

chloride from the product by fractional distillation, the dichloropentane distilled at 146.0–146.2°; yield, 7 g.; d_{25}^{25} 1.0773; n_D^{25} 1.4453.

Anal. Calcd. for $C_5H_{10}Cl_2$: Cl, 50.3. Found: Cl, 49.8.

1-Chloro-3-Bromopropanol-2.—The fraction boiling at 100–105° (20 mm.) from the preparation of 1-chloropentanol-2 was refractionated under reduced pressure into a part boiling at 95–98° (15 mm.) which was the glycerol chlorobromohydrin described by Fourneau and Tiffeneau.³ The compound was colorless when freshly distilled but darkened rapidly on exposure to light. It boiled with much decomposition at 190–200° (740 mm.), and for this reason was best purified by distillation under diminished pressure; d_{25}^{25} 1.7456; n_D^{25} 1.5140.

Anal. Calcd. for C_3H_5OClBr : Cl, 20.4; Br, 46.1. Found: Cl, 20.1; Br, 45.3.

No effort was made to secure the maximum yield of this compound. Presumably, however, about 100 g. of it was available from a run of one mole of epichlorohydrin, since the total weight of reaction product was about 140 g. and about 23 g. of chloropentanol was obtained from this. The intermediate fractions weighed 10–15 g.

The chlorobromohydrin was further identified by preparing the known 1,3-diphenoxypropanol-2 from it by the procedure described by Rössing⁹ for the preparation of this substance from α -dichlorohydrin. The melting point of the diphenoxy compound after recrystallization from alcohol was 80–81°.

Summary

1. It has been shown that ethylmagnesium bromide reacts with epichlorohydrin to give a chloro-amyl alcohol as well as glycerol chlorobromohydrin.

2. The chloro-amyl alcohol which is formed has been found to be 1-chloropentanol-2.

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STUDIES ON HYDRAZINE. THE HYDROLYSIS OF DIMETHYLKETAZINE AND THE EQUILIBRIUM BETWEEN HYDRAZINE AND ACETONE

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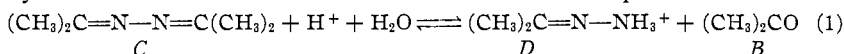
One of the most important properties of hydrazine and its organic substitution products is their capacity to react with the carbonyl group of ketones and aldehydes, forming hydrazones or azines by elimination of water. This reaction takes place most generally in neutral or alkaline solution, while in acid the product is to a greater or less extent, depending on the particular components, hydrolyzed. A study of this type of hydrolysis, using the product formed in the reaction of hydrazine with the simplest ketone, acetone, has been made in the work here presented.

⁹ Rössing, *Ber.*, 19, 64 (1886).

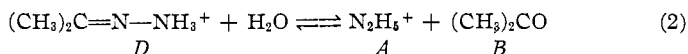
¹ Fellow of the John Simon Guggenheim Memorial Foundation.

When hydrazine and acetone are brought together under the proper conditions, two molecules of acetone combine with one of hydrazine to form dimethylketazine.² This ketazine dissolves readily in water and the solution becomes alkaline. If the free hydroxyl ion is neutralized with acid, more OH^- is then formed. In the presence of strong mineral acids the compound is completely hydrolyzed. The hydrolysis takes place with measurable velocity and the progress of the reaction may be followed by measuring the amount of acid necessary to replace the H^+ which has reacted with the ketazine, adding the acid at such a rate as to maintain a constant P_{H} in the solution. Examination of the reaction, however, showed the probability of there being present also acetone hydrazone, containing one molecule of acetone and one of hydrazine. In addition to this the reaction proved to be highly reversible, coming to equilibrium at P_{H} 5.0 when from 30 to 70% of the ketazine had been hydrolyzed, the extent depending not only on the P_{H} but also on the original concentration of ketazine.

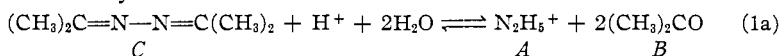
The entire reaction may be formulated, therefore, either as a reaction between dimethylketazine and water to form the acetone hydrazone, which is in turn hydrolyzed to hydrazine and acetone, or as a direct hydrolysis of the ketazine to acetone and hydrazine, with the hydrazone formed by a side reaction between the two latter. The equations are



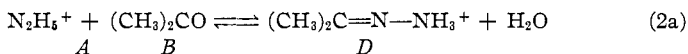
followed by



or, alternatively



and



Denoting by subscripts the equations for which the equilibrium constants are valid, the following relations exist

$$K_1 \times K_2 = K_{1a} \text{ and } K_{2a} = 1/K_2$$

The problem may therefore be resolved into three parts: (1) to determine the conditions of Equilibrium 2 or 2a; (2) to determine the conditions of Equilibrium 1 or 1a; (3) to study the kinetics of the hydrolysis. These will be taken up in the order named.

Part I

The Equilibrium between Acetone, Hydrazine and Acetone Hydrazone.—Since Reaction 1 or 1a involves H^+ on the left-hand side of the

² Curtius and Thun, *J. prakt. Chem.*, **44**, 164 (1891).

equation, it is evident that by adding sufficient acid this equilibrium may be shifted completely to the right, while 2 or 2a will be unaffected by acid and may thus be studied independently. This was done by two different procedures.

1A. Determination of Equilibrium 2a by Solubility Measurements.—

It has previously been found that hydrazine picrate³ is an easily prepared salt sufficiently insoluble to be suited for measurements of solubility. The salt moreover contains only one equivalent of acid for each molecule of hydrazine, *i. e.*, it contains the ion $N_2H_5^+$. By measuring the increase in solubility of the salt when acetone is added to the solvent, the equilibrium between acetone, hydrazine and acetone hydrazone readily may be determined. The acidity must be adjusted so that no dimethylketazine is formed. The thermodynamic mass action law applied to Equation 2a yields the expression

$$K_{2a} = \frac{C_{\text{acetone hydrazone}^+}}{C_{N_2H_5^+} \times C_{\text{acetone}}} \times \frac{f_1}{f_1 \times f_0} \quad (3)$$

where f_1 stands for the activity coefficients of the two monovalent ions and f_0 for that of acetone. At low concentrations this factor would be of little import, but some salt effect upon the equilibrium would be expected at higher concentration. It has been shown,⁴ however, that in solutions of sufficiently high ionic strength the activity coefficient factor may be neglected and concentration values employed directly in the mass action law and it was thought best to employ this expedient rather than introduce the activity coefficients.

TABLE I
SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°
Solvent 0.2 M NaCl + 0.02 M HCl + acetone

(a) Solubility						
Orig. concn. of acetone	Total hydrazine	Orig. concn. of acetone	Total hydrazine	Orig. concn. of acetone	Total hydrazine	
0	0.01480	0.04388	0.01745	0.09654	0.02102	
0	.01476	.06582	.01871	.1097	.02198	
0	.01480	.07898	.01985	.1097	.02211	
0.0392	.01712	.07679	.01980	.1097	.02211	
.0400	.01715	.08776	.02030	.09404	.02082	
.05485	.01813	.09524	.02113	.1097	.02181	
.05480	.01803	.09873	.02122	.1097	.02211	
(b) Equilibrium Data						
B_0 acetone	Total Pic. - (A + D)	$K_{s.p.} \times 10^4$	A	D	B	K_{2a}
0.040	0.01738	2.24	0.01289	0.00449	0.03551	9.80
.070	.01921	2.28	.01184	.00737	.06263	9.92
.100	.02147	2.31	.01078	.01069	.08931	11.1
						Mean 10.3

³ Gilbert, *J. Phys. Chem.*, **33**, 1235 (1929).

⁴ Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); Brönsted and Pedersen, *ibid.*, **103**, 307 (1922).

The solubility of hydrazine picrate was therefore determined at 15° in the presence of acetone, 0.2 *M* sodium chloride and 0.02 *M* hydrochloric acid (the latter to prevent formation of dimethylketazine). Results are given in Table I. These were further confirmed by measurements in acetone, 0.2 *M* sodium chloride, and 0.01 *M* hydrochloric acid, Table II; in acetone and 0.04 *M* picric acid, Table III; and finally in acetone, 0.133 *M* sodium chloride, 0.067 *M* sodium picrate and 0.0033 *M* hydrochloric acid, Table IV.

TABLE II
SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°
Solvent: 0.2 *M* NaCl-0.01 *M* HCl-acetone

(a) Solubility						
Original acetone concn.	0	0	0.05485	0.1097	0	
Total hydrazine	0.01443	0.01447	0.01799	0.02177	0.01443	
(b) Equilibrium Data						
<i>B</i> ₀ , acetone	Total Pic. ~ (<i>A</i> + <i>D</i>)	<i>K</i> _{s.p.} × 10 ⁴	<i>A</i>	<i>D</i>	<i>B</i>	<i>K</i> _{2a}
0.040	0.01702	2.13	0.01245	0.00457	0.03543	10.38
.070	.01896	2.17	.01145	.00751	.06249	10.50
.100	.02107	2.20	.01045	.01062	.08938	11.35
					Mean	10.74

TABLE III
SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°
Solvent: 0.04 *M* Picric acid-acetone

(a) Solubility							
Orig. acetone concn.	0	0	0.0439	0.0658	0.0878	0.1097	0.1097
Total hydrazine	0.00448	0.00448	0.00630	0.00687	0.00826	0.00938	0.00943
(b) Equilibrium Data							
<i>B</i> ₀ acetone	<i>A</i> + <i>D</i>	Total pic. ~	<i>K</i> _{s.p.} × 10 ⁴	<i>A</i>	<i>D</i>	<i>B</i>	<i>K</i> _{2a}
0.040	0.00607	0.0461	2.05	0.00445	0.00162	0.03738	9.74
.070	.00738	.0474	2.08	.00438	.00300	.06700	10.23
.100	.00887	.0489	2.10	.00430	.00457	.09543	11.10
						Mean	10.3

TABLE IV
SOLUBILITY OF HYDRAZINE PICRATE AND EQUILIBRIUM WITH ACETONE AT 15°
Solvent: 0.1333 *M* NaCl-0.0667 NaPic-0.003 *M* HCl-acetone

(a) Solubility								
Original acetone concentration	0		0.05485		0.1080			
Total hydrazine	0.00420		0.00677		0.00933			
(b) Equilibrium Data								
<i>B</i> ₀ , acetone	<i>A</i> + <i>D</i>	Total pic. ~	<i>K</i> _{s.p.} × 10 ⁴	<i>A</i>	<i>D</i>	<i>B</i>	<i>K</i> _{2a}	<i>K</i> _{2a} corr.
0.05485	0.00677	0.07344	3.03	0.00413	0.00264	0.0559	11.44	10.9
.1080	.00933	.07600	3.07	.00404	0.00529	0.1027	12.75	11.6

(a) **Materials.**—Hydrazine picrate was prepared as previously described and rotated in water at 15° until succeeding samples of the solution gave the same value for the solubility. This material was used for subsequent determinations. Acetone was

the best product obtainable, "zur Analyse," and was twice redistilled. A stock solution was made by weighing acetone in sealed ampules and breaking these under the surface of water in a volumetric flask.

(b) **Procedure.**—Solutions to be used as solvents for the hydrazine picrate were made by dilution of stronger stock solutions to give the desired concentration of each reagent. Care was taken to minimize loss of acetone by volatilization. Solubility measurements were made for the most part in sealed tubes. Some of the later ones were made in well stoppered bottles. In a few cases to serve as a check against volatilization losses, small weighed ampules of acetone were broken in the solubility bottle after closing it. All of the methods gave concordant results. Hydrazine was determined by the iodic acid method.⁵ Previous tests had shown that picric acid does not interfere with this method.³

It was necessary to remove acetone. This was done by acidifying the solution and boiling for several minutes to decompose acetone hydrazone and drive off the acetone. Tests were made to prove the efficacy of this procedure. Additional tests were made to ensure that acetone did not have a solvent effect additional to that caused by reaction with hydrazine. This was done by determination of the solubility of a similar salt, potassium picrate, in 0.2 *M* sodium chloride and then in 0.2 *M* sodium chloride plus 0.1 *M* acetone. No increase in solubility was found in the acetone solvent.

(c) **Calculations.**—The values of the solubility were plotted on a large scale and a curve was drawn through the points. Interpolated values were taken from this for the calculations. Since acetone hydrazone is decomposed by boiling before titration, the concentration of hydrazine found by titration represents the sum of the $N_2H_5^+$ (*A*) and the acetone hydrazone (*D*) and therefore also the concentration of the picrate ion (Pic^-). The concentration (*A*) at equilibrium is found by dividing the solubility product of hydrazine picrate by (Pic^-). Acetone hydrazone (*D*) is then obtained by subtracting (*A*) from the total hydrazine (*A* + *D*) found by titration. The acetone concentration (*B*) is equal to the original concentration of acetone in the solvent, minus (*D*).

In solutions which contain added sodium picrate or picric acid (in the solvent) allowance must be made for this in determining $K_{s,p.}/Pic^- = N_2H_5^+ = (A)$. Furthermore, our earlier work has shown that small amounts of picrate ion have a marked specific effect on the solubility of picrates with the result that the solubility product increases considerably due to the additional hydrazine picrate dissolved by the acetone, even in the small range covered in these determinations of solubility. Approximate correction was made for this increase and the $K_{s,p.}$ used in calculating is given in each case.⁶

⁵ Bray and Cuy, *THIS JOURNAL*, **46**, 858 (1924).

⁶ This correction was made as follows:

$$\text{at } 15^\circ K_{s,p.} N_2H_5Pic. \text{ in } 0.2 M NaCl + 0.02 M HCl = 2.19 \times 10^{-4} \quad (1)$$

$$\text{at } 15^\circ K_{s,p.} N_2H_5Pic. \text{ in } 0.2 M NaCl + 0.01 M HCl = 2.08 \times 10^{-4} \quad (2)$$

$$\text{at } 15^\circ K_{s,p.} N_2H_5Pic. \text{ in } 0.2 M NaCl = 1.99 \times 10^{-4} \quad (3)$$

$$\text{by interpolation } N_2H_5Pic. \text{ in } 0.2 M NaCl + 0.0033 M HCl = 2.01 \times 10^{-4} \quad (4)$$

$$\text{by expt. } N_2H_5Pic. \text{ in } \left\{ \begin{array}{l} 0.133 M NaCl \\ 0.067 M NaPic. \end{array} \right\} + 0.0033 M HCl = 2.98 \times 10^{-4} \quad (5)$$

From (4) and (5) it may be seen that changing Pic^- from 0.0709 to 0.0142 *M* causes

The values of the equilibrium constant calculated from measurements in 0.0033 *M* hydrochloric acid were rather high (Table IV), but when the constant for the equilibrium between hydrazine, acetone and dimethylketazine was determined (Part 2) it was seen that this acid concentration is so low that appreciable amounts of ketazine were present, in addition to the acetone hydrazone. When allowance was made for this, much better agreement was obtained, as noted in the "corrected *K*," Table IV.

1B. Determination of Equilibrium 2a from Distribution Experiments.—Mainly as a check on the solubility method the equilibrium was determined also by the distribution of acetone between benzene and solutions containing 0.2 *M* sodium chloride and 0.02 *M* hydrochloric acid, without and with addition of hydrazine hydrochloride. Knowing the distribution ratio when no hydrazine was present, the amount of free acetone in the equilibrium solution when hydrazine is present readily may be calculated. The difference gives the amount which has combined to form acetone hydrazone. The results are summarized in Table V.

TABLE V
EQUILIBRIUM FROM DISTRIBUTION OF ACETONE BETWEEN BENZENE AND HYDRAZINE
HYDROCHLORIDE SOLUTIONS

Solvent: 0.2 <i>M</i> NaCl-0.02 <i>M</i> HCl with or without 0.02 <i>M</i> N ₂ H ₅ Cl				
Concn. acetone in water layer, with no N ₂ H ₅ present	Concn. acetone in water layer with 0.02 <i>M</i> N ₂ H ₅ Cl	<i>A</i>	<i>D</i>	<i>K</i> _{2a}
0.0593	0.0510	0.0117	0.0083	(13.9)
.0297	.0260	.0163	.0037	8.74
.0297	.0262	.0165	.0035	8.10
.0593	.0513	.0120	.0080	(13.0)
.0297	.0258	.0161	.0039	9.4

(a) **Procedure.**—The strong stock solutions were diluted to give the proper concentration of each reagent and 50 cc. each of benzene and the solution were rotated together for eighteen hours at 15°. Fifteen cc. samples were then taken and the acetone in the benzene layer was determined by Messinger's method.⁷

The validity of the distribution method depends upon the assumption that no hydrazine or acetone hydrazone passes into the benzene layer. Since the solution is acid, both should be present as salts. There is reason to believe that the salts would be little soluble in benzene but several benzene samples were carefully tested for the presence of hydrazine after boiling with 3 *M* acid. The results were entirely negative, proving the absence of hydrazine, hydrazone and ketazine from the benzene layer. The high solubility of acetone in benzene reduced the available concentration of 0.97 × 10⁻⁴ in the *K*_{s.p.}. It was assumed that this increase would be linear and that smaller changes in *Pic.*— such as would be met when acetone is added to the solvent (increasing the solubility) would cause a proportional change.

⁷ Goodwin, THIS JOURNAL, 42, 39 (1920).

tration in the water layer so much that small errors are magnified in obtaining the equilibrium data, but the results give good confirmation for the solubility measurements.

The mean value of K_{2a} from all the experiments, both solubility and distribution, is 10.3, but in view of the uncertainty regarding salt effects which may exist it is reasonable to round it off to 10.0. This will be used in the subsequent calculations.

Having thus established the relation existing between acetone, hydrazine and acetone hydrazone, it is possible to determine the hydrolysis equilibrium of dimethylketazine.

Part II

Determination of the Equilibrium Constant for the Hydrolysis of Dimethylketazine.—The hydrolysis was studied with the use of a device previously described,⁸ by which the investigators followed the addition of anions to the ethylene oxides. The essential part consisted of a microburet with a very fine tip from which acid was run into the solution at a rate just sufficient to replace the H^+ used in the hydrolysis of the ketazine. The previous reaction differed from the present in that it was independent of the hydrogen-ion concentration, while in our work the hydrogen ion was one of the reactants. It was necessary therefore to have a much closer regulation of the P_H in this case.

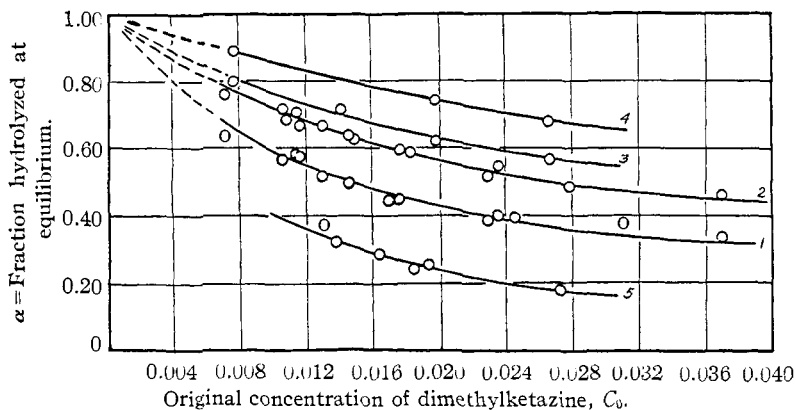
(a) **Procedure.**—The vessel containing the ketazine solution was placed in a narrow, transparent, constant-temperature bath and sky light reflected through it. A suitable amount of indicator (brom cresol green) was placed in the reacting solution, and in similar vessels on each side were placed, with the same amount of indicator, phthalate buffer solutions differing by 0.1 P_H unit (greater and less) from the P_H desired for the equilibrium mixture. A mechanical stirrer was provided, operating through a stopper, and acid (0.8089 M) was run in from the buret at a rate to keep the color of the indicator within the limits set by the standards on either side. The readings of the buret were taken from time to time and they furnished a record of the velocity of the reaction for Part 3. The final reading was taken after a matter of hours in order to ensure attainment of equilibrium. It would appear that the best results one might hope for would be not closer than 0.1 P_H unit, but by working only when the light was good much better results than this were actually realizable, as the curves show.

(b) **Results.**—Equilibrium data were obtained at 15° over a range of ketazine concentration from 0.007 to 0.037 M at P_H 5.35 and 4.95;⁹ at P_H 5.00 and 4.60 with M sodium chloride as solvent instead of water, and, finally, at 20°, at P_H 5.35, using in all cases brom cresol green as indicator. The reacting solution had a volume of 51 cc. (50 in a few runs) to which were added during the reaction varying amounts of perchloric acid—never more than 1.10 cc. This was corrected for in calculating the

⁸ Brönsted, Kilpatrick and Kilpatrick, *THIS JOURNAL*, **51**, 428 (1929).

⁹ These P_H values have been corrected as suggested by Kolthoff, *J. Phys. Chem.*, **32**, 1820 (1928), for differences between reacting salt concentration and the concentration of the standard buffers.

constants. In Fig. 1 there is plotted as ordinate the fraction " α " of dimethylketazine which has been hydrolyzed at equilibrium; as abscissa the total concentration of ketazine, hydrazine and acetone hydrazone. This was determined by boiling a measured sample of the equilibrium mixture with dilute acid to decompose the acetone compounds and volatilize



1, P_H 5.35, temp., 15°; 2, P_H 4.95, temp., 15°; 3, P_H 5.00, temp., 15°, 1.0 M NaCl; 4, P_H 4.60, temp., 15°, 1.0 M NaCl; 5, P_H 5.35, temp., 20°, add 0.30 to ordinates.

Fig. 1.—Variation of hydrolysis equilibrium with concentration of ketazine.

the acetone, and then titrating the hydrazine. This gives C_0 , the original concentration of ketazine with allowance made for dilution by the added acid. For the sake of economy of space not all the data for Fig. 1 are included but Table VI gives typical results, together with the percentage deviation of the individual points from the smooth curve. For only one point in Fig. 1 is the deviation greater than 5%. Since by our device

TABLE VI
TYPICAL EXPERIMENTAL POINTS FOR EQUILIBRIUM CURVES IN FIG. 1

(a) Temp., 15°; P_H , 4.95 (curve 2)				(b) Temp., 20°; P_H , 5.35 (Curve 5)			
Orig. concn. of ketazine, C_0	Fraction reacted at equilibrium	Curve	Deviation, %	Orig. concn. of ketazine, C_0	Fraction reacted at equilibrium	Curve	Deviation, %
0.007	0.752	0.784	-4.0	0.02346	0.548	0.526	+4.2
.01054	.714	.700	+2.0	.02780	.481	.493	-2.3
.01073	.683	.695	-1.7	.03697	.460	.448	+2.7
.01125	.717	.688	+4.2				
.01144	.688	.673	-0.7				
.01290	.664	.657	+1.1	.01300	.672	.642	+4.7
.01482	.626	.642	-2.5	.01375	.620	.628	-1.3
.01450	.638	.632	+1.0	.01624	.597	.598	...
.01756	.594	.588	+1.0	.01840	.540	.558	-3.2
.01820	.588	.580	+1.6	.01923	.553	.549	+0.7
.02285	.514	.531	-3.2	.02730	.530	.536	-1.1

the H^+ is kept constant during any series of runs, the reaction becomes essentially monomolecular to the right (see Equations 1 and 1a), and bi- or trimolecular in the reverse direction. Dilution will thus favor the hydrolysis, and as C_0 approaches zero, α will approach 1.0. This fact was taken into consideration in drawing the best curve for each set of points.

(c) **Calculations.**—For the calculation of the hydrolysis equilibrium there were in each case four quantities available: (1) C_{H^+} , which was constant and used only in the final calculation (ordinarily it was included with the constant); (2) the sum of the equilibrium concentrations of ketazine, acetone hydrazone and hydrazine ($C + D + A$) (This is equal to C_0 , the total ketazine if no hydrolysis had taken place.) (3) the concentration of acid needed to bring the system to equilibrium at the desired P_H . (This is equal to the concentration of the hydrazine plus that of acetone hydrazone ($D + A$) and also equal to αC_0 = amount of ketazine hydrolyzed); (4) the equilibrium constant, K_{2a} , which fixes the relation between acetone, hydrazine and acetone hydrazone.

$$K_{2a} = \frac{D}{A \times B} = 10.0 \text{ or } \frac{A \times B}{D} = 0.1 \quad (4a)$$

With these at hand calculation was made as follows: Equations 1 and 2 show that if neither hydrazine nor acetone is added from without

$$\text{the concentration } (B) \text{ of acetone at equilibrium} = 2A + D \quad (6)$$

for if $A = 0$, $B = D$; if $D = 0$, $B = 2A$. Then

$$\frac{A \times (2A + D)}{D} = 0.1 \quad (4a)$$

but

$$A + D = \alpha C_0 \text{ and } D = (\alpha C_0 - A) \quad (7)$$

Substituting this value for D in (4a) and solving

$$N_2H_5^+ = A = \frac{-(\alpha C_0 + 0.1) + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2} \quad (8)$$

Using (8), (7) and (6), the quantities needed for the calculation of K_1 or K_{1a} may be obtained from the two experimental figures C_0 and α .¹⁰

The constant so obtained contains in it the constant factor C_{H^+} . Introducing a numerical value for C_{H^+} gives a value for K_{1a} which may be used for the calculation of the hydrolysis under any desired condition of acidity. Table VII gives the results at different P_H and temperatures. They may be summarized as indicated in Table VIII.

¹⁰ The concentration of acid added will only be equal to that of the hydrazine and hydrazone formed by hydrolysis if the unhydrolyzed ketazine itself does not act as a base. To test this, acetone was added to dimethylketazine, with a small amount of water. This served to prevent hydrolysis of the ketazine. When no indicators were added to the solution, it was found to be slightly acid to brom thymol blue, slightly basic to brom cresol green, and neutral to brom cresol purple, showing that the ketazine itself does not, under these conditions at least, function as a base.

TABLE VII
EQUILIBRIUM CONSTANT FOR HYDROLYSIS OF DIMETHYLKETAZINE, K_{1a}
(a) P_H , 5.00; temp., 15°; solvent 1 M NaCl

C_0	$C = (1 - \alpha)C_0$	$A + D$	A	D	$B = 2A + D$	$K_{1a} C_H^+ \times 10^4$
0.007	0.001319	0.005681	0.00510	0.00058	0.01078	4.5
.010	.00240	.00760	.00665	.00095	.01425	5.6
.015	.00465	.01035	.00870	.00165	.01905	6.8
.020	.00748	.01252	.01020	.00232	.02272	7.1
.025	.01050	.01450	.01155	.00295	.02605	7.5
.030	.01374	.01626	.01265	.00361	.02891	7.6

Mean 6.93

(b) P_H , 5.35; temp., 15°; solvent, H_2O

0.007	0.002294	0.004706	0.00432	0.000394	0.00903	1.6
.010	.00412	.00588	.00529	.000590	.01117	1.6
.015	.00764	.00736	.00645	.000910	.01381	1.6
.020	.01150	.00850	.00734	.00116	.01584	1.6
.025	.01550	.00950	.00810	.00140	.01758	1.6
.030	.01956	.01044	.00880	.00169	.01919	1.7
.035	.02365	.01135	.00940	.00195	.02075	1.7
^a	.0172401585	.00219	.01389	1.8
^a	.0193501550	.00207	.01307	1.4

Mean 1.64

(c) P_H , 5.35; temp., 20°; solvent, H_2O

0.010	0.00300	0.00700	0.0062	0.00080	0.01320	3.6
.015	.00590	.00910	.0078	.00130	.01690	3.8
.020	.00920	.01080	.0090	.00180	.01980	3.8
.025	.01268	.01232	.01005	.00227	.02237	3.97

Mean 3.8

(d) P_H , 4.95; temp., 15°; solvent, H_2O

0.007	0.00150	0.005495	0.00498	0.000515	0.01047	3.6
.010	.00288	.00712	.00630	.00082	.01342	3.9
.015	.00564	.00936	.00802	.00134	.01738	4.3
.020	.00880	.01120	.00930	.00190	.02051	4.4
.025	.01215	.01285	.01045	.00240	.02331	4.6
.030	.01560	.01440	.01145	.00295	.02580	4.9
.035	.01911	.01589	.01239	.00350	.02829	5.2
^a	.01498	.02194	.01830	.00364	.02024	5.0

Mean 4.5

(e) P_H , 4.60; temp., 15°; solvent, 1 M NaCl

0.007	0.00073	0.00627	0.00560	0.00067	0.01187	(10.8)
.010	.00145	.00855	.00740	.00115	.01595	(13.0)
.015	.00309	.01191	.00980	.00211	.02171	15.0
.020	.00520	.01480	.01170	.00310	.02650	16.0
.025	.00765	.01735	.01332	.00403	.03067	16.0
.030	.01044	.01956	.01455	.00501	.03411	16.0

Mean 16.0

^a 0.01 M N_2H_5 added before the run.

(d) Discussion.—The equilibrium may be calculated either on the basis of

$$\frac{C_{N_2H_5^+} \times C_{Acetone}^2}{C_{Ketazine}} = K_{1a} \cdot C_H^+, \text{ or}$$

$$\frac{C_{Acetone\ hydr.}^+ \times C_{Acetone}}{C_{Ketazine}} = K_1 \cdot C_H^+$$

As seen in Table VIII the constant in the second case will be 10 times that in the first, since $K_1 = K_{1a} \cdot K_{2a} = 10K_{1a}$. Since K_{1a} deals with the

TABLE VIII
HYDROLYSIS CONSTANTS FOR DIMETHYLKETAZINE AT 15°

p_H	Solvent	$K_1 \cdot C_{H^+}$	$K_{1a} \cdot C_{H^+}$	K_{1a}
5.35	Water	1.64×10^{-3}	1.64×10^{-4}	36.5
4.95	Water	4.5×10^{-3}	4.5×10^{-4}	37.5
5.00	1 M NaCl	6.93×10^{-3}	6.93×10^{-4}	73.8
4.60	1 M NaCl	15.9×10^{-3}	15.9×10^{-4}	69.3
5.35 (20°)	Water	3.8×10^{-3}	3.8×10^{-4}	84.4

final simple products of the reaction, it is perhaps preferable to K_1 and the tables have been so prepared. For some purposes K_1 is better. Thus from Table VIII we can find that in water at 15° K_1 has a mean value of 370. If now a value of 0.01 is taken for C_{H^+} and some typical results are chosen from Table II; $A = 0.01245$, $B = 0.03543$ and $D = 0.00457$; then C , the concentration of ketazine present, will be $(0.00457 \times 0.0345) / (C \times 0.01) = 370$; $C = 0.00004 M$. This is less than 1% of the acetone hydrazone present and may therefore be neglected in calculating K_{2a} (as in Part 1) when 0.01 M acid is present.

On the other hand, if $C_{H^+} = 0.0033$, as in Table IV, C becomes an appreciable quantity. Using typical data

$$C = \frac{0.02264 \times 0.0559}{370 \times 0.0033} = 0.00012$$

The ketazine = $0.00012 / 0.00264 \times 100 = 4.5\%$ of the hydrazone present. This explains the fact that using uncorrected figures for the concentration of hydrazone in this solvent a very high value for K_{2a} is obtained. Allowance for the ketazine brings K_{2a} into agreement with the values found in the presence of stronger acid where the ketazine concentration is negligible.

A rise in temperature shifts the equilibrium greatly to the right, favoring the hydrolysis.

The use of a concentrated (1 M) sodium chloride solution as solvent gives a large positive salt effect on the equilibrium constant, the value being approximately double what it is in the solutions of low ionic strength. Writing the equilibrium

$$K_{1a} = \frac{C_{N_2H_5^+} \times C_{Acetone}^2}{C_{Ketazine} \times C_{H^+}} \times \frac{f_1 f_0^2}{f_0 f_1}$$

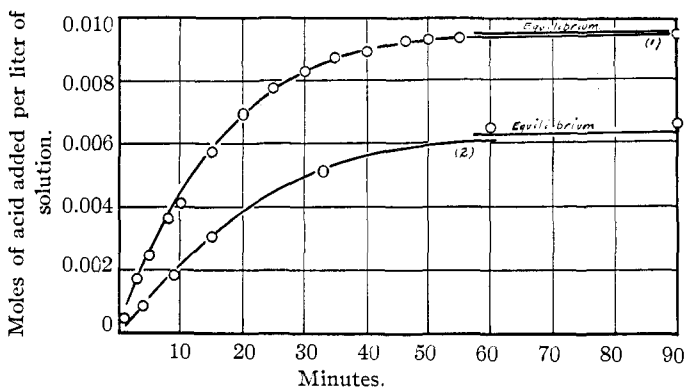
it is seen that in quite dilute solution there will be approximate equality between f_1 in the numerator and f_1 of H^+ in the denominator; likewise between the activity coefficient of the acetone and ketazine, so the factor reduces to f_0 , simply. These assumptions will not hold in such a strong solution as 1 M and the calculation of salt effect would be difficult.

Finally, inspection of the tables shows that at low acidity such as used in this work there is in all cases sufficient of both hydrazine and acetone

hydrazone present so that neither may be neglected. All of the equilibria must be taken into account simultaneously. Having thus established the conditions of equilibrium it is possible to study the kinetics of the reaction.

Part III

The Kinetics of the Hydrolysis of Dimethylketazine.—This hydrolysis is representative of a large group of reactions where H^+ or OH^- is taken up at a measurable rate. The method as used here is applicable only in cases where the P_H may be kept low enough for the proper functioning of indicators, but where applicable gives a valuable method of approach as it effects a considerable simplification of the kinetics.



1, at 20°; 2, at 15°. Note: Run 2 went past the equilibrium point. The curve was drawn below the last two points, but tangent to equilibrium line. This is necessary since the mean K_E is used in the calculation.

Fig. 2.—Velocity of hydrolysis of dimethylketazine at P_H 5.35.

(a) **Procedure.**—The rate of hydrolysis was followed by reading at intervals from the buret (as in Part 2) the amount of acid which had been added. At P_H 5.35 the rate was such that it could be readily followed both at 15 and at 20°. The buret was calibrated and a graph constructed by which readings could be translated into cubic centimeters, and thence to moles of acid per liter of solution.

(b) **Results.**—In Fig. 2 the concentration of acid added, in moles per liter, is plotted as ordinate against time for two representative runs. The data are given in Tables IX and X. Constants were calculated at points read from the curves.

(c) **Calculations.**— C_{H^+} is maintained constant during the reaction and the hydrolysis will proceed as a first-order reaction opposed by a bimolecular reaction (Equation 1), or by a trimolecular reaction (Equation 1a). Since the data are interdependent and both reactions are repre-

sented in the final state of equilibrium, the kinetics will give no indication and the data will fit both assumptions.

TABLE IX

EXPERIMENTAL DATA AND CALCULATION FOR VELOCITY CONSTANT AT 15°; P_H , 5.35

Time, minutes	Buret reading	Moles $HClO_4$ added to 50 cc. of reacting soln. $\left(\text{Buret reading} \times \frac{1.022}{20} \times \frac{0.8089}{1000} \right)$
0	0	
1	0.52	0.0000215
4	1.00	.0000415
9	2.20	.0000913
16	3.92	.0001625
33	6.18	.0002560
60	7.90	.0003275
85	8.10	.0003351
91	8.30	.0003440

Calculation

Time	αC_0 , mole/liter	$(1 - \alpha)C_0$	$\frac{d\alpha C_0}{dt}$ $\times 10^4$	A	B	k_2
0	0	0.01145
5	0.00116	.01029	2.21	0.00113	0.00229	131.2
10	.00238	.00907	1.95	.00227	.00464	135.0
15	.00308	.00837	1.67	.00291	.00599	131.8
20	.00385	.00760	1.37	.00358	.00743	130.7
25	.00450	.00695	1.19	.00412	.00862	142.7
30	.00500	.00645	0.88	.00457	.00957	137.5
35	.00540	.00605	.63	.00490	.01030	137.0
					Mean	135.0

$$k_1 = K_{1a} \cdot k_2 = 0.000164 \times 135.0 = 0.0221/C_H.$$

TABLE X

EXPERIMENTAL DATA AND CALCULATION FOR VELOCITY CONSTANT AT 20°; P_H , 5.35

Time, minutes	Buret reading	Moles $HClO_4$ added to 50 cc. of reacting soln. $\left(\text{Buret reading} \times \frac{1.022}{20} \times \frac{0.5395}{1000} \right)$
0	0
3	3.10	0.000086
5	4.45	.000124
8	6.52	.000182
10	7.40	.000206
15	10.40	.000289
20	12.50	.000347
25	14.00	.000389
30	14.92	.000415
35	15.80	.000439
40	16.10	.000448
47.5	16.60	.000462
50	16.80	.000467
55	16.85	.000468
90	17.10	.000476

TABLE X (Concluded)

Time	αC_0 mole/liter	$(1 - \alpha)C_0$	Calculation			
			$\frac{d(\alpha C_0)}{dt} \times 10^4$	A	B	k_2
0	0	0.01614
10	0.00432	.01182	3.19	0.00410	0.00842	74.0
16	.00600	.01014	2.43	.00540	.01140	77.0
25	.00774	.00840	1.45	.00668	.01442	81.0
35	.00874	.00740	0.69	.00747	.01621	81.0
					Mean	78.0

$$k_1 = K_{1a} \cdot k_2 = 0.000380 \times 78.0 = 0.0294/C_H.$$

As pointed out in Part 2, the buret reading at time "t" gives $A + D = \alpha C_0$; acetone concentration $(B) = 2A + D$, and

$$A = \frac{-(\alpha C_0 + 0.1) + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2}$$

Final titration of a sample for total hydrazine present gives C_0 and $C = (1 - \alpha)C_0$. Then

$$\frac{d(\alpha C_0)}{dt} = k_1(C_0 - \alpha C_0)C_{H^+} - k_2 \cdot A \cdot B^2 \quad (9)$$

or

$$\frac{d(\alpha C_0)}{dt} = k_1(C_0 - \alpha C_0)C_{H^+} - k_2' \cdot B \cdot D \quad (10)$$

Since the values of A , B and D are all expressed in terms of αC_0 , the equation becomes awkward to treat analytically and the purpose is well served by a graphical solution: $K_{1a} = k_1/k_2$ in (9), while in (10) $K_1 = k_1/k_2'$.

For the reason given in Part 2, K_{1a} and Equation 9 have been employed in calculations. The final result is the same in either case.¹¹ Substituting

¹¹ It has been suggested by the reviewer that since the expression $K_{1a} = k_1/k_2' = (A)(B)^2/(C)(H^+)$ may also be stated $K_{1a} = k_1'/k_2' = \frac{(A)(B)}{(C)(H^+) / (B)}$ the velocity may be expressed by the equation (using the alphabetical symbols adopted in the paper)

$$-d(C)/dt = k_1'(C)(H^+)/ (B) - k_2'(A)(B) \quad (x)$$

as distinct from the one actually used, which was based on Equation 9, *i. e.*

$$-d(C)/dt = k_1(C)(H^+) - k_2(A)(B)^2 \quad (y)$$

Equation (x) involves a reverse reaction of the second order, while (y) is based upon a reverse reaction of the third order. When the experimental values are substituted, constant values are obtained for k_1 and k_2 (Equation y) while a drift of several hundred per cent. is observed in the values of k_1' and k_2' (Equation x).

KINETICS OF HYDROLYSIS AT 15°; P_H 5.35

"t"	(C)	$-d(C)dt$	(A)	(B)	k_2	k_2' (Eq. x)
0	0.01145
5	.01029	0.000221	0.00113	0.00229	131.2	0.30
10	.00907	.000195	.00227	.00464	135.0	0.63
15	.00837	.000167	.00291	.00599	131.8	..
20	.00760	.000137	.00358	.00743	130.7	..
25	.00695	.000119	.00412	.00862	142.7	1.2
30	.00645	.000088	.00457	.00957	137.5	..
35	.00605	.000063	.00490	.01030	137.0	1.5

$k_1 = K_{1a} \cdot k_2$ in (9), also the values of A and B in terms of αC_0 and solving for k_2 , the velocity constant for the reverse reaction

$$k_2 = \frac{\frac{d(\alpha C_0)}{dt}}{C_H + K_{1a}(C_0 - \alpha C_0) - \left[\frac{-(\alpha C_0 + 0.1) + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2} \right]} \times \frac{1}{\left[\frac{\alpha C_0 - 0.1 + \sqrt{(\alpha C_0 + 0.1)^2 + 0.4\alpha C_0}}{2} \right]^2}$$

Tangents drawn at suitable points on the curves give $d(\alpha C_0)/dt$ with sufficient accuracy.

By this method is obtained a value of $k_2 = 78.0$ at 20° and 135.0 at 15° ; $k_1 \cdot C_H$ becomes 0.0294 at 20° and 0.0221 at 15° . This corresponds to a temperature coefficient of 2.65 for a 10° rise for the hydrolysis. On the other hand, the reverse reaction has a lower constant at 20° than at 15° . A rise in temperature will therefore shift the whole equilibrium markedly to the right, favoring the hydrolysis.

Having at hand the values of the equilibrium constant at two temperatures, ΔH may be found from the expression

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}. \quad \text{From the data, } \Delta H = 9100 \text{ cal.}$$

It is also interesting to calculate the standard free energy change ΔF° for the reactions involved. For Equation 1a the formation of one mole of hydrazine ion and two moles of acetone from one mole of dimethylketazine, one mole of H^+ and two of water

$$\begin{aligned} \Delta F_{238}^\circ &= -RT \ln K_{1a} = -1323 \log 37.0 \\ \Delta F_{288}^\circ &= -2075 \text{ cal.} \end{aligned}$$

For Equation 1, the formation of one mole of acetone hydrazone and one mole of acetone from one mole of ketazine, one mole of H^+ and one mole of water

$$\begin{aligned} \Delta F_{238}^\circ &= -RT \ln K_1 = -1323 \log 370 \\ \Delta F_{288}^\circ &= -3400 \text{ cal.} \end{aligned}$$

These values are small, as would be expected with a reversible reaction, but taken as they stand would indicate that Reaction 1 is a more probable course for the reaction than 1a, and hydrolysis of dimethylketazine gives first acetone and acetone hydrazone, followed by hydrolysis of the hydrazone to give hydrazine ion and more acetone.

The author wishes to express his gratitude to the John Simon Guggenheim Memorial Foundation and the Regents of the Oregon State College for providing the opportunity for this study. He is especially indebted to Professor Brønsted for the hospitality of his laboratory and for suggestions in the prosecution of the work.

Summary

1. The hydrolysis of dimethylketazine has been studied at 15 and at 20° by a kinetic method.
2. The reaction is reversible and an equilibrium is reached involving H⁺, dimethylketazine, acetone hydrazone, acetone and hydrazine.
3. Equilibrium constants have been evaluated under several conditions.
4. The kinetics of the reaction have been studied at the two temperatures and velocity constants for the forward and reverse reactions obtained.
5. Some of the free energy values have been calculated.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE RICE INSTITUTE]

THE EFFECT OF STRUCTURE OF ORGANIC HALIDES ON THEIR RATE OF REACTION WITH INORGANIC HALIDES.

III. THE EFFECT OF THE PHENYLTHIO, ALPHA-NAPHTHOXYL AND BETA-NAPHTHOXYL GROUPS

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Previous papers published from this Laboratory on the effect of structure of organic chlorides on their rate of reaction with potassium iodide in absolute acetone solution have included the effect of the phenoxy and methylthio groups,¹ and it seemed of interest to determine how these rates would be affected by substituting an α - and β -naphthoxy group for a phenoxy, and a phenylthio group for a methylthio group. The data also give a comparison of the relative effect of an oxygen and sulfur atom in compounds of the structure $C_6H_5O(CH_2)_nCl$ and $C_6H_5S(CH_2)_nCl$. These comparisons are summarized in Table I.

A study of this table brings out the following relationships of structure to reactivity. 1. A chlorine atom in the β -position to a given group has a reactivity which is in every case less than the reactivity of the chlorine atom when in the γ -position to the same group. The ratio of these reactivities at 50° varies between 1:1.53 for the phenyl group, which is the smallest ratio, to 1:6.14 for the α -naphthyl group, which is the greatest.

2. The temperature coefficient A is in every case higher in the compounds with two carbon atoms between the chlorine and the activating group than in the corresponding compounds with three carbon atoms. The values for A in the first case average approximately 4600 and approximately 4150 in the second case.

3. A phenylthio group in the β - or γ -position to a chlorine atom causes the reactivity of that chlorine atom to be about twice as great as when a

¹ Kirner, THIS JOURNAL, 48, 2745 (1926); *ibid.*, 50, 2446 (1928).