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Ultraviolet Spectra of Hydrazide Solutions and Their Hydrolysis. II. Hydrolysis of Formhydrazide in Alkaline Solutions

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The aparent first-order rate constants of the base catalyzed hydrolysis of formhydrazide have been determined by ultraviolet absorption measurements. Three cases of hydrolysis applicable to three different ranges of NaOH concentrations were recognized. The activation entropies have been calculated from the change of rate constant with temperature. The effects of solvent basicity and temperature on the absorption spectra have also been studied.

Recently, the effects of amide structure, hydroxide ion concentration, temperature, and other variables on the kinetics of base-catalyzed hydrolysis of amides have been studied by a number of investigators.[1] Similar effects on the kinetics of alkaline hydrolysis of hydrazides have not been reported.

The hydrazides are expected to undergo hydrolysis catalyzed by both acid and base. The acidic hydrolysis of formhydrazide has been reported.[2] In the present work we have examined the effects of hydroxide ion concentration and temperature on the kinetics of base-catalyzed hydrolysis of formhydrazide.

Experimental

Materials and apparatus have been described.[2] The alkaline solvents were made by diluting the stock solution of NaOH (reagent grade) immediately before each set of measurements.

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[1] *Cf.*, *e.g.*, R. H. DeWolfe and R. C. Newcomb, *J. Org. Chem.*, **36**, 3870 (1971).

[2] M. Mashima and F. Ikeda, This Bulletin, **46**, 1366 (1973).

Results

Apparent First-Order Rate Constant (k_{obs}). The dependence of k_{obs} upon NaOH concentrations is shown in Table 1 and Fig. 1. The values of k_{obs} increase with increasing NaOH concentration up to a certain value, levelling off near *ca.* 0.5 mol/l, and then decrease gradually.

TABLE 1. RATE CONSTANTS OF THE BASE-CATALYZED HYDROLYSIS OF FORMHYDRAZIDE AT 25°C

NaOH molarity	$k_{\mathrm{obs}} \times 10^2$ (min^{-1})	NaOH molarity	$k_{\mathrm{obs}} \times 10^2$ (min^{-1})
0.101	0.200	0.905	2.24
0.0153	0.282	1.02	2.24
0.0198	0.373	1.36	2.23
0.0253	0.465	1.60	2.16
0.0355	0.691	2.02	2.11
0.0510	1.14	2.51	2.02
0.102	1.27	3.05	1.97
0.130	1.48	3.34	1.94
0.162	1.65	4.05	1.80
0.202	1.87	4.48	1.70
0.250	2.09	5.09	1.65
0.308	2.15	5.51	1.51
0.404	2.26	6.35	1.46
0.510	2.32	8.24	1.05
0.604	2.38	9.16	0.985
0.805	2.27		

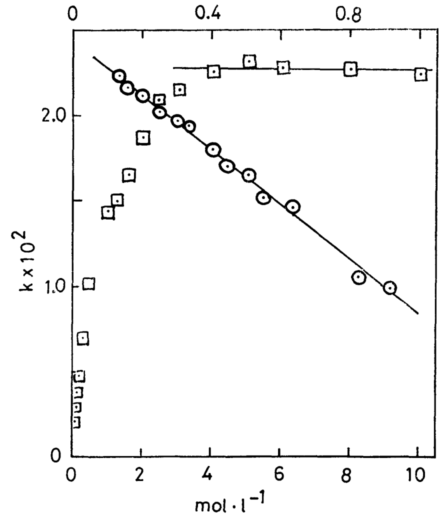

Fig. 1. The plot of k_{obs} *vs.* [NaOH]. ⊡: lower [NaOH] used the upper scale of abscissa, ⊙: higher [NaOH] used the down scale.

Kinetics in Dilute NaOH Solutions. In NaOH solutions ($<$*ca.* 0.5 mol/l) the reaction scheme is given by the following equations. NH_2NHCHO molecule and OH^- ion combine reversibly to form a complex (1) which decomposes slowly to form products (2).

$$NH_2NHCHO + OH^- \rightleftharpoons NH_2NHC^-(OH)OH \qquad \text{equil. const. } K \qquad (1)$$

$$NH_2NHC^-(OH)OH \longrightarrow HCOO^- + NH_2NH_2 \qquad \text{rate const. } k \qquad (2)$$

Rate laws and K are given by

$$-\mathrm{d}[F]/\mathrm{d}t = k[A^-] \qquad (3)$$

$$-\mathrm{d}[F]/\mathrm{d}t = k_{\mathrm{obs}}[F] \qquad (4)$$

$$K = \frac{[A^-]}{[A]}\,\frac{\gamma_{A^-}}{\gamma_A a_{OH^-}}, \qquad (5)$$

where A and A^- stand for NH_2NHCHO and $NH_2NHC^-(OH)OH$, respectively; F=total hydrazide ($A+A^-$); γ and a are activity coefficient and activity, respectively. The overall rate constant k_{obs} is readily combined with both k and K.

$$1/k_{\mathrm{obs}} = 1/k + (1/kK) \times (\gamma_{A^-}/\gamma_A a_{OH^-}) \qquad (6)$$

A plot of $1/k_{\mathrm{obs}}$ *vs.* $\gamma_{A^-}/(\gamma_A \times a_{OH^-})$ gives a straight line with a slope $1/kK$ and intercept $1/k$ (Fig. 2). The values of a_{OH^-} were assumed to be equal to those of mean activity ($a_\pm$) of NaOH, calculated by using mean activity coefficient obtained by interpolation from the values of Åkerlöf and Kegeles;[3] the values of γ_{A^-} were calculated from the approximate Debye-Hückel equation $\log \gamma_{A^-} = -0.510 \times z^2 \times (I)^{1/2}/(1+1.15\times(I)^{1/2})$, where z is the valency of A^- (equal to unity) and I is the ionic strength of aqueous NaOH solutions. A good extrapolation was obtained giving $k=3.03\times10^{-2}\ \mathrm{min}^{-1}$. With this value the slope gives $K=7.76$. Consequently, the linear plot indicates that in the region of NaOH concentration lower than *ca.* 0.5 mol/l the reaction scheme is given by equations 1 and 2, the rate-determining step being the unimolecular decomposition of the complex (Eq. 2). The true reaction mechanism will be complicated because of the change in hydration in passing from the reactants ($NH_2NHCHO+OH^-$) to the complex and to the resultants.

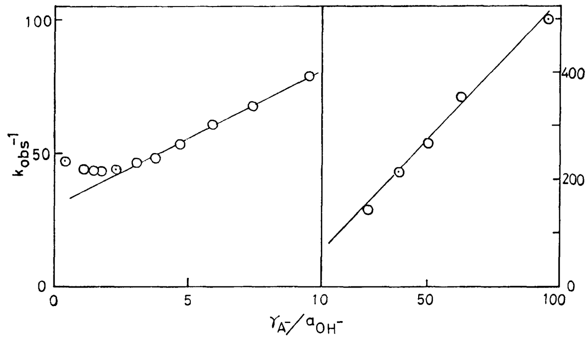

Fig. 2. The $1/k_{\mathrm{obs}}$ *vs.* γ_{A^-}/a_{OH^-} plot.

Kinetics in Moderately Concentrated NaOH Solutions. A possible mechanism for the base catalysis is one in which the attacking species is hydroxide ion, the reaction scheme being given by

$$NH_2NHCHO + OH^- \overset{\text{slow}}{\rightleftharpoons} HCOO^- + NH_2NH_2 \qquad (7)$$

In this case the overall rate constant k_{obs} can be combined with OH^- concentration by $k_{\mathrm{obs}}=k[OH^-]$. As seen from Fig. 1, the plot of k_{obs} *vs.* $[OH^-]$ (taken as equal to the stoichiometric concentration of NaOH) shows that k_{obs} is nearly constant in the narrow range of [NaOH], *ca.* 0.5—1 mol/l. Above *ca.* 1.5 mol/l k_{obs}

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[3] G. Åkerlöf and G. Kegeles, *J. Amer. Chem. Soc.*, **62**, 620 (1940).

decreases linearly with increasing [NaOH]. Thus, the base-catalyzed hydrolysis would proceed by Eq. (7) in these regions of [NaOH], the changes of hydration numbers being disregarded.

Dependence of Rate Constant on Temperature. Temperature effects were examined at 15, 20, 25, 30, and 35 °C for reaction solutions made with 0.250, 0.582, and 3.34 mol/l [NaOH] (substrate concentrations 1.5—0.6×10^{-3} mol/l). These concentrations lie in the three ranges where the hydrolysis proceeds in different ways. The Arrhenius plot, $\log k_{\mathrm{obs}}$ *vs.* $1/T$ is shown in Fig. 3 and the values of k_{obs} in Table 2. The data give a straight line, the Arrhenius activation energy of 51.3 kcal/mol being obtained from its slope. The entropy of activation, 112 e.u., was calculated for 25 °C by means of the equation given by Bunnett.[4]

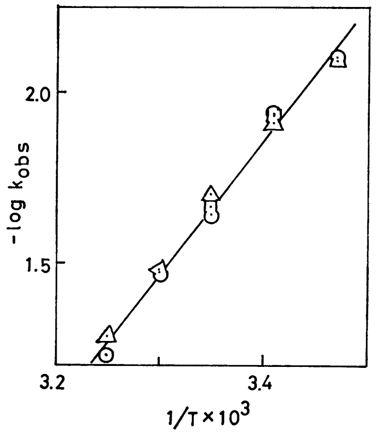

Fig. 3. Arrhenius plot, $\log k_{\mathrm{obs}}$ *vs.* $1/T$.
⊡: 0.250, ⊙: 0.582, △: 3.34 mol/l.

Table 2. Temperature effects on k_{obs}

Temperature (°C)	$k_{\mathrm{obs}}\times10^2$, min^{-1} NaOH concentration, mol/l		
	3.34	0.582	0.250
15	0.799	0.788	—
20	1.23	1.15	1.16
25	1.94	2.27	2.09
30	3.30	3.35	—
35	5.22	5.93	—

Behavior of Absorption Maxima. The primal absorption maximum of reaction solutions shifts successively to longer wavelengths with increasing NaOH concentration and rising temperature. The temperature effects on $\lambda_{\max}$ is shown in Fig. 4 (the ordinate scale is not available for a comparison of absorption intensity). Figure 5 shows the plot of $\lambda_{\max}$ for a series of [NaOH] against the logarithm of mean activity $a_{\pm}$ of NaOH. At lower NaOH concentration the values of $\lambda_{\max}$ vary linearly with increase in $\log a_{\pm}$, but at higher concentration a negative deviation from the line takes place. It is of interest that the change in the value of $\lambda_{\max}$ might be connected with this simple thermodynamic character of solvents.

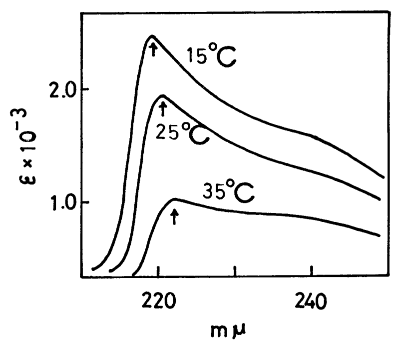

Fig. 4. Temperature effect on absorption of reaction solutions made by 0.582 mol/l NaOH.

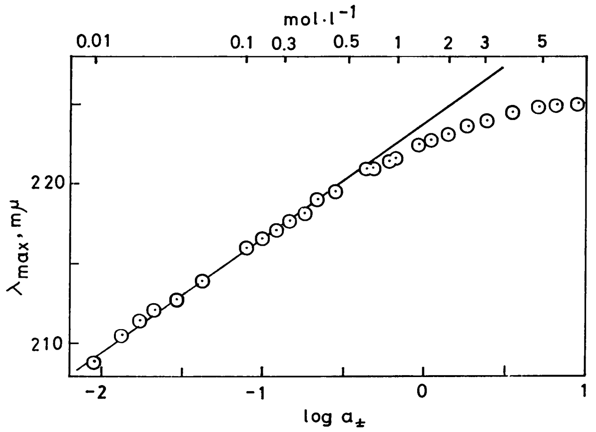

Fig. 5. The plot of $\lambda_{\max}$ *vs.* $\log a_{\pm}$.

Discussion

Mechanism of Hydrolysis. The products of alkaline hydrolysis of the hydrazides $RCONHNH_2$ would be carboxyl ions and hydrazine:

$$RCONHNH_2 + OH^- \longrightarrow RCO_2^- + NH_2NH_2. \quad (8)$$

We see that the reaction involves rate-determining unimolecular decomposition of the complex in dilute solutions,

$$S + OH^- \rightleftharpoons SOH^-$$

$$SOH^- \xrightarrow{\text{slow}} \ddagger \longrightarrow \text{products}$$

and the rate-determining nucleophilic attack of OH^- in moderately concentrated solutions,

$$S + OH^- \xrightarrow{\text{slow}} \ddagger \longrightarrow \text{products.}$$

Although the value of activation entropy is based on pseudo-first-order rate constants independent of solvent basicity, the observed medium independence of $\Delta S^{\ddagger}$ over the range of basicities 0.25—3.34 mol/l would not be expected to lead to such a constancy, provided a mechanism change is involved.

Correlation of k_{obs} with Acidity Function H_-. Yagil and others[5] summarized the formulation of rate expressions of eight types of base-catalyzed reactions, which can be divided into three groups. Our results (Eqs. 1, 2, and 7) belong to the group containing

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[4] J. F. Bunnett, "Technique of Organic Chemistry," Vol. VIII, Part I, ed. by A. Weissberger, Interscience, New York, N. Y. (1961), p. 201.

[5] M. Anbar, M. Bostelsky, D. Samuel, and G. Yagil, *J. Amer. Chem. Soc.*, **85**, 2380 (1963).

reactions expected to give a linear plot of $\log k_{\mathrm{obs}}$ *vs.* $H_{-}+\log C_{\mathrm{w}}$,[6] with about unit slope. The plot for our results is shown in Fig. 6 together with the Zucker-Hammett type plot, $\log k_{\mathrm{obs}}$ *vs.* H–. Both plots indicate that, in the range of NaOH concentration shown in Fig. 6, two linear parts can be obtained with slopes (<0.3) deviating greatly from unity, with a boundary point between them.

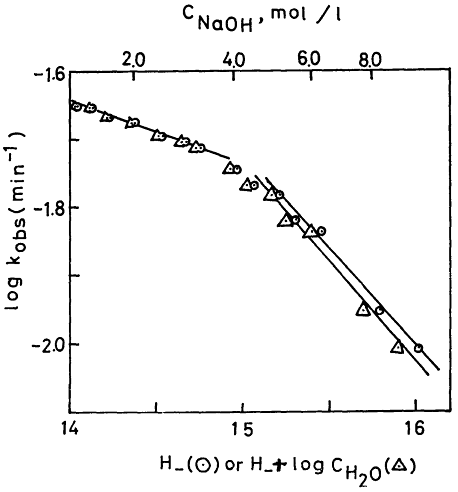

Fig. 6. The plot of $\log k_{\mathrm{obs}}$ *vs.* H_{-} (⊙) or $H_{-}+\log C\mathrm{w}$ (△).

By analogy with the Bunnett treatment[7] of the acid-catalyzed reactions, $\log k_{\mathrm{obs}}-H_{-}$ was plotted against the logarithm of water activity a_{W} (Fig. 7) for the hydrolysis in reaction solutions except for ones prepared with very dilute NaOH solutions. Three linear parts were obtained; in dilute NaOH solutions ($<$*ca.* 0.8 mol/l) with slope 40, in the range *ca.* 1—3 mol/l with 20 and $>$*ca.* 5 mol/l with 5.6. Assuming that these parts correspond to three types of hydrolysis, one is the rate-determining unimolecular decomposition of the complex $\mathrm{NH_2NHC^-(OH)OH}$, and the other two due to the rate-determining nucleophilic attack of $\mathrm{OH^-}$ with different values of slope of the plot k_{obs} *vs.* [NaOH], the results being consistent with those given in the preceeding paragraph. As Rochester[8] has pointed out,

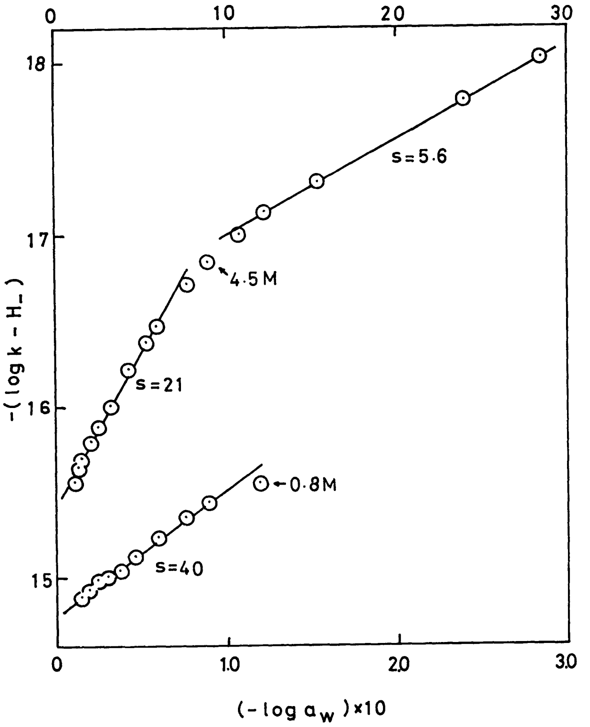

Fig. 7. The plot of $\log k_{\mathrm{obs}}-H_{-}$ *vs.* $\log a_{\mathrm{w}}$. The upper scale of abscissa is used for the upper plots and the lower scale for the lower ones.

the values of slopes of the linear plot, $\log k-H_{-}$ *vs.* $\log a_{\mathrm{w}}$, would provide useful criteria for the mechanism of reactions in basic media.

Behavior of Absorption Maxima. Smith and Symons[9] ascribed the red-shifts of the first electronic absorption band of solvated iodide ions with temperature rise to an increase in the average radius of the solvent shell. As shown in Fig. 4, the maximum of primary absorption of reaction solutions shifts to longer wavelengths with temperature rise. The effect is ascribable to the change in energy levels of hydrated molecular or ionic species of formhydrazide and to the change of the water shell. It is of interest that there is a linear correlation between λ_{max} and $\log a_{\pm}$ of NaOH in the range $<$*ca.* 0.8 mol/l of basicities, where the rate constants have also been combined with $a_{\pm}$.

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[6] For C_{w} denoting the concentration of free water, see G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, **85**, 2376 (1963).

[7] J. F. Bunnett, *ibid.*, **83**, 4956, 4968, 4973, 4978 (1961).

[8] C. H. Rochester, "Acidity Functions," Academic Press, London (1970), p. 243.

[9] M. Smith and H. C. R. Symons, *Discuss. Faraday Soc.*, **24**, 206 (1957).