Ultraviolet Spectra of Hydrazide Solutions and Their Hydrolysis. I. Hydrolysis of Formhydrazide in Acid Solutions

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The protonation constant 1.99 of formhydrazide (pK_{BH^+}) has been obtained from measurements of its ultraviolet absorption in dilute sulfuric acid. From the absorption in concentrated sulphuric and perchloric acids, the apparent first-order rate constants of acid-catalyzed hydrolysis have been determined. The reaction mechanism of rate-determining steps has been proposed by means of the plots of Zucker-Hammett and Bunnett.

Ultraviolet absorption spectra and hydrolysis of amides have been of interest to a number of investigators. However, little is known about the ultraviolet spectra and hydrolysis of hydrazides. Edward, Hutchison and Meacock[1] determined the rate constants for the hydrolysis of acethydrazide in aqueous hydrochloric acid. They obtained the first-order rate constants which increase with the increase of acid concentration. For acethydrazide in 0.1 N HCl, Lindegren and Niemann[2] determined the apparent ionization constant of $AcNHNH_3^+$ by potentiometric titration and obtained 3.24 for pK_{BH^+}. Recently, the present authors[3] have investigated ultraviolet spectra of some hydrazides in various solvents and have reported on the behavior of a band with maximum at about 190 mμ.

A series of works has been made for examining systematically the spectral change of hydrazides in aqueous solutions by adding electrolytes and nonelectrolytes, and for determining the rate constant of the hydrolysis of hydrazides in acid- and alkali-media. The present communication deals with spectroscopical measurements of the protonation constant of formhydrazide and its rate constant of hydrolysis in sulphuric and perchloric acids.

Experimental

Materials and Apparatus. Formhydrazide was synthesized with methylformate and hydrazinehydrate and purified by recrystallization from ether–ethanol mixture: mp 54 °C. Formhydrazidehydrochloride was precipitated from a solution of formhydrazide dissolved in an aqueous hydrochloride by addition of ethanol and the precipitates were washed repeatedly with ethanol: mp 139 °C. Aqueous acid solutions were prepared by dilution of reagent-grade acids with water. They were standardized by titration with standard sodium hydroxide solution. Organic solvents, methanol and dioxane, were of spectrograde.

The ultraviolet solution spectra were measured with a Hitachi EPS-3T Recording Spectrophotometer equipped with a thermostated cell compartment. All the measurements were carried out at 25±0.01 °C.

Rate Measurements. Reactions were followed by recording the change in absorbance A with time. The apparent first-order rate constant k' was calculated graphically from plots of log $(A-A_\infty)$ *vs.* time (min) or by means of a computer program which gives, by adjustment of A_∞, the first-order rate constant which best fits the observed data. In view of the highly dilute reaction solutions, 10^{-3} M (mol/l), used for spectrophotometric examination, no attempt was made to isolate reaction products from the reaction solutions. It is expected that the products are formic acid and hydrazine (or hydrazinium ions). To check the A_∞, the absorption spectra of these materials dissolved in reaction media were examined and compared with those of reaction solutions.

Results and Discussion

Absorption Spectra. The ultraviolet solution spectra of formhydrazide and its hydrochloride are shown in Fig. 1. In water formhydrazide gives a broad absorption band asymmetrically broadened to the low energy side, having probably four component bands with maxima at about 188, 189, 192, and 193 mμ. Such an absorption is characteristic of the hydrazides in water.[3] For formhydrazide this band red-shifts to 203 mμ in methanol and to 212 mμ in dioxane (curves 2 and 3, Fig. 1). It has been tentatively assigned[3] to the π→π* transition of the carbonyl π-electron system perturbed by the π-electron system of $NHNH_2$ group. If this is the case, the result is not in line with the view that the π→π* transition band red-shifts by hydrogen bonding in hydroxylic solvents.[4]

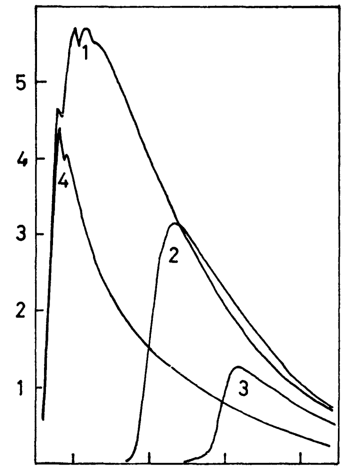

Fig. 1. Ultraviolet spectra of formhydrazide (1, in water; 2, in methanol; 3, in dioxane) and its hydrochloride (4, in water).

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[1] J. T. Edward, H. P. Hutchison and S. C. R. Meacock, *J. Chem. Soc.*, **1955**, 2520.

[2] C. R. Lindegren and C. Niemann, *J. Amer. Chem. Soc.*, **71**, 1504 (1949).

[3] M. Mashima and F. Ikeda, *Chem. Lett.*, **1972**, 209.

[4] G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco (1960), Chap. 4.

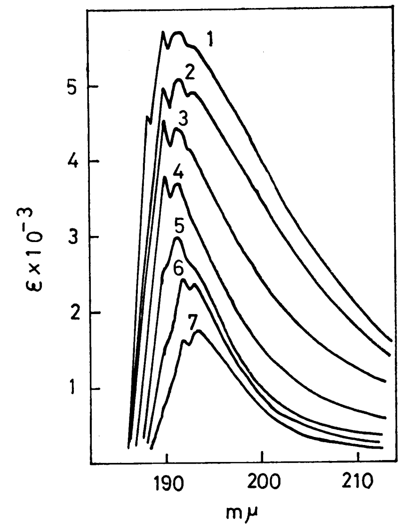

Fig. 2. Spectral changes of formhydrazide in dilute aqueous sulphuric acid.
The acid concentrations are (1) 0, (2) 0.5768×10^{-3}, (3) 0.2884×10^{-2}, (4) 0.1154×10^{-1}, (5) 0.5047×10^{-1}, (6) 0.5678×10^{-1}, (7) 0.1131N.

Formhydrazide hydrochloride in water shows two bands with maxima at 188 and 189 mμ. They are ascribable to electronic transition in formhydrazidinium ion, $HCONHNH_3^+$, which is expected to have two electronic transitions with nearly equal energies.

Spectral Changes in Highly Dilute Sulphuric Acid. Spectral changes in sulphuric acid more dilute than about 0.1N, are shown in Fig. 2. It is seen that the broad band absorbed by formhydrazide in water does not shift but the extinction coefficients are lowered successively with increasing acid concentrations. In such a dilute acid no change in absorbance was observed with time, but a delayed spectral change at about 0.1N (Fig. 3) and a marked change was observed at still higher concentration. The spectral changes with time indicate that the hydrolysis occurs in concentrated acid solutions.

The behavior of two bands absorbed by formhydrazide hydrochloride dissolved in sulphuric acid is shown in Fig. 4. When the concentration of acid is smaller than that of hydrochloride, no change of shape was observed but the two bands red-shift to 190 and 191 mμ, respectively. When the acid concentration exceeds that of hydrochloride, the absorption is similar, in both shape and positions of component peaks, to that of formhydrazide dissolved in water; it indicates that both formhydrazide in water and its hydrochloride in sulphuric acid of an appropriate concentration have the same absorbing species (compare curve 3, Fig. 4 with curve 1, Fig. 1). At still higher acid concentration, *e.g.* about 0.14N, the band is similar in both shape and positions of peaks to those of formhydrazide in about 0.11N of sulphuric acid (compare curve 4, Fig. 4 with curve 7, Fig. 2). Thus, both these solutions seem to have the same absorbing species differing from that contained in the aqueous solution of formhydrazide hydrochloride. The latter would be $HCONHNH_3^+$ or its hydrated species, and the former $HCONHNH_2$ or its hydrated species. From a comparison of 2, 3, and 4 in Fig. 4, it seems that at least two absorbing species are present in the solution giving curve 3. Consequently, in aqueous formhydrazide solution there will be an ionization equilibrium:

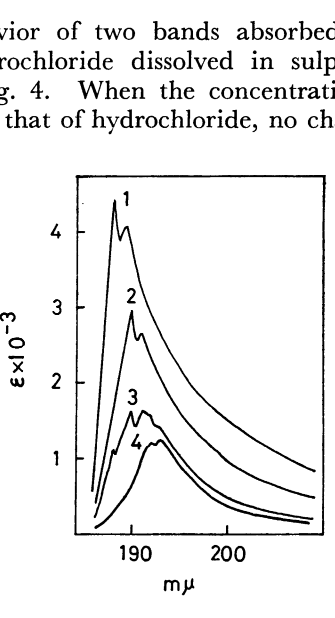

Fig. 4. Ultraviolet spectra $HCONHNH_2$–HCl in aq. H_2SO_4.
(1) 0; (2) 0.1442×10^{-2}; (3) 0.1048×10^{-1}; (4) 0.1442N.

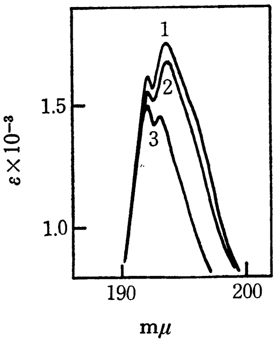

Fig. 3. Spectral change in 0.1132N H_2SO_4.
(1) 14 min (2) 2 hr (3) 17 hr after preparing the solution.

$$HCONHNH_3^+ + H_2O \rightleftharpoons HCONHNH_2 + H_3O^+,$$

between hydrated molecular species and hydrated ionic species.

Calculation of Thermodynamic Protonation Constant. The ionized species shows the 190 mμ peak which is weakened with the increase of acid concentration (Fig. 2). Therefore, the extinction coefficients at 190 mμ seem to be suitable for calculating the equilibrium constant.

By measuring the extinction coefficient of a base, at any given wavelength, it is possible to calculate the value of pK_{BH^+} for the base from the following equation.[5]

$$pK_{BH^+} = \log\{(\varepsilon-\varepsilon_i)/(\varepsilon_m-\varepsilon)\} + \log(\gamma_i/\gamma_m) - \log a_{H^+}$$

where pK_{BH^+} is the negative logarithm of the thermodynamic dissociation constant for the equilibrium $BH^+ \rightleftharpoons B + H^+$, γ_i and γ_m are the activity coefficients of the acid cation BH^+ and the base B, respectively, a_{H^+} is the activity of hydrogen ion; ε_i and ε_m are the extinction coefficients of BH^+ and B, respectively; ε is that due to absorbing species in an appropriate solutions. The values of $\log\gamma_i$ at 25 °C were calculated from the

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[5] L. A. Flexer, L. P. Hammett, and A. Dingwall, *J. Amer. Chem. Soc.*, **57**, 2103 (1935).

approximate Debye-Hückel equation $\log \gamma_i = -0.510 \times z^2 \times I/(1+1.32 \times I)$, where z is the valency of BH^+ (equal to unity in the present study) and I is the ionic strength of the medium. The values of I were calculated by assuming that in such a dilution as considered here sulphuric acid is almost completely ionized.[6] It was assumed that $\gamma_m = 1$. The values of a_{H^+} were assumed to be equal to those of the mean activity of sulphuric acid, $a_\pm (= m_\pm \gamma_\pm)$, whose values were calculated by using the mean activity coefficients obtained by interpolation from the values in literature.[7] The values of ε_i and ε_m were adjusted by means of a computer program to give the values of pK_{BH^+} which best fit the observed data of ε; the results of calculation are summarized in Table 1. In view of the value of pK_{BH^+} it would appear that formhydrazide is a weaker base than acethydrazide ($pK_{BH^+} = 3.24$).[2] This seems to be in line with the fact that formic acid is a stronger acid than acetic acid.

Table 1. Values of pK_{BH^+} at 25 °C

Molality H_2SO_4	$\log\{(\varepsilon-\varepsilon_i)/(\varepsilon_m-\varepsilon)\}$[a]	$\log \gamma_i$	$\log a_{H^+}$	pK_{BH^+}
0.2892×10^{-3}	−1.37	−0.01	3.37	1.99
0.7231×10^{-3}	−0.95	−0.02	3.01	2.04
0.1446×10^{-2}	−0.71	−0.03	2.74	2.00
0.2893×10^{-2}	−0.45	−0.04	2.48	1.99
0.4339×10^{-2}	−0.37	−0.05	2.34	1.92
0.5788×10^{-2}	−0.27	−0.06	2.25	1.92
1.443×10^{-2}	+0.19	−0.08	1.94	2.05
				m. 1.99±0.04

a) ε_i and ε_m were assumed to be 5130 and 1450, respectively.

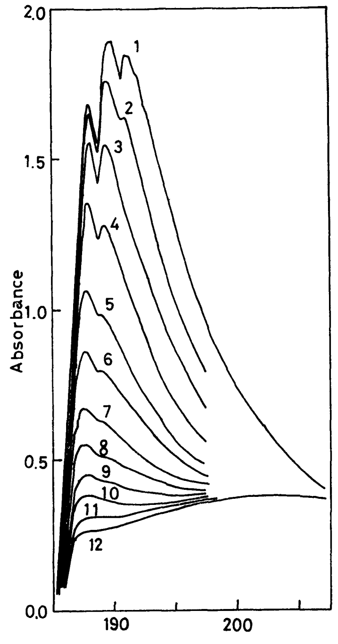

Fig. 5. Spectral changes of $HCONHNH_2$ in 8.51 M H_2SO_4. (1) 12.0, (2) 13.8, (3) 15.3, (4) 16.8, (5) 18.7, (6) 20.3, (7) 22.3, (8) 24.0, (9) 26.0, (10) 28.0. (11) 33.0, (12) 43.0 min after preparing the solution.

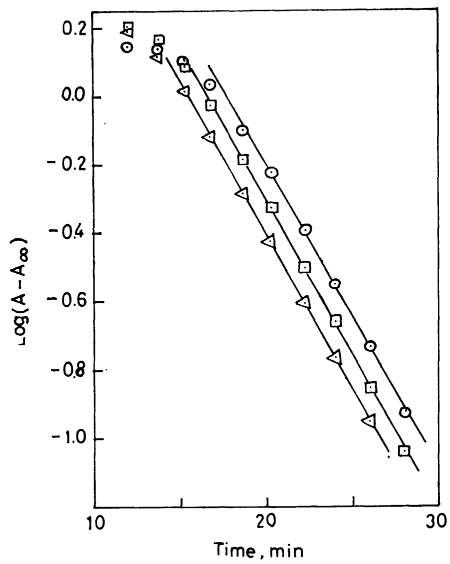

Fig. 6. The log $(A-A_\infty)$ vs. t plots for the hydrolysis of $HCONHNH_2$ in 8.51 M H_2SO_4.
⊙: at 188 mμ, ⊡: at 190 mμ, △: at 191 mμ.

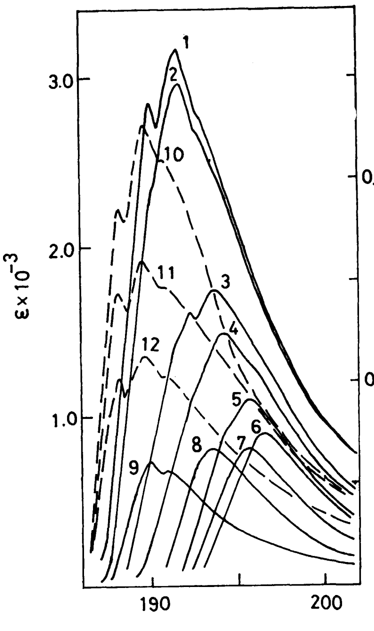

Fig. 7. Spectral changes of $HCONHNH_2$ in aq H_2SO_4 with increasing acid concentration.
(1) 0.01420, (2) 0.02523, (3) 0.05655, (4) 0.1419, (5) 0.5235, (6) 1.627, (7) 2.501, (8) 4.125, (9) 6.593, (10) 7.435, (11) 7.870, (12) 9.360 M.

Hydrolysis in Sulphuric Acid. The change of absorbance with time was observed for the solutions of formhydrazide dissolved in sulphuric acid above about 0.1 N. Typical one is shown in Fig. 5 for a reaction solution of formhydrazide (*ca.* 8×10^{-3} M) dissolved in sulphuric acid (*ca.* 8 M). The log $(A-A_\infty)$ *vs.* t plots at the wavelengths where three peaks are shown primarily by the reaction solution are shown in Fig. 6. The plots give good straight lines having nearly the same slope except for some initial points. The slope therefore definitely gives the apparent first-order rate constant. The presence of points deviating

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6) T. F. Young and L. A. Blatz, *Chem. Rev.*, **44**, 93 (1949).

7) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd. Ed., Reinhold Pub. Corp., New York (1958), p. 576.

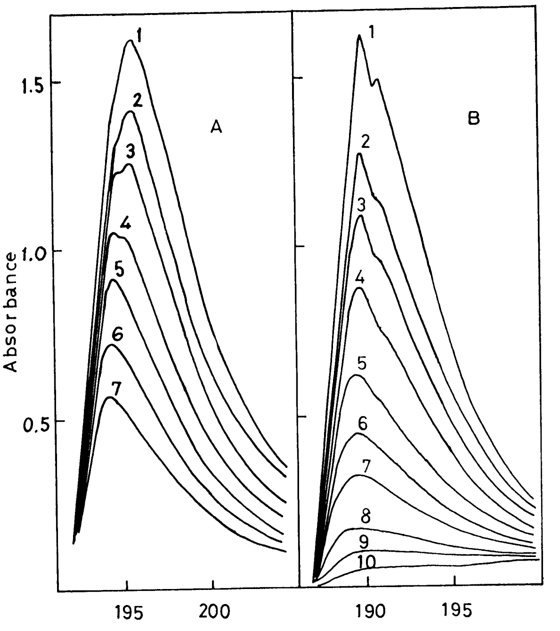

Fig. 8. Spectral changes of $HCONHNH_2$ in aq H_2SO_4.
A; 0.523 M H_2SO_4: (1) 8.25, (2) 22.1, (3) 58.3, (4) 110.6, (5) 155.1, (6) 210.1, (7) 270.1 min; B; 6.59 M H_2SO_4: (1) 9.1, (2) 11.2, (3) 12.5, (4) 14.2, (5) 16.6, (6) 18.9, (7) 21.2, (8) 26.0, (9) 30.6, (10) 42.3 min after preparing the solutions.

from the linear plot indicates that a reaction occurs prior to hydrolysis.

From a comparison of the primary absorption curves of reaction solutions, we see that both the shape of band and the potitions of component peaks change with increasing acid concentration. The initial abosrption curves are given in Fig. 7. In view of the change of the band with time, it is useless to compare the values of extinction coefficient with each other, but the positions of peaks are useful for examining the effects of acidity on the formhydrazide absorption. We give the following comments. (1) At relatively low acidity the absorption band has an intense peak with another rather weak peak (or a shoulder) on the high energy side. This band red-shifts with increasing acid concentration up to about 2 M, and further increasing acid concentration brings about a blue-shift. Moreover, the above main peak disappears prior to hydrolysis and the subpeak is weakened gradually with progress of hydrolysis (Fig. 8A). Thus, it would appear that in this region of acid concentrations the reaction solution contains initially two absorbing species affected by acid media. (2) Another case of typical changes of absorbance with time is shown in Fig. 8B which contains the absorption curves for reaction solutions made up of about 6 M sulphuric acid. The reaction solution shows initially the band with two peaks (the main peak on the high energy side and a subpeak on the low side). A similar band was observed in all the reaction solutions. Therefore, this band may be ascribed to the substrate hydrolyzed immediately. (3) Above about 7 M acid concentration, the reaction solution initially gives a broad absorption band with component peaks at the same positions as those of formhydrazide in water (compare curve 1, Fig. 5 with curve 1, Fig. 1) and increasing acid concentration does not affect the position of component peaks (see dashed cruves in Fig. 7). This indicates that the electronic states of formhydrazide are affected by structures or characters of water molecules in aqueous sulphuric acid. The band, composed of several component bands and observed in sulphuric acid above 7 M, is expected to arise from two absorbing species, one absorbing the band with two peaks at 188 and 189 mμ and the other at 190 and 191 mμ. With the progress of reaction two bands at higher wavelengths, 190 and 191 mμ, disappear first followed by the band at 188 mμ (Fig. 5).

Table 2. First-order rate constant (k') for hydrolysis of formhydrazide

Sulfuric acid		Perchloric acid	
Molarity[a]	$10^2 \times k'$ (min^{-1})	Molarity	$10^2 \times k'$ (min^{-1})
0.1420	0.145	1.002	0.448
0.2465	0.216	1.861	1.03
0.4068	0.332	2.690	1.84
0.5235	0.4123	3.449	2.45
0.8715	0.785	4.916	3.55
1.140	1.18	5.833	4.08
1.627	1.65	6.783	4.68
2.034	2.31	7.883	5.45
2.551	3.66	8.633	5.88
3.015	5.02	9.009	6.12
3.717	6.88	9.384	6.30
4.125	7.73		
4.766	8.93		
5.746	11.7		
6.592	15.3		
7.435	17.4		
7.870	19.1		
8.510	20.4		
9.360	23.1		

a) Because of the velocity being too high, k' values in concentrations higher than those in the present study could not be determined.

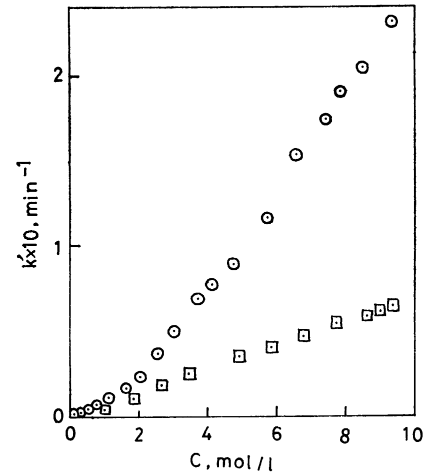

Fig. 9. Dependence of rate constants on acid concentration.
⊙: H_2SO_4, ⊡: $HClO_4$

Rate Constants of Hydrolysis in Sulphuric and Perchloric Acids. The apparent first-order rate constant k' was determined for formhydrazide in sulphuric and perchloric acids. The values of k' are given in Table 2 and the plot of k' *vs.* acid concentration (M) is shown in Fig. 9. The rate constant depends on the acid concentration but not in the same way for both acids. Thus the hydrolysis of formhydrazide seems to be acid catalyzed.

Zucker and Hammett[8] treated quantitavely rate-acidity dependence in acids for the first time. They grouped reactions into two categories, depending on whether the logarithm of the pseudo first-order rate constants were linear either $-H_0$ (negative Hammett's acidity function) or $\log C_{H^+}$ (molar concentration of hydrogen ion), with approximately unit slope. They assumed that reactions of the first type involved rate-determining unimolecular decomposition of protonated substrate (Al mechanism) and those of the second type involved rate-determining attack on protonated substrate by a water molecule (A2 mechnism).[9]

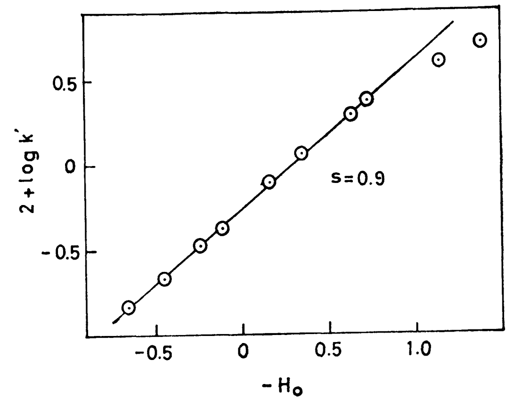

Fig. 10. Log k' *vs.* $-H_0$* plot for the hydrolysis of $HCONHNH_2$ in 0.1—3.0 M H_2SO_4.

* The H_0 values were obtained by interpolation from the values presented in Ref. 9a in the text.

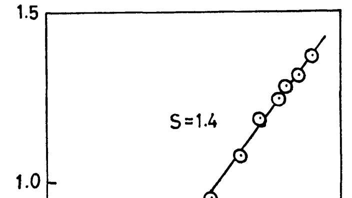

Fig. 11. Log k' *vs.* log M plot for the hydrolysis of $HCONHNH_2$ in moderately concentrated H_2SO_4 and $HClO_4$. ⊙: H_2SO_4, ⊡: $HClO_4$.

In a limited range of acid concentrations (0.1—2.0 M), the k' *vs.* $-H_0$ plot (Fig. 10) is straight with a 0.9 slope; at high acid concentration above *ca.* 2 M, the log k' *vs.* log M plot (Fig. 11) is straight with a 1.0 slope (in perchloric acid) and a 1.4 slope (in sulphuric acid). According to the Zucker-Hammett hypothesis, the Al mechanism seems to be suitable for the rate-determining stage of the hydrolysis of formhydrazide at low acid-concentrations; the A2 mechanism seems to be suitable at high acid-concentrations. However, objection to the Zucker-Hammett hypothesis was discussed theoretically and experimentally by Taft, Deno, and Shell[10] and by later workers.[11]

Bunnett[12] found empirically that, for a large number of reactions, plots of $\log k' + H_0$ *vs.* the logarithm of the activity of water ($\log a_w$) in the reaction medium are linear or very nearly linear. The slopes w of these plots vary over a wide range. From a comparison with reactions of known mechanism it was possible to classify reactions into three types according to the magnitude of w values and the role of water in the rate-determining step, as shown in Table 3.

TABLE 3. MECHANISTIC INTERPRETATION OF w (after Bunnett[12])

Range of w value	Role of water in the rate-determining step
-2.5 to 0.0	not involved
$+1.2$ to $+3.3$	acts as a nucleophile
$>+3.3$	acts as a proton transfer agent

For the acid-catalyzed hydrolysis of formhydrazide in concentrated acid solutions, the Bunnett plot is given in Fig. 12 which contains the plot in sulphuric acid above 2.5 M and in perchloric acid above 1.8 M. It is of interest to see that the Zucker-Hammett plot (Fig. 11) gives only a straight line in the range of acid concentration examined in the present study, while the Bunnett plot gives straight lines composed of two parts. According to the Bunnett treatment the w values indicate the following reaction mechanisms of hydrolysis. In moderately strong acid solutions, 2.5—7 M sulphuric acid (w=5.0) and 1.5—6 M perchloric acid (w=5.5), the reaction mechanism contains proton transfer in rate-determining steps. Gillespie[13] has shown on the basis of results of Raman and NMR measurements that perchloric acid dissociates completely up to about 6 M.[14] He compared the H_0 values for these acids

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[8] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, **61**, 2791 (1939).

[9] For comprehensive treatment, see a) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957); b) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

[10] R. W. Taft, N. C. Deno, and P. S. Shell, *Ann. Rev. Phys. Chem.*, **9**, 287 (1958).

[11] Contains an extensive bibliography, H. Zollinger, *ibid.*, **13**, 391 (1962).

[12] J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1961).

[13] R. J. Gillespie, "Physico Chemical Progresses in Mixed Aqueous Solvents," ed. by F. Franks, Heineman, London (1967), pp.129— 140.

[14] See Figs. 7 and 6 in Ref. 13.

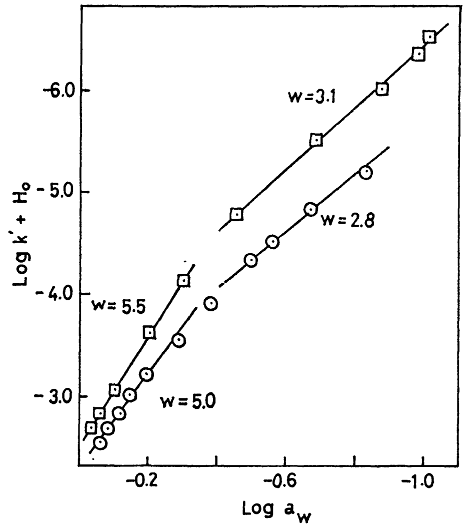

Fig. 12. Log k' + H_0 *vs.* log a_w* plot for the hydrolysis of $HCONHNH_2$. ⊙: H_2SO_4, ⊡: $HClO_4$.

* The a_W values were obtained by interpolation from the values given in Ref. 12 in the text.

at concentrations at which ionization is incomplete, and pointed out that the $HClO_4$ molecule and perhaps also the H_3O^+ ion have a greater proton donating ability in this medium than in H_2SO_4. This is consistent with our results: the rate-determining steps contain proton transfer in the range 1.5—6 M of perchloric acid concentration and the w value in perchloric acid is higher than that in sulphuric acid.

At a still higher acid-concentration than 7 M, water acts as a nucleophile in the slow step. The conclusion depends on the w value of 2.8 for sulphuric acid and of 3.1 for perchloric acid. In this region of acid concentration, both acids would be incompletely ionized. Wyatt[15] interpreted the incomplete ionization of sulphuric acid by postulating that the H_3O^+ ion tends to retain a molecule of hydration. The postulation seems to be consistent with the role of water.

Conclusion

Using a spectrophotometric method, we determined the protonation constant and the apparent first-order rate constant of the acid-catalyzed hydrolysis for formhydrazide.

The number 1.99 has been obtained for pK_{BH^+} of formhydrazide in highly dilute sulphuric acid. Hydrolysis occurs in relatively low dilution (0.1—2.0 M) and involves rate determining unimolecular decomposition of protonated substrate (A1 mechanism), using the Zucker-Hammett, log k' *vs.* $-H_0$ plot. However, in concentrated acid media the Bunnett, log $k'+H_0$ *vs.* log a_w plot is preferable for inspecting the reaction mechanism. Consequently, we have proposed the following mechanism: in the acid media 2—6 M the rate-determining steps contain proton transfer and above about 7 M water acts as a nucleophile.

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[15] P. A. H. Wyatt, *Disc. Faraday Soc.*, **24**, 162 (1957).