

TEMPERATURE COEFFICIENTS OF RATE OF HYDROLYSIS  
OF SEVERAL MONOSUBSTITUTED DIPHENYL KETIMINE  
HYDROCHLORIDES

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By

YAO CHIANG

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Bachelor of Science

Hangchow Christian College

Hangchow, Chekiang, China

1937

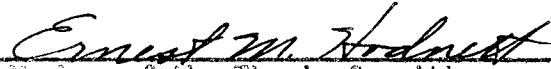
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Chairman, Thesis Committee



Member of the Thesis Committee



Head of the Department



Dean of the Graduate School

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## A C K N O W L E D G M E N T

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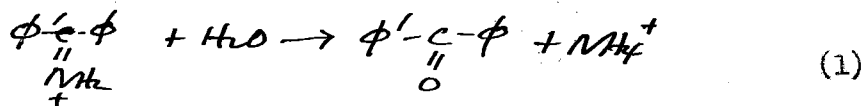
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## INTRODUCTION

The hydrolysis of several monosubstituted diphenyl ketimine hydrochlorides as studied by Professor Culbertson and his co-workers<sup>3</sup> shows a dependence of rate upon the relative positions as well as the nature of the substituted groups in the molecule. For the ortho compounds, proximity effect is observed and Stieglitz suggested that this relative stability might be due to an imine-enamine tautomerism, which is supported by studies of absorption in the near ultraviolet regions<sup>4</sup>. Hammett and his co-workers<sup>6,8,10</sup>, by postulating a theory which assumes a rigid structure for the transition state complex, have related the entropy of activation to the rigidity of the reacting substances. Thus, for a given class of reaction, other things being equal, a rigid molecule should have an entropy of activation greater than a non-rigid one. These considerations have suggested that a study of temperature coefficients of the rate of formations of several monosubstituted diphenyl ketones from the hydrolytic reactions of their respective ketimine hydrochlorides



and the corresponding values of the entropies of activation might reveal a possible extension of Hammett's rigid structure theory of transition complex.

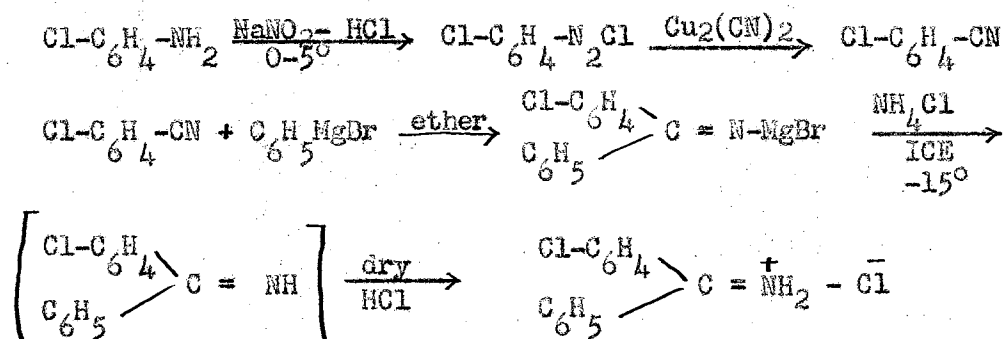
The rate of hydrolysis, equation (1) can be measured by the conductivity method since the diphenyl ketimmonium ion,  $(C_6H_5)_2C = \overset{+}{N}H_2$  is less mobile than the ammonium ion. Benzophenone is found not to adsorb

any of the ions. This reaction is pseudo-unimolecular in the concentrations studied, about 10 mg. per 10 cc. of water.

## EXPERIMENTAL

Materials.

o-Chloro-, m-chloro-, p-chloro-, o-methyl-, p-methyl-, and unsubstituted diphenyl ketimine hydrochlorides were prepared and purified for reaction rate studies. These compounds were made from nitriles via the Grignard reaction and the nitriles (with the exception of benzonitrile) from substituted anilines via the Sandmeyer reaction. The following represents a typical scheme of synthesis for all the compounds:

Preparation of Monosubstituted Benzonitriles.

o-Tolunitrile (b.p. 204°), m-tolunitrile (b.p. 214°) and p-tolunitrile (needles, m.p. 29.5°) were made by the Vogel procedure<sup>11</sup>. Yields were 40-50% of the theoretical.

o-Chlorobenzonitrile (m.p. 42-3°, sublimes, needles), m-chlorobenzonitrile (m.p. 40-1°) and p-chlorobenzonitrile (m.p. 92°, needles) were prepared by the Clarke and Read procedure<sup>2</sup>. Yields are 75-80% of the theoretical.

Some difficulty was encountered in diazotizing p-chloroaniline. When ice was added to the concentrated hydrochloric acid solution, the reaction stopped because of dilution. It was found best to cool the mixture to 0-5° in this case by placing the reaction vessel in an ice bath.



Preparation of Diphenyl Ketimine Hydrochloride.<sup>7,9</sup>

The following quantities of materials were used in each experiment: 0.20 mole of bromobenzene, 0.21 atom of magnesium, 130 cc. or about 6 molecular equivalents of ether, a crystal of iodine which weighed about 0.04 g., and 0.15 mole of benzonitrile or substituted benzonitrile in 15 cc. of ether.

In a 0.5-l. three-neck flask fitted with a dropping funnel, reflux condenser, and stirrer were placed 4.8 g. (0.21 atoms) of magnesium turnings and a crystal of iodine. A mixture of 5.1 g. of bromobenzene and 20 cc. of dry ether was added and the flask warmed gently with the palm until the reaction became rapid. Stirring was then started, and the vessel was surrounded by a dish of cold water. A mixture of 26.9 g. of bromobenzene (total 32 g., 0.20 moles) and 110 cc. of dry ether (total 130 cc., 1.20 moles) was run in at such a rate (about 15 drops per ten seconds at the very beginning) as to cause vigorous refluxing. When the addition was complete (16 min.) the whole was stirred for ten minutes. The solution was cooled in ice and 15.5 g. (0.15 mole) of benzonitrile in 15 cc. of dry ether was added with stirring. A white powder appeared and the mixture was heated on a water bath for 8 hours. The mixture was then cooled in the ice box over night. The white crystalline powder was washed with dry ether four times by decantation. To the flask containing a suspension of the powder in ether, a freezing mixture (ammonium chloride, 19% + ice, 81%) at  $-15^{\circ}$  was added carefully with agitation. During this hydrolysis the ketimine which formed was continuously taken up with ether. The ether extracts containing ketimine were immediately dried with anhydrous sodium sulfate; they were then

saturated with dry hydrogen chloride gas. The diphenyl ketimine hydrochloride (appearing as crystals) were separated and dissolved in a minimum amount of hot dry methanol and filtered to remove impurities. The hydrochloride was then reprecipitated as pure crystals by cooling. The yield of pure crystals was 50% of the theoretical.

A derivative of diphenyl ketimine hydrochloride was made by heating a small quantity (about 2 g.) of the solid with 50 cc. of 10% hydrochloric acid solution for two hours. The purified benzophenone thus obtained melted at 48.5°.

#### Preparation of o-Methyldiphenyl Ketimine Hydrochloride.

The method was the same as described under Preparation of Diphenyl Ketimine Hydrochloride except that 17.5 g. (0.15 mole) of *o*-tolunitrile was used in place of 15.5 g. (0.15 mole) of benzonitrile. The yield was 72%.

A similar derivative was made as described above. The purified *o*-methyldiphenyl ketone thus obtained was an oil which formed an oxime, anti-phenyl *o*-tolyl ketoxime (m.p. 69°).

#### Preparation of p-Methyldiphenyl Ketimine Hydrochloride.

The method was the same as described under Preparation of Diphenyl Ketimine Hydrochloride except that 17.5 g. (0.15 mole) of *p*-tolunitrile was used in place of 15.5 g. (0.15 mole) of benzonitrile. The yield was 23%.

A similar derivative was made as described above. The purified *p*-methyldiphenyl ketone thus obtained melted at 59-60° (stable form).

Preparation of o-Chlorodiphenyl Ketimine Hydrochloride.

The method was the same as described under Preparation of Diphenyl Ketimine Hydrochloride except that 20.6 g. (0.15 mole) of o-chlorobenzonitrile was used in place of the benzonitrile. The yield was 32%.

A similar derivative was made as described above. The purified o-chlorodiphenyl ketone thus obtained melted at 45.5°.

Preparation of m-Chlorodiphenyl Ketimine Hydrochloride.

The method was the same as described under Preparation of Diphenyl Ketimine Hydrochloride except that 20.6 g. (0.15 mole) of m-chlorobenzonitrile was used in place of the benzonitrile. The yield was 21%.

A similar derivative was made as described above. The purified m-chlorodiphenyl ketone thus obtained melted at 82-83°.

Preparation of p-Chlorodiphenyl Ketimine Hydrochloride.

The method was the same as described under Preparation of Diphenyl Ketimine Hydrochloride except that 20.6 g. (0.15 mole) of p-chlorobenzonitrile was used in place of 15.5 g. (0.15 mole) of benzonitrile. The yield was 19%.

A similar derivative was made as described above. The purified p-chlorodiphenyl ketone thus obtained melted at 75.5-76°.

Attempted Preparation of m-Methyldiphenyl Ketimine Hydrochloride.

m-Tolunitrile did not add to the Grignard reagent,  $C_6H_5MgBr$ , and hence we were unable to prepare the ketimine. A private communication from Dr. Culbertson indicated however that this ketimine can be made by this series of reactions.

## Kinetic Measurements.

### Apparatus.

A student-type conductance measurement set-up was used. It was composed of: (1) a standard resistance (L and N #4745) which was a four-dial unshielded A C resistance box, total resistance 11,110 ohms, steps of 10 (1 - 10 - 100 - 1000) ohms, accuracy  $\pm 0.1\%$ ; (2) a circular slidewire (L and N #4261), length about 35 cm., resistance about 100 ohms, scale divided into 100 divisions which may be read to 0.1 division, error  $\pm 0.5$  division, the resistance of the end coils is 4.5 times the resistance of the slide; (3) an audio oscillator, General Radio Co., Type 813A, a 1000-cycle oscillator of the tuning fork type, output about 25 milliwatts, with no more than 1% harmonics; (4) an amplifier, composed of an electronray tube 6A8GT as null point indicator and four other tubes converted from a radar set; (5) switches, battery for powering oscillator and Freas type conductivity cells.

### Procedure.

Ten cubic centimeters of distilled water was pipetted into a Freas conductivity cell in a thermostat (at  $0 \pm 0.02^\circ$ ,  $20 \pm 0.02^\circ$  and  $35 \pm 0.02^\circ$ ). The thermometer used was compared with one calibrated at the U. S. Bureau of Standards. After allowing the cell to age for twenty minutes at constant temperature, 10 mg. of powdered diphenyl ketimine hydrochloride or one of its substituted salts were added, accompanied by constant shaking (for about 3 minutes) with the right hand while the stop watch was started by the left. The number of readings taken on the decade resistance box depended upon the rate of hydrolysis. In general, readings were taken up to the half period.

### Method of Calculation.

The method used to compute the rate constant from the conductivity of the solution depends on the fact that as the hydrolysis proceeds the relatively large, slow-moving ketiminium ion is replaced by the smaller, more rapid-moving ammonium ion:



consequently the conductivity of the solution increases and the resistance decreases.

The resistance  $\underline{R}$  of a solution in a conductivity cell whose cell constant is  $\underline{K}$  is related to the concentration of the electrolyte  $\underline{c}$  and the equivalent conductance  $\underline{\Delta}$  of the electrolyte at the concentration  $\underline{c}$  through the equation:

$$\frac{\underline{K}}{\underline{R}} = \frac{\underline{c} \underline{\Delta}}{1000} \quad (2)$$

While  $\underline{\Delta}$  varies with  $\underline{c}$  for a solution containing a single electrolyte this variation (for a strong electrolyte) results principally from the change in the ionic strength of the solution. In the problem at hand the ionic strength is sensibly constant throughout the hydrolysis and consequently  $\underline{\Delta}$  for each electrolyte will be practically constant.

Consequently one may write:

$$\text{at } t = 0 \quad \frac{1000 \underline{K}}{\underline{R}_0} = a \underline{\Delta}_{ket.} \quad (3)$$

where  $a$  = initial concentration of ketimine.

$$\text{at } t = t \quad \frac{1000 \underline{K}}{\underline{R}_t} = (a-x) \underline{\Delta}_{ket.} + x \underline{\Delta}_{NH_4Cl} \quad (4)$$

where  $x$  = concentration of ammonium chloride.

$$\text{at } t \rightarrow \infty \quad \frac{1000 \underline{K}}{\underline{R}_\infty} = a \underline{\Delta}_{NH_4Cl} \quad (5)$$

Substituting equations (3) and (5) into equation (4) one obtains

$$\frac{1}{R_t} = \frac{1}{R_0} - \frac{x}{a} \frac{1}{R_0} + \frac{x}{a} \frac{1}{R_\infty} \quad (6')$$

$$\text{or } a \left( \frac{1}{R_t} - \frac{1}{R_0} \right) = x \left( \frac{1}{R_\infty} - \frac{1}{R_0} \right) \quad (6)$$

The rate equation applicable to the pseudo first order reaction at hand is of the form

$$kt = \ln a/a-x$$

which becomes, when proper substitution from equation (6) is made:

$$kt = \ln R_0 - R_\infty/R_0 - \ln R_t/R_t - R_\infty$$

Hence a plot of  $\log R_t/R_t - R_\infty$  vs.  $t$  should give a straight line whose slope is equal to  $0.4343k$ . One therefore measures the conductivity as a function of time to determine values of  $R_t$ . After allowing the reaction mixture to stand for several half lives (greatly expedited for the slower reactions by raising the temperature) the resistance is again measured and when further change in the resistance is no longer noted the value is taken as  $R_\infty$ .

## RESULTS

Sample Data.

Table I. Sample #498301, Rate of Hydrolysis of o-Methyldiphenyl Ketimine Hydrochloride at 25.00  $\pm$  0.02°C., 10 mg. per 10 cc. H<sub>2</sub>O (Fig. 1,a)

Time (min.)	R <sub>t</sub> (ohms)	$\frac{R_{\infty}}{R_t}$	$\log \frac{1}{1 - R_{\infty}/R_t}$
10	1111	0.709	0.5361
20	1091	0.721	0.5544
30	1070	0.736	0.5784
40	1044	0.754	0.6091
50	1028	0.766	0.6308
60	1913	0.776	0.6498
70	998	0.789	0.6757
80	986	0.800	0.6990
90	974	0.809	0.7190
100	962	0.819	0.7423
110	952	0.828	0.7645
120	942	0.836	0.7852
130	933	0.845	0.8097
$\infty$	788	-----	-----

From Fig. 1, a, two readings were used for calculating the velocity constant,

$$\begin{aligned}
 k_{25^{\circ}} &= 2.303 \times \frac{\left[ \log \frac{1}{1 - \frac{R_{\infty}}{R_2}} \right]_{t_2} - \left[ \log \frac{1}{1 - \frac{R_{\infty}}{R_1}} \right]_{t_1}}{t_2 - t_1} \\
 &= 2.303 \times \frac{0.8097 - 0.6091}{130 - 40} = 5.23 \times 10^{-3} \text{ min.}^{-1}
 \end{aligned}$$

It should be noted that these two readings lie on the best straight line which one may draw through the experimental points.

Figure 1  
 Hydrolysis of o-methyldiphenyl ketimine HCl  
 25°C. 0.1% Soln.

○ a  
 ● b

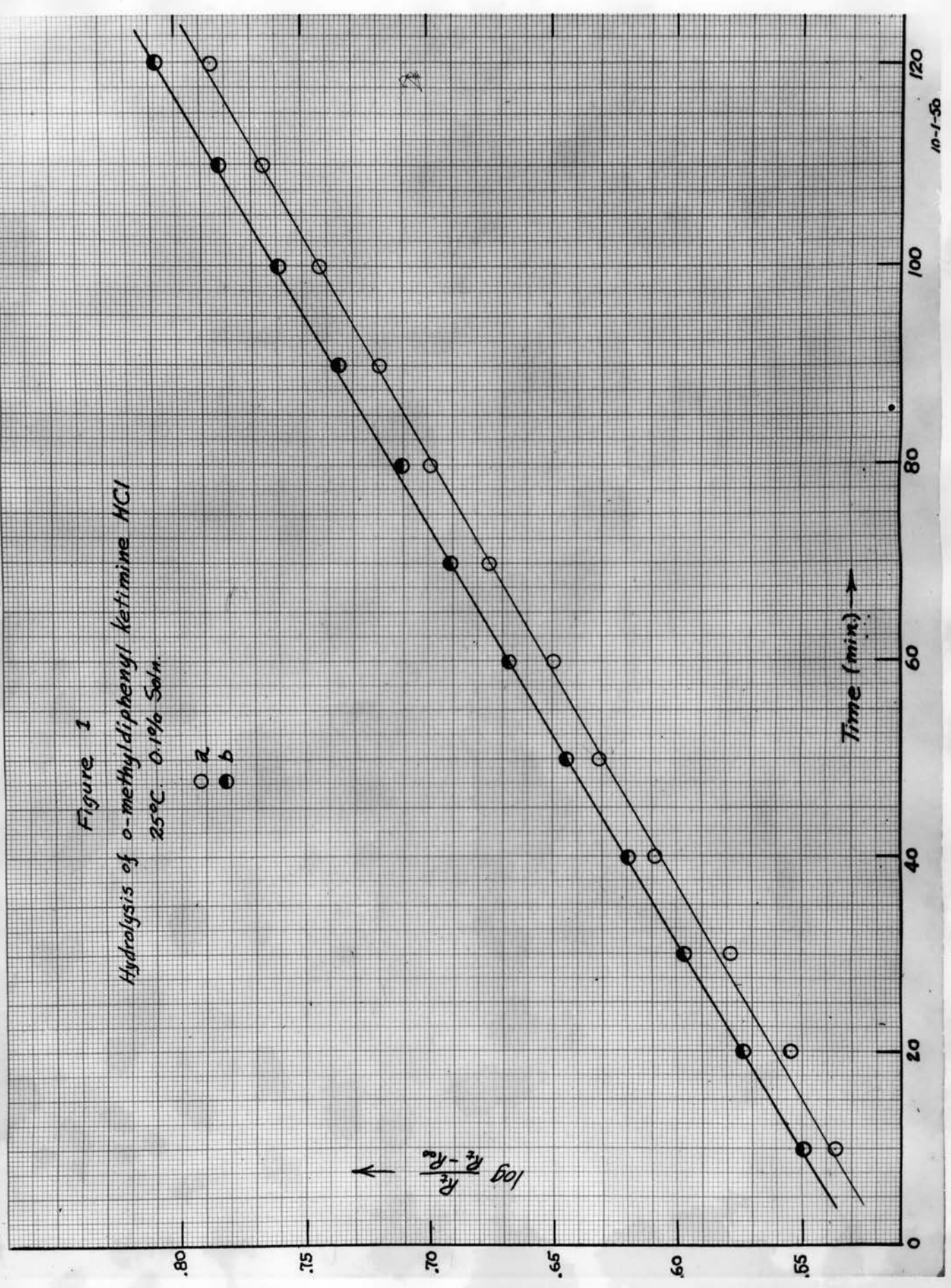




Table II. Sample #498311, Rate of Hydrolysis of *o*-Methyldiphenyl  
Ketimine Hydrochloride at 25.00  $\pm$  0.02°C., 10 mg. per 10 cc. H<sub>2</sub>O (Fig. 1, b)

Time (min.)	R <sub>t</sub> (ohms)	$\frac{R_{\infty}}{R_t}$	$\log \frac{1}{1 - R_{\infty}/R_t}$
10	1058	0.718	0.5498
20	1036	0.733	0.5735
30	1017	0.747	0.5969
40	998	0.760	0.6198
50	982	0.773	0.6440
60	967	0.785	0.6676
70	954	0.796	0.6904
80	942	0.805	0.7100
90	930	0.816	0.7352
100	919	0.826	0.7595
110	909	0.835	0.7825
120	900	0.844	0.8069
130	892	0.851	0.8268
$\infty$	759	-----	-----

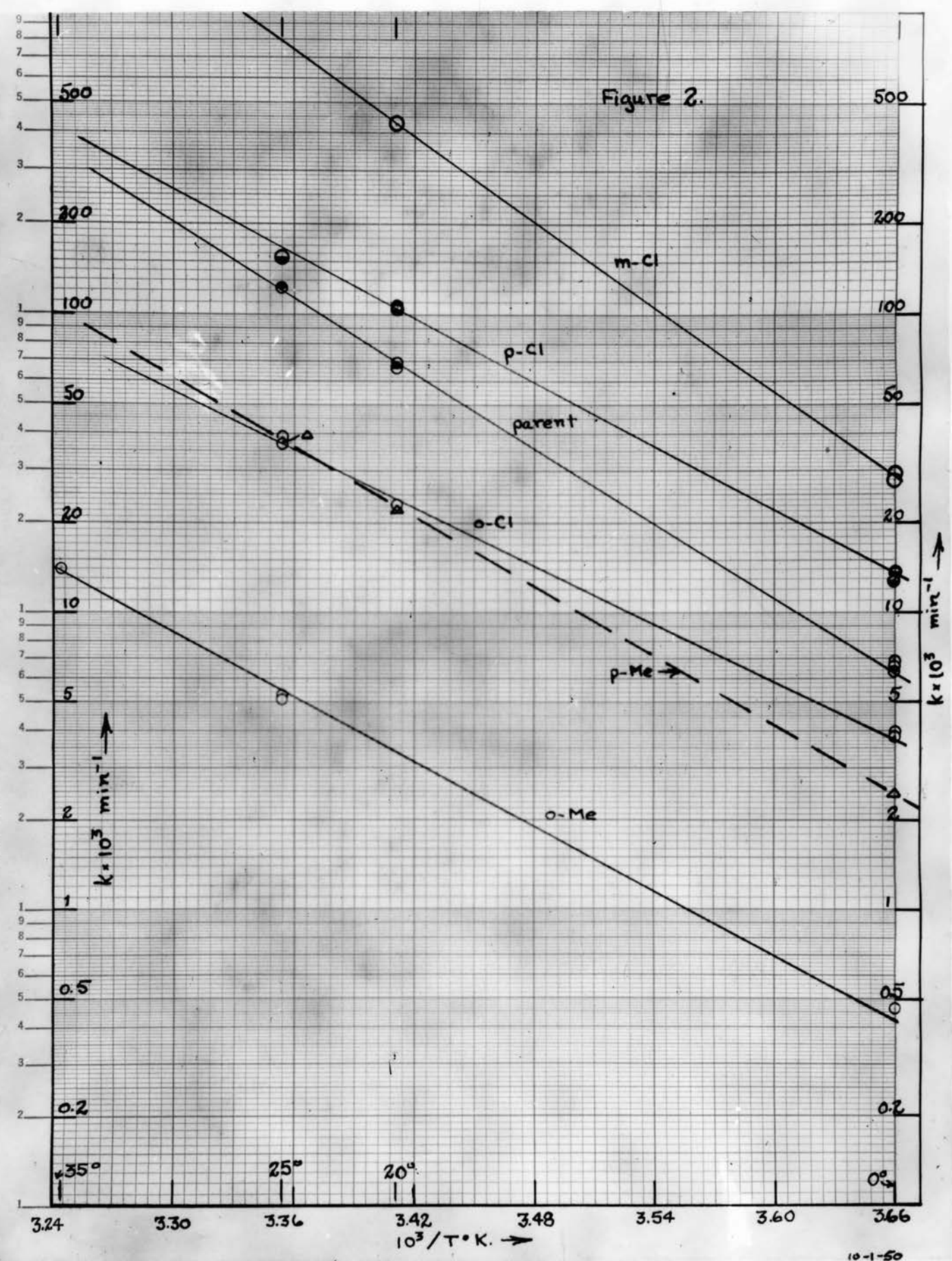
From Fig. 1, b, two readings were taken for calculating the velocity  
constant,  $k_{25^{\circ}}$ :  $t_1 = 30$  min. and  $t_2 = 110$  min.

$$k_{25^{\circ}} = 2.303 \times \frac{\left[ \log \frac{1}{1 - \frac{R_{\infty}}{R_t}} \right]_{t_2} - \left[ \log \frac{1}{1 - \frac{R_{\infty}}{R_t}} \right]_{t_1}}{t_2 - t_1}$$

$$= 2.303 \times \frac{0.7825 - 0.5969}{110 - 30} = 5.33 \times 10^{-3} \text{ min.}^{-1}$$

By assuming no error in  $t$  but a variation of plus or minus one ohm in  $R_t$ ,  
we find an uncertainty in  $k$  of about five per cent. The above values of  
 $k_{25^{\circ}}$  lie within the experimental error.

Figure 2.



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Table III. Rate Constants,  $k \times 10^3$  in  $\text{min.}^{-1}$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta F^\ddagger$  for  
Hydrolysis of Diphenyl Ketimine Hydrochlorides.

<u>Unsubstituted</u>				$\Delta H^\ddagger$ cal.	$\Delta S^\ddagger$ cal./°C.	$\Delta F^\ddagger$ cal.
$k_{0^\circ}$	$k_{20^\circ}$	$k_{25^\circ}$	$k_{35^\circ}$			
6.85	68.75	123.3				
6.31	66.1	121.0				
6.62				18,700	58.3	2100
<u>6.96</u>						
Av. 6.69	<u>67.4</u>	<u>122.2</u>				
<u>o-Cl</u>						
3.77	22.65	39.35				
<u>3.95</u>	<u>23.0</u>	<u>37.0</u>		14,600	42.5	2500
Av. 3.86	22.8	38.2				
<u>o-Me</u>						
0.458		5.13	14.05			
		<u>5.33</u>	<u>13.71</u>	16,200	44.1	3600
Av. 0.458		5.23	13.88			
<u>p-Cl</u>						
12.92	106.7	156.0				
12.75	100.5	154.9				
<u>13.58</u>				16,200	50.5	1800
Av. 13.08	<u>103.6</u>	<u>155.5</u>				
<u>p-Me</u>						
2.39	21.7	37.4				
2.43	22.4	38.1		17,800	53.0	2700
<u>2.43</u>						
Av. 2.41	<u>22.1</u>	<u>37.7</u>				
<u>m-Cl</u>						
27.95	432					
<u>29.4</u>	<u>440</u>			21,600	72.2	1000
Av. 28.7	436					

The logarithm of the mean rate constant plotted against the reciprocal of the absolute temperature gave a series of good straight lines (Fig. 2). These lines have been drawn by the least-squares method giving the proper statistical weight to each point. The corresponding rate equations were found to be:

$k_{\text{unsubst'd.}}$	= 10	12.8 ± 0.3	exp.(18,700 ± 500)/RT	min. <sup>-1</sup>
$k_{\text{o-Cl}}$	= 10	9.3 ± 0.3	exp.(14,600 ± 400)/RT	min. <sup>-1</sup>
$k_{\text{o-Me}}$	= 10	9.0 ± 0.1	exp.(16,200 ± 100)/RT	min. <sup>-1</sup>
$k_{\text{p-Cl}}$	= 10	11.0 ± 0.5	exp.(16,200 ± 500)/RT	min. <sup>-1</sup>
$k_{\text{p-Me}}$	= 10	11.6 ± 0.1	exp.(17,800 ± 100)/RT	min. <sup>-1</sup>
$k_{\text{m-Cl}}$	= 10	15.7 ± 0.3	exp.(21,600 ± 300)/RT	min. <sup>-1</sup>

The error limits in these equations were fixed<sup>1,5</sup> as follows. It was assumed that all the error resided in the log k values and none in the temperature measurements. The root mean square of the deviations of the logarithms of the mean velocity constants from the least squares line was then applied positively and negatively to the two ends of the least squares line at the extreme temperatures of the experimental range to give the error limits shown.

The error thus introduced into the entropy of activation differences is about 1.3 cal./°C. (corresponds to the exponent 0.3 in most of the equations above), and into the heat of activation differences about 100-500 cal., and into the free energy of activation differences about 300 cal.

## DISCUSSION

Table III emphasizes the interdependence of both the potential energy ( $\Delta H^\ddagger$ ) and the internal kinetic energy ( $\Delta S^\ddagger$ ) on substituents. These quantities taken together are a measure of the free energies of activation ( $\Delta F^\ddagger$ ). It is important to remember that the effect of a change in structure of reactant upon rate of reaction can be explained in terms of internal electron displacements or of external electrical fields due to a substituting group, in terms that is, of potential energies alone, only when there is a cancellation of other effects due to the internal kinetic energies of the reactants. It may be shown that the quantity

$$\Delta S_1^\ddagger - \Delta S_2^\ddagger = -\frac{\partial}{\partial T} \left( RT \ln \frac{k_1}{k_2} \right)$$

should vanish (where 1 and 2 refer to reactants and k, the rate constant) when the internal kinetic energies cancel. Thus the reactivity of o-chlorodiphenyl ketimine hydrochloride can be compared with o-methyl-diphenyl ketimine hydrochloride but not p-chlorodiphenyl ketimine hydrochloride. Similarly, that of p-chlorodiphenyl ketimine hydrochloride can be compared with p-methyldiphenyl ketimine hydrochloride but not o-methyldiphenyl ketimine hydrochloride. Unfortunately, the m-chloro-diphenyl ketimine hydrochloride is left uncomparred because we were unable to prepare m-methyldiphenyl ketimine hydrochloride.

Both of the ortho substituents exhibit a lowering of entropy of activation and a decreased value of heat of activation. Apparently the influence of entropy of activation is here alone responsible and hence a decrease in rate constant.

## SUMMARY

(1) A simple conductivity method has been applied satisfactorily to the measurement of the rate of hydrolysis of diphenyl ketimine hydrochlorides.

(2) The rate constants for the hydrolysis of the monochloro- and monomethyldiphenyl ketimine hydrochlorides have been determined at temperatures of 0°, 20° and 25° (and 35° in one case).

(3) From the rate constant measurements the energies, entropies and free energies of activation have been computed for the three monochloro-, the *o*-methyl-, the *p*-methyl- and the unsubstituted diphenyl ketimine hydrochlorides.

(4) There is no apparent simple relation between the energies of activation and the effect of substituents due to variation in the entropy of activation from one compound to another.

(5) The steric or proximity effect noted in the ortho substituted compounds is not simply an entropy effect.

## BIBLIOGRAPHY

- (1) Barton and Onyon, *Trans. Faraday Soc.*, 45, 728 (1949).
- (2) Blatt, "Organic Synthesis", Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1925, p. 69.
- (3) Culbertson, A Study of Tautomerism of Aromatic Ketimines, Abstracts of Theses, The University of Chicago, Science Series, 6, 135-42 (1927-8). See also C. A., 25, 1231; 27, 1810; 29, 2522, 3582; 36, 3415.
- (4) Culbertson, *Proc. Iowa Acad. Sci.*, 49, 281-2 (1942), via C. A., 37, 5653.
- (5) Crumpler and Yoe, "Chemical Computations and Error", John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 131, 132.
- (6) Gettler and Hammett, *J. Am. Chem. Soc.*, 65, 1824 (1943).
- (7) Gilman, Zoellner and Dickey, *J. Am. Chem. Soc.*, 51, 1576 (1929).
- (8) Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 118-20.
- (9) Moureu and Mignonac, *Ann. chim.*, (9) 14, 322-59 (1920), via C. A., 15, 1495.
- (10) Price and Hammett, *J. Am. Chem. Soc.*, 63, 2387-93 (1941).
- (11) Vogel, "A Textbook of Practical Organic Chemistry", Longmans, Green and Co., New York, N. Y., 1948, pp. 582, 583.

Typed by:

Mrs. J. O. Richardson