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The Hydroxylation Equilibrium Constant for 2,4 Dichlorobenzaldehyde at Various Temperatures

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THE HYDROXYLATION EQUILIBRIUM CONSTANT
FOR 2,4 DICHLOROBENZALDEHYDE AT VARIOUS TEMPERATURES

by

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Kevork V. Nahabedian

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TABLE OF CONTENTS

LIST OF TABLES AND GRAPHS

SUMMARY

The primary objective of this work was to examine the temperature dependence of dissociation constants of hydroxylated substituted benzldehydes. The equilibrium of 2,4 dichlorobenzaldehyde in aqueous sodium hydroxide solutions has been studied at 35°C with varying hydroxide ion concentrations ($[OH^-]$).

$$\text{I} \quad + OH^- \quad \xrightarrow{\text{Fast}} \quad \text{II}$$
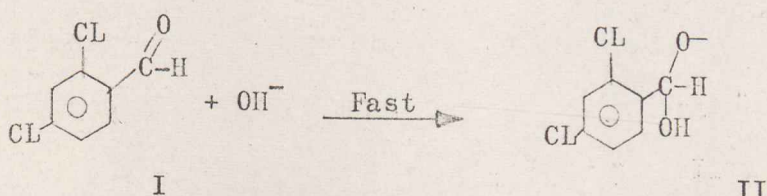
Timed readings of the absorbancy of the indicator base solutions were made on the Beckman D.U. Spectrophotomerer or on the Perkin-Elmer recording spectrophotometer. Plots of absorbance vs. time were extrapolated to zero time and these absorbancies were related to the ratio $[II] / [I]$. James MacGregor (1) had previously developed the expression:

$$\frac{[II]}{[I]} = \frac{[DOH]}{[D]} = \frac{E_D - E_b}{E_b - E_{DOH^-}}$$

where D refers to the free indicator, I, DOH^- refers to the hydroxylated indicator, II, and E_b refers to the absorptivity of a given basic solution of the indicator.

A plot of log $\frac{E_D - E_b}{E_b - E_{DOH^-}}$ - log $[OH^-]$ vs. $[OH^-]$ extrapolated to zero base concentration gave a value of pK_{DOH^-} for the dissociation of the hydroxylated aldehyde. The pK_{DOH^-} value may easily be related to the dissociation constant by the simple expression:

$$pK_{DOH^-} = \log \frac{1}{K_{DOH^-}} = - \log K_{DOH^-}$$

The standard enthalpy, ΔH°, and the standard entropy, ΔS°, for the reaction were determined for equations (1) and (3):

$$(\text{I}) \quad \log K_{(DOH^-)_2} / K_{(DOH^-)_1} = \frac{\Delta H^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$(\text{II}) \quad \Delta S^\circ = 2.303 \, R \log K_{(DOH^-)_1} + \frac{\Delta H^\circ}{T_1}$$

$$(\text{III}) \quad \Delta S^\circ = 2.303 \, R \log K_{(DOH^-)_2} + \frac{\Delta H^\circ}{T_2}$$

in which $K_{(DOH^-)_2}$ equaled the dissociation constant at 35°C, $K_{(DOH^-)_1}$ represented the dissociation constant at 25°C, T_1 referred to 25°C or 298°K, and T_2 equaled 35°C or 308°K. The determined value of K_{DOH^-} at 35°C is .776 and the values of ΔH° and ΔS° are -5.28 Kcal mole^{-1} and -17.65 entropy units, respectively.

HISTORY AND THEORY

The H_o acidity function was proposed by Hammett and Deyrup (2) in 1932. This function dealt with the equilibrium:
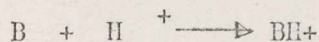
$$B + H^+ \longrightarrow BH+$$

where B is neutral indicator base and BH+ is its conjugated acid. The dissociation constant for the equilibrium was expressed as the following ratio of activities:

$$K_{BH+} = \frac{A_B \, A_{H+}}{A_{BH+}}$$

Hammett and Deyrup defined the H_o function as:

$$H_o = -\log A_{H+} \cdot \frac{f_B}{f_{BH+}} = pK_{BH+} - \log \frac{[BH+]}{[B]}$$

in which f_B and f_{BH+} are activity coefficients. The H_o function allowed quantative measurements of acidity to be made in strongly acid media outside the pH range.

Westheimer and Kharasch (3) developed a function very similar to the H_o function. The function is called the J_o function and deals with the equilibrium:

$$ROH + H+ \longrightarrow R+ + H_2O$$
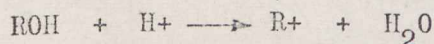
in which ROH is an indicator base. The J_o function was defined analogous to the H_o function as follows:

$$J_o = -\log \frac{A_{H+} - A_{ROH}}{A_{H_2O} - f_{R^+}} = pK_{ROH} - \log \frac{[R+]}{[ROH]}$$

James MacGregor (1) combined the ideas of Hammett and

Deyrup, and Westheimer and Kharasch with those of his own to

develop the D_o^1 function for aqueous sodium hydroxide solutions,

the D_o^1 function deals with the equilibrium:

$$D + OH^- \; - \; DOH^-$$
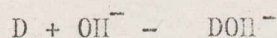
in which D is a neutral Lewis acid indicator and DOH^- is the

hydroxylated form of the indicator.

MacGregor defined the D_o function in a manner comparable

to Hammett and Deyrup's definition of the H_o function as

follows:

$$K_{DOH^-} = \frac{A_D \; A_{OH^-}}{A_{DOH}} = \frac{[D]}{[DOH]} \cdot \frac{f_D \; A_{OH^-}}{f_{DOH^-}}$$

$$A_{OH^-} \cdot \frac{f_D}{f_{DOH^-}} = K_{DOH^-} \cdot \frac{[DOH^-]}{[D]}$$

$$D_o^1 = -\log A_{OH^-} \cdot \frac{f_D}{f_{DOH^-}} = -\log K_{DOH^-} - \log \frac{[DOH^-]}{[D]}$$

$$(IV) \quad D_o^1 = pK_{DOH^-} - \log \frac{[DOH^-]}{[D]}$$

The method for evaluating pK_{DOH^-} can be realized by

considering its definition:

$$pK_{DOH^-} = \log \frac{[DOH^-]}{[D] \; [OH^-]} + \log \frac{f_{DOH^-}}{f_D \; f_{OH^-}}$$

MacGregor states, "the concentration of the indicator is always very small and activity coefficients approach unity at zero concentration " (1). He presented an altered form for the definition of pk_{DOH^-} :

$$pk_{DOH^-} = \lim_{[OH^-] \to 0} \left[\log \frac{[DOH^-]}{[D]} - \log [OH^-] \right]$$

For those indicators that are partically hydroxylated in base concentrations of $0 - 2\,M$, a plot of $\log \frac{[DOH^-]}{[D]} - \log [OH^-]$ vs. $[OH^-]$ extrapolated to zero $[OH^-]$ yielded a value for pK_{DOH^-}.

The last step in determining a pK_{DOH^-} value is the evaluation of the indicator ratio $\frac{[DOH^-]}{[D]}$ by the use of ultraviolet spectroscopy. The total absorbancy of any solution containing a partically hydroxylated form of an indicator can be expressed as follows:

$$A_b = E_{ArCHO}\, C_{ArCHO} + E_{ArCHO^-(OH)}\, C_{ArCHO^-(HO)} + E_{ArCH_2OH}$$

$$C_{ArCH_2OH} + E_{ArCO_2^-}\, C_{ArCO_2^-} + E_{ArC(HO^-)O}\, C_{ArC(HO^-)O} +$$

$$E_{ArCHO_2^-}\, C_{ArCHO_2^-}$$

where E is the molar absorptivity, C is the concentration, $E_{ArCHO}\, C_{ArCHO} = A_D$ which represents the absorbancy due to the free form of the indicator, and $E_{ArCHO^-(OH)}\, C_{ArCHO^-(OH)} = A_{DOH^-}$ which equals the absorbancy due to the hydroxylated form of the indicator. The equation $(E_D\, C_D = A_D)$ is a slightly modified form of the Beer-Lambert law. The concentration of the indicator was kept around $10^{-4}\,M$ to insure the validity of Beer's Law.

E_{ArCH_2OH} C_{ArCH_2OH} and $E_{ArCO_2^-}$ $C_{ArCO_2^-}$ are

considered to be negligible and $E_{ArC(OH)O^-}$ $C_{ArC(OH)O^-}$ and

$E_{ArCHO_2^-}$ $C_{ArCHO_2^-}$ are considered to make only a small

contribution to the total absorbancy up to a 50% change from

the absorbancy reading in neutral solutions. Thus the

absorbancy of a given basic solution of the indicator is

given by:

$$A_b = A_D + A_{DOH^-} = E_D C_D + E_{DOH^-} C_{DOH^-}$$

$$A_b = ([D] + [DOH^-]) E_b$$

in which E_b is the molar absorptivity of the entire solution.

Substituting for A_b, separation of variables, and combining

of terms leads to the expression of the indicator ratio as

the appropriate ratio of molar absorptivities.

$$E_b [DOH^-] - E_{DOH^-} [DOH^-] = E_D [D] - E_b [D]$$

$$E_b - E_{DOH^-} [DOH^-] = (E_b - E_D) [D]$$

(V)
$$\frac{[DOH^-]}{[D]} = \frac{E_D - E_b}{E_b - E_{DOH^-}}$$

The molar absorptivities of the various basic indicator

solutions were determined and the corresponding indicator

ratio was determined.

The pK_{DOH^-} value was transformed into K_{DOH^-} by the

expression:

$$pK_{DOH^-} = \log {^1/K_{DOH^-}} = - \log K_{DOH^-}$$

ABSORBTION MEASUREMENTS

MacGregor (1) developed a group of eight different
substituted benzaldehyde indicators that would be of use
when dealing with absorbancies of sodium hydroxide solutions.
The sodium hydroxide solutions used had a maximum absorbtion
below 220 - 230 mμ whose magnitude depended on the hydroxide
ion concentration. The indicator used absorbed in another
region of the ultraviolet spectrum. The 2,4 dichlorobenzaldehyde
used in this project had a maximum absorbtion at 264 mμ.
The indicators did not undergo the Cannizzaro reaction to any
appreciable extent. Nevertheless, extrapolations to zero
time of absorbancy vs. time plots were made to counteract
slight variations in absorbtion readings with time possibly
caused by the Cannizzaro reaction.

2,4 dichlorobenzaldehyde was purified by recrystallization
from ethanol until a melting point of 71°C was observed. Aldehyde
solutions were kept under a nitrogen atmosphere because of
oxidizing action of air on aldehydes. All indicator solutions
were kept stoppered and nitrogen gas was bubbled through the
solution if it was exposed to the air. Indicator solutions
were prepared directly from the solid form on the day of
intended use. Water, deaereated by boiling, was used in the
preparation of all solutions.

The method of preparing the indicator solutions was
proposed by Gedansky (4) for indicators that are slightly
soluble in water. Generally, this method included the following
steps.

1. The preparation of a 1×10^{-2} M solution of 2,4 dichlorobenzaldehyde in methanol. The solid indicator was weighed on an analytical balance.

2. A 10^{-3} M indicator solution containing 10% methanol was prepared by diluting 10 ml of the 10^{-2} M solution to 100 ml with water.

3. Ten milliliters of the 10^{-3} M 2,4 dichlorobenzaldehyde solution was added to 10 ml of deaereated and equilibrated in a constant temperature water bath at 35° for 20 minutes. One hundred milliliters of sodium hydroxide solution was equilibrated in a like manner. Thermally equilibrated solutions were mixed to facilitate constant absorbancy readings. Water jackets were attached to both the Beckman D.U. and to the Perkin-Elmer 202 spectrophotometers to insure a temperature of 35 ±1°C during the timed measurements of absorbance. After the base and indicator solutions had come to temperature, they were mixed and an aliquot was taken for absorbancy measurements.

FIGURE 1.

Absorbancy vs Time for 1.471M NaOH Soln.

.280 → Zero Extrapolation Value (.280)

Absorbancy

Time (min)
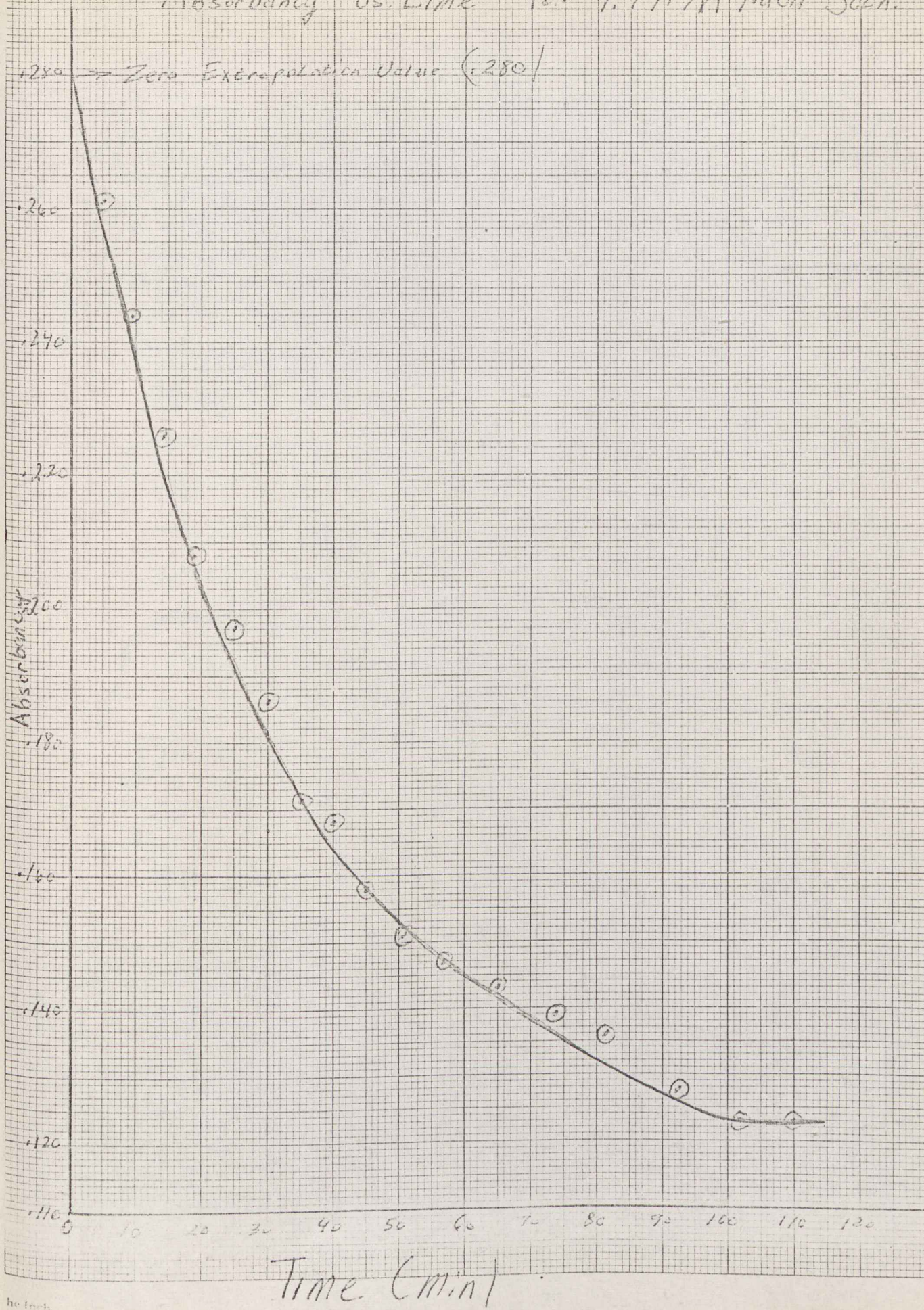
DETERMINATION OF K_{DOH^-}, ΔH° AND ΔS°

The values of E_D have been determined for 35°C and were lower in magnitude than at 25°C. An average value of E_D was used in the calculations since a slight variation of A_D readings was observed for different concentrations of the indicator. E_{DOH^-} was not measured at 35°C, but instead we have assumed that E_{DOH^-} has the same value as at 25°C. This assumption wasn't serious because even if E_{DOH^-} is neglected completely, the magnitude of $E_b - E_{DOH^-}$ for the measurements made would be affected by at most 5%. The determination of E_b involved a solvent correction that varied with the concentration of sodium hydroxide. The solvent corrections necessary were obtained from MacGregor's solvent correction curve for 2,4 dichlorobenzaldehyde (1). Thus E_b was obtained from the following equation:

$$E_b = \frac{A_b - \text{solvent correction}}{[OH^-]}$$

Table 2 has the calculation of $\log \frac{[DOH^-]}{[O]}$.

The value of pK_{DOH^-} from the plot shown in figure 3 of $\log \frac{[DOH^-]}{[D]} - \log [OH^-]$ vs. $[OH^-]$ extrapolated to zero base concentration gave a pK_{DOH^-} value of 0.75.

$$pK_{DOH^-} = \log K_{DOH^-}$$

$$K_{DOH^-} = .177 \text{ at } 35°C$$

MacGregor found a pK_{DOH^-} value of 0.98 at 25°C from a similar plot. The corresponding value at 25°C for K_{DOH^-} is 0.105.

The work of Bunnett, Miles, and Nahabedian (6) with 2,6 dihalobenzaldehydes suggests that at 35°C the K_{DOH^-} value would be less than that at 25°C.

The reason for this discrepancy was obvious when MacGregor's graph of log $\frac{[DOH^-]}{[D]}$ - log $[OH^-]$ vs $[OH^-]$ at 25°C was compared to our plot at 35°C. MacGregor's plot showed an almost linear array of points, through which a linear extrapolation to zero hydroxide ion concentration was easily made to determine pK_{DOH^-}. Figure 3 shows that at 35°C the scattering of plotted points makes it difficult to make a linear extrapolation. A value of pK_{DOH^-} could have been selected almost arbitrarily. The value 0.75, would have an error of at least ± 0.25 units or 33%.

If activity coefficients are neglected, K_{DOH^-} can be expressed as:

$$K_{DOH^-} = \frac{[ArCHO]\ [OH^-]}{[ArCHO^-\ OH]}$$

Since

$$\frac{[ArCHO^-\ (OH)]}{[ArCHO]} = \frac{E_{ArCHO} - E_{OH^-}soln.}{E_{OH^-}soln - E_{ArCHO^-}(OH)} = \frac{E_D - E_b}{E_b - E_{DOH^-}}$$

then

$$K_{DOH^-} = \frac{E_b - E_{DOH^-}}{E_D - E_b}\ [OH^-]$$

and a plot of $\dfrac{E_D - E_b}{E_b - E_{DOH^-}}$ vs $[OH^-]$ would have the slope

K_{DOH^-} and the intercept zero.

The values of K_{DOH^-} at 35°C and 25°C were computed from the plots shown in figures 4 and 5, respectively, and the values obtained were 0.78 and 1.04 respectively.

The relative magnitudes of these values are qualitatively
in agreement with the demonstrated temperature dependence
of hydroxylation equilibrium constants (6).

The evaluation of the standard enthalpy (ΔH°) and the
standard entropy (ΔS°) for the dissociation was made using
the relationships

$$2.303 \; RT \; \log K_{DOH^-} = -\Delta F^\circ = -\Delta H^\circ + T\Delta S$$

and

$$\log K_{DOH^-} = -\frac{\Delta H^\circ}{2.303 \; RT} + \frac{\Delta S^\circ}{2.303R} \; .$$

If we assumed that ΔH° is insensitive to temperature, then
a plot of $\log K_{DOH^-}$ vs. $1/T$ is linear and has the slope $-\Delta H^\circ/2.303R$
and the intercept $\Delta S^\circ/2.303R$. This plot would be of primary
use for a series of K_{DOH^-} values at different temperatures.

When dealing with only two K_{DOH^-} values, the following
modified equations must be used to find ΔH:

$$(I) \quad \log K_{(DOH^-)_2} / K_{(DOH^-)_1} = \frac{\Delta H^\circ}{2.303 \; R} \left(1/T_1 - 1/T_2 \right)$$

then, at T_1:

$$(II) \; \Delta S^\circ = 2.303 \; R \; \log K_{(DOH^-)_1} + \frac{\Delta H^\circ}{T_1}$$

and at T_2:

$$(III) \; \Delta S^\circ = 2.303R \; \log K_{(DOH^-)_2} + \frac{\Delta H^\circ}{T_2}$$

Values of ΔH° and ΔS° previously found for similar
reactions with 2,6 dihalobenzaldehydes are in the neighborhood
of -8 Kcal mole^{-1} and -21 eu mole^{-1} respectively (6).

The H° value from this work is -5.28 Kcal mole^{-1} and S° is -14.65 eu/mole. An error of at least $\pm 25\%$ must be introduced in our $\triangle H^{\circ}$ and $\triangle S^{\circ}$ values because they are accurate to only one significant figure. The large error factor has arisen because only two K_{DOH^-} values were used in the computation of $\triangle S^{\circ}$ and $\triangle H^{\circ}$. If $\triangle H^{\circ}$ and $\triangle S^{\circ}$ measurements were made for similar reactions at a series of different temperatures, the $\triangle H^{\circ}$ and $\triangle S^{\circ}$ values would probably approach more closely the previously measured values.

TABLE 1. DATA FOR 2,4 DICHLOROBENZALDEHYDE

λ_{max} = 264 mu   T = 35°C

Sol No.	Indicator Concentration	OH⁻ Molarity	Time		Absorbancy
0	0.5521×10^{-4} M	0	1 1/2	min	.662
			4 1/4	"	.662
			7 3/4	"	.656
			11 1/2	"	.652
			15 1/2	"	.648
			20 3/4	"	.642
			71 1/4	"	.618
1	0.5521×10^{-4} M	0.05146	2	"	.665
			4	"	.665
			6 1/2	"	.662
			9 1/4	"	.662
			12 3/4	"	.652
			14 3/4	"	.652
			18 1/4	"	.644
			23 1/2	"	.638
			27 1/2	"	.623
			31 3/4	"	.623
0^1	0.5545×10^{-4} M	0	1	"	.631
			3	"	.631
			6 1/2	"	.631
			9	"	.631
			11	"	.629
2	0.5545×10^{-4} M	0.07788	3/4	"	.514
			5	"	.514
			10	"	.508
			15	"	.491
			20	"	.480
			25	"	.480
3	0.5545×10^{-4} M	.1016	1	"	.541
			5	"	.541
			10	"	.541
			15	"	.539
			20	"	.539

TABLE 1. (Continued)

Sol No.	Indicator Concentration	OH$^-$ Molarity	Time		Absorbancy
0^{11}	0.5541×10^{-4} M	0	1 1/2	min	.744
			2 1/2	"	.744
			5	"	.744
			10	"	.744
			16	"	.735
			21	"	.735
4.	0.5541×10^{-4} M	0.1415	1 1/2	"	.721
			4	"	.721
			9 1/4	"	.719
			15	"	.709
			20 3/4	"	.700
			24 1/4	"	.696
5	0.5545×10^{-4} M	0.1687	1	"	.462
			5	"	.462
			10	"	.462
			15	"	.460
			20	"	.459
0^{111}	0.5543×10^{-4} M	0	1 1/4	"	.657
			4 1/2	"	.658
			7 3/4	"	.658
			11 1/2	"	.655
			15 3/4	"	.648
6	0.5543×10^{-4} M	0.2042	1	"	.641
			3	"	.643
			5 3/4	"	.638
			9	"	.633
			12	"	.628
			15 1/4	"	.624
			17 1/2	"	.617
			20 1/4	"	.609
			25 1/4	"	.601
			29	"	.597
			36 3/4	"	.592
			44 1/4	"	.582
0^{1111}	0.5541×10^{-4} M	0	1	"	.640
			2 1/2	"	.640
			5 1/2	"	.640
			8 1/2	"	.630
			10 3/4	"	.630
			13 1/2	"	.615
			16 1/2	"	.630
			21	"	.612
			25 1/4	"	.611

TABLE 1. (Continued)

Sol No.	Indicator Concentration	OH⁻ Molarity	Time		Absorbancy
7	0.5541×10^{-4} M	0.2377	1	min	.545
			3	"	.544
			5	"	.543
			7 3/4	"	.538
			10 3/4	"	.535
			13	"	.531
			16 1/4	"	.526
			20	"	.522
			24 1/2	"	.519
			28 1/4	"	.513
			32 1/2	"	.508
8	0.5545×10^{-4} M	0.3780	1	"	.544
			2 3/4	"	.544
			4 1/2	"	.543
			6 3/4	"	.543
			9	"	.540
			12	"	.540
			15 1/2	"	.540
9	0.5545×10^{-4} M	0.4521	1	"	.512
			2 3/4	"	.514
			6	"	.520
			9	"	.528
			12	"	.528
			15	"	.528
10	0.5545×10^{-4} M	0.6009	1	"	.432
			5	"	.432
			10	"	.432
			15	"	.431
			20	"	.416

FIGURE 2

Extrapolation to Zero Time

(displacement vs time)

#10   #2   #7   #3   #4   #6
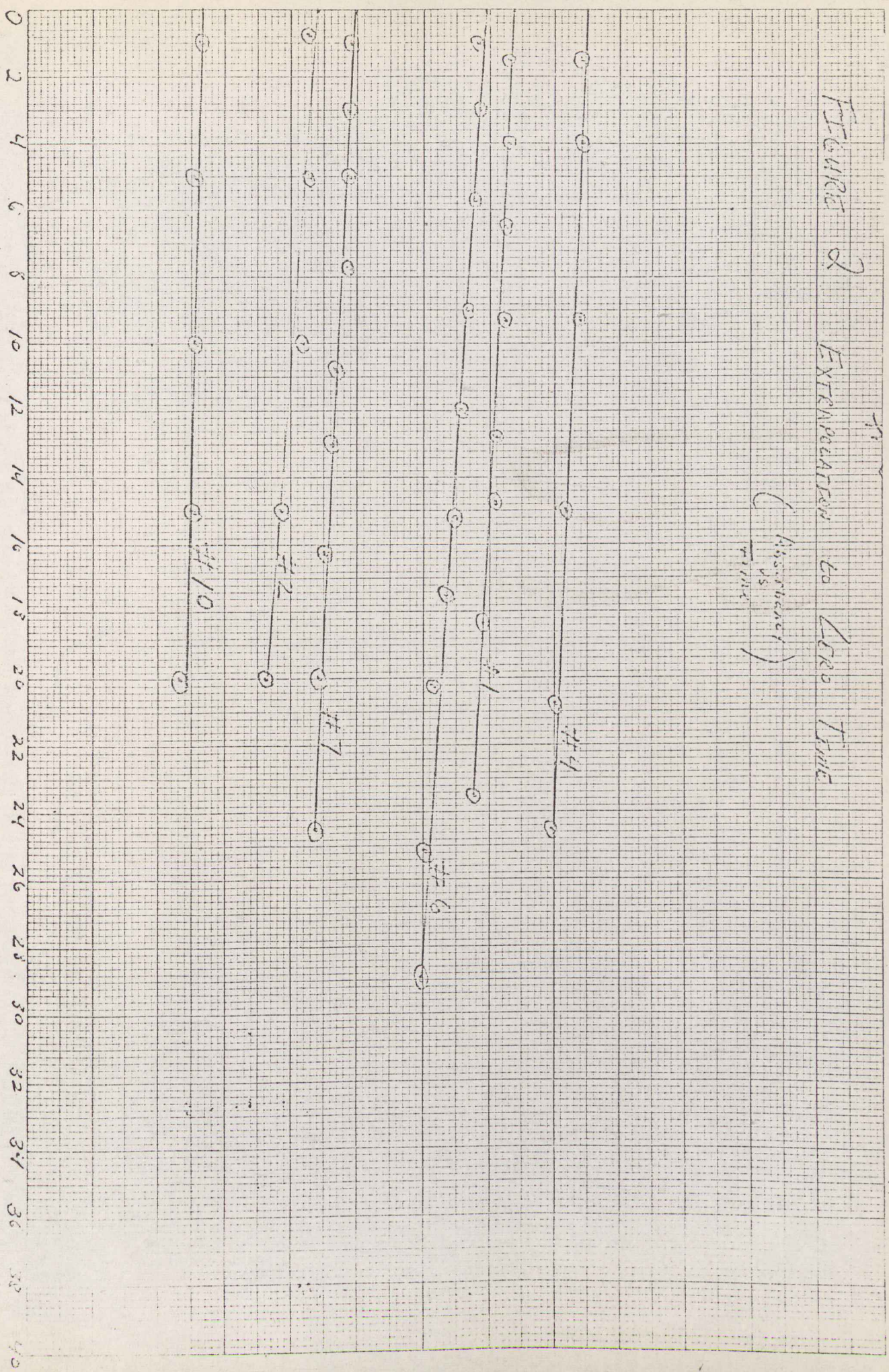
TABLE 2. CALCULATION OF LOG (INDICATOR RATIO) AND LOG (N_a OH MOLARITY)

λ max = 264 mμ E_{DOH^-} = 634 E_D = 11529

Sol No.	Molarity	Solvent Correction	A_r	E_b	$E_D - E_b$	$E_b - E_{DOH^-}$	$\dfrac{E_D - E_b}{E_b - E_{DOH^-}}$	$\log \dfrac{E_D - E_b}{E_b - E_{DOH^-}}$	$\log\ OH^-$
1	.0515	0.029	.6698	11775	-246	11145	-.0221	+1.656	-1.290
2	.0781	0.029	.5210	8875	2654	8245	.322	- .492	-1.108
3	0.102	0.030	.5410	9241	2288	8611	.266	- .575	- .930
4	0.142	0.030	.7250	12480	-1051	11950	.0880	-1.055	- .851
5	0.169	0.030	.4620	7800	3729	7170	.520	- .284	- .774
6	0.205	0.030	.6470	11144	385	10514	.0366	-1.436	- .690
7	0.238	0.030	.5490	9389	2140	8759	.244	- .612	- .525
8	0.379	0.033	.5440	9289	2240	8659	.259	- .586	- .422
9	0.453	0.035	.5280	8998	2531	8368	.302	- .520	- .345
10	0.601	0.505	.4330	7450	4079	6820	.598	- .223	- .222

TABLE 3.   DETERMINATION OF pK BY DIRECT EXTRAPOLATION

Sol No.	MOLARITY	$\text{Log } [D] - \text{Log}[OH^-]$ $\frac{[DOH^-]}{}$
1	0.05146	+ 3.946
2	0.07812	+ 1.600
3	0.1021	+ .355
4	0.1415	− .204
5	0.1687	+ .490
6	0.2049	− .746
7	0.2377	− .087
8	0.3789	− .164
9	0.4531	− .175
10	0.6009	− .001

TABLE 3.   DETERMINATION OF pK BY DIRECT EXTRAPOLATION

FIGURE 3   DETERMINATION of pK_{DH^-} by DIRECT EXTRAPOLATION

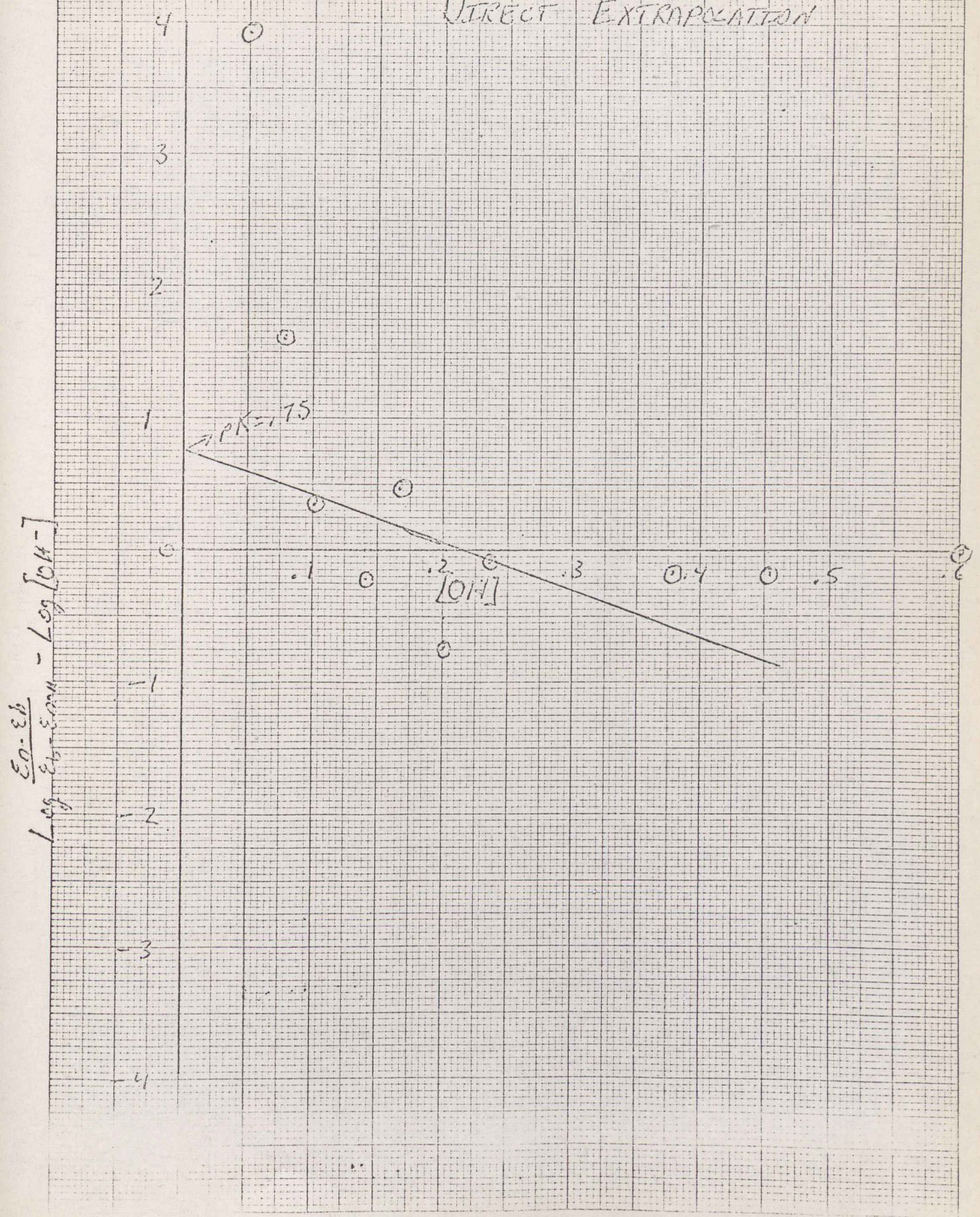FIGURE 4

DETERMINATION OF K_{OOH^-} VALUE AT 35°C
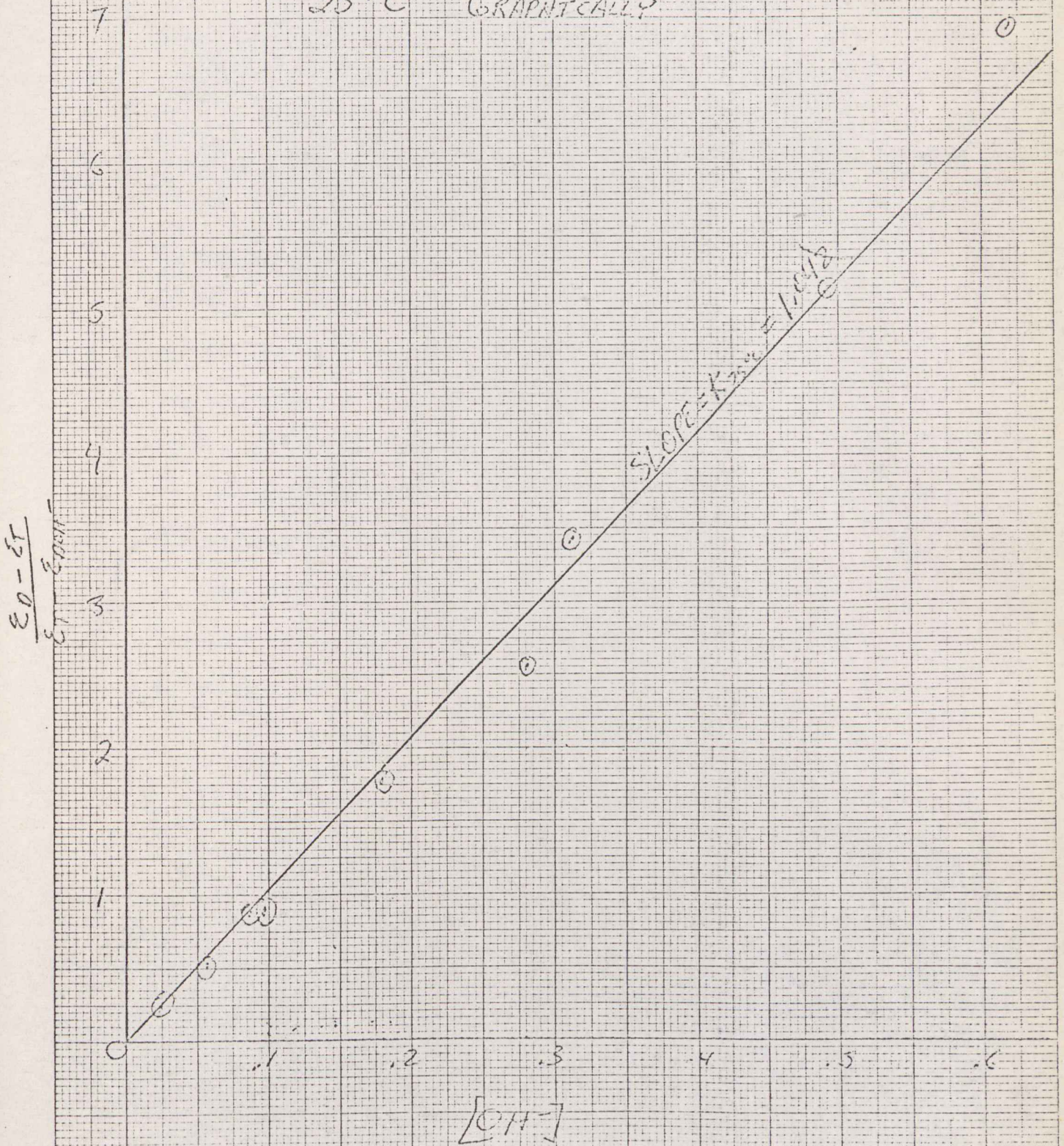
GRAPHICALLY

$\dfrac{E_b}{E_{OOH^-}}$
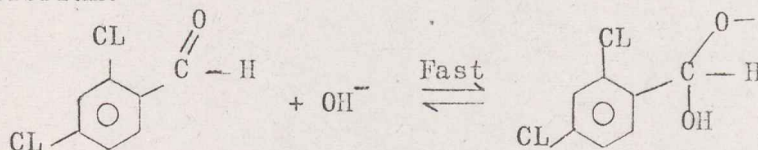
SLOPE = $K_{35°C}$ = .778
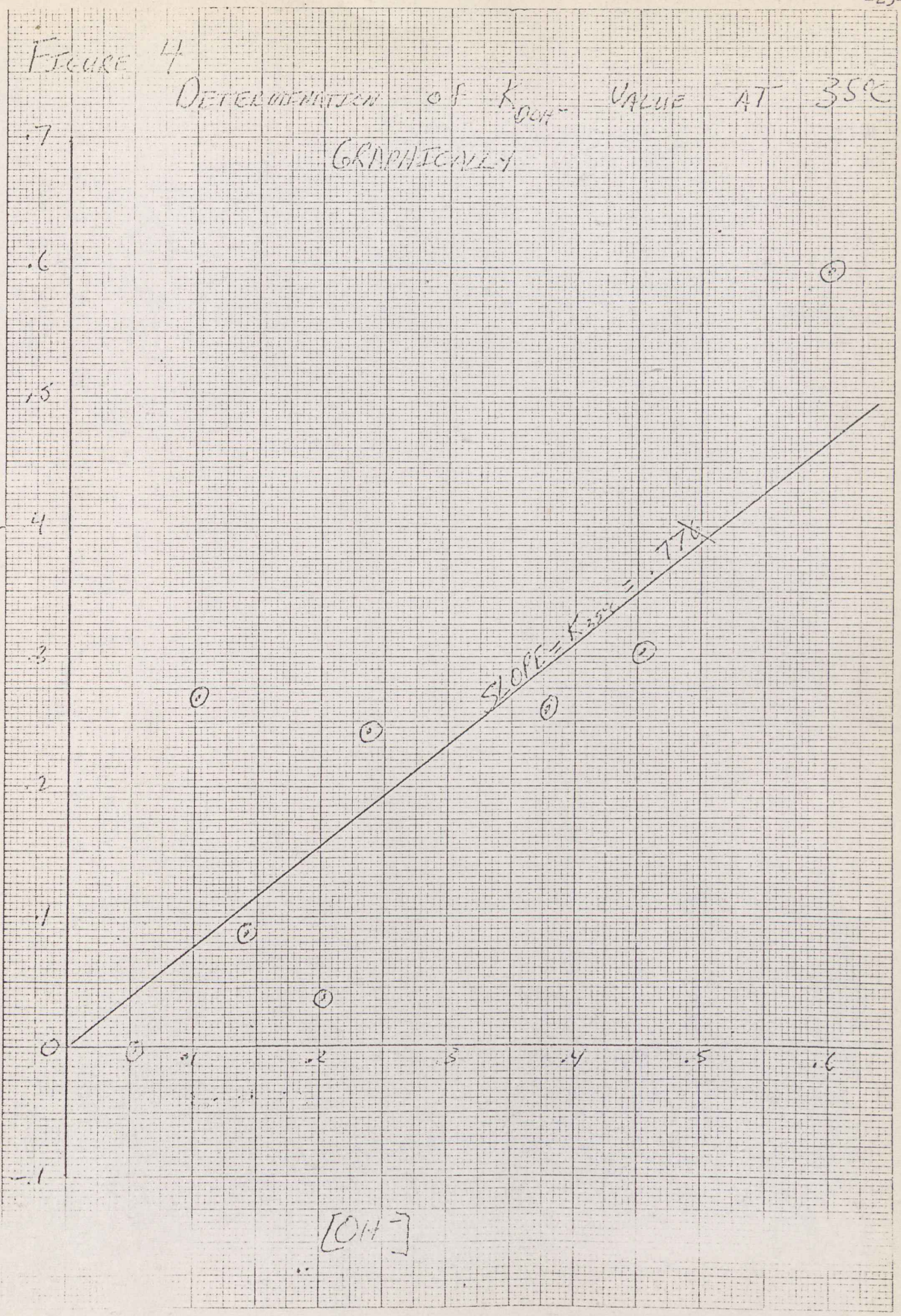
[OH⁻]

FIGURE 5

DETERMINATION OF MACGREGOR'S K_{2344} VALUE AT 25°C GRAPHICALLY
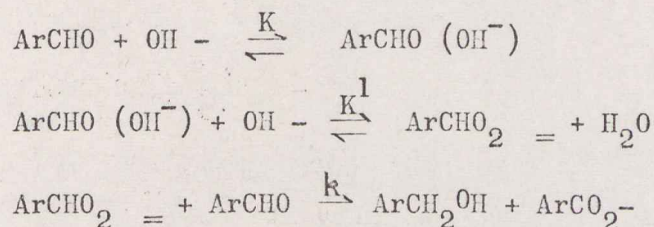
SUGGESTIONS FOR FURTHER STUDY

The relationship of the dissociation equilibrium constants at 35°C and 25°C has been studied for the equilibrium:

The dependence of K_{DOH^-} on temperature could be studied over a wide range of temperatures (i.e. 2-62 °C). The ΔH° and ΔS° should be calculated at each temperature to see if they compare more closely with those previously measured for 2,6 dihalobenzaldehydes (6).

Similar studies with the other seven indicator systems developed by MacGregor would be fruitful.

One very interesting project would be to examine the kinetics of the Cannizzaro reaction which presumably occurs by the pathway:

$$ArCHO + OH^- \overset{K}{\rightleftharpoons} ArCHO\,(OH^-)$$

$$ArCHO\,(OH^-) + OH^- \overset{K^1}{\rightleftharpoons} ArCHO_2^= + H_2O$$

$$ArCHO_2^= + ArCHO \overset{k}{\rightarrow} ArCH_2OH + ArCO_2^-$$

Second-order kinetics would be observed if a plot of $1/\left[ArCHO\right]_t$ vs time is linear and the slope of this plot would be the observed second-order rate constant.

$$\text{Rate} = K_{obs.}\left[ArCHO\right]_t^2$$

This rate law can be related to the rate law for the above

mechanism as follows:

$$\text{Rate} = k \left[\text{ArCHO}_2^=\right] \left[\text{ArCHO}\right]$$

$$= kK^1 \frac{\left[\text{ArCHO}\right]\left[\text{ArCHO}(\text{OH}^-)\right]\left[\text{OH}^-\right]}{H_2O}$$

$$= kK^1K \frac{\left[\text{ArCHO}\right]^2\left[\text{OH}^-\right]^2}{H_2O}$$

then

$$R_{obs} = \frac{kK^1K\left[\text{OH}^-\right]^2}{H_2O}$$

and

$$\log R_{obs} = \text{constant} + 2\log\left[\text{OH}^-\right] - \log\left[H_2O\right]$$

But $\left[\text{ArCHO}\right]_t$ cannot be easily related to the absorbance of

the basic solution at time t. That this might be done, can

be appreciated from a close consideration of the following

equation, in which A_b is the absorbance of the solution, E

refers to the extinction coefficient, A and C is the

concentration of the species.

$$A_b = E_{\text{ArCHO}}\ C_{\text{ArCHO}} + E_{\text{ArCH}_2\text{OH}} + E_{\text{ArCO}_2^-}\ C_{\text{ArCO}_2} + E_{\text{ArC}(\text{HO}^-)\text{O}}$$

$$C_{\text{ArC}(\text{HO}^-)\text{O}} + E_{\text{ArCHO}_2^-}\ C_{\text{ArCHO}_2^-}$$

If $E_{\text{ArCH}_2\text{OH}}\ C_{\text{ArCH}_2\text{OH}}$ and $E_{\text{ArCO}_2^-}\ C_{\text{ArCO}_2}$ are considered to be

negligible, then since $E_{\text{ArCH}(\text{OH})\text{O}^-}\ C_{\text{ArC}(\text{OH})\text{O}^-}$ and $E_{\text{ArCHO}_2^-}$

$C_{\text{ArCHO}_2^-}$ make only a small contribution up to a 50% change in

absorbancy reading from that of the neutral solution, it can

be assumed that the absorbance is given by

$$A_b = E_{ArCHO} \, C_{ArCHO}$$

Plots of 1/ Absorbance vs. time would then be linear for second-order kinetics to be obeyed. Alternatively, the complication of absorbtion by hydroxylated forms can be removed by acidifying timed aliquotes prior to determining their absorbancies.

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