_3O^-} \, f_S}{a^n_{CH_3OH} \, f_{SOCH_3^-}} \qquad \text{(XIX)}$$

the relationship between D_0 and the concentration of methoxide ion and free methanol is given by equation (XX). By assuming various values for n and calculating the

$$D_0 = n \log C_{CH_3OH} - \log C_{CH_3O^-} - \log \frac{f_{CH_3O^-} f_S}{f^n_{CH_3OH} f_{SOCH_3^-}} \qquad (XX)$$

concentration of free methanol, D_0 values can be calculated for representative methoxide ion concentrations and compared with the experimental D_0 scale.

Objections (18) to the simple treatment of Bascombe and Bell for acidic media has resulted in a modified theory by Perrin (15). The modified theory allowed for variable hydration and stressed the use of solvent activity rather than concentration. In using the Perrin theory, equation (XX) is redefined as equation (XXI).

$$D_0 = n \log a_{CH_3OH} - \log C_{CH_3O^-} - \log \frac{f_{CH_3O^-} f_S}{f_{SOCH_3^-}} \qquad (XXI)$$

By plotting the quantity ($D_0 + \log C_{CH_3O^-}$) against $\log a_{CH_3OH}$ (21), the average solvation number, $\bar{n}$, is obtained.

Examples of kinetic investigations in moderately concentrated methanolic sodium methoxide solution are limited to the work of Ridd et al. (19,22,23) and the methanolysis of 1-chloropropane (this study). Ridd et al. studied the methanolyses of chloroform, phenylethyl chloride and 1-chloro-3,3-dimethylbutane and attempted to correlate the kinetic results with the H_- function based on nitrated aniline indicators. Since the kinetic data (19) for the same reactions was correlated with the donor function or contrived H_- function in this study, the reaction mechanisms will be discussed.

The methanolysis of chloroform proceeds by the E1CB mechanism (24) via a rapid equilibration of chloroform with its conjugate base followed by rate-determining elimination of chloride ion from the trichloromethyl anion. This mechanism

$$CHCl_3 + CH_3O^- \rightleftharpoons CCl_3^- + CH_3OH \qquad (XXII)$$

$$CCl_3^- \rightarrow CCl_2 + Cl^- \qquad (XXIII)$$

$$CCl_2 + CH_3OH \rightarrow \text{products} \qquad (XXIV)$$

is further supported by the observation that deuterium in deuterochloroform is equilibrated with hydrogen in methanolic sodium methoxide solution. The CCl_3^- anion is therefore formed by an equilibrium process, not a concerted process. A correlation of reaction rate with an H_- function is expected since the formation of CCl_3^- is dependent on the medium in the same manner as the formation of B^- (equation I). The expected correlation of H_- with reaction rate (22) can be shown (17) by applying the Bronsted equation to the rate-determining step.

$$\text{rate} = \frac{-dC_{CHCl_3}}{dt} = \frac{k^1 \, a_{CH_3O^-} \, C_{CHCl_3} \, f_{CHCl_3}}{f^{\ddagger} \, K_{CCl_3^-} \, a_{CH_3OH}} \qquad (XXV)$$

In equation (XXV), k^1 is the rate constant for reaction (XXIII) and $f^{\ddagger}$ is the activity coefficient for the transition state. Since $CHCl_3$ exists almost entirely as the uncharged form, the first-order rate constant is defined by equation (XXVI).

$$k_1 \equiv -\frac{1}{C_{CHCl_3}}\frac{dC_{CHCl_3}}{dt} = \frac{k^1\, a_{CH_3O^-}\, f_{CHCl_3}}{K_{CCl_3^-}\, a_{CH_3OH}\, f^{\ddagger}} \qquad \text{(XXVI)}$$

If H_- is defined as $-\log h_-$, H_- becomes equal to $pOCH_3$ and h_- becomes equal to $C_{CH_3O^-}$ in dilute solution. By substitution

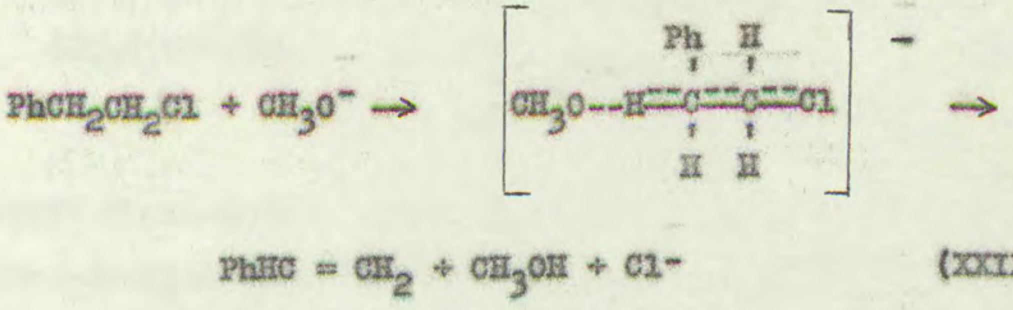
$$h_- = -\frac{a_{CH_3O^-}\, f_{BH}}{a_{CH_3OH}\, f_{B^-}\, K_{CH_3OH}} \qquad \text{(XXVII)}$$

of equation (XXVII) into equation (XXVI) and taking logs, the following equation is obtained.

$$\log k_1 = H_- - \log \frac{f_{B^-}\, f_{CHCl_3}}{f_{BH}\, f^{\ddagger}} + \text{constant} \qquad \text{(XXVIII)}$$

Assuming that the activity coefficient term remains constant, a plot of log k_1 vs. the H_- function should give a straight line having a slope of unity.

The methanolysis reaction of phenylethyl chloride in sodium methoxide solution proceeds by the E2 mechanism (19).

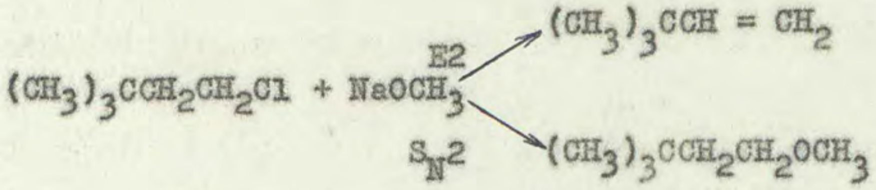


$$PhCH_2CH_2Cl + CH_3O^- \rightarrow \left[CH_3O{-}{-}H{=}{=}\overset{\overset{Ph}{|}}{\underset{\underset{H}{|}}{C}}{=}{=}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{=}{=}Cl \right]^- \rightarrow$$

$$PhHC = CH_2 + CH_3OH + Cl^- \qquad \text{(XXIX)}$$

Methoxide ion is neutralized by hydrogen and chloride is eliminated in a concerted manner. In dilute sodium methoxide solution ($<$ .2 molar), the second-order rate constants are reported (19) to be fairly constant; for methoxide ion concentrations up to 4 molar however, the calculated second-order rate constants increase constantly. The reaction rate is therefore necessarily dependent on a basicity function. The rate should not be proportional to an H_- function, as is the methanolysis of chloroform, since in the latter methoxide ion is completely neutralized before CCl_3^- undergoes the rate-determining elimination reaction. The reaction rate should to a first approximation be proportional to the D_0 function since inclusion of methoxide ion must occur in the activited complex in somewhat the same manner as in the formation of $SOCH_3^-$.

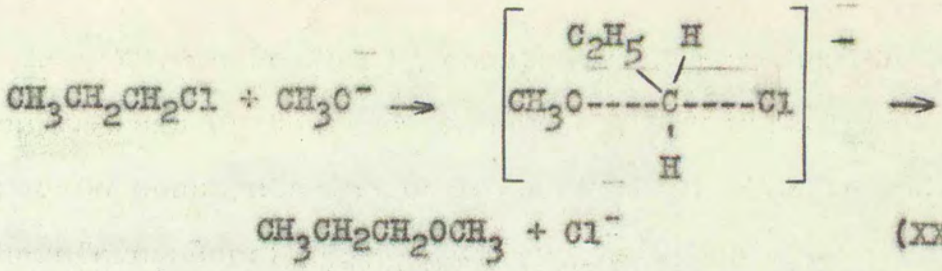
The methanolysis of 1-chloro-3,3dimethylbutane (19) proceeds by a combination of the E2 and S_N2 mechanisms. At 84.9 C the percentage of elimination was 68% in 0.6-4 molar sodium methoxide solutions. For this reaction, the



$$(CH_3)_3CCH_2CH_2Cl + NaOCH_3 \begin{cases} \xrightarrow{E2} (CH_3)_3CCH = CH_2 \\ \xrightarrow{S_N2} (CH_3)_3CCH_2CH_2OCH_3 \end{cases} \qquad (XXX)$$

pseudo first-order rate constants were proportional to the concentration of methoxide ion (k_2 for 5 runs = a constant).

The methanolysis of 1-chloropropane, by analogy with ethanolysis (25), proceeds by the S_N2 mechanism with about 5% elimination. This is the first S_N2 reaction to be studied



$$CH_3CH_2CH_2Cl + CH_3O^- \longrightarrow \left[CH_3O{-}{-}{-}{-}\overset{C_2H_5\quad H}{\underset{H}{C}}{-}{-}{-}{-}Cl \right]^- \longrightarrow CH_3CH_2CH_2OCH_3 + Cl^- \qquad (XXXI)$$

in moderately concentrated sodium methoxide media (.1-4.6 molar). The correlation of the pseudo first-order rate constants with basicity parameters should prove interesting since methoxide ion is included into the 1-chloropropane molecule in the activated complex in much the same manner as in the formation of $SOCH_3^-$.

SECTION III

EXPERIMENTAL PROCEDURE

A. Chemicals and Solutions

Benzaldehyde (Matheson, Coleman and Bell commercial grade) was purified by fractional distillation at reduced pressure. A gas-liquid chromatogram of the clear distillate (b. p., 80° C/29 mm. Hg) showed the benzaldehyde to be at least 99.9% pure. The gas-liquid chromatograph used for this and subsequent analyses was a commercial programmed temperature instrument manufactured by F. and M. Corporation. This instrument utilized helium carrier gas, thermal conductivity detectors and a four-foot column containing General Electric SE-30 silicone on Chromsorb P. The purified benzaldehyde was stored in an airtight bottle.

Practical 2,4 dichlorobenzaldehyde (Eastman Kodak) was purified by recrystallization from an ethanol-water mixture (80:20). After drying in a vacuum desiccator overnight, the needles melted sharply at 71-72° C (lit.(26) m.p., 70-71° C).

Practical p-chlorobenzaldehyde (Eastman Kodak) was purified by two recrystallizations from an ethanol-water mixture (80:20) to give needle shaped crystals that melted sharply at 46.0-46.7°C (lit. m.p.: 48°C(27), 47°C(28)). After questionable measurements were made with this sample, reexamination of the sealed sample bottle showed traces of moisture or solvent on the glass wall. A gas-liquid chromatogram of several crystals dissolved in anhydrous methanol further showed 5.7% of an unidentified impurity having a slightly higher retention time than p-chlorobenzaldehyde. The symetrical shape of the peak implies that the impurity is not p-chlorobenzoic acid.

Concentrated stock solutions of sodium methoxide (5.5-5.8 M) were prepared by reacting an excess of freshly cut sodium metal (Mallinckrodt or Fisher analytical reagent grade) with anhydrous methanol (Matheson, Coleman and Bell, A.C.S. analyzed reagent grade, 0.02-0.07% H_2O) under a nitrogen atmosphere. After stirring overnight, excess sodium was removed from the viscous, cloudy solution by a quick filtration through a coarse wire screen into a one quart polyethylene bottle. The polyethylene bottle was previously extracted with dilute sodium methoxide in order to remove all low molecular weight impurities. After the concentrated sodium methoxide solution was allowed to sit at room temperature for 10 to 14 days, the haze settled from solution to give perfectly clear and colorless sodium methoxide. The clear, concentrated sodium methoxide solutions absorb ultraviolet radiation strongly below 235 mμ and weakly (absorbance, .1-.2) from 245 to 300 mμ. Particular care must be taken to completely remove all toluene or aromatic solvents from the sodium metal since these impurities also absorb ultraviolet radiation in the range of 245 to 300 mμ.

Commercial 1-chloropropane (Eastman Kodak, 95-96%) was purified by fractional distillation. The gas-liquid chromatogram of the center cut (b.p., 46-46.5°C) showed no measurable impurities.

A stock solution of 0.100 M silver nitrate was prepared by dissolving 4.2495 g of silver nitrate (Baker analyzed reagent, 99.7% assay) in 250 cc of halide free distilled water.

Other standard solutions were prepared using conventional procedures.

B. Ultraviolet Spectra of Indicators

The U.V. Spectra of 2,4 dichlorobenzaldehyde, p-chlorobenzaldehyde, benzaldehyde and o-anisaldehyde in methanol were obtained using a recording Beckman DK-2 spectrophotometer before attempting to make accurate indicator measurements with the Beckman DU at 25°C. The molar absorptivities and the wavelength of maximum absorption for the indicators (10^{-4} M) in methanol and water are given in Table I.

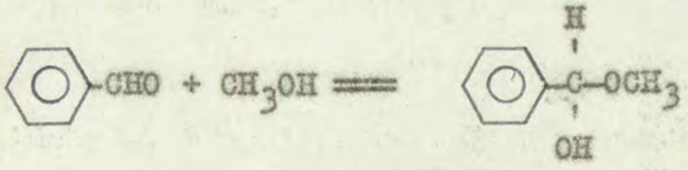
TABLE I

A Comparison of Indicator Spectroscopic Data in Methanol and Water (12)

	Water		Methanol	
Indicator	λmax. (mμ)	ϵ_S	λmax.	ϵ_S
2,4 dichlorobenzaldehyde	264	12,980	258	4,560
p-chlorobenzaldehyde	261	16,190	255	14,150
benzaldehyde	251	12,830	245	12,200
o-anisaldehyde	256.5	10,450	254	9,360

In general it was observed that the wavelength of maximum absorption (λmax.) was smaller in methanol than water by 3.5 to 8 mμ. The molar absorptivities were affected even more by the solvent change, the ϵ values being lower in methanol by 530 to 8,420. These differences can be attributed to a solvent effect (29), the nature of the substituent and degree of substitution apparently having a large effect.

The possibility that hemiacetal formation, illustrated by reaction (XXXII) for benzaldehyde, was responsible for



(XXXII)

the large differences in the ϵ values, on changing from water to methanol solvent, was discounted by noting the dependence of the ϵ values for 2,4 dichlorobenzaldehyde in methanol on the amount of water present. The measured ϵ values for methanol-water mixtures at the $\lambda_{max.}$ for the particular solution were as follows: 100% CH_3OH, 4,560; 96% CH_3OH 4,770; 50% CH_3OH, 7,710; 10% CH_3OH, 12,000 and 0.5% CH_3OH, 13,000. The ϵ value for 0.5% CH_3OH is in excellent agreement with MacGregor's value (12) in 1% CH_3OH (12,980). This variation can be accounted for by a solvent effect without the complication of hemiacetal formation.

Another unusual observation relates to the spectrum of o-anisaldehyde (Figure I) in concentrated methanolic sodium methoxide solution where a considerable portion of the indicator exists as $SOCH_3^-$. The other indicators gave spectra like that shown for benzaldehyde (Figure II), where the only observed effect of the sodium methoxide medium is a decrease in benzaldehyde (S) absorbance. The peak at 270 mμ (shoulder

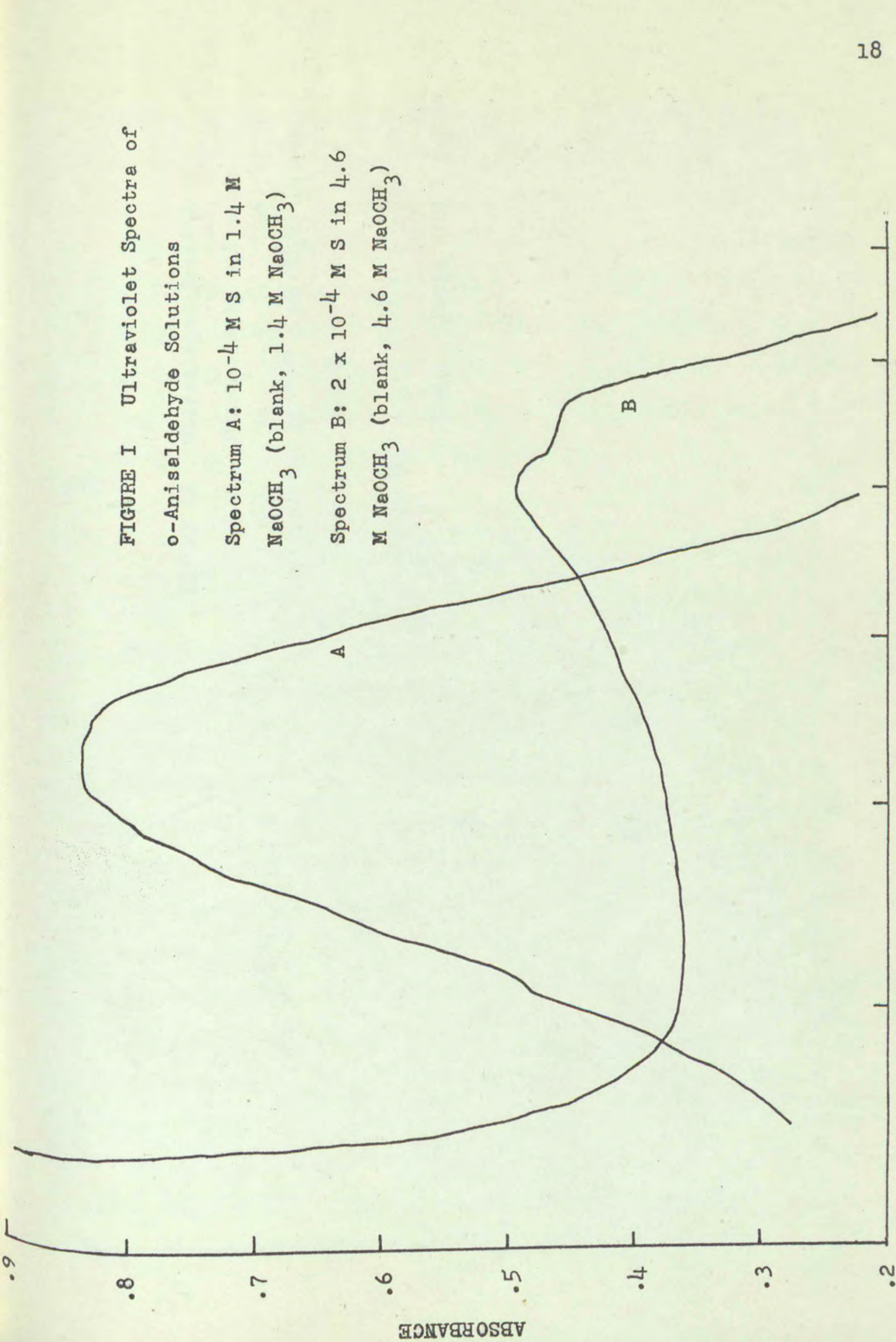


FIGURE I Ultraviolet Spectra of o-Aniseldehyde Solutions

Spectrum A: 10^{-4} M S in 1.4 M $NaOCH_3$ (blank, 1.4 M $NaOCH_3$)

Spectrum B: 2 x 10^{-4} M S in 4.6 M $NaOCH_3$ (blank, 4.6 M $NaOCH_3$)

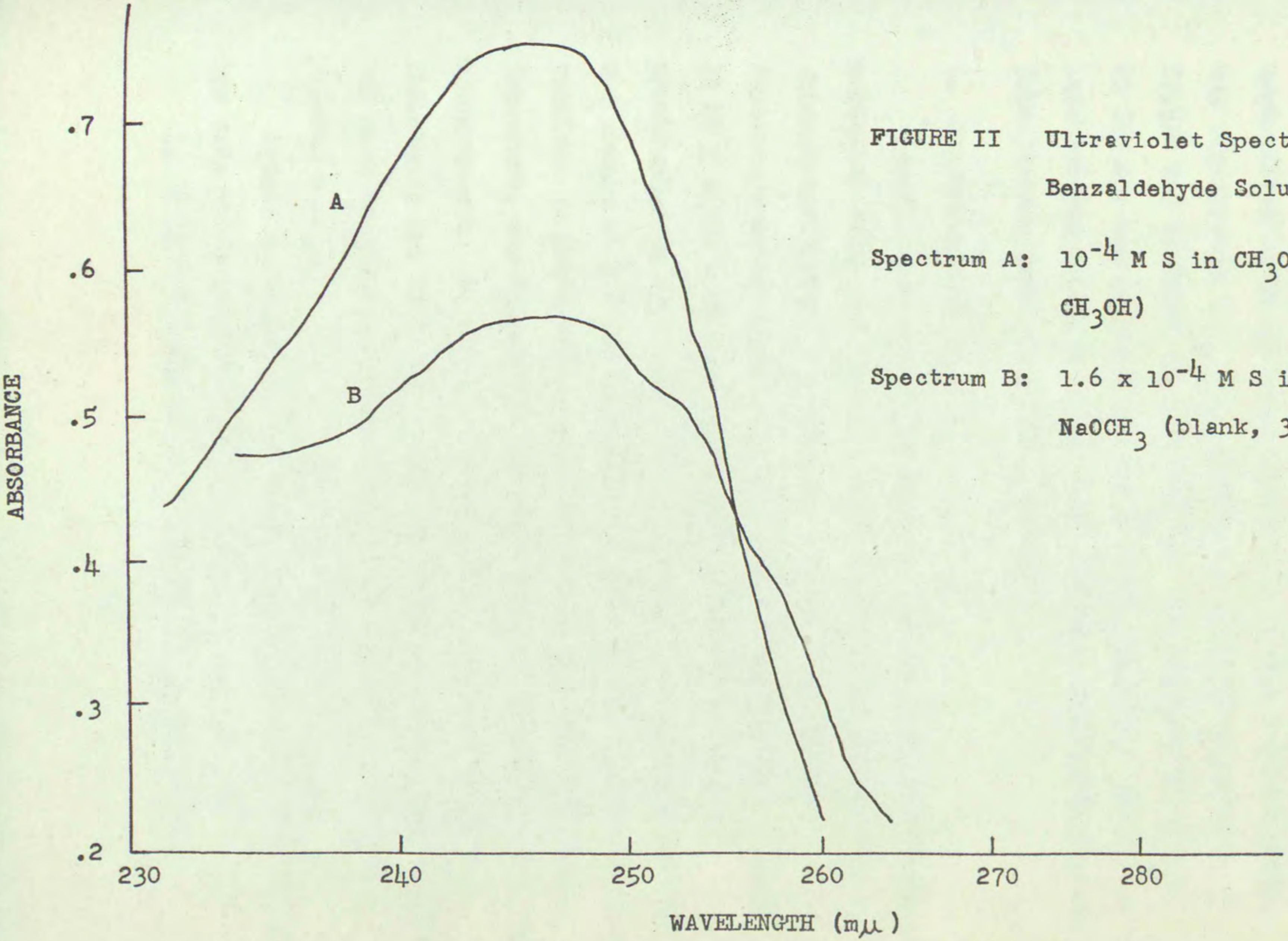


FIGURE II Ultraviolet Spectra of Benzaldehyde Solutions

Spectrum A: 10^{-4} M S in CH_3OH (blank, CH_3OH)

Spectrum B: 1.6×10^{-4} M S in 3.4 M $NaOCH_3$ (blank, 3.4 M $NaOCH_3$)

275 mμ) for o-anisaldehyde in 4.6 M $NaOCH_3$ (Figure I, Spectrum A) is believed to be due to $SOCH_3^-$. When a portion of a 4.5 M $NaOCH_3$ solution containing o-anisaldehyde was neutralized after 45 min., almost all of the o-anisaldehyde was regenerated ($\epsilon_{meas.}$ = 9,620 for 2% CH_3OH solution: ϵ = 10,450 for 1% CH_3OH solution (12)). No evidence of a peak at 270 mμ was observed in the neutral solution. Indicator measurements at 254 mμ for o-anisaldehyde were made without interference from the peak at 270 mμ.

C. Measurement of D_0

Quantitative indicator measurements in methanolic sodium methoxide media were made using 2,4 dichlorobenzaldehyde, p-chlorobenzaldehyde, benzaldehyde and o-anisaldehyde. Absorbance measurements were made in the ultraviolet region at 25°C using a thermostatically controlled Beckman DU spectrophotometer. Absorbance readings were constant and did not change with time, and neutralization of the basic solutions resulted in quantitative regeneration of the free aldehyde. Therefore, the Cannizzaro reaction does not interfere with the measurements. A sodium methoxide blank was used since the absorbance due to sodium methoxide alone is strong below 240 mμ and weak to moderate (depending on impurities) in the range 245-260 mμ.

Actual indicator measurements were made using essentially the same procedure as MacGregor (12):

1. A 10^{-2} M solution of aldehyde was prepared by

accurately weighing the purified aldehyde into a nitrogen flushed, 50 ml. volumetric flask. Nitrogen degased methanol was used for making dilutions.

2. A portion of the 10^{-2} M aldehyde solution was diluted to 10^{-3} M with nitrogen degased methanol.
3. An aliquot of stock sodium methoxide solution (5.6-5.8 M) was pipeted into a volumetric flask along with an aliquot of the 10^{-3} M aldehyde solution. Nitrogen degased methanol was used to dilute to the mark. A blank solution (less aldehyde) was prepared in the same manner. The initial concentration of aldehyde ranged from 1 to 3×10^{-4} M depending on the amount of $SOCH_3^-$ formed. The concentration of sodium methoxide was determined by titration with standard HCl using phenolphthalein indicator.
4. One centimeter quartz cells were dried and flushed with nitrogen before filling. The cells were sealed while measurements were being made.

The molar absorptivities (ϵ S) for the free aldehydes were calculated from absorbance measurements in methanol containing no sodium methoxide by using equation (XXXIII). The determination of molar absorptivity ($\epsilon_{SOCH_3^-}$) values for the

$$A = \epsilon bc \qquad \text{(XXXIII)}$$

methoxylated aldehydes will be discussed in Section IV.

D. Deuterium Exchange in the Methanolysis of Chloroform

In order to predict that the rate of methanolysis of chloroform should be proportional to an H_- function, it was necessary to know that chloroform is equilibrated with the trichloromethyl anion. While equilibration of hydrogen had been proven by deuterium exchange studies in aqueous sodium hydroxide solution (24), the corresponding experiment had not been run in methanolic sodium methoxide solution.

An excess of deuterochloroform (1.10 M) was reacted with sodium methoxide (0.553 M) for about 20 hours at 40°C. Titration of an aliquot with standard acid indicated that 95.4% of the sodium methoxide was consumed. A 10 cc portion of the reaction mixture was then shaken with 2 cc of isooctane and 25 cc of water. After another water wash, the infrared spectrum of the isooctane extract was recorded using a Perkin Elmer 137 Infracord. Examination of published chloroform spectra (30) showed that the following bands could be used to measure the $CHCl_3/CDCl_3$ ratio: 4.15 and 8.23 μ for $CHCl_3$ and 11.05 μ for $CDCl_3$. The 11.05 μ $CDCl_3$ band was shifted to 10.98 μ in isooctane solution but this did not affect absorbance measurements. Synthetic mixtures of chloroform, deuterochloroform and isooctane (31) were analyzed in the same manner as the isooctane extract of the reaction mixture. The absorbance ratios for the synthetic samples and unknown are given in Table II.

TABLE II

Infrared Analysis of Chloroform Solutions

Sample	Ratio $CHCl_3/CDCl_3$	$\frac{A^{10.98\mu}_{CDCl_3}}{A^{8.23\mu}_{CHCl_3}}$	$\frac{A^{10.98\mu}_{CDCl_3}}{A^{4.15\mu}_{CHCl_3}}$
A. 5.00 cc isooctane, .05 cc $CDCl_3$, and .25 cc $CHCl_3$.	5	0.62	25
B. 5.00 cc isooctane, .02 cc $CDCl_3$, and .35 cc $CHCl_3$.	18	0.15	6.0
isooctane extract of reaction mixture	18(calc.)	0.15	—
	25(calc.)	—	4.3

The ratio of $CHCl_3/CDCl_3$ of about 22 confirms that chloroform is rapidly equilibrated with its conjugate base prior to a rate-determining step in methanolic sodium methoxide solution.

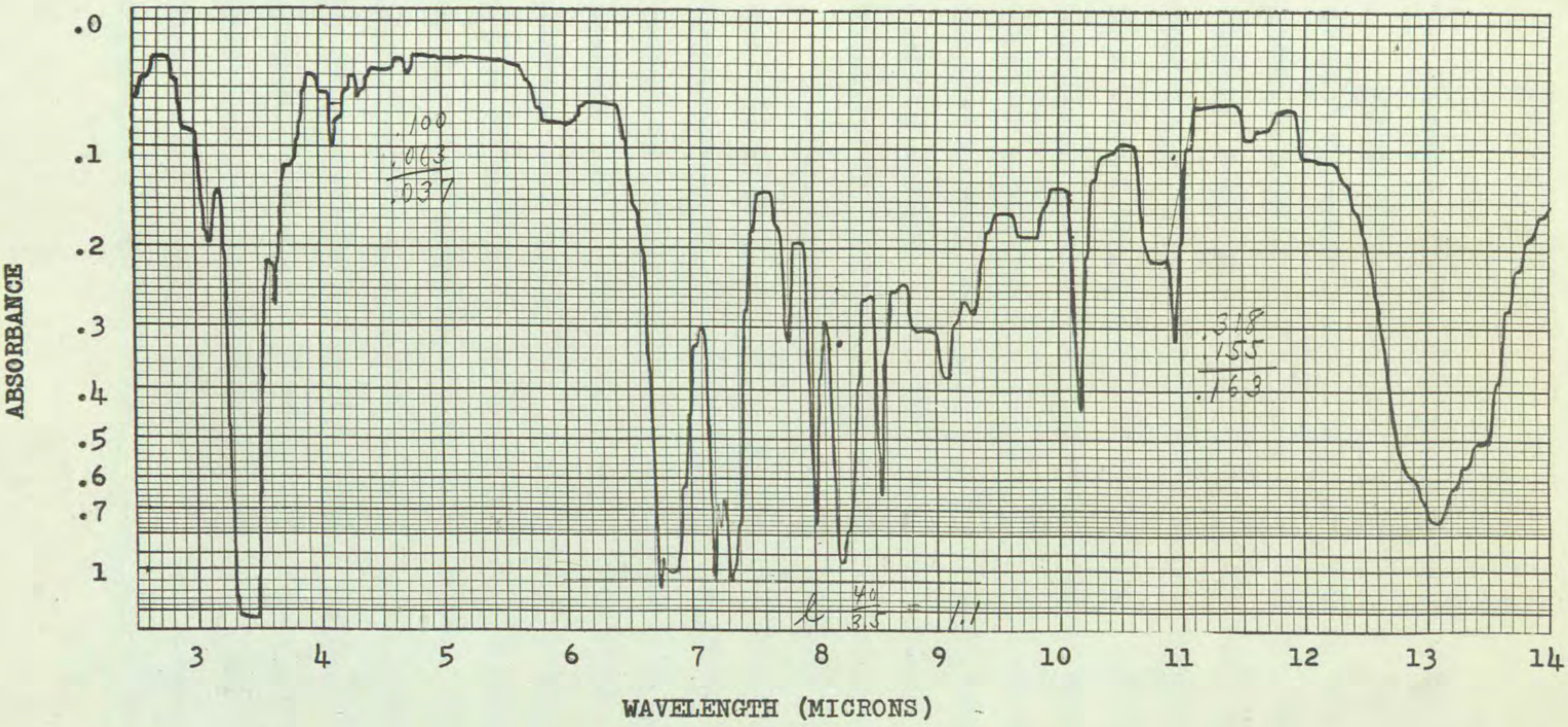


FIGURE III

Infrared Spectrum of Chloroform-Deuterochloroform Mixture in Isooctane (.106 mm cell)

E. Kinetics of the Methanolysis of 1-Chloropropane

Pseudo first-order rate constants for the S_N2 reaction of 10^{-2} M 1-chloropropane were measured in 0.11 to 4.6 M sodium methoxide solutions at 76.0 ± .03° C. The six gallon constant temperature bath was equipped with a primary 300 watt heater, a 100 watt secondary heater which was connected to a mercury thermoregulator and relay, a calibrated N.B.S. thermometer and an efficient air driven stirrer. Sealed glass ampoules with polypropylene inserts were used to carry out the reactions so that reaction of the base with the glass could be avoided. The reactions were followed by potentiometric titration of chloride ion with standard silver nitrate.

A stock solution of about .1 M 1-chloropropane in methanol was used to prepare each of the reaction mixtures. The concentration of the stock solution was determined from the average of infinite time chloride determinations for three separate runs (.1210, .1190, and .1245 molar). The reaction mixtures were prepared in 50 cc volumetric flasks by adding a 5 cc aloquot of the stock .1215 M 1-chloropropane solution to the sodium methoxide solution at 0-10° C. After the reaction mixture warmed to room temperature, 5 cc aliquots were placed in the polypropylene lined ampoules. The ampoules were then protected with a calcium sulfate tube, chilled and sealed. Zero time (t_0) was denoted at the instant when the sealed ampoules were immersed in the oil bath. Ampoules were then withdrawn at timed intervals, chilled and opened. The

E. Kinetics of the Methanolysis of 1-Chloropropane

Pseudo first-order rate constants for the S_N2 reaction of 10^{-2} M 1-chloropropane were measured in 0.11 to 4.6 M sodium methoxide solutions at 76.0 ± .03° C. The six gallon constant temperature bath was equipped with a primary 300 watt heater, a 100 watt secondary heater which was connected to a mercury thermoregulator and relay, a calibrated N.B.S. thermometer and an efficient air driven stirrer. Sealed glass ampoules with polypropylene inserts were used to carry out the reactions so that reaction of the base with the glass could be avoided. The reactions were followed by potentiometric titration of chloride ion with standard silver nitrate.

A stock solution of about .1 M 1-chloropropane in methanol was used to prepare each of the reaction mixtures. The concentration of the stock solution was determined from the average of infinite time chloride determinations for three separate runs (.1210, .1190, and .1245 molar). The reaction mixtures were prepared in 50 cc volumetric flasks by adding a 5 cc aloquot of the stock .1215 M 1-chloropropane solution to the sodium methoxide solution at 0-10°C. After the reaction mixture warmed to room temperature, 5 cc aliquots were placed in the polypropylene lined ampoules. The ampoules were then protected with a calcium sulfate tube, chilled and sealed. Zero time (t_0) was denoted at the instant when the sealed ampoules were immersed in the oil bath. Ampoules were then withdrawn at timed intervals, chilled and opened. The contents of the polypropylene tube were carefully washed into a clean bottle with 125 cc of glacial acetic acid (Dupont reagent grade). The glacial acetic acid neutralized the sodium methoxide and served as a good solvent (32) for running micro-potentiometric chloride determinations. Chloride ion was determined in a total of 175 cc of glacial acetic acid by titration with aqueous .0100 M $AgNO_3$. The end point was detected using a Corning Model 10 pH meter with commercial glass electrodes. The precision was very good, and the end points could be located to within 0.01 cc of 0.0100 M $AgNO_3$.

SECTION IV

EXPERIMENTAL RESULTS AND DISCUSSION

A. Measurement of $pK_{SOCH_3^-}$ Values

Spectroscopic data for 2,4 dichlorobenzaldehyde, p-chlorobenzaldehyde, benzaldehyde and o-anisaldehyde in .023-5.04 molar sodium methoxide solutions is given in Tables III to VI.

The molar absorptivities for $SOCH_3^-$ and SOH^- (12) are given in Table VII along with the base concentration of the medium in which the value was determined. The best available value for $\epsilon_{SOCH_3^-}$ is given in column four. The molar absorptivity for 2,4 dichlorobenzaldehyde was taken to be 438 since this was lower than ϵ_{SOH^-} (634) but it is not necessarily the correct value. For p-chlorobenzaldehyde, the ϵ_{SOH^-} value was used as the best $\epsilon_{SOCH_3^-}$ value since the measured $\epsilon_{SOCH_3^-}$ values were still decreasing at the highest base concentration. Benzaldehyde gave the best agreement between $\epsilon_{SOCH_3^-}$ and ϵ_{SOH^-}, and the slightly lower value was used. In methanolic sodium methoxide solution, o-anisaldehyde is too weak an acid ($pK_{SOCH_3^-} = -1.43$, $pK_{SOH^-} = -.96$) to be converted completely to $SOCH_3^-$ even in 5.04 M $NaOCH_3$. The ϵ_{SOH^-} value was therefore taken to be the best $\epsilon_{SOCH_3^-}$ value. In fact, it has been shown (12) that the molar absorptivities for SOH^- and the aromatic substrate without the aldehyde group are roughly equivalent.

Data used to determine $pK_{SOCH_3^-}$ values is given in Tables VIII to XI. The indicator ratio, R, was determined using equation XI, as discussed in Section II. Values for ϵ_T were taken from Tables III to VI.

The dependence of the indicator ratio on the sodium methoxide concentration is shown for all indicators in Figure IV, where log R is plotted vs. $NaOCH_3$ molarity. The plots are roughly parallel except for p-chlorobenzaldehyde, thus showing that the indicator ratio is independent of the indicator used, but is characteristic of the medium. Since it was later discovered that p-chlorobenzaldehyde was impure (refer to Section III), measurements with this indicator will not be considered valid.

Figure V shows a plot of (log R -log $NaOCH_3$ M) vs. $NaOCH_3$ M for the indicators. The plots are remarkably linear up to about 3.5 M $NaOCH_3$, thus allowing for an accurate extrapolation to infinite dilution. Apparently the general effects of interionic attraction on the activity coefficients in equation (XII) cancel out up to 3.5 M $NaOCH_3$. In acidic media (1), pK_{BH^+} can usually be determined only up to 2 M H^+ by the extrapolation procedure. The $pK_{SOCH_3^-}$ values obtained by the extrapolation procedure are given in Table XII and compared with the corresponding pK_{SOH^-} values (12) for aqueous solution. The $pK_{SOCH_3^-}$ values are smaller than the pK_{SOH^-} values, except for p-chlorobenzaldehyde, where an impurity problem exists.

It was impossible to determine $pK_{SOCH_3^-}$ values accurately using the method of direct comparison, since the indicator ratios do not overlap in Figure IV by a sufficient amount. If $pK_{SOCH_3^-}$ for benzaldehyde was evaluated from .75 - 1.25 M $NaOCH_3$ using the extrapolated $pK_{SOCH_3^-}$ value for 2,4 dichlorobenzaldehyde, $pK_{SOCH_3^-}$ values from -1.01 to -.91 were obtained. The extrapolation procedure gave a $pK_{SOCH_3^-}$ value of -1.43 for o-anisaldehyde, while direct comparison with the $pK_{SOCH_3^-}$ value for 2,4 dichlorobenzaldehyde at 1.25 M $NaOCH_3$ gave -1.38. By comparing o-anisaldehyde with benzaldehyde at 1.5, 2.5 and 3.5 M $NaOCH_3$, the $pK_{SOCH_3^-}$ values: -1.40, -1.44 and -1.42 were obtained, in good agreement with the -1.43 value obtained by extrapolation.

TABLE III

Spectroscopic Data for 2,4 Dichlorobenzaldehyde Solutions

λmax. = 258 mμ T = 25°C

Soln. No.	S(10^4 M)	$NaOCH_3$ (M)	Absorbance	$10^{-3}\epsilon$
1	0.890	nil	.403	4.53
2	1.228	nil	.564	4.59
3	1.228	0.0228	.506	4.12
4	1.228	0.0569	.446	3.63
5	1.228	0.1138	.361	2.94
6	1.228	0.2277	.270	2.20
7	1.228	0.5693	.131	1.07
8	1.228	1.149	.087	0.708
11	1.780	2.290	.078	0.438

TABLE IV

Spectroscopic Data for p-Chlorobenzaldehyde Solutions

$\lambda_{max.}$ = 255 mμ   T = 25°C

Soln. No.	$S(10^{4}$ M)	NaOCH$_3$ (M)	Absorbance	$10^{-3}\epsilon$
1	.5860	nil	.830	14.2
2	.970	nil	1.370	14.1
4	.970	.1149	1.261	13.0
5	.970	.3448	1.086	11.2
6	.970	1.165	.603	6.22
7	1.940	2.327	.486	2.50
8	1.940	3.446	.224	1.15
9	1.940	4.598	.143	.737
b	.970	nil	1.375	14.2
1b	.970	.1452	1.240	12.8
2b	.970	.4329	1.035	10.7
3b	.970	.7084	.830	8.56
4b	3.490	3.751	.319	.914

TABLE V

Spectroscopic Data for Benzaldehyde Solutions

λmax. = 245 mμ T = 25°C

Soln. No.	S(10^4 M)	$NaOCH_3$ (M)	Absorbance	$10^{-3}\epsilon$
1	.832	nil	1.020	12.3
1a	.842	nil	1.045	12.4
1b	1.03	nil	1.235	12.0
2	.832	.6870	.896	10.8
3	.832	1.054	.814	9.78
4	.832	1.763	.598	7.19
5	1.664	2.341	.896	5.38
6	1.664	3.412	.450	2.70
7	1.664	4.515	.171	1.03
8	6.66	5.466	.385	.578
9	5.99	3.751	1.035	1.73
10	5.99	4.473	.605	1.01
11	6.66	5.041	.454	.682

TABLE VI

Spectroscopic Data for o-Anisaldehyde Solutions

λmax. = 254 mμ T = 25°C

Soln. No.	S(10^4 M)	$NaOCH_3$ (M)	Absorbance	$10^{-3}\epsilon$
2	1.095	nil	1.025	9.36
3	.981	nil	.913(.925)	9.30(9.43)
4	.981	1.439	.791	8.06
5	.981	1.826	.750	7.64
6	.981	2.318	.637	6.49
7	1.96	2.961	.965	4.92
8	1.96	3.448	.710	3.62
9	1.96	4.568	.285	1.45
11	4.20	3.751	1.00	2.38
12	4.20	4.473	.558	1.33
13	4.04	5.041	.429	1.06

TABLE VII

Molar Absorptivities for $SOCH_3^-$ and SOH^- (12)

Indicator	ϵ SOH^-	ϵ $SOCH_3^-$	ϵ $SOCH_3^-$ used
2,4 dichlorobenzaldehyde	634 (1.57 M OH^-)	438 (2.29 M CH_3O^-)	438
p-chlorobenzaldehyde	324 (10.45 M OH^-)	737 (4.60 M CH_3O^-)	324
benzaldehyde	596 (10.55 M OH^-)	578 (5.46 M CH_3O^-)	578
o-anisaldehyde	463 (11.34 M OH^-)	1020 (5.04 M CH_3O^-)	460

TABLE VIII

Data for the Determination of $pK_{SOCH_3^-}$ for 2,4 Dichlorobenzaldehyde

$\epsilon_{SOCH_3^-} = 438$ $\epsilon_S = 4,560$

Soln. No	R	Log R	Log $NaOCH_3$ M	Log R - Log $NaOCH_3$ M
3	.120	-.921	-1.642	.721
4	.291	-.536	-1.245	.709
5	.648	-.188	-.944	.756
6	1.34	.127	-.643	.770
7	5.52	.742	-.245	.987
8	14.3	1.15	.060	1.09

TABLE IX

Data for the Determination of $pK_{SOCH_3^-}$ for p-Chlorobenzaldehyde

$\epsilon_{SOCH_3^-} = 324$ $\epsilon_S = 14,150$

Soln. No.	R	Log R	Log $NaOCH_3$ M	Log R - Log $NaOCH_3$ M
4	.0907	-1.04	-.940	-.103
5	.271	-.567	-.462	-.104
6	1.34	.129	.0663	.0624
7	5.35	.729	.367	.362
8	15.7	1.20	.537	.660
9	32.5	1.51	.663	.849
1b	.108	-.960	-.838	-.128
2b	.332	-.479	-.364	-.115
3b	.679	-.168	-.150	-.018
4b	22.4	1.35	.574	+.777

TABLE X

Data for the Determination of $pK_{SOCH_3^-}$ for Benzaldehyde

$\epsilon_{SOCH_3^-} = 578$ $\epsilon_S = 12,200$

Soln No.	R	Log R	Log $NaOCH_3$ M	Log R - Log $NaOCH_3$ M
2	.140	-.854	-.163	-.691
3	.262	-.582	.0228	-.605
4	.758	-.120	.246	-.366
5	1.42	.152	.369	-.217
6	4.47	.650	.533	+.117
7	24.8	1.394	.655	+.739
9	9.09	.959	.574	+.385
10	25.9	1.413	.651	+.762
11	110.7	2.045	.702	+1.343

TABLE XI

Data for the Determination of $pK_{SOCH_3^-}$ for o-Anisaldehyde

$\epsilon_{SOCH_3^-} = 460$ $\epsilon_S = 9,360$

Soln. No.	R	Log R	Log $NaOCH_3$ M	Log R - Log $NaOCH_3$ M
4	.171	-.767	.158	-.925
5	.239	-.622	.261	-.883
6	.476	-.322	.365	-.687
7	.995	-.002	.471	-.473
8	1.82	.260	.538	-.278
9	7.99	.902	.660	.242
11	3.63	.560	.574	-.014
12	9.23	.965	.651	-.314
13	13.8	1.399	.702	-.697

TABLE XII

A Comparison of pK_{SOH^-} and $pK_{SOCH_3^-}$ Values

Indicator	$pK_{SOCH_3^-}$	pK_{SOH^-}	(pK_{SOH^-} − $pK_{SOCH_3^-}$
2,4 dichlorobenzaldehyde	0.70	0.97	0.27
p-chlorobenzaldehyde	-0.20	-0.32	-0.12
benzaldehyde	-0.91	-0.68	0.23
o-anisaldehyde	-1.43	-0.96	0.47

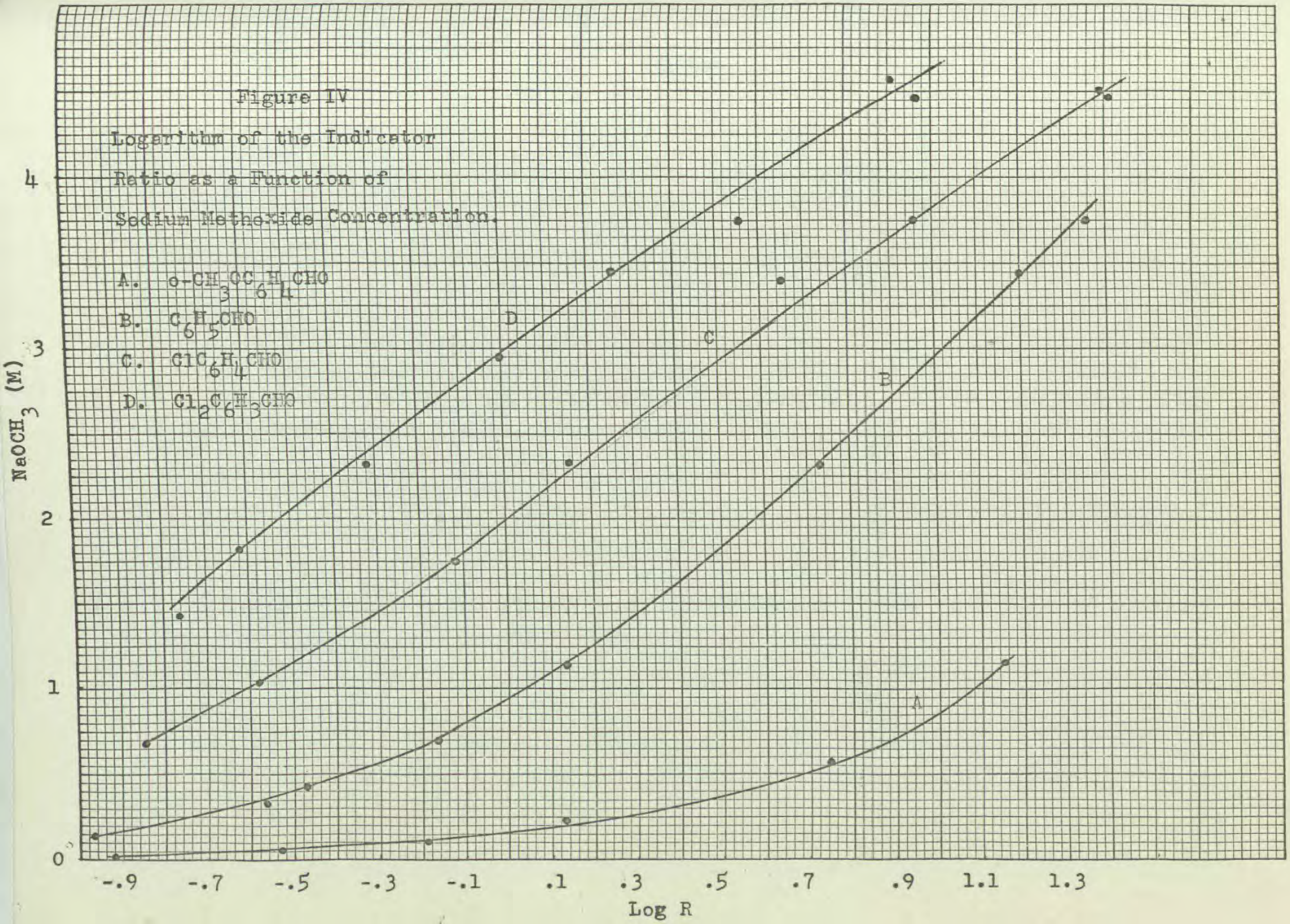


Figure IV

Logarithm of the Indicator Ratio as a Function of Sodium Methoxide Concentration.

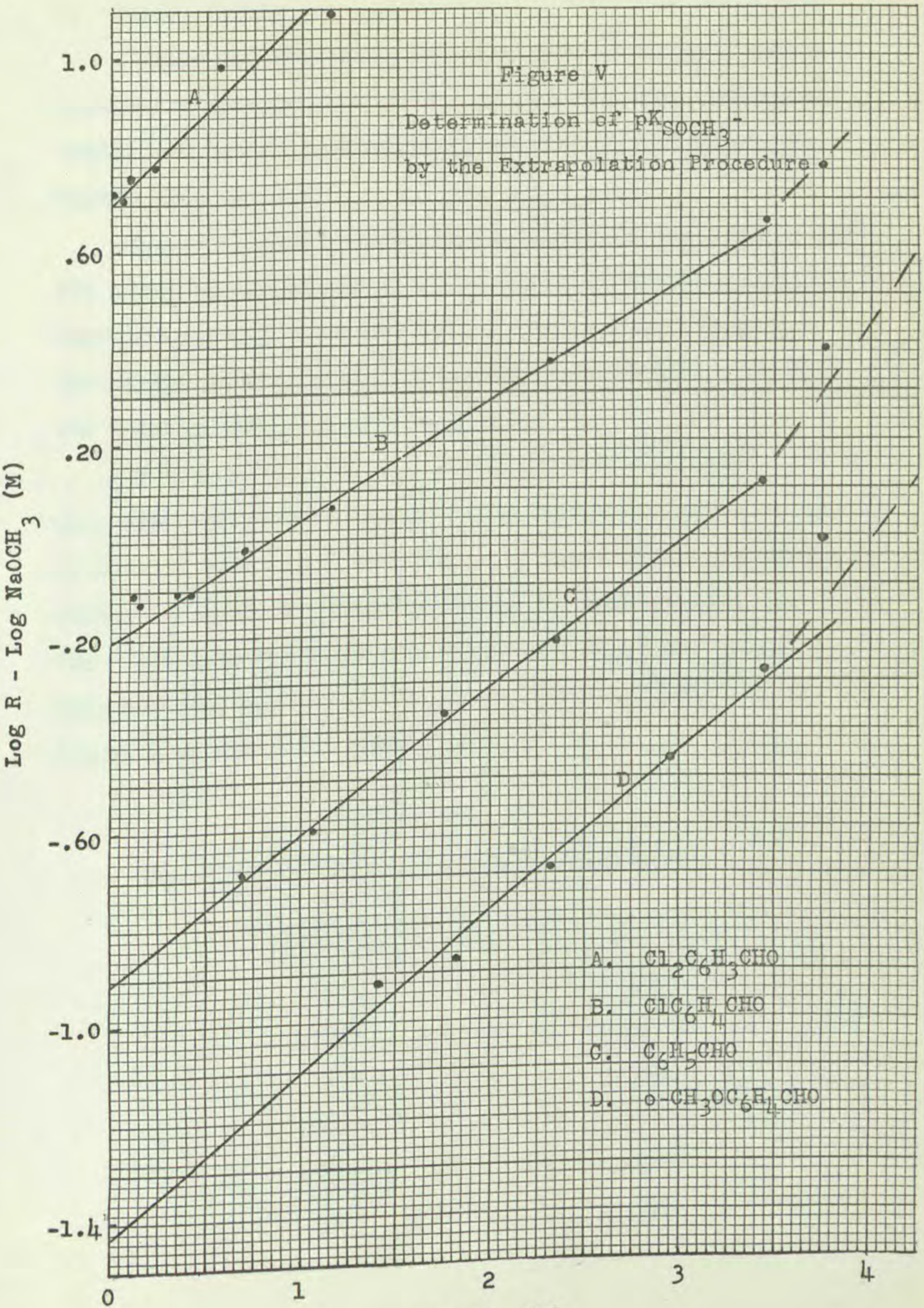


Figure V

Determination of $pK_{SOCH_3^-}$ by the Extrapolation Procedure

B. The D_0 Scale

Values for the donor function were calculated using equation X and the data in Tables VIII to XII. Tabulated values for D_0 are shown for the individual indicators in Tables XIII to XVI.

Figure VI shows the D_0 scale, which is the line of best fit using 24 experimental points for 2,4 dichlorobenzaldehyde, benzaldehyde and o-anisaldehyde. The agreement between indicators is pretty good since the average deviation from the line is less than .05 D_0 unit.

In Figure VII, D_0 is plotted against -log $NaOCH_3$ (M) to show that basicity in concentrated sodium methoxide solutions is nowhere near equal to $pOCH_3$. If basicity was dependent on $pOCH_3$, as shown by the solid line, the experimental plot and the solid line would be superimposed. The donor function does however, approach $pOCH_3$ as a measure of basicity in dilute solution (.1 M $NaOCH_3$).

TABLE XIII

D_0 Values Using 2,4 Dichlorobenzaldehyde

$NaOCH_3$ (M)	D_0
.0228	1.62
.0569	1.24
.1138	0.89
.2277	0.57
.5693	-0.04
1.149	-0.45

TABLE XIV

D_0 Values Using p-Chlorobenzaldehyde

$NaOCH_3$ (M)	D_0
.1149	.84
.3448	.37
1.165	-.33
2.327	-.93
3.446	-1.40
4.598	-1.71
.1452	.77
.4329	.28
.7084	-.03
3.751	-1.55

TABLE XV

D_0 Values Using Benzaldehyde

$NaOCH_3$ (M)	D_0
.6870	-.06
1.054	-.33
1.763	-.79
2.341	-1.06
3.412	-1.56
4.515	-2.30
3.751	-1.87
4.473	-2.32
5.041	-2.95

TABLE XVI

D_0 Values Using o-Anisaldehyde

$NaOCH_3$ (M)	D_0
1.439	-.66
1.826	-.81
2.318	-1.11
2.961	-1.43
3.448	-1.69
4.568	-2.33
3.751	-1.99
4.473	-2.39
5.041	-2.83

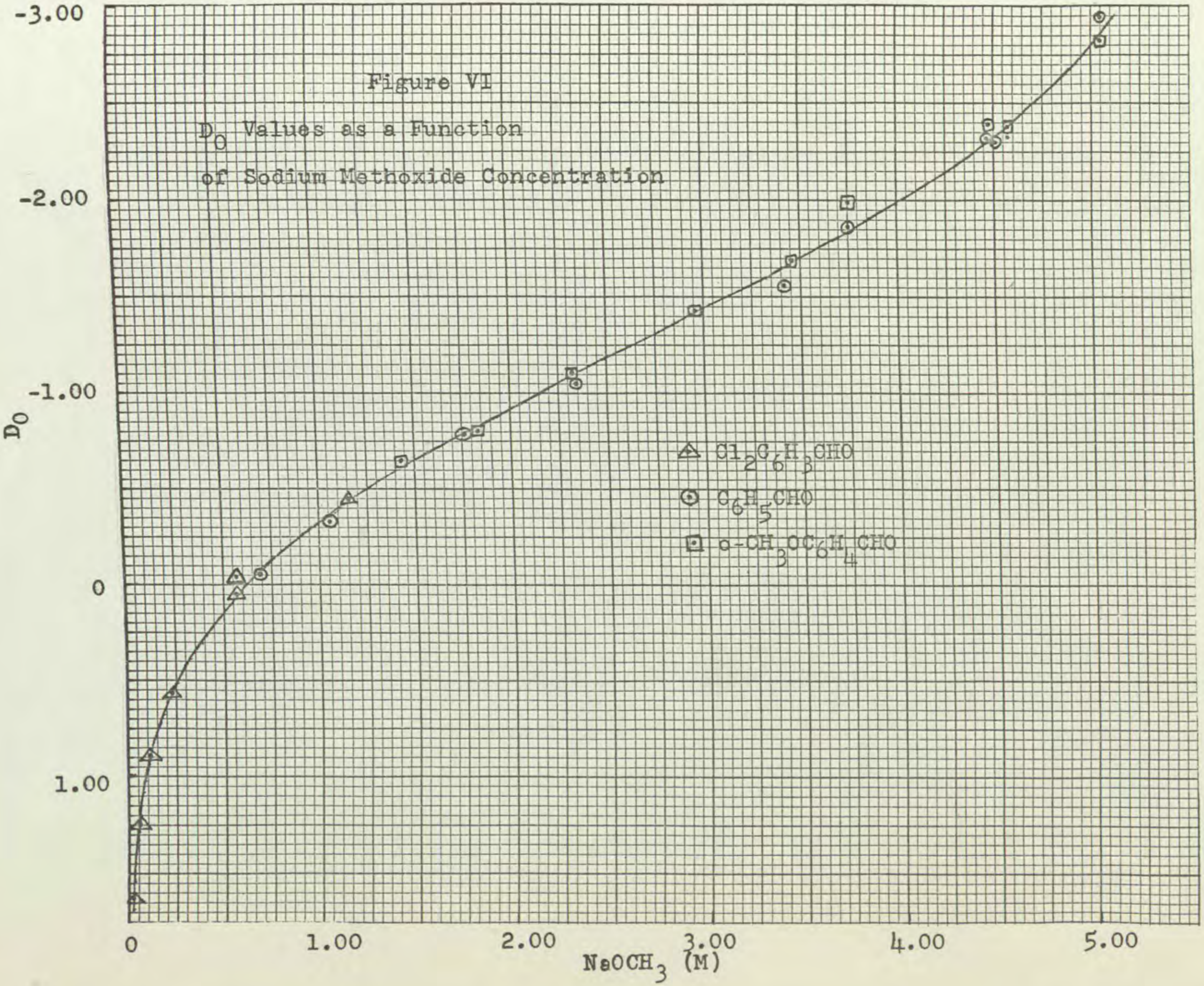
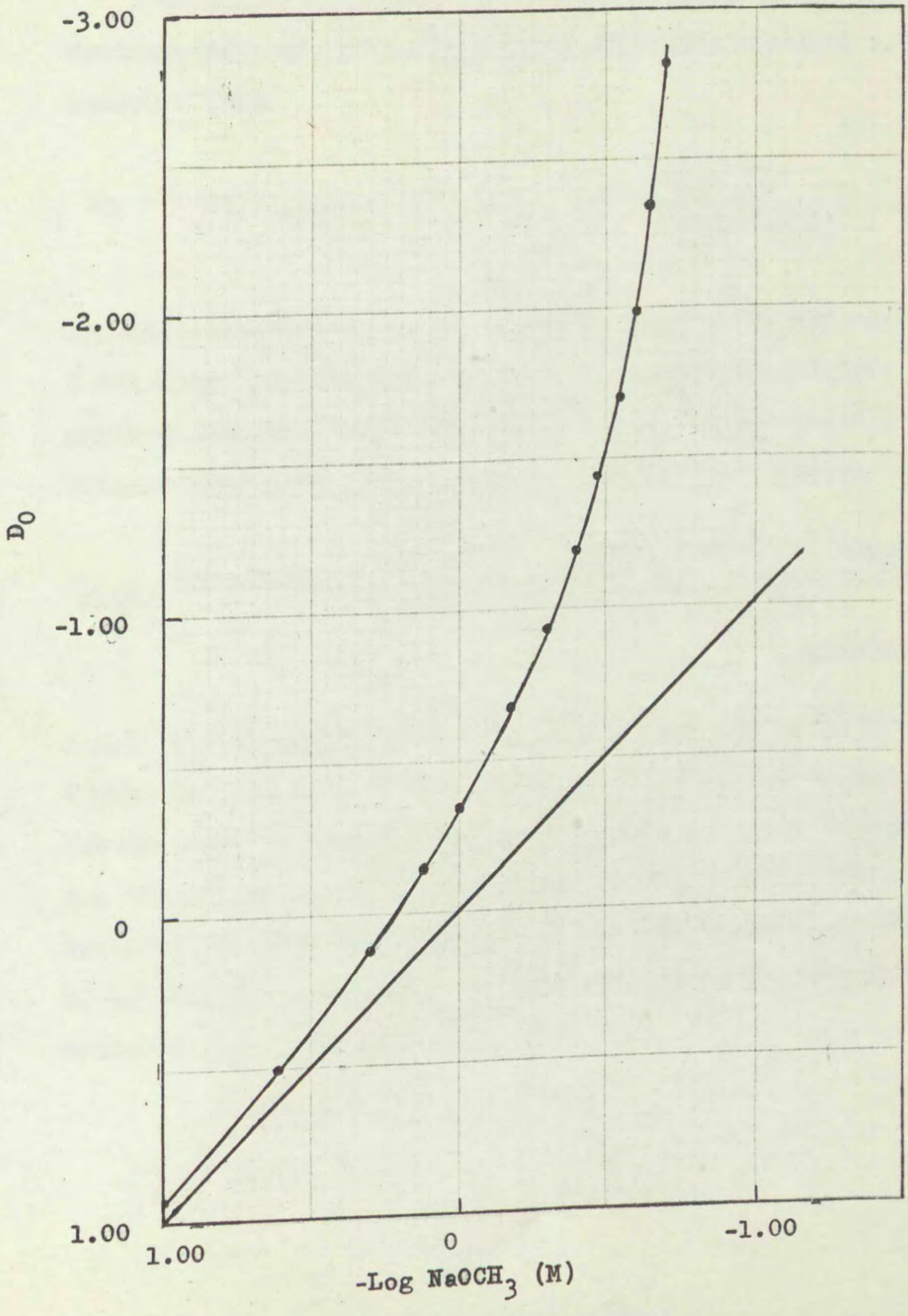


Figure VI

D_0 Values as a Function of Sodium Methoxide Concentration

Figure VII

Comparison of D_0 and -Log $NaOCH_3$ (M) as a Measure of Basicity



C. Solvation of the Methoxide Ion

The Bascombe and Bell theory was applied to the D_0 function data in methanolic sodium methoxide solution using equation (XX).

$$D_0 = n \log C_{CH_3OH} - \log C_{CH_3O^-} - \log \frac{f_{CH_3O^-} f_S}{f^n_{CH_3OH} f_{SOCH_3^-}} \quad (XX)$$

The solvation number (n) was determined by trial and error. A value for n was assumed, and the concentration of free methanol was determined using the density of the solution (Figure VIII, data from reference 21) and the equation,

$$C_{CH_3OH} \text{ (normalized)} = \frac{\text{dens.} - .001(54.03 + 32.04\ n)\ C_{CH_3O^-}}{32.04 \times 24.54 \times .001} \quad (XXXIV)$$

A plot of log C_{CH_3OH} for n = 3.2 vs. $NaOCH_3$ (M) is given in Figure IX; the use of this plot will be discussed later. For the sake of comparison, D_0 values for n = 3.0, 3.2 and 3.4 from .5 to 5 M $NaOCH_3$ are given in Table XVII. The agreement between calculated D_0 values for a solvation number of 3.2 and the experimental D_0 scale is fair, the average deviation being 0.1 D_0 unit.

TABLE XVII

Solvation of the Methoxide Ion Using the Bascombe and Bell Theory

		D_0(calc.)		
$C_{CH_3O^-}$ (M)	D_0 (exp.)	n = 3.0	n = 3.2	n = 3.4
.50	+.13	+.21	+.20	+.19
1.0	-.34	-.19	-.21	-.18
1.5	-.67	—	-.52	—
2.0	-.93	-.72	-.78	-.85
2.5	-1.19	—	-1.05	—
3.0	-1.44	-1.21	-1.31	-1.43
3.5	-1.70	—	-1.60	—
4.0	-1.98	-1.73	-1.92	-2.14
4.5	-2.34	—	-2.31	—
5.0	-2.82	-2.45	-2.80	-3.23

The Perrin theory was applied to our data by plotting (D_0 + log $C_{CH_3O^-}$) vs. log a_{CH_3OH} (obtained by interpolation of the data of Freeguard (21), which is plotted in Figure X), using the data from Table XVIII.

TABLE XVIII

Solvation of the Methoxide Ion Using the Perrin Theory

$C_{CH_3O^-}$ (M)	-(D_0 + log $C_{CH_3O^-}$)	-Log a_{CH_3OH}
.5	.17	0
1.0	.34	.035
1.5	.49	.072
2.0	.63	.112
2.5	.79	.155
3.0	.96	.199
3.5	1.16	.250
4.0	1.38	.301
4.5	1.69	.354
5.0	2.12	.410

The plot is remarkably linear up to 4 M $NaOCH_3$ as shown in Figure XI. The increase in slope (presumably the solvation number) from 4 to 5 M $NaOCH_3$ is unexpected since solvent becomes continuously less available with increasing base concentration. By using the data from .5 to 4.5 M $NaOCH_3$, a least squares procedure using a computer gave a solvation number of 4.1 (σ = .1).

Use of the two theories gave different solvation numbers (3.2 and 4), in good agreement with solvation numbers (3 and 4) obtained for the hydroxide ion using the D_0 function for aqueous solution (12). Previous investigators, using the H_- scale for nitrated anilines (10), have obtained a methoxide ion solvation number of 4 (10) using the Bascombe and Bell theory, and unreasonably high numbers (21) using the Perrin theory. While the $CH_3O(CH_3OH)_3^-$ ion can be pictured as resulting from the interaction of methanol protons with the unshared electron pairs from the methoxide ion, it is harder to visualize the compound $CH_3O(CH_3OH)_4^-$.

Crystalline sodium methoxide has been shown (33) to exist as $NaOCH_3(CH_3OH)_2$ and $NaOCH_3$ but evidence on the structure of methoxide ion in methanol solution is not conclusive. P.M.R. and Raman spectra (34) of methanolic sodium methoxide solutions have indicated only that the methoxide ion gives no new peaks, OH splitting does not occur, and strong hydrogen bonds exist between methoxide ion and methanol.

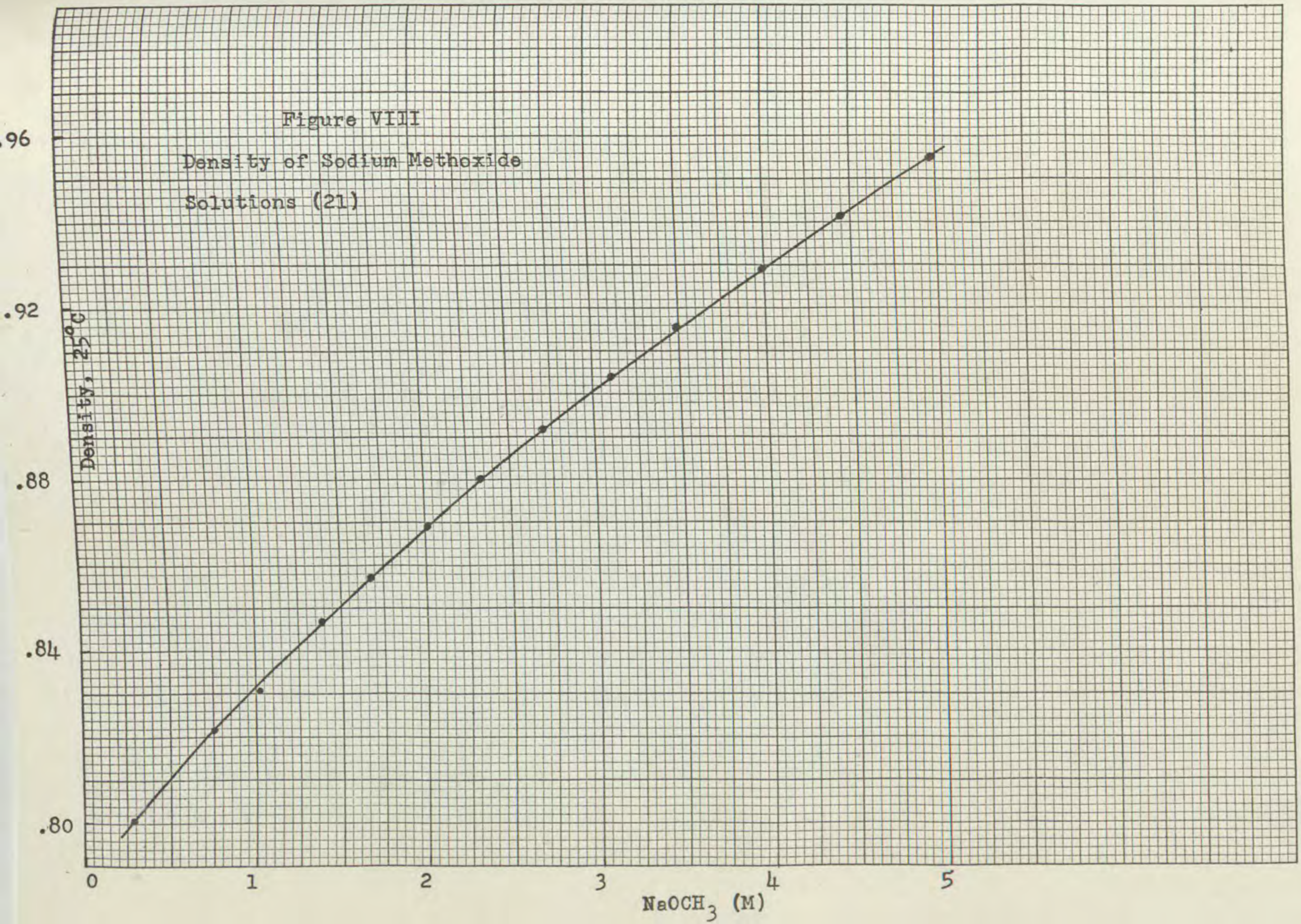


Figure VIII

Density of Sodium Methoxide Solutions (21)

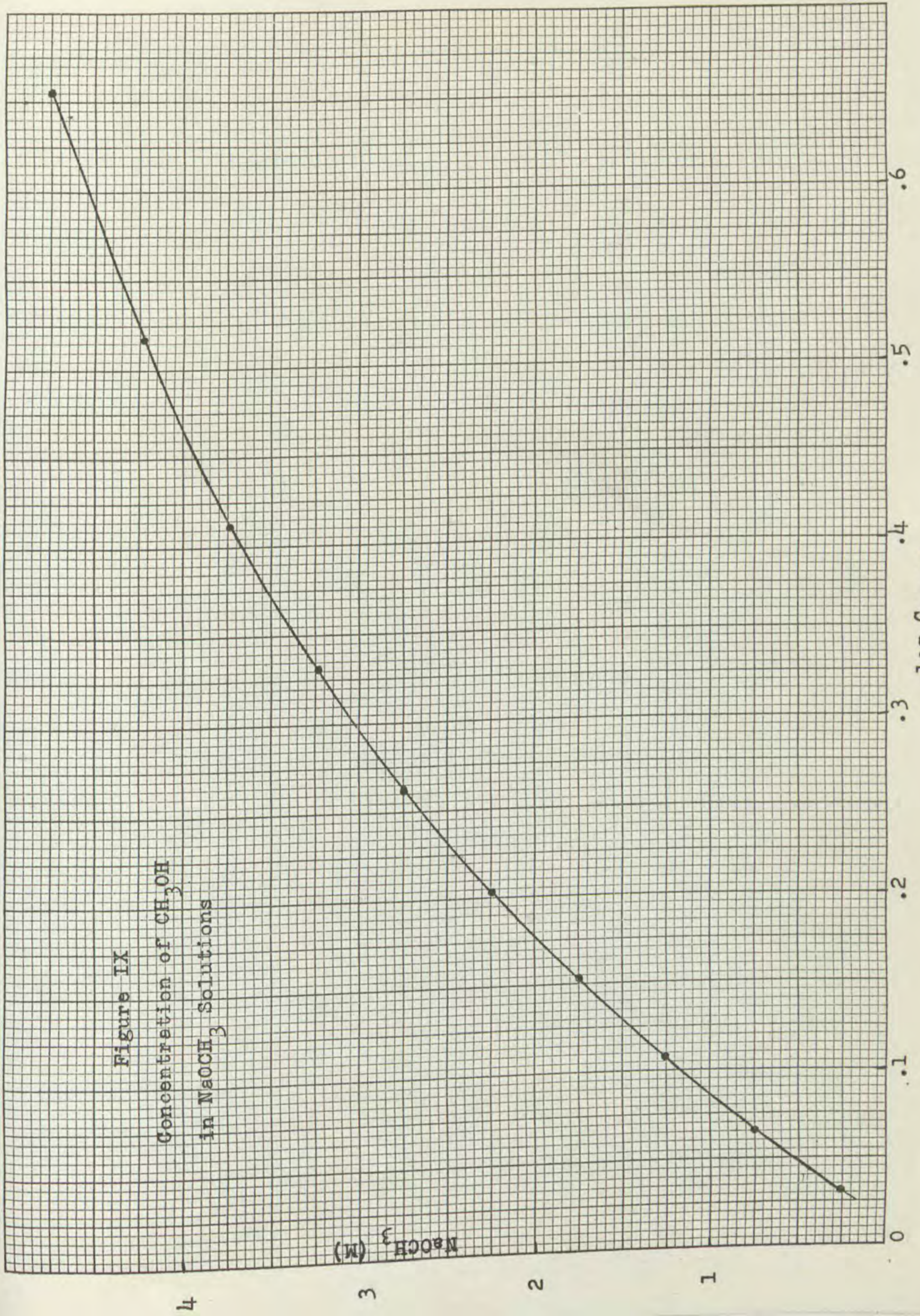


Figure IX

Concentration of CH_3OH

in $NaOCH_3$ Solutions

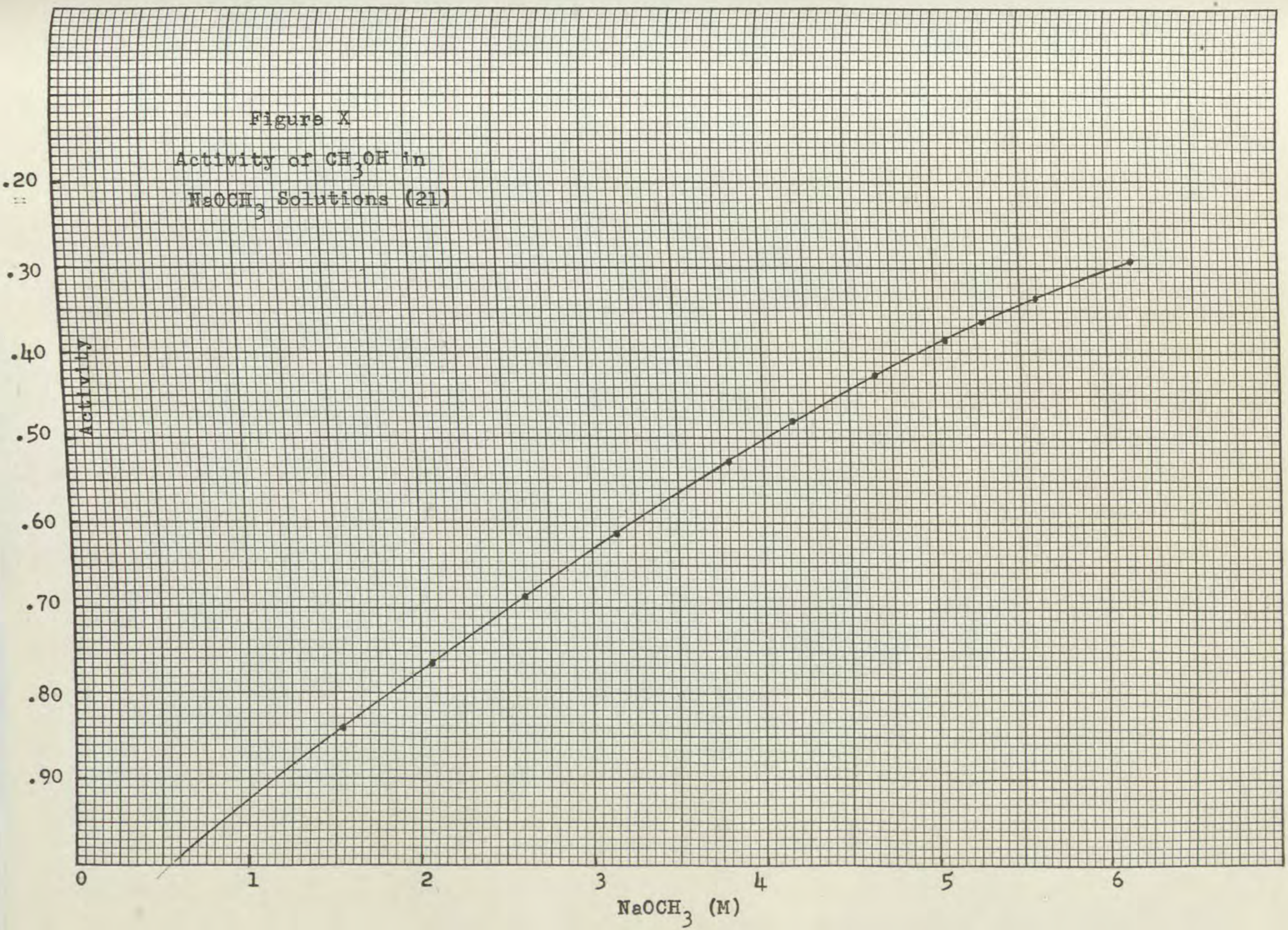


Figure X

Activity of CH_3OH in

$NaOCH_3$ Solutions (21)

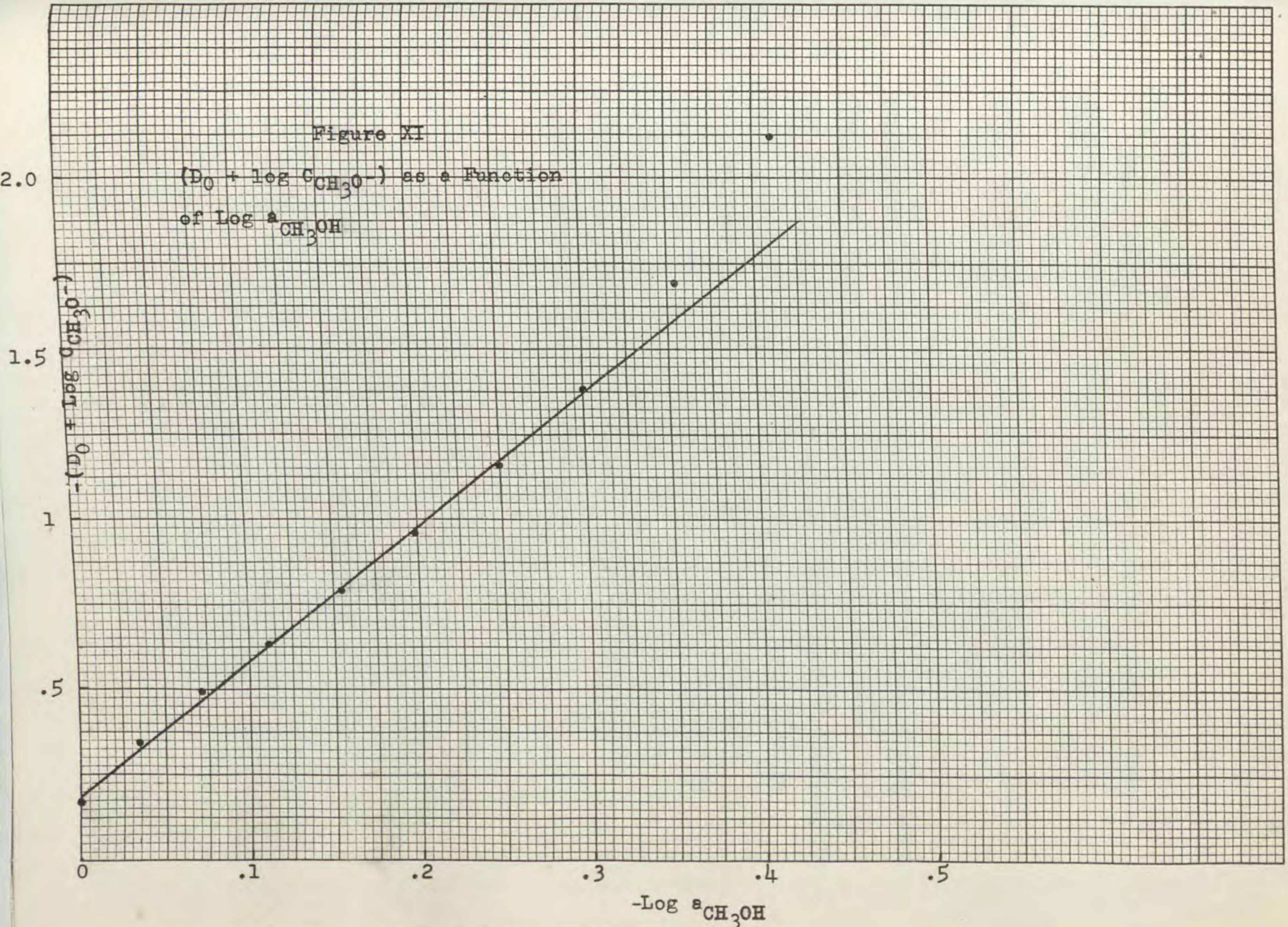


Figure XI

$(D_0 + \log C_{CH_3O^-})$ as a Function of Log a_{CH_3OH}

D. The Contrived H_- Function

The contrived H_- function was obtained using equation (XV) as discussed in Section II. Table XIX compares this

$$-(D_0 + \mathrm{Log}\ a_{CH_3OH} - pK_{CH_3OH}) = H^- + \log \frac{f_{B^-}\ f_S}{f_{BH}\ f_{SOCH_3^-}} \qquad (XV)$$

contrived H_- function with two experimental H_- scales determined with nitroanilines (10) and t-butylphenols (11) as indicators. The comparison shows that the contrived H_- function approximates the H_- scale obtained from phenol indicators more closely than the experimental H_- scales approximate each other. At 3 M $NaOCH_3$, the H_- scale from phenols appears, however, to be increasing more rapidly than the contrived H_- scale, but at the higher base concentrations the phenol indicators become increasingly less stable (11).

TABLE XIX

A Comparison of D_0 and H_- Functions

		a b	H_-	
$NaOCH_3$ (M)	$-D_0$	$-(D_0 + \log a_{CH_3OH} - pK_{CH_3OH})$	Amines	Phenols
.50	-.13	16.57	16.66	16.50
1.00	.34	17.07	17.23	16.93
1.50	.67	17.44	17.71	17.30
2.00	.93	17.74	18.10	17.64
2.50	1.19	18.04	18.52	18.06
3.00	1.44	18.34	18.98	18.50
3.50	1.70	18.65	19.53	——
4.00	1.98	18.98	20.20	——
4.50	2.34	19.39	——	——
5.00	2.82	19.93	——	——

a. a_{CH_3OH} taken from Figure X; reference 21.

b. $pK_{CH_3OH} = 16.70$; reference 35.

E. Methanolysis of Chloroform

A comparison of the contrived H_- function with the rates of methanolysis of chloroform at 45.1° C (19) is of interest, since this was the first reaction to serve as a test for basicity functions in methanolic sodium methoxide solution. Correlation of the rate by an H_- function is anticipated from the mechanism of the reaction as discussed in Section II.

Table XX gives rate data for the methanolysis of chloroform at 45.1° C (19) from 1.04 M to 3.99 M $NaOCH_3$, the contrived H_- values from Table XIX (based on a_{CH_3OH}), and another derived H_- scale based on the free methanol concentration from Figure IX.

Figure XII shows a nearly ideal dependence of the rate of methanolysis of chloroform on the contrived H_- function (slope = 1.04, σ = .01). A plot of (D_0 + Log C_{CH_3OH} - pK_{CH_3OH}) against log k_1 also gave an excellent correlation (slope = 1.00, σ = .01), but this derived H_- function is not as theoretically sound as the contrived H_- function based on thermodynamic activity. By using the H_- function from nitrated anilines (10) to correlate the same rate data, More O'Ferrall and Ridd (19) obtained a curved line whose average slope was 0.8. Since the contrived H_- function correlates the rate of methanolysis of chloroform almost perfectly, this function is presumably an accurate measure of the basicity of the medium in the Bronsted sense. This result is analogous to that found in aqueous media, in that a contrived D_0 function, ($H_- + \log C_{H_2O} - pK_{H_2O}$), correlates the rates of an S_N2 and an E2 reaction (20) more effectively than the experimental D_0 function. The implication is that the contrived D_0 function in aqueous media is a more accurate measure of basicity in the Lewis sense.

TABLE XX

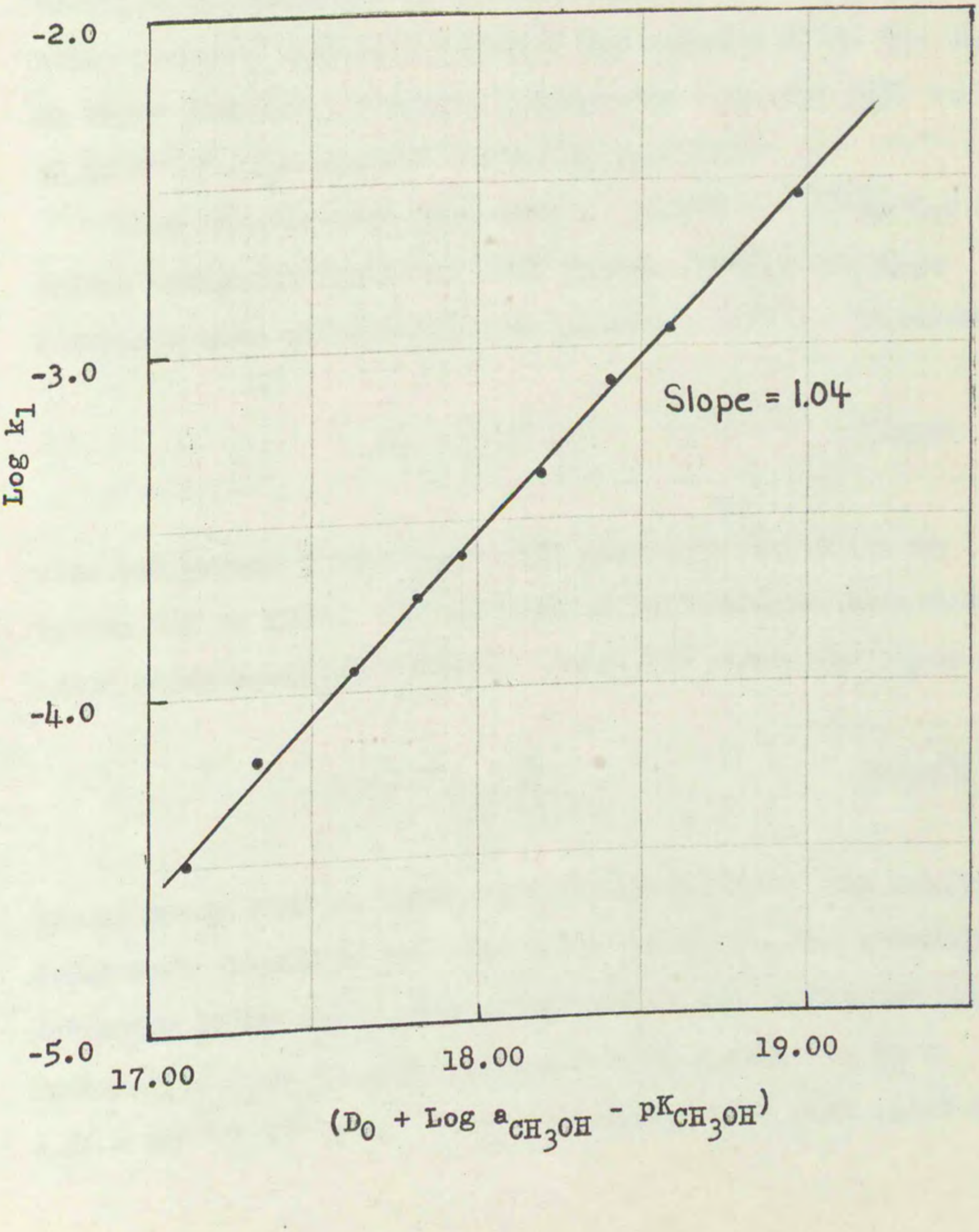
Methanolysis of Chloroform at 45.1°C (19)

$NaOCH_3$ (M)	$-\log k_1$	$(D_0 + \text{Log } a_{CH_3OH} - pK_{CH_3OH})$	$(D_0 + \text{Log } C_{CH_3OH}$[a] $- pK_{CH_3OH})$
1.04	4.507	17.12	17.15
1.36	4.211	17.34	17.37
1.79	3.951	17.63	17.66
2.13	3.742	17.82	17.86
2.34	3.609	17.96	18.01
2.74	3.375	18.20	18.25
3.12	3.105	18.41	18.47
3.40	2.951	18.59	18.66
3.99	2.548	18.98	19.09

[a] C_{CH_3OH} values were taken from Figure IX.

Figure XII

Rate of Methanolysis of Chloroform at 45.1°C as a Function of the Contrived H_- Function



F. Methanolysis of 1-Chloropropane

The S_N2 reaction of 10^{-2} M 1-chloropropane was studied in .11 to 4.6 M $NaOCH_3$ solutions at 76.0°C according to the experimental procedure described in Section III. The reaction was followed by determination of chloride ion; the other products were not isolated but assumed to be the same as those resulting from the ethanolysis reaction (25) at 74.95°C (95% S_N2 product and 5% E2 product).

Nine kinetic runs were made at 76.0°C in .11 to 4.6 M sodium methoxide solution. The pseudo first-order rate constants were calculated using equation (XXXV). Experimental

$$k_1 = \frac{1}{t} \ln \frac{C_0}{C} \qquad \text{(XXXV)}$$

data and pseudo first-order rate constants are given in Tables XXI to XXIX. Second-order rate constants were calculated using equation (XXXVI). Table XXX shows the first- and

$$k_2 = \frac{k_1}{NaOCH_3\ (M)} \qquad \text{(XXXVI)}$$

second-order rate constants for the nine runs; the second-order rate constants are remarkably constant, the standard deviation being 0.25. The second-order rate constants for methanolysis are in good agreement with a reported $k_2 = 6.86 \times 10^{-3}$ l M^{-1} min.$^{-1}$ for ethanolysis (25) with .1617 M ethoxide at a slightly lower temperature (74.95°C), since ethoxide is about twice as effective a nucleophile as the methoxide ion.

The linear dependence of the pseudo first-order rate constants for the methanolysis of 1-chloropropane on concentration of methoxide ion is analogous to the nature of the rate dependence of the methanolysis of 1-chloro-3,3-dimethylbutane (19) on methoxide ion concentration in methanol solvent. These results are contrary to those obtained in aqueous media. Anbar et al. (20) have reported that the rates of E2 hydrolysis for dl-serine phosphate and S_N2 hydrolysis for ethyl iodide are proportional to a contrived D_0 function ($H_- + \log C_{H_2O} - pK_{H_2O}$). Apparently the effect of the reaction medium on the rates of at least some S_N2 reactions is great enough so that extremes can be observed in the very nature of rate dependence on basicity parameters.

TABLE XXI

Methanolysis of .01215 M[a] 1-Chloropropane in .1118 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	$10^4\ k_1$ (min.$^{-1}$)
0	.01209	——	——
140	.01121	1.078	5.36
200	.01087	1.112	5.31
290	.01049	1.157	5.03
444	.00965	1.252	5.06
558	.00905	1.335	5.18
690	.00859	1.407	4.95
735	.00833	1.451	5.07
		average	5.14

a. The concentration of the stock solution was deduced from the average of infinite time chloride determinations for three runs.

TABLE XXII

Methanolysis of .01215 M[a] 1-Chloropropene in .2236 M $NaOCH_3$ at 76.0° C

time (min.)	n-PrCl (M)	C_0/C	$10^4 k_1$ (min.$^{-1}$)
0	.01209	———	———
120	.01079	1.120	9.45
180	.01013	1.193	9.80
270	.00933	1.295	9.58
421	.00803	1.505	9.71
670	.00647	1.868	9.33
715	.00599	2.018	9.82
		average	9.61

[a] The concentration of the stock solution was deduced from the average of infinite time chloride determinations for three runs.

TABLE XXIII

Methanolysis of .01215[a]M 1-Chloropropane in

.5464 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	$10^4\ k_1$ (min.$^{-1}$)
0	.01209	———	———
60	.01051	1.150	23.3
116	.00903	1.338	25.1
204	.00733	1.649	24.5
264	.00639	1.892	24.1
382	.00461	2.622	25.2
515	.00361	3.349	23.5
			average 24.3

a. The concentration of the stock solution was deduced from the average of infinite time chloride determinations for three runs.

TABLE XXIV

Methanolysis of .01215 M[a]1-Chloropropane in

1.157 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	$10^4\ k_1$ (min.$^{-1}$)
0	.01207	———	———
59	.00911	1.324	47.6
141	.00603	2.001	49.2
222	.00417	2.894	47.9
290	.00289	4.176	49.3
			average 48.5

a. The concentration of the stock solution was deduced from the average of infinite time chloride determinations for three runs.

TABLE XXV

Methanolysis of .01245 M[a] 1-Chloropropane in

2.208 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	$10^4\ k_1$ (min.$^{-1}$)
0	.01235	———	———
35	.00899	1.374	90.8
45	.00825	1.497	89.7
65	.00661	1.868	96.1
85	.00543	2.274	96.7
135	.00351	3.518	93.2
395	.00115	10.74	60.1
		average (excluding last result)	93.3

a. The initial concentration was deduced from the average of two infinite time chloride determinations (.01250 and .01240 M Cl^-).

TABLE XXVI

Methanolysis of .01210 M[a] 1-Chloropropane in

2.867 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	$10^4\ k_1$ (min.$^{-1}$)
0	.01200	———	———
30	.00856	1.401	112
42	.00718	1.671	122
50	.00650	1.846	122
60	.00586	2.048	119
86	.00398	3.015	128
115	.00290	4.138	123
		average	121

a. The initial concentration was deduced from a single infinite time chloride determination.

TABLE XXVII

Methanolysis of .01215 M[a] 1-Chloropropane in 4.047 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	$10^4\ k_1$ (min.$^{-1}$)
0	.01215	——	——
30	.00745	1.631	163
58	.00443	2.742	174
89	.00227	5.352	188
150	.00193	6.295	123
	average (excluding last result)		175

a. The concentration of the stock solution was deduced from the average of infinite time chloride determinations for three runs.

TABLE XXVIII

Methanolysis of .01190 M[a] 1-Chloropropane in 4.164 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	$10^4\ k_1$ (min.$^{-1}$)
0	.01178	——	——
27	.00740	1.592	172
35	.00578	2.038	203
46	.00452	2.633	210
70	.00290	4.103	202
107	.00160	7.437	187
		average	195

a. The initial concentration was deduced from a single infinite time chloride determination.

TABLE XXIX

Methanolysis of .01098 M[a] 1-Chloropropane in

4.681 M $NaOCH_3$ at 76.0°C

time (min.)	n-PrCl (M)	C_0/C	10^4 k_1 (min.$^{-1}$)
0	.01086	———	———
25	.00686	1.583	184
36	.00478	2.272	228
45	.00370	2.935	239
60	.00262	4.145	237
81	.00178	6.101	223
107	.00100	10.86	223
		average (excluding first result)	230

a. The initial concentration was deduced from the average of two infinite time chloride determinations (.01092 and .01104 M Cl^-).

TABLE XXX

First-and Second-Order Rate Constants for the Methanolysis of 1-Chloropropane in .11 to 4.7 M $NaOCH_3$ at 76.0°C

$NaOCH_3$ (M)	10^4 k_1 (min.$^{-1}$)	10^3 k_2 (1 M^{-1} min.$^{-1}$)
.1118	5.14	4.60
.2236	9.61	4.30
.5464	24.3	4.45
1.157	48.5	4.19
2.208	93.3	4.22
2.876	121	4.22
4.047	175	4.32
4.164	195	4.68
4.681	230	4.91
		average 4.43 (σ = .25)

G. Methanolysis of Phenylethyl Chloride

More O'Ferrall and Ridd (19) have shown that the rate of E2 methanolysis of phenylethyl chloride at 59.7°C is not proportional to the concentration of sodium methoxide; the second-order rate constants increased constantly in .235 to 4.28 M $NaOCH_3$ solution. Of interest is a comparison of D_0 with log k_1 using the data from Table XXXI. Figure XIII shows a linear relationship, but the slope of .76(σ = .02) indicates that the reaction is not correlated by D_0.

TABLE XXXI

Methanolysis of Phenylethyl Chloride at 59.7°C

$NaOCH_3$ (M)	10^5 k_2	-log k_1	$-D_0$
.235	3.26	5.116	-.53
.840	3.60	4.520	.22
1.71	5.14	4.056	.72
2.38	7.02	3.777	1.14
2.88	9.05	3.583	1.38
3.12	10.10	3.502	1.50
3.71	13.30	3.307	1.81
4.28	18.57	3.100	2.18

Since the reaction is not correlated by either D_0 or the concentration of sodium methoxide, it is of interest to determine what modification of the present treatment will give a good correlation (where the slope of a plot of log k_1 vs.

the parameter gives a straight line having a slope of 1.00).

If the argument (18,19), that a difference in the solvation of reactants and the transition state is responsible for the dependence of reaction rate on the medium is valid, it is reasonable that (1) an E1CB reaction is correlated by H_- because methoxide ion is completely neutralized before the rate-determining step, (2) an E2 or S_N2 reaction could be proportional to D_0 because methoxide ion loses solvent, possibly by a preequilibrium process, before new bond formation is completed and (3) an E2 or S_N2 reaction could be proportional to the concentration of methoxide ion because solvent is retained in the activated complex of the rate-determining step. It is then possible to visualize the situation where a reaction is dependent on a function somewhere between H_- and the concentration of methoxide ion, where some fraction, or all, of the bound methanol is lost in forming the activated complex. A function of the form $\boxed{D_0 - (4-x) \log a_{CH_3OH}}$, or $\boxed{D_0 - (3-x) \log C_{CH_3OH}}$ would compress the D_0 scale and increase the slope of a log k_1 vs. basicity function plot, as x is decreased. A comparison of the slopes obtained for plots of the various functions (for all whole number values of x) vs. log k_1, using a least squares procedure, is shown in Table XXXII.

TABLE XXXII

A Correlation of Functions Based on n Solvated Methoxide Ions with log k_1 for Phenylethyl Chloride

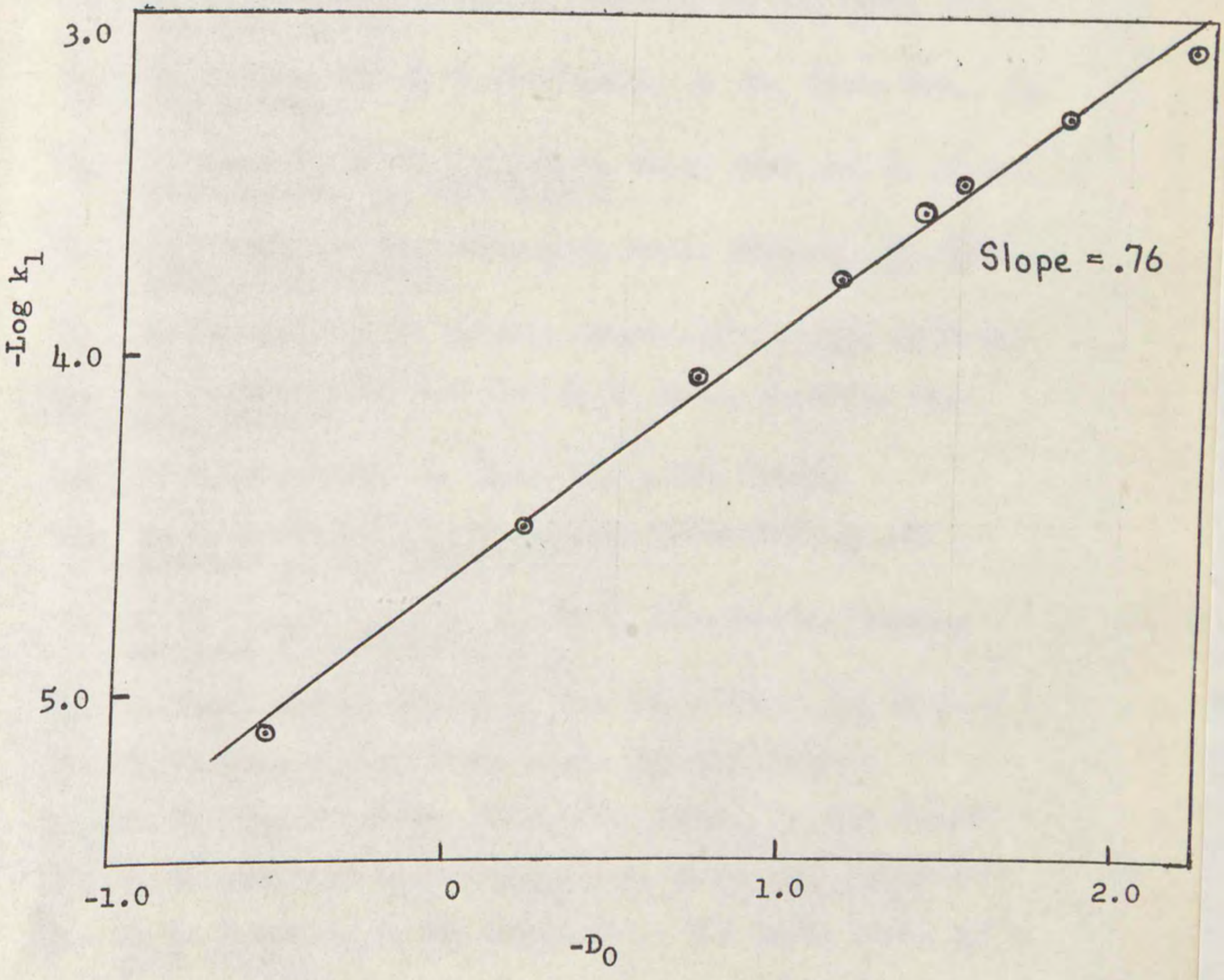
Functions	CH_3OH Molecules Released Before the Rate-Determining Step	Slope
H_-	4, or 5	curved
D_0	3, or 4	.76, σ = .01
D_0 - Log C_{CH_3OH}	2	.91, σ = .01
D_0 - 2 Log C_{CH_3OH}	1	1.13, σ = .04
D_0 - Log a_{CH_3OH}	3	.87, σ = .02
D_0 - 2 Log a_{CH_3OH}	2	1.01, σ = .02
D_0 - 3 Log a_{CH_3OH}	1	1.21, σ = .06

The rate is apparently best correlated by (D_0 - 2 log a_{CH_3OH}), the implication being that one-half of the bound methanol is lost during the formation of the activated complex.

This simple explanation for the dependence of reaction rate on a basicity function is meaningless unless a tri- or tetra-solvated methoxide ion can be shown to exist by some analytical measurement. The fact that the donor function can be explained by a solvated methoxide ion, does not prove its existence. Studies of reaction rate in concentrated methanolic sodium methoxide solution have only begun. Considerable work is required in order to begin answering many of the questions concerning dependence of reaction rate on basicity parameters.

Figure XIII

Rate of Methanolysis of Phenylethyl Chloride at 59.7°C as a Function of D_0



BIBLIOGRAPHY

1. M. A. Paul and F. A. Long, Chem. Rev., 57, 1 (1957).

2. G. Schwarzenbach and R. Sulzberger, Helv. Chem. Acta, 27, 348 (1944).

3. J. T. Edward and I. C. Wang, Cand. J. Chem., 40, 399 (1962).

4. N. C. Deno, J. Am. Chem. Soc., 74, 2039 (1952).

5. C. H. Langford and R. L. Burwell, J. Am. Chem. Soc., 82, 1503 (1960).

6. R. Stewart and J. P. O'Donnell, J. Am. Chem. Soc., 84, 494 (1962).

7. R. Stewart, J. P. O'Donnell, D. J. Cram and B. Rickborn, Tetrahedron, 18, 917 (1962).

8. R. Schall and G. Lambert, J. Chim. Physics, 59, 1151, 1164, 1170 (1962).

9. G. Lambert and R. Schaal, Compt. Rend., 255, 2256 (1962).

10. R. A. More O'Ferrall and J. H. Ridd, J. Chem. Soc., 5030 (1963).

11. C. H. Rochester, J. Chem. Soc., 676 (1965).

12. J. T. MacGregor, B. S. Thesis, Union College and University, May 1965.

13. K. N. Bascombe and R. P. Bell, Discussions Faraday Society, 24, 158 (1957).

14. G. Yagil and M. Anbar, J. Am. Chem. Soc., 85, 2376 (1963).

15. C. Perrin, J. Am. Chem. Soc., 86, 256 (1964).

16. E. M. Arnett, Progr. Phys. Org. Chem., 1, 233 (1963).

17. F. A. Long and M. A. Paul, Chem. Rev., 57, 935 (1957).

18. J. F. Bunnett, J. Am. Chem. Soc., 83, 4956, 4968, 4973, 4978 (1961).

19. R. A. More O'Ferrall and J. H. Ridd, J. Chem. Soc., 5035 (1963).

20. M. Anbar, B. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, J. Am. Chem. Soc., 85, 2380 (1963).

21. G. F. Freeguard, R. B. Moodie, and D. J. G. Smith, J. Appl. Chem., 15 (1965).

22. J. H. Ridd, Chemistry and Industry, 1268 (1957).

23. M. F. L. Allison, C. Bamford and J. H. Ridd, Chemistry and Industry, 718 (1958).

24. J. H. Hine, "Physical Organic Chemistry", McGraw Hill, Inc., New York, 1962, p. 484.

25. C. A. Vernon, J. Chem. Soc., 4462 (1954).

26. "Beilsteins Handbuch Der Organischen Chemie", 7, Berlin, 1925, p. 236.

27. "Tables for Identification of Organic Compounds", The Chemical Rubber Co., Cleveland, 1964, p. 87.

28. "Beilsteins Handbuch Der Organischen Chemie", 7, Berlin, 1925, p. 235.

29. H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley Inc., New York, 1962, p. 173.

30. N. B. Colthup, L. H. Daly and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964, p. 459.

31. Catalog of Infrared Spectral Data, Serial No. 577, American Petroleum Research Project 44, Chemical Thermodynamic Properties Center, Texas A and M University, Texas.

32. J. A. Magnuson, G. E. Silicone Products Dept. private communication.

33. P. J. Wheatley, J. Chem. Soc., 4270 (1960).

34. Zbigniew Kecki and Jan Witanowski, Roczniki Chem., 37, 888 (1963).
C. A., 60, 7592 (1964).

35. R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, New York, 1959, p. 43.