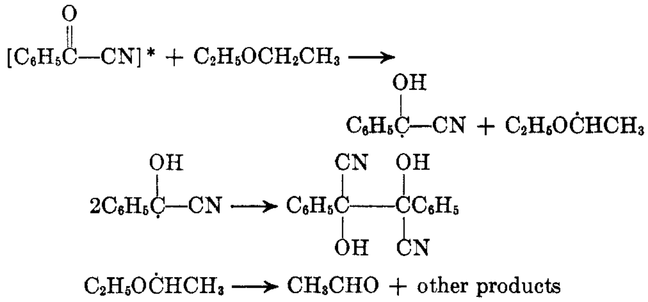
aroyl cyanides. The choice of solvents was limited, because aroyl cyanides are reactive toward hydroxylic compounds. A hydrogen-donating organic solvent is essential; no reaction occurs in carbon tetrachloride. In ether, triplet benzoyl cyanide reacts with hydrogen from diethyl ether in a manner that is perhaps comparable with that proposed[3] for the photoreduction of pyruvic acid in methanol; the reactions are as shown below.



$$[C_6H_5\overset{O}{\overset{\|}{C}}—CN]^* + C_2H_5OCH_2CH_3 \longrightarrow C_6H_5\underset{\cdot}{\overset{OH}{\overset{|}{C}}}—CN + C_2H_5O\dot{C}HCH_3$$

$$2C_6H_5\underset{\cdot}{\overset{OH}{\overset{|}{C}}}—CN \longrightarrow C_6H_5\overset{CN}{\underset{OH}{C}}—\overset{OH}{\underset{CN}{C}}C_6H_5$$

$$C_2H_5O\dot{C}HCH_3 \longrightarrow CH_3CHO + \text{other products}$$

It has not been determined whether the benzildicyanohydrin isolated from the irradiation products of benzoyl cyanide is racemic, *meso*, or a mixture of both. Notwithstanding the difference among the "melting points" previously reported for benzildicyanohydrin, the same modification is obtained regardless of the method of preparation.

All the dicyanohydrins obtained from the irradiation of aroyl cyanides decompose on heating or prolonged irradiation to benzil (or substituted benzils) and hydrogen cyanide. It has not been possible to account for the formation of benzoin. It is apparent, as a result of the tracer studies, that benzoin is not an intermediate in the formation of benzil, and, in this sense, the reaction differs from that for the photochemically induced oxidation of acetoin to biacetyl.[3]

The photochemical decomposition of benzildicyanohydrin is not reversible. However, equilibrium between benzil, hydrogen cyanide, and benzildicyanohydrin is readily attained at 95° in a sealed glass tube or at 25° in the presence of powdered glass. In both instances reaction is catalyzed by the glass surface. The synthesis in which powdered glass is used as the catalyst is certainly the most satisfactory method for preparing benzildicyanohydrin.

TABLE I

PRODUCTS OBTAINED IN THE IRRADIATION OF AROYL CYANIDES[a]

Compd irradiated	Major products	Overall yield, %
$C_6H_5COCN^b$	$C_6H_5COCOC_6H_5$	40
	$C_6H_5COCHOHC_6H_5$	19
C_6H_5COCN	$C_6H_5COCOC_6H_5$	90
$C_6H_5COCN^c$	No reaction	. . .
$C_6H_5COCN^d$	$C_6H_5COH(CN)COH(CN)C_6H_5$	50
p-$CH_3C_6H_4COCN$	*p*-$CH_3C_6H_4COCOC_6H_4$-*p*-CH_3	60
m-$CH_3C_6H_4COCN$	*m*-$CH_3C_6H_4COCOC_6H_4$-*m*-CH_3	23
o-$CH_3C_6H_4COCN$	*o*-$CH_3C_6H_4COH(CN)COH$-$(CN)C_6H_4$-*o*-CH_3	<5
	(Recovered *o*-$CH_3C_6H_4COCN$)	>70
p-$CH_3OC_6H_4COCN$	*p*-$CH_3OC_6H_4COCOC_6H_4$-*p*-OCH_3	27
	p-$CH_3OC_6H_4COH(CN)COH$-$(CN)C_6H_4$-*p*-OCH_3	18
p-ClC_6H_4COCN	*p*-$ClC_6H_4COCOC_6H_4$-*p*-Cl	13
	p-$ClC_6H_4COH(CN)COH(CN)$-C_6H_4-*p*-Cl	17
p-$NO_2C_6H_4COCN^e$	No identifiable products	. . .
α-Naphthoyl[f] cyanide	No reaction	. . .
α-Naphthoyl[g] cyanide	α-$C_{10}H_7COCO$-α-$C_{10}H_7$	11
Furoyl cyanide	No reaction	. . .

[a] Sensitizer, benzophenone; solvent, diethyl ether except as noted; irradiation time, 6 hr except as noted. [b] Irradiation time, 2 hr. [c] Solvent, carbon tetrachloride. [d] Benzoyl chloride present. [e] Tetrahydrofuran added to increase solubility of *p*-nitrobenzoyl cyanide. [f] Irradiation time, 14 hr. [g] Sensitizer, acetophenone; irradiation time, 24 hr.

The photochemical reactions described in this paper do not have completely general applicability for the preparation of substituted benzils. However, they are useful for the preparation of unhindered benzils that are not readily obtained by way of the benzoin condensation–oxidation sequence.

Acknowledgment.—The author is indebted to Dr. C. J. Collins and Dr. J. F. Eastham for helpful comments and discussion.

The Kinetics and Mechanism of the Hydrolysis of Benzohydroxamic Acid[1]

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The rate of hydrolysis of benzohydroxamic acid has been determined as a function of hydronium and hydroxide ion concentrations at high concentrations of these catalytic agents. First-order dependence on hydronium ion is observed in the acid-catalyzed reaction. Both first- and second-order dependence on hydroxide ion is inferred in the base-catalyzed reaction. Mechanisms consistent with the rate data are proposed.

The alkaline hydrolysis of an amide, trifluoroacetanilide, which contains a weakly acidic hydrogen attached to nitrogen has recently been investigated.[2] We now wish to report an investigation of the acidic and alkaline hydrolysis of benzohydroxamic acid. This substance contains two weakly acidic hydrogen—its conjugate base is a tautomeric mixture.[3]

Results and Discussion

All kinetic measurements were carried out with excess hydronium or hydroxide ion thus ensuring that all rates were pseudo first order. The results for the acid- and base-catalyzed hydrolyses in aqueous solution are listed in Tables I and II, respectively. The

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[1] From the M.A. Thesis of R. L. Fuller, Western Michigan University, 1966.

[2] P. M. Mader, *J. Am. Chem. Soc.*, **87**, 3191 (1965).

[3] G. M. Steinberg and R. Swidler, *J. Org. Chem.*, **30**, 2362 (1965).

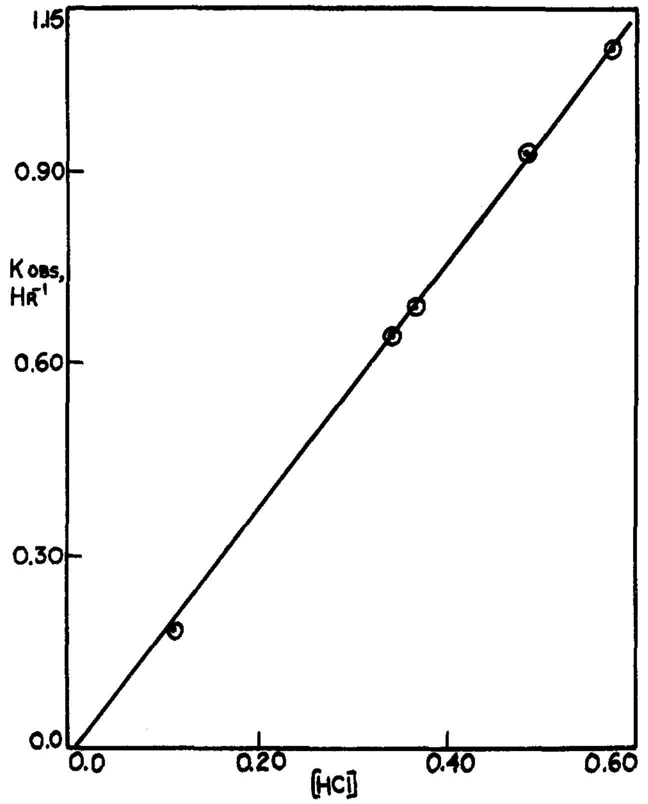


Figure 1.—Pseudo-first-order rate constants as a function of hydrochloric acid concentration at 88.6°.

Table I

Pseudo-First-Order Rate Constants for the Acidic Hydrolysis of Benzohydroxamic Acid

[HCl], mole/l.	Rate constant,[a] hr^{-1} 78.6°	88.6°
0.577		1.09
0.485	0.394	0.928
0.369		0.689
0.341	0.290	0.643
0.109	0.0861	0.187

[a] Average value of three determinations except in two cases, average of two runs each. Ionic strength maintained at 0.577 *M* with potassium chloride.

Table II

Pseudo-First-Order Rate Constants for the Alkaline Hydrolysis of Benzohydroxamic Acid

[NaOH], moles/l.	Rate constant,[a] hr^{-1} at 88.6°
2.179	0.0678
1.757	0.0630
1.578	0.0592
0.985	0.0533
0.609	0.0476
0.119	0.0421

[a] Average of three or four determinations except one case, average of two. Ionic strength maintained at 2.179 *M* with potassium chloride.

rate constants are those corresponding to the rate law, $-dS/dt = k_{obsd}S$, where S is the total stoichiometric amount of hydroxamic acid present at any time. Graphs of k_{obsd} *vs.* hydronium and hydroxide ion concentrations are shown in Figures 1 and 2, respectively. The corresponding rate laws are given by eq 1 and 2, respectively. Equation 1 is written on the basis that the intercept in Figure 1 is zero within experimental accuracy and the fact that the reaction is extremely slow in the absence of added catalyst (*vide infra* 2). Mechanisms consistent with eq 1 and 2 follow.

$$k_{obsd} = 1.92[H_3O^+] \qquad (1)$$

$$k_{obsd} = 0.0405 + 0.0125[^-OH] \qquad (2)$$

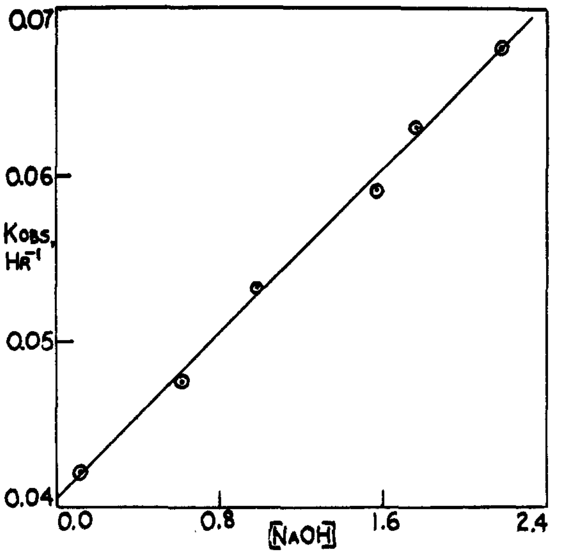
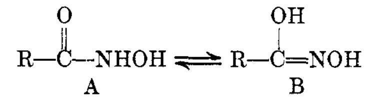


Figure 2.—Pseudo-first-order rate constants as a function of sodium hydroxide concentration at 88.6°.

Acidic Catalysis.—Hydroxamic acids can exist in two tautomeric forms (eq 3). Spectral evidence indicates that A is the predominant form.[4] Accordingly, structure A will be assumed in the following discussion although B might also be important. In any case the form of the rate law corresponding to the mechanistic scheme below will be the same whether or not one or more tautomers and/or protonated species are involved. Protonation of A at the carbonyl oxygen is likely by analogy to the protonation of amides.[5] Protonation at other positions may occur and might be kinetically important; however, the form of the rate law will be the same. The proposed general mechanism for acidic catalysis consistent with eq 1 is shown (eq 4 and 5).



$$\underset{A}{R-\overset{O}{\overset{\|}{C}}-NHOH} \rightleftharpoons \underset{B}{R-\overset{OH}{\overset{|}{C}}=NOH} \qquad (3)$$

$$A + H_3O^+ \overset{K_1}{\rightleftharpoons} AH^+ + H_2O \qquad (4)$$

$$AH^+ + H_2O \xrightarrow{k_1} \text{products} \qquad (5)$$

By analogy to the hydrolysis of other carboxyl derivatives,[6,7] it is likely that tetrahedral intermediates exist in the present system. These intermediates (except for a few special cases) exist in only very small amounts in solution;[6] furthermore, protonated species such as AH^+ will be present in only very small amounts in the acid range (Table I) studied; *e.g.*, benzamide is only half-protonated in 34% sulfuric acid.[5] Thus the total stoichiometric amount of benzohydroxamic acid will be essentially equal to that in the nonprotonated form (see eq 6). (The concentration of water has been treated

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[4] R. E. Plapinger, *J. Org. Chem.*, **24**, 802 (1959), and references in footnote 3.

[5] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[6] M. L. Bender, *Chem. Rev.* **60**, 53 (1960).

[7] M. L. Bender and R. J. Thomas, *J. Am. Chem. Soc.*, **83**, 4183 (1961).

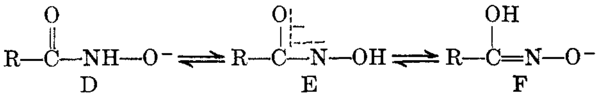
$$k_{\text{obsd}} = k_1K_1 \tag{6}$$

as a constant and is included in rate and equilibrium constants where appropriate.) Equation 6 is of the form of eq 1.

The step shown in eq 7 is not included in the mechanism, since no detectable reaction of benzohydroxamic acid was observed at 88.6° in pure water in 24 hr whereas the half-life in 0.109 *M* acidic solution is 3.71 hr.

$$\text{A} + \text{H}_2\text{O} \longrightarrow \text{products} \tag{7}$$

Basic Catalysis.—In aqueous solution the benzohydroxamate anion can potentially exist in three forms (eq 8). D and E exist in approximately equal proportions and F, if it exists at all, is 10^{-3} to 10^{-4} times the concentration of D and E.[3] F will not be included in the following discussion; its inclusion would not change the form of the derived rate law. The proposed general mechanism for base-catalyzed hydrolysis consistent with eq 2 is shown in eq 9–14. The water concentration is treated as a constant as before. Consequently we have eq 15 and 16 where $1/[^-\text{OH}]$ is very small compared to $K_2 + K_3$ in the range studied[8] and may be neglected. Therefore eq 16 is the form of the observed rate law, eq 2. In eq 2 and 16 for the above mechanism, the intercept and slope are related, respectively, to the amount of hydroxamic acid reacting *via* the one hydroxide ion pathway and the two hydroxide ion pathway. The expression (slope)$[^-\text{OH}]$/intercept $= 0.31[^-\text{OH}]$ gives the ratio of the amount of hydroxamic acid reacting *via* the two hydroxide to that *via* the one hydroxide ion pathway at 88.6°.



$$\underset{\text{D}}{\text{R—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—NH—O}^-} \rightleftharpoons \underset{\text{E}}{\text{R—}\overset{\overset{\text{O}^-}{|}}{\text{C}}\text{—N—OH}} \rightleftharpoons \underset{\text{F}}{\text{R—}\overset{\overset{\text{OH}}{|}}{\text{C}}\text{=N—O}^-} \tag{8}$$

$$\text{A} + {}^-\text{OH} \overset{K_2}{\rightleftharpoons} \text{D} + \text{H}_2\text{O} \tag{9}$$

$$\text{A} + {}^-\text{OH} \overset{K_3}{\rightleftharpoons} \text{E} + \text{H}_2\text{O} \tag{10}$$

$$\text{D} + \text{H}_2\text{O} \xrightarrow{k_2} \text{products} \tag{11}$$

$$\text{E} + \text{H}_2\text{O} \xrightarrow{k_3} \text{products} \tag{12}$$

$$\text{D} + {}^-\text{OH} \xrightarrow{k_4} \text{products} \tag{13}$$

$$\text{E} + {}^-\text{OH} \xrightarrow{k_5} \text{products} \tag{14}$$

$$S = A(1 + K_2[^-\text{OH}] + K_3[^-\text{OH}]) \tag{15}$$

$$k_{\text{obsd}} = \frac{k_2K_2 + k_3K_3 + (k_4K_2 + k_5K_3)[^-\text{OH}]}{1/[^-\text{OH}] + K_2 + K_3} \tag{16}$$

A step in the mechanism corresponding to eq 7 has not been included since no detectable reaction of benzohydroxamic acid in pure water was observed at 88.6° in 24 hr whereas the half-life in 0.119 *M* hydroxide solution is 16.5 hr.

Evidence for tetrahedral intermediates in the hydrolysis of amides has been presented.[6,10,11] It is presumed that similar intermediates exist in the present system. Concurrent first- and second-order dependence on hydroxide ion has been observed in the hydrolysis of anilides and the corresponding intermediates have been proposed.[2,7,12] The discreet existence of dianionic intermediates (postulated to account for second-order dependence on hydroxide ion) in amide hydrolysis has been questioned and they may instead be part of the transition state structure for general base-catalyzed decomposition of monoanionic intermediates.[13]

Experimental Section

Materials.—Benzohydroxamic acid, mp 128–129°, was prepared according to the literature procedure.[14] The hydrochloric acid and sodium hydroxide solutions were prepared from analytical reagent grade materials and compression distilled water. Acid and base strengths were determined by titration using potassium acid phthalate as primary standard. The ferric chloride solution used in the colorimetric procedure was prepared by dissolution of 10 g of ferric chloride hexahydrate in 1 l. of distilled water containing a sufficient amount of hydrochloric acid to prevent ferric hydroxide formation and to render acidic a mixture of 10 ml of the ferric chloride solution and 1 ml of the sodium hydroxide solution to be used in the hydrolysis rate measurements.

Kinetic Measurements.—Temperature control was ±0.05°. Polypropylene test tubes with caps were used as reaction vessels for alkaline solutions and glass stoppered test tubes for acidic solutions. Solutions for rate measurements were prepared by adding a preweighed sample of benzohydroxamic acid to the appropriate temperature-equilibrated acidic or basic solution; initial concentration was 0.012 *M*. The rates were determined colorimetrically by use of the well-known maroon Fe^{III} hydroxamic acid complex. A 1.0-ml aliquot of the reaction solution was periodically removed during at least 2 half-lives and added to 10.0 ml of ferric chloride solution and the resulting solution was diluted to 25.0 ml and its absorbance determined with a Klett–Summerson photoelectric colorimeter. Beer's law is obeyed by the system.

The pseudo-first-order rate constants were calculated from the slope of the first-order graphs using the appropriate form of the first-order rate law for this colorimetric procedure.[15] Good first-order graphs were obtained. The deviations of the individual rate constants from the appropriate average value for all entries of Tables I and II are 3% or less except for three values in which the maximum deviation is 5.6%.

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(8) K_3 may be estimated as follows where $[\text{H}_2\text{O}]$ is included in the constant: $K_3 = K_{\text{ion}}/K_{\text{W}} = 10^{3.8}$ where K_{ion} is the ionization constant for formation of D estimated[3] at 30° and K_{W} is the ionization constant of water[9] at 90°. Similarly, $K_4 = 10^{3.5}$. These values are large by comparison with $1/[^-\text{OH}]$ which has a maximum value of 10 in the range studied.

(9) A. N. Martin, "Physical Pharmacy," Lea and Febiger, Philadelphia, Pa., 1960, p 223.

(10) M. L. Bender and R. D. Ginger, *J. Am. Chem. Soc.*, **77**, 348 (1955).

(11) R. L. Schowen, H. Jayaraman, and L. Kershner, *Tetrahedron Letters*, **No. 5**, 497 (1966).

(12) S. S. Biechler and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4927 (1957).

(13) R. L. Schowen and G. W. Zuorick, *ibid.*, **88**, 1223 (1966).

(14) C. R. Hauser and W. B. Renfrow, Jr., "Organic Syntheses," Coll. Vol. II, E. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 67.

(15) D. C. Berndt and H. Shechter, *J. Org. Chem.*, **29**, 916 (1964).