the usual manner except that benzene was used for the extractions. The product was obtained as white crystals, m.p. 69–71°, yield, 165 mg. (6%). Crystallization from methanol gave white plates, m.p. 76°. The melting point reported for bicinnamyl is 81–82°.[14] The trinitrobenzene complex formed orange needles, m.p. 143–144°, reported[14] m.p. 145°.

p-Methoxybenzyltrimethylammonium Trifluoroacetate.—A solution of the salt (9 g., 0.03 mole) in DMA (100 ml.) was electrolyzed at an average current of 0.11 amp. (The initial current of 0.17 amp. fell to 0.05 amp. during the course of the electrolysis.) The cell contents were poured into water and filtered. An off-white solid, 526 mg. (15%), was obtained. After crystallization from ethanol the m.p. was 124°; m.p. reported[15] for *p,p'*-dimethoxybibenzyl, 125°.

Fluorenyltrimethylammonium Nitrate.—A solution of the salt (14.3 g., 0.05 mole) in DMF (100 ml.) was electrolyzed for 10 hr. at a current of 0.2 amp. The cell contents were poured into water and filtered with suction. The resultant dark solid was digested with benzene, and the benzene was removed *in vacuo*. The residue was digested four times with hexane, and the hexane was evaporated to give an orange-white solid, 2.15 g. (26.1%). Two crystallizations from benzene–ethanol gave material with m.p. 233–236°; mixed m.p. with authentic bifluorenyl, 235–237°.

***d*-α-Phenylethyltrimethylammonium Nitrate.**—A solution of the dextrorotatory salt (7.0 g.) in DMF (100 ml.) was electrolyzed for 17.8 hr. at 0.4 amp. The initial voltage was 65 v., and the final voltage necessary to maintain the current constant was 100 v. The cell contents were poured into salt water (1000 ml.). The solution was extracted four times with ether, and the ether extracts were washed successively with water, 1:1 hydrochloric acid, water, saturated sodium bicarbonate solution and water. After drying over magnesium sulfate, the ether was distilled through a Vigreux column, and the residue was taken up in a small amount of hot methanol. On cooling, a white solid (355 mg.) was obtained, m.p. 121–122°; mixed m.p. with authentic *meso*-2,3-diphenylbutane, 122–123°. The methanol was distilled from the mother liquor, and the residue was distilled *in vacuo* through a short-path still to yield 624 mg. of product, $n^{20}D$ 1.5512. The total yield of 2,3-diphenylbutanes was 30%.

The above liquid product was completely devoid of optical activity. It was analyzed by v.p.c. and shown to consist almost entirely of mixed 2,3-diphenylbutanes, containing a maximum of 15% of the *meso*-isomer. A very small amount of acetophenone also was present. These analytical results were confirmed by infrared spectroscopy. Repeat experiments gave the same optical results, and the same percentages of *meso*- and *dl*- products were obtained with the *dl*-salt.

Two experiments demonstrate that α-phenylethyltrimethylammonium nitrate is optically stable under the experimental conditions. The *d*-salt (15% in DMF) had $[\alpha]^{25}D$ equal to +18.0° initially and $[\alpha]^{25}D$ equal to +17.7° after standing in solution for 50 hr. at room temperature. In a second experiment a solution of 19.9 g. (0.088 mole) of the *l*-salt ($[\alpha]^{25}D$ −18.4°) in 130 ml. of DMF was electrolyzed for 3.9 hr. at 0.4 amp. with an applied voltage of 75 v. The observed rotation for this solution was −2.82°. If the current efficiency were 100%, 5.9 hr. would be required for total reaction. After electrolysis the light yellow solution was filtered, and the observed rotation was −2.37°. The DMF was distilled *in vacuo* and the residual oil was distributed between water and ether. The ether layer was dried over magnesium sulfate and distilled. The product, consisting of mixed 2,3-diphenylbutanes (infrared spectrum), amounted to 0.771 g. (0.00367 mole). Using the amount of product isolated as a measure of the extent of decomposition of *l*-α-phenylethyltrimethylammonium nitrate, the optical activity of the unreacted salt was calculated; $[\alpha]^{25}D$ −16.9° (*l* 1 dm., 14% in DMF). The aqueous layer was concentrated to a tan oil which could not be induced to crystallize. It was sucked as dry as possible and its optical rotation was determined; $[\alpha]^{25}D$ −15.6° (*l* 1 dm., 17% in DMF). Since the salt was not pure, this is a minimum value and less reliable than the previous rotation.

Acknowledgment.—We are indebted to Dr. E. Robert Coburn of Bennington College for the resolution of α-phenylethylamine and Mr. John E. Barry of these laboratories for the infrared spectra.

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(14) J. v. Braun and Z. Kohler, *Ber.*, **51**, 79 (1918); R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 144 (1928).

(15) J. S. Buck and S. S. Jenkins, THIS JOURNAL, **51**, 2162 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT SANTA BARBARA]

Mechanism of Hydrolysis of N,N'-Diarylformamidines in Acidic Solutions

BY ROBERT H. DEWOLFE

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The effects of aryl substituents, temperature, solvent polarity, solvent acidity and nucleophilic catalysts on the rate of hydrolysis of symmetrically substituted N,N'-diarylformamidines have been investigated. In solutions of mineral acids, rate of hydrolysis is given by the equation $k_1 = C \cdot c_{H_3O^+} a_{H_2O}/h_0$. This fact and other experimental observations indicate that diarylformamidine hydrolysis in acidic solutions involves nucleophilic attack by water on hydrated amidinium ions.

Mechanisms of hydrolysis and saponification of amides have been worked out in some detail.[1] Very little information is available concerning hydrolysis reactions of amidines, however. These compounds (I)

$$RN{=}CR'{-}NR''R'''$$
I

are nitrogen analogs of amides, and undergo many of the same reactions, such as hydrolysis, saponification and aminolysis. They differ from amides primarily in being much more basic.

(1) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 784; (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 295; (c) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 365; (d) J. T. Edwards and S. C. R. Meacock, *J. Chem. Soc.*, 2000 (1957).

The only kinetic investigation of formamidine hydrolysis yet reported is that of DeWolfe and Roberts,[2] who studied the hydrolysis of N,N'-diphenylformamidine in acidic aqueous dioxane. This reaction (equation 1, Ar = C_6H_5, R = H) yields aniline and formanilide

$$ArN{=}CR{-}NHAr + H_2O = ArNH_2 + ArNHCOR \quad (1)$$

The formanilide hydrolyzes, more slowly, to aniline and formic acid. Hydrolysis of this amidine was found to be general acid-catalyzed in buffer solutions. In dilute hydrochloric acid solutions, the rate of hydrolysis was nearly independent of hydrogen ion concentration and ionic strength. The reaction was found to obey the rate equation

(2) R. H. DeWolfe and R. M. Roberts, THIS JOURNAL, **75**, 2942 (1953).

$$\text{rate} = [C_6H_5N{=}CHNHC_6H_5] \sum_{i} k_i[A_i]$$

where k_i are the catalytic coefficients of the various acidic species, A_i, present in the reaction solution. The kinetic analysis is complicated by the fact that the amidine is basic, and hence its concentration in the reaction solutions is *p*H dependent. This rate equation is rationalized equally well in terms of general acid-catalyzed hydrolysis of the free base or general base-catalyzed hydrolysis of its conjugate acid, diphenylformamidinium ion.[3]

Since the kinetic data of the earlier study do not permit an unambiguous assignment of mechanism to the hydrolysis reaction, a more detailed study of diarylformamidine hydrolysis was undertaken. The effects of aryl substituents, temperature, solvent acidity, solvent polarity and nucleophilic catalysts on rate of hydrolysis of symmetrically substituted N,N′-diarylformamidines were systematically investigated. The results obtained show that both of the previously postulated mechanisms are oversimplifications. A new mechanism of diarylformamidine hydrolysis is proposed which is compatible with all of the experimental data.

Experimental

The dioxane used in the reaction solutions was purified by the procedure of Fieser.[4] The symmetrically substituted N,N′-diarylformamidines used in this study were prepared from triethyl orthoformate and the appropriate aromatic primary amines by the method of Claisen,[5] and are known compounds. Reagent grade inorganic chemicals were used throughout. All organic chemicals were redistilled or recrystallized before use.

Diarylformamidines and their salts are only sparingly soluble in water, so aqueous dioxane was used as the reaction solvent for most of the kinetic runs. Reaction solutions were prepared by pipetting the desired volume of a very dilute solution of the amidine in dioxane into a 25-ml. volumetric flask, adding the desired volumes of aqueous acid and salt solutions, and then filling the flask to the calibration mark with water. Most rate measurements were made in "20%" dioxane, that is, 5 ml. of dioxane made up to 25 ml. with water and aqueous solutions. Diphenylformamidine hydrochloride is sufficiently soluble in aqueous hydrochloric acid solution for its rate of hydrolysis to be measured in aqueous solutions.

Reaction rates were determined spectrophotometrically, using a Beckman model DU spectrophotometer equipped with thermospacers. Reactions were carried out in stoppered absorption cells in the cell housing of the spectrophotometer. The temperature of the cell housing was maintained constant at the desired value by circulating water from a constant-temperature bath through the thermospacers. The temperature of the inside of the cell housing was measured directly, to allow for heat losses occurring between the bath and the cell housing.

The hydrolysis reactions are first order, and rates were determined by measuring the rate of disappearance of the amidine. This is accomplished easily, since the amidines (with the exception of N,N′-di-*m*-nitrophenylformamidine) absorb light to longer wave lengths than the amines and anilides formed by their hydrolysis. Rate constants were calculated from slopes of the excellent straight lines obtained in plots of ln A (absorbance) *vs.* time (in seconds), or, in the case of N,N′-di-*m*-nitrophenylformamidine, from plots of ln $(A_t - A_\infty)$ *vs.* time, where A_t is the value of absorbance at time t, and A_∞ is the final absorbance.

The rate constants given in Table I are averages of at least two runs. In general, agreement between runs was better than 3%. Data for hydrolysis of N,N′-diphenylformamidine in 20% dioxane–0.415 N HCl are illustrative of the results obtained.

T, °C.	k_1, sec.$^{-1}$ Run I	Run II	Average
25.0	3.47×10^{-5}	3.48×10^{-5}	3.48×10^{-5}
39.7	1.63×10^{-4}	1.58×10^{-4}	1.60×10^{-4}
54.6	5.64×10^{-4}	5.75×10^{-4}	5.70×10^{-4}

Arrhenius activation energies were calculated from the least-squares slopes of log k_1 *vs.* $1/T$ plots. Entropies of activation were calculated for 25°, using the equation

$$\Delta S^* = 2.303R\left[\log k_1 + \frac{E_a - RT}{2.303RT} - \log (kT/h)\right]$$

Activation energies and entropies of activation for hydrolysis reactions in 20% dioxane–0.415 N HCl are shown in Table II.

Results

Effects of Aryl Substituents on Reaction Rate.—A number of symmetrical N,N′-diarylformamidines were hydrolyzed in 20% dioxane which was 0.415 N in hydrochloric acid. In most cases rate determinations were made at three of four temperatures. The kinetic data are summarized in Table I.

TABLE I

HYDROLYSIS OF N,N′-DIARYLFORMAMIDINES ($XC_6H_4N{=}CHNHC_6H_4X$) IN 20% DIOXANE–AQUEOUS 0.415 N HCl

X	T: 5.6°	10.1°	10^5k_1, sec.$^{-1}$ at T°C. 25.0°	39.7°	54.6°	69.2°
p-CH_3O			0.25	1.07	3.98	14.8
p-CH_3			0.751	3.45	13.3	46
m-CH_3			2.44	10.3	39.6	120
H			3.48	16.0	57.0	
m-C_2H_5O			10.6			
p-Cl			21.8	92.3	298	
p-Br			30.0	127	403	
m-Cl		19.1	74	307	980	
m-NO_2	203		1020			
o-CH_3			0.756	3.23	11.1	
o-Cl		71.5	285	918		

A Hammett $\rho\sigma$ plot (ref. 1*c*, p. 184 ff.) of the kinetic data at 25° yields a straight line of slope +3.64 (Fig. 1), showing that the reaction is strongly accelerated by electron-withdrawing aryl substituents. The value of ρ is approximately independent of temperature: at 39.7°, ρ = 3.78, and at 54.6°, ρ = 3.63.

Energies and Entropies of Activation.—Arrhenius activation energies and entropies of activation at 25°, derived from the kinetic data of Table I, are given in Table II. It is evident that the large positive value of ρ for the reaction is due to lowering of the activation energy by electron-

TABLE II

THERMODYNAMIC QUANTITIES OF ACTIVATION FOR HYDROLYSIS OF N,N′-DIARYLFORMAMIDINES ($XC_6H_4N{=}CHNHC_6H_4X$) IN 20% DIOXANE–AQUEOUS 0.415 N HCl

X	E_a, kcal.	ΔS^*, e.u.
p-CH_3O	18.6	−24
p-CH_3	18.8	−21
m-CH_3	17.9	−21
H	18.4	−19
p-Cl	17.2	−20
p-Br	17.1	−19
m-Cl	16.4	−20
m-NO_2	14	−24
o-CH_3	17.6	−25
o-Cl	15.2	−21

(3) R. H. DeWolfe, Ph.D. Thesis, The University of Texas, 1953.

(4) L. F. Fieser, "Experiments in Organic Chemistry," Third Edition, D. C. Heath and Co., New York, N. Y., 1955, p. 284.

(5) L. Claisen, *Ann.*, **287**, 366 (1895).

withdrawing substituents. The entropy of activation has a large negative value of about −20 entropy units, which does not vary in any systematic way with the structure of the aryl group. The two *o*-substituted diarylformamidines studied yield ΔS^* values similar to those of the *m*- and *p*-substituted compounds.

Effect of Solvent Polarity and Ionic Strength on Reaction Rate.—The rate of hydrolysis of N,N'-di-*m*-chlorophenylformamidine in aqueous dioxane–0.415 *N* HCl was found to have a maximum in about 60% dioxane (Table III).

TABLE III

HYDROLYSIS OF N,N'-DI-*m*-CHLOROPHENYLFORMAMIDINE IN AQUEOUS DIOXANE–0.415 *N* HCl SOLUTIONS AT 25.0°

Dioxane, %	$10^3 k_1$, sec.$^{-1}$
0	0.165
20	0.74
40	1.89
60	3.72
80	2.21

Dioxane concentration exerts a similar influence on rate of hydrolysis of N,N'-diphenylformamidine: at 25°, the rate of hydrolysis is 1.84×10^{-5}/sec. in aqueous 0.745 *N* HCl, and 3.48×10^{-5}/sec. in 20% dioxane–0.415 *N* HCl. At 40°, the rate in 0.415 *N* HCl solutions is 1.60×10^{-4}/sec. in 20% dioxane and 2.54×10^{-4}/sec. in 37% dioxane.

The ionic strength of the reaction solution has little or no effect on rate of hydrolysis of N,N'-diphenylformamidine.[2]

Influence of Acidity on Reaction Rate.—The rate of hydrolysis of N,N'-diphenylformamidine is approximately independent of hydrogen ion concentration in dilute solutions of hydrochloric acid.[2] The reaction rate drops off rapidly when the acid concentration is increased into the range where Hammett's acidity function (ref. 1c, p. 267) diverges from hydrogen ion concentration.

Table IV shows the effect of perchloric acid concentration on rate of hydrolysis of N,N'-di-*m*-chlorophenylformamidine in 40% dioxane at 25°. An increase in acid concentration from 0.37 to 3.3 *N* results in almost a hundred-fold decrease in reaction rate. Also given in the table are h_0 values for the different acid concentrations used. In the same concentration range, h_0 increases by a factor of approximately 200.

TABLE IV

HYDROLYSIS OF N,N'-DI-*m*-CHLOROPHENYLFORMAMIDINE IN 40% DIOXANE PERCHLORIC ACID SOLUTIONS AT 25°

$HClO_4$	$10^4 k_1$, sec.$^{-1}$	h_0[a]
0.369	10	0.0725
.554	7.8	.138
0.739	6.0	.224
1.108	3.5	.50
1.662	1.71	1.32
3.32	0.111	14.8

[a] C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

More extensive data were obtained for the hydrolysis of N,N'-diphenylformamidine in aqueous hydrochloric acid solutions at 25.0° (Table V).

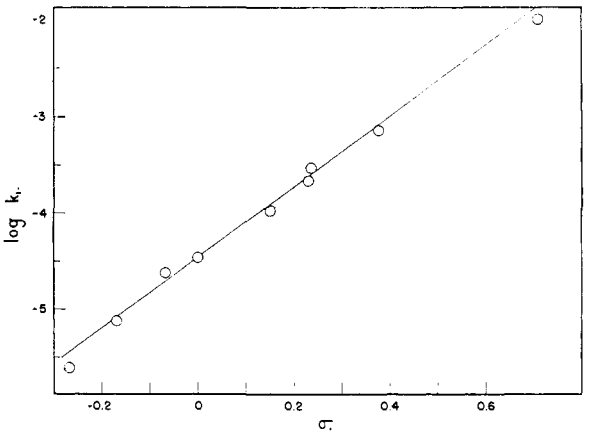


Fig. 1.—Hammett plot for hydrolysis of N,N'-diarylformamidines in acidic 20% dioxane at 25°.

In addition to the rate data, values of the activity of water and of h_0 are given for each hydrochloric acid concentration used. In going from 0.745 *N* HCl to 5.71 *N* HCl, hydrolysis rate decreases nearly thirty-fold, while h_0 increases a hundred-fold. The significance of these observations will be discussed in detail later.

TABLE V

HYDROLYSIS OF N,N'-DIPHENYLFORMAMIDINE IN AQUEOUS HCl AT 25.0°

[HCl]	$10^6 k_1$, sec.$^{-1}$	a_{H_2O}[a]	h_0[b]	$10^6 k_1 h_0 / c_{H_2O} a_{H_2O}$
0.754	18.4	0.973	1.0	25.4
1.24	14.4	.950	2.14	26.2
1.74	11.4	.927	3.80	26.9
2.24	9.37	.899	5.90	27.4
2.73	6.43	.870	8.9	24.1
3.22	4.61	.838	13.5	23.1
3.72	3.33	.804	20.4	22.7
4.22	2.23	.765	30.9	21.4
5.21	1.03	.683	67.6	19.6
5.71	0.743	.640	102	20.$^-$

[a] M. Randall and E. K. Young, THIS JOURNAL, **50**, 1002 (1928). [b] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 12 (1957).

Rate Studies in Buffer Solutions.—Hydrolysis of N,N'-diphenylformamidine is subject to general acid–base catalysis in acetate and *p*-nitrophenolate buffers.[2] This reaction also exhibits general catalysis in formic acid–formate buffers[3] and anilinium ion–aniline buffers (Table VI). For each buffer, Table VI lists the buffer ratio [HB]/[B] (which determines the *p*H of the solution) and the concentration of the conjugate base of the buffer acid ($[RCO_2^-]$ for carboxylate buffers, $[C_6H_5NH_2]$ for aniline buffers).

Table VI also gives data for hydrolysis of N,N'-di-*m*-chlorophenylformamidine in acetate, chloroacetate and dichloroacetate buffers. These data show that hydrolysis of N,N'-di-*m*-chlorophenylformamidine is also subject to general acid–base catalysis, and permit calculation of the catalytic coefficients of the buffer bases.

In solutions of sufficiently low *p*H for essentially all of the amidine to be present as amidinium ion,

TABLE VI

HYDROLYSIS OF $XC_6H_4N{=}CHNHC_6H_4X$ IN AQUEOUS DIOXANE HB–B BUFFER SOLUTIONS

[HB]/[B]	[B]	10^4k_{1i}, sec.$^{-1}$
N,N′-Diphenylformamidine in 30% dioxane HCO_2H–HCO_2^- buffers at 35° (μ 0.160)[a,b]		
0.302	0.160	3.83
.302	.107	3.13
.302	.0537	2.43
.743	.160	3.73
.743	.107	3.13
.743	.0537	2.52
1.17	.160	3.81
1.17	.107	3.12
1.17	.0537	2.55
N,N′-Diphenylformamidine in 20% dioxane $C_6H_5NH_3^+$–$C_6H_5NH_2$ buffers at 40° (μ 0.127)		
1.44	0.174	2.17
1.44	.116	2.06
1.44	.058	1.90
N,N′-Di-*m*-chlorophenylformamidine in 20% dioxane $CHCl_2CO_2H$–$CHCl_2CO_2^-$ buffers at 25° (μ 0.127)		
0.520	0.127	1.11
.520	.085	1.07
.520	.0425	1.03
N,N′-Di-*m*-chlorophenylformamidine in 20% dioxane CH_2ClCO_2H–$CH_2ClCO_2^-$ buffers at 25° (μ 0.127)		
1.86	0.127	1.36
1.86	.085	1.26
1.86	.0425	1.12
0.430	.127	1.33
.430	.085	1.23
.430	.0425	1.08
N,N′-Di-*m*-chlorophenylformamidine in 20% dioxane CH_3CO_2H–$CH_3CO_2^-$ buffers at 25° (μ 0.127)		
0.472	0.127	7.38
.472	.085	6.01
.472	.0425	4.41
.975	.127	10.5
.975	.085	9.05
.975	.0425	6.73
1.94	.127	12.6
1.94	.085	10.8
1.94	.0425	8.0

[a] μ is ionic strength. [b] Data from ref. 3.

both of the compounds studied obey the rate law

$$k_1 = k_0 + \sum^{i} k_{Bi}\cdot[B_i]$$

where k_0 is the rate of the "water reaction," k_{B_i} are the catalytic coefficients of the basic species present, and $[B_i]$ are their concentrations. The catalytic coefficients of the buffer bases may be evaluated by plotting k_1 *vs.* [B] and calculating the slopes of the resulting lines. For diphenylformamidine hydrolysis in 30% dioxane formate buffers at 35°, $k_{HCO_2^-} = 1.3 \times 10^{-3}$ l./mole sec.; the value of $k_{HCO_2^-}$ is independent of buffer ratio, indicating that the amidine is almost completely protonated at the *p*H of the buffer solutions. The catalytic coefficient of aniline for this reaction in 20% dioxane at 40° is 2.3×10^{-4} l./mole sec.

The catalytic coefficients of acetate ion, chloroacetate ion, and dichloroacetate ion for hydrolysis of N,N′-di-*m*-chlorophenylformamidine in 20% dioxane at 25° are 1.0×10^{-2}, 2.9×10^{-3} and 1.0×10^{-3} l./mole sec., respectively. The amidine is not completely protonated in the acetic acid–sodium acetate buffers and $k_{CH_3CO_2^-}$ is estimated on the assumption that when the buffer ratio is 1.94, the amidine is approximately 50% protonated, as indicated by the intercept of the k_1 *vs.* $[CH_3CO_2^-]$ plot. These catalytic coefficients conform to the Brönsted catalysis law.[6] A plot of log k_B *vs.* log K_B ($K_B = 1/K_i$, where K_i, is the ionization constant of the buffer acid in water at 25°) gives a straight line described by the equation

$$\log k_B = 0.29 \log K_B - 3.37$$

Discussion

The kinetic data of this study and of the earlier investigation of N,N′-diphenylformamidine hydrolysis[2] can be rationalized equally well in terms of either general acid-catalyzed hydrolysis of the free amidines, or general base-catalyzed hydrolysis of the amidinium ions. The first of these mechanisms, general acid-catalyzed hydrolysis of the unprotonated amidine, can now be rejected with a fair degree of confidence.

Due primarily to resonance stabilization of their conjugate acids

$$\overset{+}{\text{ArNH}}{=}\text{CH}{-}\text{NHAr} \longleftrightarrow \text{ArNH}{-}\text{CH}{=}\overset{+}{\text{NH}}\text{Ar}$$

diarylformamidines are substantially more basic than the aromatic amines from which they are derived. Thus, for N,N′-diphenylformamidine in 30% dioxane, $K_B = 1.4\times10^6$ at 35°,[2] while for aniline, $K_B \cong 4 \times 10^{4}$.[7] In the 0.4 *N* hydrochloric acid solutions used in the kinetic experiments, the amidines would be present almost exclusively as amidinium chlorides, $(ArNH{=}CHNHAr)^+Cl^-$. This fact alone suggests that the observed reaction is hydrolysis of the amidinium ion. In addition, a general acid-catalyzed reaction would require a rate-determining proton transfer to a basic nitrogen atom, which seems unlikely.

Diarylformamidine hydrolysis in 20% dioxane–0.415 *N* HCl has one of the largest positive ρ-values yet reported for a reaction.[8] The strong rate-accelerating effect of electron-withdrawing aryl substituents is predicted by a mechanism involving hydrolysis of the amidinium ion. If the reaction involved rate-determining proton transfer to the unprotonated amidine, electron-withdrawing substituents would increase the concentration of the free amidine in acidic solutions (by lowering its basicity), but should simultaneously decrease the rate of proton transfer to it. These two factors would oppose each other, and the result should be a small positive, or even a negative, value of ρ. The large positive value of ρ supports the idea that the rate-controlling step of the reaction involves attack by water on the amidinium ion or some species whose concentration is proportional to that of the amidinium ion.

(6) J. N. Brönsted and K. Pedersen, *Z. physik. Chem.*, **A108**, 185 (1923).

(7) N. A. Lange, "Handbook of Chemistry," Ninth Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1956, p. 1202; $K_B = K_i/K_w$. It is assumed that the basicity constant will not be greatly affected by the change in solvent polarity.

(8) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

Such attack would be facilitated by electron-withdrawing substituents.

The kinetic data for hydrolysis of diarylformamidines in strongly acidic solutions (Tables IV and V) shed light on the detailed mechanism of the reaction. These data show that the reaction rate is an unusually complicated function of the acidity of the reaction medium. For hydrolysis of N,N'-diphenylformamidine in aqueous hydrochloric acid solutions, the reaction rate is directly proportional to the concentration of hydronium ion and the activity of water, and inversely proportional to h_0 (ref. 1c, p. 267), as shown by the relative constancy of the quantity $k_1h_0/c_{H_3O^+}a_{H_2O}$. That is

$$k_1 = Cc_{H_3O^+}a_{H_2O}/h_0 \qquad (2)$$

where C is a constant. In dilute acid solutions, $c_{H_3O^+} \cong h_0$, and $a_{H_2O} \cong 1$, so that $k_1 \cong C$, in agreement with experimental observation. The same relationship probably holds for hydrolysis of N,N'-di-*m*-chlorophenylformamidine in 40% dioxane perchloric acid solutions, but this cannot be tested in the absence of data for the activity of water in these solutions.

If equation 2 is valid, the transition state for the hydrolysis reaction must include the amidine molecule, a proton, and two molecules of water. This requires a more complicated mechanism than a concerted attack by water on the amidinium ion, which would involve a transition state containing only one molecule of water. The following mechanism rationalizes the data satisfactorily

$$ArN{=}CH{-}NHAr + H_3O^+ \overset{K_1}{\rightleftharpoons} Ar\overset{+}{N}H{=}CH{-}NHAr + H_2O$$

$$Ar\overset{+}{N}H{=}CH{-}NHAr + H_2O \overset{K_2}{\rightleftharpoons} Ar\overset{+}{N}H_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}NHAr$$

$$Ar\overset{+}{N}H_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}NHAr + H_2O \overset{K\ddagger}{\rightleftharpoons} Ar\overset{\delta+}{N}H_2\cdots\underset{\displaystyle HO}{\underset{|}{C}}\cdots O^{\delta+}H \quad (NHAr\ H)$$

$$\downarrow k_3$$

$$ArNH_2 + ArNHCHO + H_3O^+$$

To simplify the later discussion this mechanism may be abbreviated

$$B + H_3O^+ \overset{K_1}{\rightleftharpoons} BH^+ + H_2O$$

$$BH^+ + H_2O \overset{K_2}{\rightleftharpoons} BH_3O^+$$

$$BH_3O^+ + H_2O \overset{K}{\rightleftharpoons} \ddagger \xrightarrow{k_3} \text{products}$$

Activities are denoted by a, concentrations by c, and activity coefficients by f. According to this mechanism

$$v = k_3c\ddagger = k_3K\ddagger a_{BH_3O^+}a_{H_2O}/f\ddagger$$

$$a_{BH_3O^+} = K_2c_{BH^+}f_{BH^+}a_{H_2O}$$

$$k_1 = v/c_{BH^+} = k_3K\ddagger K_2a_{H_2O}^2\frac{f_{BH^+}}{f\ddagger}$$

but

$$f_{BH^+} = a_{H^+}f_B/h_0, \text{ and } a_{H^+}a_{H_2O} = a_{H_3O^+} = c_{H_3O^+}f_{H_3O^+}$$

therefore

$$k_1 = k_3K\ddagger K_2a_{H_2O}c_{H_3O^+}\cdot\frac{f_Bf_{H_3O^+}}{h_0f\ddagger}$$

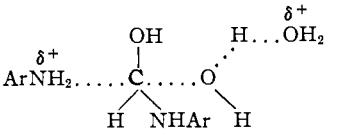
where k_1 is the observed first-order rate constant. If it is assumed that $f_Bf_{H_3O^+}/f\ddagger$ is independent of $c_{H_3O^+}$,[9] equation 3 is equivalent to equation 2, with

$$C = k_3K\ddagger K_2f_Bf_{H_3O^+}/f\ddagger$$

The rate data of Table V are somewhat more closely described by the equation

$$k_1 = C\cdot a_{H_2O}^2c_{H_3O^+}/h_0 \qquad (4)$$

than by equation 2, although the rate and h_0 data are not sufficiently precise to permit a decision between the two. Equation 4 would require a more complex transition state, such as



Alternative paths for assembling the transition state required by the kinetics would also lead to expressions equivalent to equation 2 (or equation 4), but the proposed mechanism seems in excellent agreement with all of the experimental observations.

This mechanism would account for the large positive value of ρ for the reaction. In a bimolecular reaction of the hydrated amidinium ion with water, both the bond-breaking and the bond-making processes should be facilitated by electron-withdrawing substituents on the aryl groups.

Long, Pritchard and Stafford[10] recently suggested that entropy of activation is a valuable diagnostic tool for assigning mechanisms to acid-catalyzed hydrolysis reactions. Unimolecular acid-catalyzed hydrolysis reactions of esters, ortho esters, epoxides and acetals consistently have entropies of activation which are much more positive than those of bimolecular hydrolyses. This is plausible, since a greater constraint is placed upon the reaction system in forming the transition state of a bimolecular reaction than in forming that of a unimolecular reaction. In acid-catalyzed ester hydrolyses, reactions occurring by the Al mechanism (ref. 1a, p. 779) have positive or small negative entropies of activation (*e.g.*, +13.3 e.u. for *t*-butyl mesitoate and +9.6 e.u. for *t*-butyl benzoate in 60% acetone[11]; −1.8 e.u. for the *p*-methoxydiphenylmethyl acetate in 70% dioxane[12]), while those occurring by the $A_{Ac}2$ mechanism have large negative entropies of activation, ranging from about −20 to about −40 e.u.[13]

The large negative entropy of activation of diarylformamidine hydrolysis is thus in agreement with the postulated bimolecular rate-determining

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 281.

(10) F. A. Long, J. G. Pritchard and F. E. Stafford, THIS JOURNAL, **79**, 2362 (1957).

(11) V. R. Stimson, *J. Chem. Soc.*, 2010, 2673 (1955).

(12) C. A. Bunton and T. Hadwick, *ibid.*, 3043 (1957).

(13) (a) V. R. Stimson, *ibid.*, 4020 (1955); E. W. Timm and C. N. Hinshelwood, *ibid.*, 862 (1938).

step. It is also significant that the two *o*-substituted diarylformamidines yielded ΔS^* values similar to those of the *m*- and *p*-substituted compounds. *o*-Substituents do not sterically hinder the reaction, indicating that the central carbon atom of the amidine group is far enough from the aromatic rings for hindrance by *o*-substituents to be negligible.

The rate of hydrolysis of N,N′-di-*m*-chlorophenylformamidine was found to increase with increasing dioxane content of the reaction medium, up to 60 or 70% dioxane. This acceleration in rate with diminishing solvent polarity is predicted by the proposed mechanism, according to which charge is dispersed on going from reactants to transition state (ref. 1a, p. 349). The decrease in rate above about 60% dioxane probably is due simply to the reduced concentration of water.

Kinetic studies in buffer solutions show that hydrolysis of diarylformamidinium ions is general base-catalyzed. The mechanism of the general base catalysis probably is similar to that proposed for the reaction in mineral acid solutions, with the buffer base replacing water in either the addition step or the bimolecular displacement step. In either case a highly reactive intermediate would be formed which on hydrolysis would yield the observed products. The fact that aniline catalyzes the hydrolysis of N,N′-diphenylformamidine is an argument against the buffer base participating in the displacement step

$$\mathrm{Ar\overset{+}{N}H_2{-}CH(OH){-}NHAr + B: \longrightarrow ArNH_2 + \overset{+}{B}{-}CH(OH){-}NHAr}$$

since in this case a displacement of aniline by aniline would result in no net change, and hence no catalysis. The observed catalysis is thus evidence for the formation of the conjugate acid of trianilinomethane as an intermediate in the reaction. However, the evidence is not conclusive; the general catalysis is small, and the rate change may be due to decreasing the polarity of the solvent by replacing water with aniline.

It seems likely that the catalysis by aniline is real. The highest aniline concentrations used correspond to about 1.6% by weight of aniline. It can be estimated that increasing the dioxane concentration of the reaction medium by 1.6% would increase the reaction rate by a factor of 1.11, which is only half the increase observed in aniline solutions. Since aniline has a higher dielectric constant than dioxane (ref. 7, p. 1222), the medium effect may actually be smaller than this.

The mechanism proposed for acid hydrolysis of diarylformamidines is similar to the $A_{Ac}2$ mechanism of ester hydrolysis. It is probably also similar to the mechanism of acid hydrolysis of amides[1] and imidic esters. According to Edwards and Meacock,[14] the rates of hydrolysis of benzamide and methyl benzimidate are described by the equation

$$k_1 = C \cdot c_{BH^+} c_{H_3O^+} / h_0 \qquad (5)$$

where C is a constant and c_{BH^+} is the concentration of the conjugate acid of the amide or imidic ester. They do not give numerical rate data, but inspection of their graphs indicates that their results may be more closely described by equation 3 than by equation 5, in which case the mechanisms of the hydrolysis reactions may be strictly analogous to that proposed for diarylformamidine hydrolysis.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Thermochromism of Two Disulfides

BY ROBERT EARL DAVIS[1] AND CHARLES PERRIN[2]

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The thermochromism of 2,2′-dibenzothiazolyl disulfide and of tetramethylthiuram disulfide has been examined in homogeneous solution in the temperature range of 25 to 100°. Beer's law is obeyed by both compounds at 25 and at 100°, thus indicating that no reversible dissociation has taken place. The thermochromism is attributed to thermal broadening of the absorption band caused by increasing population of the higher vibrational states of the ground state. Radical dissociation of the disulfides has been shown to play no part. The mode of radical decomposition of tetramethylthiuram disulfide has been discussed. Thermodynamic and quantum mechanical criteria have been used to clarify reactions involving elemental sulfurs.

Introduction

Many aryl disulfides, thiocarbonyl compounds and various other sulfur compounds are weakly thermochromic, becoming yellow or deepening in color on heating. In many cases the change is reversible and the original compound is obtained on cooling. Considerable polemic discussion[3-6] has been generated concerning whether or not a *re-*

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