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Kinetics and Mechanism of Acylhydrazine Hydrolysis in Sulfuric Acid-Water Mixtures

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The rates of acid-catalyzed hydrolysis of formylhydrazine, acetylhydrazine, chloroacetylhydrazine, propionylhydrazine, butyrylhydrazine, and octanoylhydrazine in sulfuric acid–water mixtures have been investigated over a wide range of acidities (about 1—18 M H_2SO_4) by means of spectrophotometric methods. First-order kinetics were obtained in all cases, and the pseudo-first-order rate constants showed one of two types of acidity dependences: (i) a rate maximum at intermediate acidities, followed by slow hydrolysis in highly concentrated acids; (ii) a rate maximum at intermediate acidities, followed by a sharp increase in rate at high acidities. This result was treated as a function of the Hammett acidity function, the water activity, and the total concentration of hydrogen ion to yield reaction parameters which are explicable in terms of a change in mechanism at a high acidity from A-2 to A-1. The mechanism change also was deduced from a criterion based on the values of activation entropies.

The rates of acid-catalyzed hydrolysis of amides have been studied systematically, but only a few results[1,2] have been obtained for those of acylhydrazines. Hydrazidinum ion $RCONHNH_3^+$, which is expected to exist in acid solutions,[1,3,4] would have a planar skeleton of O–C–N–N having two π-electrons and two lone-pair electrons. It is of interest to test how this electron system affects the kinetics.

Mechanisms of reaction in strong acid solutions have been recently reviewed in detail by Rochester[5] and Liler.[6] Empirical criteria of acid-catalyzed hydrolysis have been developed in terms of the acidity function, the water activity, the total concentration of hydrogen ions of acid media, and further in terms of the change of hydration number between reactants and transition states. For the hydrolysis containing pre-equilibrium, the value of the dissociation constant of the conjugate acid may also control the rate-determining step. Sulfuric acid-water mixtures are an exceptionally suitable medium to examine the factors affecting the kinetics of acid-catalyzed hydrolysis over a wide range of acid concentrations.

Experimental

Materials and Apparatus. The acylhydrazines were synthesized with methyl or ethyl esters of the corresponding acids and hydrazine hydrates, and purified by recrystallization from ether–ethanol mixtures. Purity was assured by melting point. Sulfuric acid–water mixtures were made by dilution of reagent grade acid with distilled water. The acid solutions were standardized by titration against a standard sodium hydroxide solution, exccpt for highly concentrated acids of which concentrations were determined by measurements of density. Molarities were calculated by calibration on the basis of the literature data of densities.[7]

The ultraviolet solution spectra were measured with a Hitachi EPS-3T Recording Spectrophotometer equipped with a thermostated cell compartment. The temperature in this compartment was controlled within ±0.1 °C.

Rate Measurements. Reactions were followed by recording the change in absorbance A with time at the absorption maximum. Pseudo-first-order rate constants k were 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 diluted reaction solutions, about 10^{-3} M ($1 \text{ M}=1 \text{ mol dm}^{-3}$), used for spectrophotometric examination, no attempt was made to isolate reaction products from the reaction solutions. In order to check the A_∞, the absorption spectra of the prepared mock solutions were examined and compared with those of reaction solutions.

Results

Rate Profiles. The rate-acidity dependences of hydrolysis of the acylhydrazines were found to fit into one of two categories. The dependence of formylhydrazine and chloroacetylhydrazine is characterized by an initial rate increase with the acid concentration, passing through a maximum, followed by a rate decrease with further increasing acid concentration. Other acylhydrazines resemble this, except that the final increase occurs steeply at higher acid concentrations. It has been confirmed that the acylhydrazine hydrolysis also shows a rate maximum as amide[8] and ester[9] hydrolysis do, but at relatively high acidities: about 12 M H_2SO_4 for formylhydrazine, in contrast to about 5 M H_2SO_4 for formamide.[8a] The values of rate constants and acid concentrations at the maximum rate have been estimated graphically and collected in Table 2.

An important difference in reaction activities is found between the first two members of the aliphatic series $RCONHNH_2$, and an anomaly is found among the first three members, as pointed out for aliphatic acid amide homologues;[10] acetylhydrazine is less active than propionylhydrazine, but the difference is not very large. It also should be noted that the chlorine-substitution in the acyl group changes the reactivity in the low acidity region very little but does affect the reactivity at the very high acidity region.

Treatment of Rate Data. The pseudo-first-order rate constants, k, of hydrolysis of formylhydrazine and acetylhydrazine at 25 °C have been used in order to test several treatments which are useful for obtaining mechanistic conclusions in terms of the values of acidity function H_0,[11] activity of water a_w,[12] total concentration of hydrogen ion $[H^+]$,[13] and pK_{SH^+} of conjugate acid.[1,3]

One criterion of the reaction mechanism has been presented by Bunnett and Olsen,[14] who have found a

TABLE 1. PSEUDO-FIRST-ORDER RATE CONSTANTS OF HYDROLYSIS OF ACETYLHYDRAZINES $RCONHNH_2$ IN SULFURIC ACID–WATER MIXTURES

T / °C	$[H_2SO_4]$ / M	$10^2 k$ / min^{-1}	T / °C	$[H_2SO_4]$ / M	$10^2 k$ / min^{-1}
	$R=H$			$R=CH_3$	
25.0	1.04	1.73	25.0	1.66	0.122
	1.66	2.64		2.67	0.180
	2.67	4.53		3.67	0.239
	3.67	6.23		4.18	0.269
	3.99	6.69		4.79	0.306
	4.18	7.24		5.70	0.352
	4.79	8.51		7.33	0.465
	5.70	10.9		8.15	0.517
	6.32	12.4		8.83	0.527
	7.74	16.0		9.40	0.499
	8.15	16.8		9.90	0.483
	8.40	17.4		11.1	0.356
	9.25	19.8		12.3	0.251
	10.2	22.1		13.7	0.144
	10.9	24.1		14.7	0.189
	11.2	24.7		15.6	0.572
	11.7	26.0		16.2	0.950
	12.4	24.5		16.5	1.41
	13.4	17.8		16.7	1.78
	13.7	16.4		17.5	6.10
	14.9	9.94		17.7	7.03
	15.5	6.35		17.9	8.70
	16.3	2.90	55.0	0.780	0.554
	16.5	2.03		1.38	0.992
	17.1	1.36		1.94	1.46
55.0	0.368	5.54		2.72	1.87
	0.510	7.64		3.67	2.73
	0.770	11.3		4.22	3.20
	1.04	15.3		5.10	4.03
	1.38	21.0		6.32	4.96
	1.54	23.7		7.80	6.42
	1.94	29.8		8.83	6.75
	2.85	43.9		9.63	6.80
	3.16	49.5		10.6	6.24
	3.67	55.9		11.1	5.98
	4.79	75.6		11.9	5.49
	5.70	92.1		12.6	4.78
	7.34	119		13.3	4.06
	8.92	142		14.0	4.14
	9.77	156		14.8	9.79
	11.2	181		15.9	20.7
	12.4	186		16.1	23.9
	13.2	162		16.7	39.6
	14.0	137		17.6	74.1
	14.8	105		17.9	98.2
	15.6	74.4			
	16.5	46.1			
	17.5	24.7			

T / °C	$[H_2SO_4]$ / M	$10_2 k$ / min^{-1}	T / °C	$[H_2SO_4]$ / M	$10^2 k$ / min^{-1}
	$R=CH_2Cl$			$R=CH_3CH_2$	
55.0	0.947	0.865	55.0	1.66	1.23
	1.40	1.32		2.72	2.14
	1.99	1.88		3.28	2.74
	2.72	2.72		4.39	3.40
	3.70	3.41		5.01	4.47
	4.64	4.23		6.19	5.66
	6.19	5.53		7.33	6.53
	7.80	6.09		8.58	7.25
	8.92	6.41		9.77	7.18
	10.3	6.57		10.6	6.85
	11.9	6.36		11.4	6.33
	13.3	5.64		12.3	5.51
	14.8	4.14		13.1	5.34
	15.8	3.11		14.0	6.95
	16.2	2.48		14.9	14.9
	17.0	1.60		15.9	30.3
	17.6	1.03		16.5	47.7
				17.3	94.8
	$R=CH_3(CH_2)_2$			$R=CH_3(CH_2)_6$	
55.0	0.974	0.967	55.0	1.99	0.661
	1.40	1.03		2.90	0.994
	1.99	1.44		4.45	1.73
	2.90	2.23		5.10	1.93
	3.70	2.84		6.19	2.43
	5.10	3.84		7.46	3.28
	6.19	4.45		7.95	3.44
	7.46	5.09		8.92	3.59
	8.92	4.86		9.77	3.56
	9.77	4.34		10.8	3.22
	10.8	3.85		11.7	3.01
	11.7	3.18		12.3	3.21
	12.3	2.90		13.1	4.21
	13.1	2.70		14.0	9.23
	14.0	5.33		14.8	17.7
	15.0	14.6		15.5	34.2
	15.5	21.1		15.9	46.8
	16.2	32.4		16.5	81.9
	16.5	42.2		17.3	143
	16.7	59.3			
	17.1	84.5			
	17.6	121			

linear correlation of $\log k+H_o$ *vs.* $H_o+\log[H^+]$ and proposed the values of the proportionality slope parameter ϕ as useful to characterize the medium dependence of rate constants. Typical ϕ plots are illustrated in Fig. 1, which shows the following: for formylhydrazine the points below 12 M H_2SO_4 give a good straight line ($\phi=0.95\pm0.01$), and above 13 M H_2SO_4 another straight line ($\phi=1.37\pm0.01$) can be drawn through the remaining points; for acetylhydrazine the similar linearities are obtained below about 10 M H_2SO_4 ($\phi=1.00\pm0.01$) and in the middle region of about 11—14 M H_2SO_4 ($\phi=1.29\pm0.00$), and one more linearity ($\phi=0.09\pm0.00$) is found above about 14 M H_2SO_4. It has been deduced[14,15] that for substrates

Table 2. Values of rate constant and acid concentration at maximum rate of hydrolysis of acetylhydrazines in sulfuric acid–water mixtures

R	$10^2 k$ / min^{-1}	$[\mathrm{H_2SO_4}]$ / M	T / °C
H	26	12	25
	187	12	55
CH_3	0.53	9.1	25
	6.9	9.4	55
CH_2Cl	6.5	10	55
CH_3CH_2	7.3	9.0	55
$CH_3(CH_2)_2$	5.2	8.0	55
$CH_3(CH_2)_6$	3.6	9.2	55

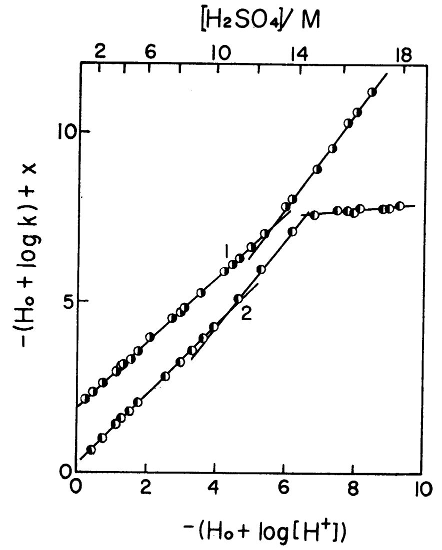

Fig. 1. Plots of H_0+log k_{obsd} *vs.* H_0+log $[H^+]$ for hydrolysis in sulfuric acid at 25 °C; vertical displacement values $x=0$ for formylhydrazine (1) and $x=-3$ for acetylhydrazine (2).

protonated on N or O atom the ranges of ϕ values for different modes of water involvement in the rate-determining step are: $-0.34<\phi<0$ for water not involved, $0.18<\phi<0.47$ for water acting as a nucleophile, and $\phi>0.47$ for water acting as a proton transfer agent. Applying this criterion, the ϕ values obtained imply that the hydrolysis of formylhydrazine proceeds by the mechanism (A-2) involving water as a proton transfer agent over all the range of acid concentration studied; acetylhydrazine is hydrolyzed by the same mechanism up to about 14 M H_2SO_4, and above the acid concentration the hydrolysis mechanism changes into the one involving no water (A-1). A mechanistic conclusion similar to that for formylhydrazine is obtained for chloroacetylhydrazine, and a conclusion similar to that for acetylhydrazine is obtained for propionylhydrazine butyrylhydrazine and caprylylhydrazine (refer to the ϕ values in Table 3).

Bunnett[16] noted that $\log k + H_0$ was correlated

Table 3. Values of Φ, w, and w^* parameters[a] for the hydrolysis of acetylhydrazines $RCONHNH_2$ in sulfuric acid–water mixtures

R	T	Φ	w	w^*
H	25	0.95±0.01 (1.04—11.7)	8.85±0.03 (1.04—2.67)	
		1.37±0.01 (13.4—17.1)	3.37±0.03 (3.99—8.15)	Not linear
			1.81±0.03 (10.23—17.1)	
	55	0.98±0.00 (0.510—9.77)	8.75±0.02 (0.150—3.16)	
		1.15±0.01 (11.2—17.5)	3.58±0.03 (3.67—8.92)	Not linear
			1.50±0.03 (12.4—17.5)	
CH_3	25	1.00±0.01 (1.66—9.90)	8.35±0.01 (1.66—3.67)	Not linear
		1.29±0.00 (11.1—13.7)	3.61±0.02 (4.18—8.83)	
		0.09±0.00 (14.7—17.9)	2.33±0.04 (9.90—13.7)	−1.96±0.02 (13.7—17.9)
			0.10±0.01 (14.7—17.9)	
	55	0.97±0.01 (0.780—7.80)	9.24±0.01 (0.780—1.94)	Not linear
		1.13±0.01 (8.83—13.3)	3.56±0.03 (4.22—8.83)	
		0.35±0.01 (14.0—17.9)	2.21±0.01 (10.6—13.3)	−1.78±0.04 (13.3—17.9)
			0.44±0.01 (14.0—17.9)	
CH_2Cl	55	1.02±0.01 (0.97—8.92)	8.74±0.01 (0.974—2.72)	
		1.11±0.00 (11.9—17.6)	3.62±0.01 (4.64—8.92)	Not linear
			1.47±0.05 (11.9—17.6)	
CH_3CH_2	55	0.95±0.01 (1.66—7.33)	8.48±0.01 (0.974—2.72)	
		1.10±0.00 (8.58—13.1)	3.53±0.00 (4.39—7.33)	Not linear
		0.37±0.00 (14.0—17.3)	2.41±0.08 (8.58—13.1)	
			0.64±0.01 (14.0—17.3)	−1.87±0.03 (14.0—17.3)
$CH_3(CH_2)_2$	55	1.00±0.01 (0.974—7.46)	9.67±0.00 (0.974—2.78)	
		1.15±0.00 (8.92—13.1)	3.65±0.01 (5.10—8.92)	Not linear
		0.33±0.00 (14.0—17.6)	2.35±0.05 (9.77—13.1)	
			0.40±0.01 (14.0—17.6)	−1.77±0.01 (15.0—17.6)
$CH_3(CH_2)_6$	55	0.94±0.01 (1.99—6.19)	6.02±0.03 (1.99—4.45)	
		1.07±0.00 (7.46—12.3)	3.04±0.01 (6.19—7.95)	Not linear
		0.33±0.00 (13.1—17.3)	2.41±0.04 (8.92—12.3)	
			0.41±0.01 (13.1—17.3)	−1.90±0.03 (14.0—17.3)

a) The values of H_0, [H+] and a_w at 25 °C are used for the kinetic data at 55 °C. b) The acid concentration range in which the parameters are calculated is inserted in the parentheses.

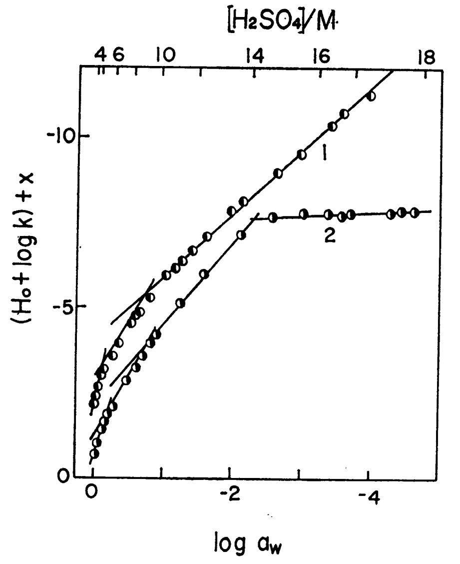

Fig. 2. Plots of H_0+log k_{obsd} *vs.* log a_w for the hydrolysis in sulfuric acid at 25 °C; vertical displacement values $x=0$ for formylhydrazine (1) and $x=-2$ for acetylhydrazine (2).

linearly with log a_w and that the values of the correlation slope parameter w were useful as the criterion of the reaction mechanism. Typical w plots are shown in Fig. 2. The plots should be divided into three (for formylhydrazine) or four (for acetylhydrazine) linear portions. The w values estimated for each portion are collected in Table 3, along with the acid concentration ranges in which the w values are calculated. A complementary parameter w^* was defined by Bunnett[16] as a useful index of the response of the reaction to the catalysis by concentrated acid, *e.g.* sulfuric acids above 4 M. The w^* plots, log $k-H_0-$log [H$^+$] *vs.* log a_w, are shown in Fig. 3. This clearly indicates that for acetylhydrazine the mechanism change expected from the magnitude of ϕ values takes place, *i.e.* for this compound a curved line similar to that for formylhydrazine can be drawn through the points up to about 14 M H_2SO_4, while a good linearity is found beyond 14 M H_2SO_4.

The applicability of the Zucker-Hammett hypothesis[17] was also examined. However, the plot of log k *vs.* H_0 showed no linearity over the range of acid concentration, except for a narrow range of very high acidity, and the plot of log k *vs.* log [H$^+$] also gave a linear portion in a narrow range at low acidities only.

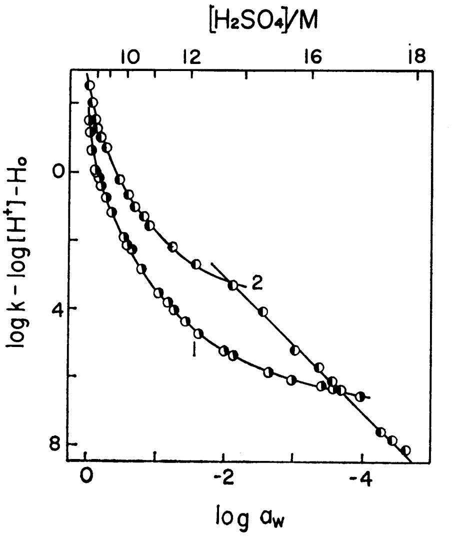

Fig. 3. Plots of log k_{obsd} $-$log [H^+]$-H_0$ *vs.* log a_w for the hydrolysis of formylhydrazine (1) and acetylhydrazine (2) at 25 °C.

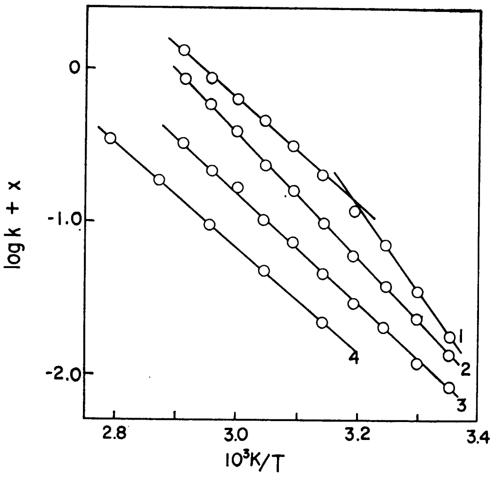

Fig. 4. Arrhenius plots for the hydrolysis of acetylhydrazine; vertical displacement value $x=0$ at 16.7 M H_2SO_4 (1), $x=0.6$ at 11.1 M (2), $x=0.2$ at 8.83 M (3), $x=0.4$ at 2.72 M (4).

Activation Parameters. The rate-temperature dependence was examined at several acid concentrations representative of linear portions in the plots mentioned in the foregoing section. Typical Arrhenius plots, log k *vs.* $1/T$, are shown in Fig. 4 for the hydrolysis of acetylhydrazine at 2.72, 8.83, 11.1, and 16.7 M H_2SO_4. The plots at high acid concentration for each substrate, except chloroacetylhydrazine, were divided into two linear portions. In these cases the rate constant-temperature dependence can be reasonably treated under the assumption that the activation heat capacities ΔC_p^* vary with temperature.[18] However, our present data do not seem to cover a sufficiently wide temperature range to do the treatment. Therefore, the values of activation parameters were calculated for each linear portion and are collected in Table 4.

After studying the acid-catalyzed hydrolysis of esters, Schaleger and Long[19] have suggested that the typical values of activation entropies are 0 to 42 J K^{-1} mol^{-1} for the A-1 mechanism and -63 to -126 J K^{-1} mol^{-1} for A-2. In fact, for the ethyl acetate hydrolysis[9] the ΔS^* value changed from a negative value (-64.0 J K^{-1} mol^{-1} at 40.2% H_2SO_4) typical of A-2 reactions to a small positive value (+9.6 J K^{-1} mol^{-1} at 98.4% H_2SO_4) typical of A-1 reactions; for the amide hydrolysis, which proceeds probably through the A-2 mechanism, the ΔS^* value[20] is -69.5 J K^{-1} mol^{-1} for formamide, -86.6 J K^{-1} mol^{-1} for acetamide, and 88.3 J K^{-1} mol^{-1} for propionamide in 1.00 M HCl.

The mechanistic change of acylhydrazine hydrolysis

TABLE 4. ACTIVATION PARAMETERS FOR HYDROLYSIS OF ACETYLHYDRAZINES $RCONHNH_2$

R	$[H_2SO_4]$ / M	ΔE[a] / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}	T[b] / °C
H	1.04	59.0 (25—65)	−121	25
	5.07	60.0 (10—40)	−92	25
	11.2	63.6	−88	25
	16.5	84.1 (25—45)	−38	25
		59.0 (55—75)	−113	55
CH_3	2.72	65.7 (45—85)	−121	55
	8.83	70.3 (25—70)	−96	25
	11.1	77.8	−71	25
	16.7	107 (25—35)	+38	25
		64.4 (57—70)	−100	55
CH_2Cl	1.99	72.0 (25—70)	−100	25
	7.80	73.2 (25—70)	−88	25
	15.8	74.5 (25—70)	−88	25
CH_3CH_2	3.28	63.2 (45—85)	−126	55
	11.4	72.0 (45—85)	−92	55
	17.3	89.1 (25—45)	−17	25
		35.1 (55—75)	−180	55
$CH_3(CH_2)_2$	5.10	64.4 (35—75)	−138	55
	11.7	74.9	−109	55
	15.5	108 (25—65)	+21	25
		26.4 (75—85)	−209	75
$CH_3(CH_2)_6$	4.45	68.2 (45—85)	−113	55
	12.3	77.4 (45—85)	−79	55
	15.5	105 (25—45)	+29	25
		54.8 (55—85)	−130	55

a) The linear Arrhenius plots were obtained in the temperature range which is indicated in the parentheses. b) The temperature at which ΔS^* was calculated.

from A-2 to A-1, at a very high acid concentration, was deduced again from the above-mentioned criterion in terms of the ΔS^* values. For each acylhydrazine the larger negative entropies were obtained in the acidity region in which the hydrolysis was expected to go through the A-2 mechanism, and in highly concentrated acids the ΔS^* values were positive or slightly negative, except for chloroacetylhydrazine. Although the ΔS^* values are based on pseudo-first-order rate constants which are dependent on acidity, the observed medium dependence of ΔS^* (see Table 4) would not be expected to lead to such a drastic change, unless a mechanism change was involved. However, for formylhydrazine no indication of the mechanism change from A-2 to A-1 was obtained from the criterion based on the reaction parameters ϕ, w, and w^*, while a relatively small negative value of ΔS^*, probably suitable to the A-1 mechanism, was obtained at a low temperature in 16.5 M H_2SO_4. This inconsistency may be due to the fact that the hydrolysis of formylhydrazine at high acidity is unimolecular (A-1), but is retarded by high activation energies. Even if this is the case, the Arrhenius plots involving two linear portions still need to be interpreted. For all the acylhydrazines with the exception of chloroacetylhydrazine, the values of activation energies and entropies, estimated from the linear portion of Arrhenius plot in higher temperature region and at high acidity, are identical with those obtained at lower acidities. This seems to indicate that change of hydrolysis mechanism occurs; in other words, there are two competing reactions, probably A-1 and A-2, which are predominant at low and high temperature, respectively.

Discussion

In the acidity region in which the hydrolysis proceeds through the A-2 mechanism, formylhydrazine has been observed to undergo hydrolysis about thirty times faster than acetylhydrazine (see Table 1). Acetylhydrazine is hydrolyzed as slow as chloroacetylhydrazine, with a k value of 4.12×10^{-1} min^{-1} at 25 °C in 7.8 M H_2SO_4 (not shown in the table). In spite of such a large rate difference, these three acylhydrazines give nearly equal values of activation energies and of entropies. Therefore, it may be said that the hydrolysis in the low acidity region is not entropy-controlled, nor is it an energy-controlled reaction. The greater stability of acetylhydrazine can not be ascribed to the electron-donating property of methyl group compared with the formyl hydrogen atom, because chloroacetylhydrazine, whose chloromethyl group has no electron-donation power, is as stable as acetylhydrazine. Thus the stability would come from the steric hindrance of the bulky acyl group which prevents it from attacking the water molecule. At high acidity, chloroacetylhydrazine shows no mechanism change from A-2 to A-1; this has been deduced from the criterion based on the reaction parameters and also from that based on activation entropies. The effect of substitution on acylhydrazine hydrolysis ought to be studied more widely. The regions of hydrolysis by the A-1 and A-2 mechanisms are usually separated by a minimum in the rate constant-acid concentration profile curves;[21] this is the case for the hydrolysis of acetylhydrazine, propionylhydrazine, butyrylhydrazine, and caprylylhydrazine.

The magnitude of the parameter used as the criterion of reaction mechanism depends upon how broad a range of acid concentration is covered by the kinetic experiments;[14] our present data, covering a sufficiently wide acidity range for the acylhydrazine hydrolysis, clearly reflect a medium change. The plots based on the linear free relationship[14] give a good linearity which covers all the examined range of acid concentration. However, the plots are divided into two or three linear portions (see Fig. 1 and Table 3). For the first one or two portions, the ϕ values are suitable to the A-2 mechanism, but the value for the higher acidity region is slightly larger than that for the lower acidity region. No acceptable interpretation of the small difference in ϕ values may be deduced from the ϕ plots only.

A striking behavior of the w^* plots, $\log k - H_0 - \log[H^+]$ *vs.* $\log a_w$, is worth noting (see Fig. 3): the plot of acetylhydrazine gives a curved line up to an acid concentration which begins to give a linear portion, and so the mechanism change from A-2 to A-1 is expected to be involved; otherwise such a sudden change in curvature is not expected. Moreover, we should pay attention to the curved line portion, because the apparently continuous change of $\log k - H_0 - \log[H^+]$

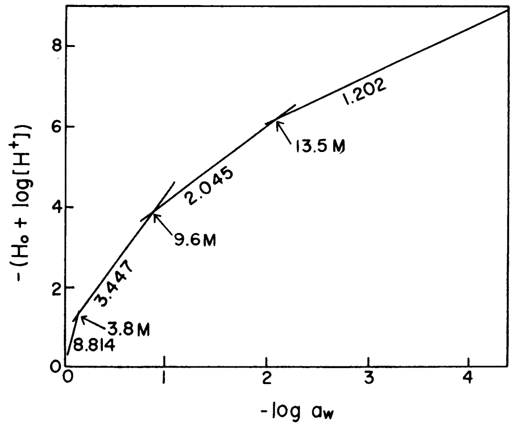

Fig. 5. The plots of $-(H_0+\log[H^+])$ *vs.* $-\log a_w$ for sulfuric acid–water mixtures.

which changing $\log a_w$ is considered to come from some affecting factors, which are continuously changed with acid concentration, on the hydrolysis rate. The relation between Hammett's acidity function and water activity has been discussed by several authors.[14,16,22,23] For sulfuric acid-water mixtures in the concentration range examined, the "excess acidity,"[23] $-(H_0+\log[\mathrm{H}^+])$, is plotted against $-\log a_w$ by the use of data[11–13] available in Fig. 5. The plot is divided into four linear portions: the initial three portions in slope value and also in the acidity region correspond to the initial three linear portions of the *w* plots, *i.e.* the local linearlities of the plot of the excess acidity against the water activity are directly reflected on the *w* plot (compare the slope values and the range of acid concentration inserted in Fig. 5 with those presented in Table 3). Since the correspondence was found for all the acylhydrazines examined, it is not considered to be accidental. This means that the plot of $\log k+H_0$ *vs.* $H_0+\log[\mathrm{H}^+]$ (the Bunnett-Olsen ϕ plot[14]) gives a straight line with the ϕ value of unity; this is equivalent to the fact that the acidity dependence of rate constants comes from the change of total concentration of hydrogen ions, that is, the linear plot of $\log k$ *vs.* $\log[\mathrm{H}^+]$ with the slope value of unity (the Zucker-Hammett hypothesis[17]) is obtainable. In fact, the ϕ values nearly equal to unity were obtained over the acid concentration range in which the acylhydrazines were hydrolyzed through the A-2 mechanism. However, the ϕ values at lower acidity regions are slightly smaller than those at higher acidity regions; this was found for all the acylhydrazines which gave ϕ values which differed slightly from each other. This seems to imply that the hydration change which occurs with protonation and/or transition of substrate molecules also affects the rate constant-acidity dependence. Finally, we can say that the w^* parameter is greatly sensitive to small deviations from the Zucker-Hammett criteria and that the ϕ parameter will provide a more reliable criterion for the interpretation of the dependences of rate constants and also of reaction mechanisms on changes in acid concentration.

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