

HYDROLYSIS OF BENZOHYDROXAMIC ACIDS

A. AHMAD, J. SOCHA and M. VEČEŘA

Department of Organic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

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Hydrolysis rate constants of 9 benzohydroxamic acids have been determined in a broad range of proton activities (60% HClO_4 to 16% NaOH). At higher temperatures acid- and base-catalyzed hydrolysis in water is also accompanied by spontaneous solvolysis. The reaction is 1. order in OH^- ion, the substituent polar effects do not practically influence the hydrolysis rate in alkaline medium. The alkaline hydrolysis is accompanied by little (1–3%) spontaneous decomposition of the anion (to give aniline). The hydrolysis rate is higher in acid than in alkaline medium, being maximum at H_0 –2 to –3, whereafter it again decreases. Polar effects of substituents are insignificant in acid medium, however they are marked in media where the substrates are fully protonated. The mechanisms of hydrolysis of benzohydroxamic acids in the media used have been discussed.

Hydrolysis of benzohydroxamic acid in aqueous sodium hydroxide (0.119 to 2.179 mol/l) at 88.6°C was found¹ to be 1. order or 2. order in OH^- ion, the spontaneous solvolysis being not observed at this temperature. The results were interpreted by the dissociated substrate (both tautomers)² reacting with water molecules (1. order in OH^-) or with hydroxyl ions (2. order in OH^-).

With respect to the chosen narrow concentration range of hydroxyl ion¹ we decided to extend this study with the aim of getting more information about the solvolysis mechanism. The reaction temperature was raised to 111°C to obtain the hydrolysis kinetic data also in the pH range 3 to 9 where the reaction is very slow. Special attention was paid to strongly basic media in order to be able to decide (confirm) whether the base-catalyzed hydrolysis proceeded as a 1. order or 2. order reaction in OH^- ion. At the same time we also followed the competing reaction *i.e.* the Lossen rearrangement (formation of the aromatic amine).

The hydrolysis of benzohydroxamic acid at 88.6°C was followed also in a low acidity range (0.1 to 0.58M-HCl) (ref.¹). In order to be able to extend this finding to hydrolysis in media where the substrate is protonated, we chose perchloric acid as catalyst and the temperature 70 to 80°C, and we followed the behaviour of further *m*- and *p*-substituted benzohydroxamic acids. During our studies there appeared a paper³ dealing with acid-catalyzed hydrolysis of benzohydroxamic acid and five *p*-substituted derivatives in perchloric acid, sulphuric acid and hydrochloric acid media. Although this study was carried out at different temperatures, we could com-

pare our results in several cases. The reaction rate was measured by decreases of the unreacted benzohydroxamic acid.

EXPERIMENTAL

Benzohydroxamic acids were prepared by the known procedure^{4,5} except for 3-bromo- and 4-bromobenzohydroxamic acids which were prepared as it follows. 0.02 mol hydroxylamine hydrochloride was dissolved in 25 ml methanol and added into a solution prepared from 0.05 mol sodium metal and 30 ml methanol, and the precipitated sodium chloride was filtered off. The methanolic hydroxylamine solution was then mixed with 0.2 mol methyl ester of the respective carboxylic acid at room temperature, and after 5 minutes the solvent was distilled off under reduced pressure. The raw sodium benzohydroxamate was dissolved in water and free acid was isolated by acidification (pH 1–2) and crystallized from methanol; m.p. of 3- and 4-bromobenzohydroxamic acids were 192 and 204°C, respectively. The melting points of the other compounds were identical with those given in ref.⁶ Most acids melted with decomposition. Purity of the products was also checked by means of NMR spectroscopy which enabled to find the presence of the respective carboxylic acids at the concentrations as low as 0.1%.

The other chemicals used were commercial products (Lachema, Brno), and their purity was checked by usual methods. The solutions of perchloric acid were prepared by diluting 70% perchloric acid (Carlo Erba, Italy), and their concentration was determined titrimetrically with a standard sodium hydroxide solution. Anilines were determined spectrophotometrically using their reaction with Ehrlich reagent⁷ (aqueous solution of 1.6 g 4-N,N-dimethylaminobenzaldehyde and 8.0 ml conc. HCl per liter) and calibration curves of the anilines concentration ranges 0 to $4.8 \cdot 10^{-5}$ mol/l.

Kinetic measurements were carried out discontinuously at the temperature chosen maintained within $\pm 0.1^\circ\text{C}$ by withdrawing samples (acid medium), by analyzing the whole reaction mixture in a glass ampoule (neutral and slightly basic media) or in a platinum crucible connected with a reflux condenser (strongly basic medium — prevention of contamination with silicic acid). The decrease of hydroxamic acid was followed spectrophotometrically using its reaction² with ferric ion. As the extinction depended on pH, constant conditions were used giving the maximum extinction *i.e.* pH 2.0 ± 0.2 and 4.0 g $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ per liter. The concentration of the respective unreacted hydroxamic acid was found from calibration curves. Rate constants were determined from the dependence of log conc. vs time by the half-life method⁸.

In a typical kinetic run benzohydroxamic acid and potassium chloride were dissolved in a buffer pH 9 to make the final concentrations 0.012 and 2.0 mol/l, respectively. About 2-ml samples of this solution were sealed in glass ampoules (the hydrolysis is negligible at room temperature) which were then placed in a bath tempered at 111°C. At definite time intervals the ampoules were taken out one by one, cooled, opened, and 1 ml of the content was pipetted into a 25 ml calibrated flask. Thereto 10 ml of ferric chloride solution was added (4 g $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ per liter and hydrochloric acid to make pH 2.0 ± 0.2 of the final solution for the extinction measurements) and water to adjust the volume. After mixing, the extinction of the solution was measured at 520 nm.

pK_a of the hydroxamic acids were determined spectrophotometrically⁹ in water at 25°C. Minimum 8 solutions of various pH were used for each acid, ionic strength being constant 0.01 mol/l. The pK_a values of the hydroxamic acids given in ref.⁶ (obtained by titration methods) are practically identical with our spectrophotometrically determined values (Table I).

TABLE I
 p*K* and Hydrolysis Rate Constants of Substituted Benzohydroxamic Acids (k_{obs} , s⁻¹)

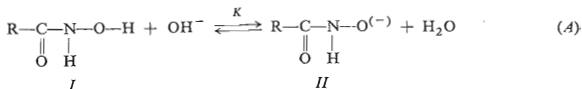
No	Substituent	p <i>K</i> ^a	$k_{\text{obs}} \cdot 10^4$			σ^d
			1 <i>M</i> -NaOH ^b	59.2% HClO ₄ ^c	10.1% HClO ₄ ^c	
1	4-OCH ₃	9.03	1.07	0.29	1.92	-0.26
2	3-CH ₃	8.93 ^e	1.09	0.39	2.10	-0.17
3	H	8.80 ^e	1.14	0.55	2.45	0.00
4	4-Cl	8.56	1.26	0.85	2.10	0.23
5	4-Br	8.57	1.26	0.89	2.10	0.23
6	3-Cl	8.42	1.32	1.23	1.92	0.39
7	3-Br	8.43	1.25	1.19	1.92	0.39
8	3-NO ₂	8.10	1.38	2.60	1.58	0.72
9	4-NO ₂	8.02 ^e	1.42	2.80	1.60	0.78

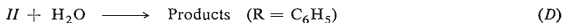
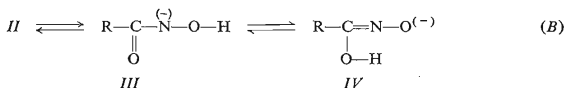
^a Determined spectrophotometrically at 20°C at ionic strength 0.01; ^b measured at 111°C at ionic strength 2.0; ^c at 80°C; ^d see ref.¹⁰; ref.⁶ gives the p*K* values 8.938, 8.80 and 8.02 for compounds 2, 3 and 9, respectively.

RESULTS AND DISCUSSION

Hydrolysis of Benzohydroxamic Acids in Basic Media

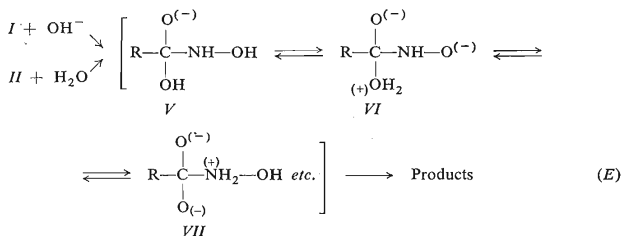
Fig. 1 gives the dependence of the 1. order rate constants (k_{obs}) of hydrolysis of benzohydroxamic acid vs hydroxyl ion concentration at 111°C (or 80°C for higher OH⁻ ion concentrations, *i.e.* 0.1 to 6.5*M*-NaOH), the dependence found by Berndt and Fuller¹ being added, too (curve 3). We have found that salt effect does not operate in the hydrolysis (additions of potassium chloride at pH 9 and 13) and the reaction is not subject to general base catalysis (no influence of added ethanolamine at pH 12 at ionic strength 2.0). Further our kinetic results show that in the basicity range of ionized benzohydroxamic acid (p*K*_a 8.8) the reaction does not depend on OH⁻ ion concentration, and the attack of OH⁻ ion on the acid anion (as given in ref.¹) is insignificant. Our kinetic data cannot differentiate between two possibilities of hydrolysis *viz.* reaction of the undissociated substrate with hydroxyl ion (Eq. (C)) and that of conjugated base of the substrate with water molecule (Eq. (D)).



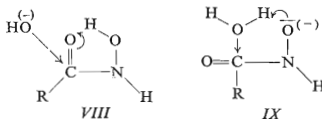


It is known² that hydroxamate anion can exist in three tautomeric forms *II*, *III* and *IV*, and in the case of benzohydroxamic acid it was found that the forms *II* and *III* were almost equally populated, whereas the form *IV*, if it was present at all, was less than 10^{-3} mol per one mol of *II*. It is presumed that, if the anion is the reacting species (Eq. (D)), the tautomer *II* is most suitable for a nucleophilic attack, the negative charge being located at the more remoted atom.

Analysis of substituent effects in acid hydrolysis of amides suggested^{10,11} a one-step mechanism of the $\text{S}_{\text{N}}2$ type, however, in alkaline media formation of the tetrahedral intermediate was proved both kinetically¹² and by isotopic exchange¹³. We presume the formation of tetrahedral intermediate in the alkaline hydrolysis of benzohydroxamic acids, too, the form *VII* being the most suitable of the possible tautomers for decomposition into the reaction products. The other tautomeric forms *V* and *VI* can be interpreted as products of OH^- ion attack on the undissociated acid and H_2O molecule attack on the acid anion, respectively.



No intermolecular general base catalysis was found in the reaction, however, intramolecular acid catalysis (*VIII*) of hydroxyl ion attack on the substrate can be presumed with respect to suitable geometry. Similarly, intramolecular general base catalysis is possible, if the tetrahedral intermediate is supposed to be formed by an attack of water molecule on the acid anion (*IX*). The kinetic isotopic effect found ($k_{\text{H}}/k_{\text{D}} = 1.37$; 0.1M-NaOH ; 111°C) suggests an assistance of water molecules in formation of the tetrahedral intermediate, which is supported also by the negative activation entropy value (-37.6 e.u.), the activation energy having usual value (16.3 kcal/mol).



Further information about the reaction mechanism was drawn from hydrolysis kinetics of *m*- and *p*-substituted benzohydroxamic acids in 1M-NaOH medium at 111°C at constant ionic strength 2.0M (KCl). Eq. (1) gives the dependence of the rate constants logarithms on the substituent constants σ (Table I).

$$\log k = 0.118\sigma - 0.062 \quad (r = 0.977; \quad s = 0.01; \quad n = 9). \quad (1)$$

The correlation is good, but the polar effects of substituents affect the rate only slightly ($\rho \approx 0.12$). This behaviour could be explained by the decomposition of the tetrahedral intermediate being rate-limiting; favourable influence of electron-withdrawing

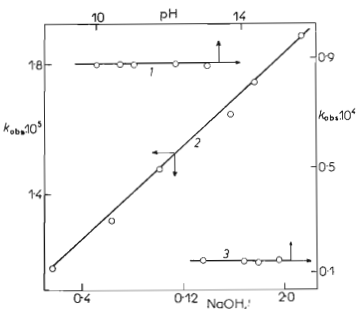


FIG. 1

Dependence of Base-Catalyzed Hydrolysis Rate of Benzohydroxamic Acid on pH (H^-) at 111°C (1) resp. 80°C (2) at Constant Ionic Strength 2.0

The straight line 3 gives the dependence of base-catalyzed hydrolysis rate constant of benzohydroxamic acid on sodium hydroxide concentration at 88.6°C at ionic strength 2.179 (according to ref.²). Concentration of NaOH in mol/l.

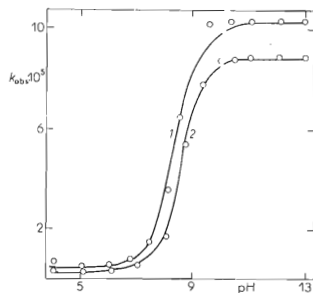


FIG. 2

Dependence of Hydrolysis Rate ($k_{obs} \text{ s}^{-1}$) of Benzohydroxamic (2) and 3-Nitrobenzohydroxamic (1) Acids on pH at 111°C at Constant Ionic Strength 2.0 (additions of KCl)

The curves represent the calculated relations, the points are experimental.

substituents on the formation of the tetrahedral intermediate would be counterbalanced by an opposite effect of the same substituents on its splitting. This explanation is, however, not very likely, as we did not find any incorporation of ^{18}O into the unreacted substrate when carrying out the hydrolysis in H_2^{18}O . A more acceptable interpretation of the low sensitivity of the alkaline hydrolysis of benzohydroxamic acids to the substituent effects is presented by the above mechanism of intramolecular base catalysis (IX). Electron-withdrawing substituents of the benzene nucleus affect favourably the attack of nucleophile (water molecule), at the same time, however, they lower the catalytic activity of the negatively charged oxygen atom.

Our experimental results agree with an alternative hydrolysis mechanism consisting in a rate-limiting (k_2) attack of OH^- ions on the undissociated substrate and subsequent rapid decomposition of the tetrahedral intermediate VII.

$$k = k_2 K_w / K_{\text{SH}} . \quad (2)$$

Kinetic equation (2) can be derived for this case, where K_{SH} stands for the equilibrium constant of the dissociation $I \rightleftharpoons II$, and it can be modified to give Eqs (3) and (4), where ρ_1 and ρ_2 are the Hammett reaction constants of acid-base equilibrium $I \rightleftharpoons II$ and addition of OH^- ion on the undissociated substrate, respectively.

$$\log (k/k_0)_{\text{exp}} = \log (k/k_0)_2 - \log (K/K_0)_{\text{SH}} , \quad (3)$$

$$\rho_{\text{exp}} \sigma = \rho_2 \sigma - \rho_1 \sigma . \quad (4)$$

The ρ_2 value about 1.0 can be estimated from the determined $\rho_{\text{exp}} = 0.1$ of the alkaline hydrolysis rate and the calculated $\rho_1 = 0.94$ from the $\text{p}K_{\text{a}}$ values given in Table I.

In strongly basic media acid-catalyzed hydrolysis of benzohydroxamic acids can be excluded, and the reaction rate can be expressed by Eq. (5), where k_1 and k_2 represent the rate constants of hydrolyses of the substrate (spontaneous solvolysis) and its conjugated base, respectively.

$$-dS/dt = k_1[S] + k_2[S^-] . \quad (5)$$

In order to be able to separate the both rate constants, we followed the hydrolyses of benzohydroxamic and 3-nitrobenzohydroxamic acids also in the pH range 9.0 to 3.0; the results (111°C, ionic strength 2.0M) are presented in Table II. The kinetic experiments were carried out in sealed glass ampoules and evaluated in the same way as the above series. It was found that, in contrast to strongly basic media, the reaction products did not contain any aniline (resp. *m*-nitroaniline), the analytical method used (Ehrlich reaction) being able to detect its concentration as low as $4 \cdot 10^{-5}$ mol/l. Fig. 2 gives the pH-profile of the hydrolysis of the both benzohydroxamic acids studied. It can be seen that in the pH range 4 to 7 the both acids are hydrolyzed practi-

cally at the same rate, then there follows a pH range where the reaction rate increases with increasing proportion of the dissociated acid, and finally in alkaline region the reaction rate is again constant. In accord with 3-nitrobenzohydroxamic acid being stronger acid, its hydrolysis rate begins to increase at a lower pH. At low pH values the second term of Eq. (5) is negligible and k_{obs} corresponds to spontaneous solvolysis; in strongly basic media, on the contrary, the first term of Eq. (5) is negligible. Thus it is possible to determine the both constants k_1 and k_2 with sufficient accuracy. By introduction of concentrations of the undissociated and dissociated forms Eq. (6) can be obtained which enables calculation of hydrolysis rates in the pH range 4 to 14 at 111°C.

$$k_{\text{obs}} = (k_1 + k_2 K / [\text{H}^+]) / (1 + K / [\text{H}^+]) \quad (6)$$

The respective constants for benzohydroxamic and 3-nitrobenzohydroxamic acids are: k_1 $3.66 \cdot 10^{-6}$ and $3.83 \cdot 10^{-6} \text{ s}^{-1}$, k_2 $8.75 \cdot 10^{-5}$ and $1.028 \cdot 10^{-4} \text{ s}^{-1}$, K (estimated from the dependence of k_{obs} vs pH) $2.51 \cdot 10^{-9}$ and $3.98 \cdot 10^{-9}$, respectively. The curves calculated according to Eq. (6) agree very well with experimental points

TABLE II

Dependence of Pseudomonomolecular Rate Constant ($k_{\text{obs}} \text{ s}^{-1}$) of Hydrolysis of Benzohydroxamic (3) and 3-Nitrobenzohydroxamic (8) Acids on pH at 111°C at Ionic Strength 2.0 (addition of KCl)

pH	$k_{\text{obs}} \cdot 10^4$	pH	$k_{\text{obs}} \cdot 10^4$
Compound 3		Compound 8	
13.00	0.875	13.00	1.030
12.20	0.880	12.01	1.050
11.00	0.882	11.00	1.040
10.86 ^a	0.888	10.30	1.030
10.60	0.885	9.50	1.030
10.00	0.875	9.06	1.050
9.10	0.770	8.50	0.663
8.75	0.555	8.04	0.320
8.50	0.346	7.50	0.128
8.01	0.160	6.80	0.083
7.05	0.037	6.00	0.038
6.00	0.037	5.00	0.033
5.07	0.042	4.01	0.063
4.00	0.015		

^a At 101 and 121°C the k_{obs} values are $0.488 \cdot 10^{-4}$ and $1.41 \cdot 10^{-4} \text{ s}^{-1}$, respectively.

TABLE III

First Order Rate Constants ($k_{\text{obs}} \cdot 10^4, \text{s}^{-1}$) of Acid-Catalyzed Hydrolysis of Benzohydroxamic (3) and 3-Nitrobenzohydroxamic (8) Acids at 70 and 80°C

HClO ₄	-H ₀	k_{obs} (3)		k_{obs} (8)	
		70°C	80°C	70°C	80°C
4.9	-0.02	0.51	1.10	0.34	0.70
10.1	0.36	1.05	2.45	0.68	1.58
15.1	0.67	1.58	3.19	1.05	2.35
20.4	1.01	2.28	5.00	1.44	3.20
30.4	1.62	2.90	6.41	2.40	5.76
39.6	2.35	2.90	5.22	2.89	6.60
45.6	2.95	2.18	5.22	2.90	7.21
50.3	3.50	1.44	3.88	2.90	7.21
54.6	4.22	0.61	1.76	2.09	5.00
59.2	5.066	0.19	0.55	1.06	2.60

for the both benzohydroxamic acids. Also the pK_a values estimated from the dependence in Fig. 2 correspond with those determined independently at 25°C (Table I).

The results given allow to conclude this section of the work by stating that two solvolytic reactions are significant in the discussed pH range. At lower pH spontane-

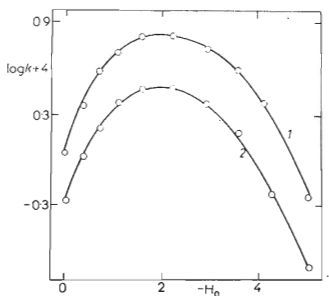


FIG. 3

Dependence of Acid-Catalyzed Hydrolysis Rate of Benzohydroxamic Acid on H₀ at 70 (2) and 80°C (1)

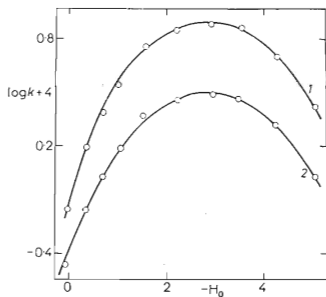


FIG. 4

Dependence of Acid-Catalyzed Hydrolysis Rate of 3-Nitrobenzohydroxamic Acid on H₀ at 70 (2) and 80°C (1)

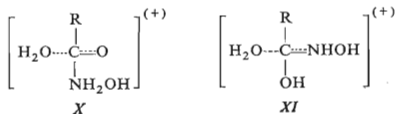
ous solvolysis takes place predominantly, whereas in strongly alkaline region the OH^- ion-catalyzed reaction predominates. From our results it follows that the most likely mechanism of hydrolysis in basic media is that involving the reaction of the conjugated base with water. The interpretation must take into account that, if the acid anion is reacting, the rate constant is a sum of rate constants of reactions of its individual tautomeric forms. Reaction of benzohydroxamic acid in basic media can produce aniline besides the hydrolysis products, *i.e.* the so-called Lossen degradation is taking place side by side¹⁴. However, under the reaction conditions used by us the amount of aniline formed was relatively small (2 to 4% aniline was found in the pH range 9 to 13 at 111°C), and, therefore, we do not consider this rearrangement in discussion of the reaction mechanism. (Reactions of certain derivatives of benzohydroxamic acids give much more rearrangement than hydrolysis products. This problem is dealt with in our further communication.)

Hydrolysis of Benzohydroxamic Acids in Acidic Media

The behaviour of benzohydroxamic and 3-nitrobenzohydroxamic acids was studied in 5 to 60% perchloric acid at 70 and 80°C. Higher perchloric acid concentrations bring about uncontrollable reactions (destruction), however, in the chosen acidity range ($H_0 - 0.02$ to -5.06) the reaction is smooth, and no rearrangement to aniline (*resp.* *m*-nitroaniline) takes place. The 1. order rate constants (k_{obs}) are given in Table III. The dependence of $\log k_{\text{obs}}$ vs H_0 are presented in Figs 3 and 4 for the both hydroxamic acids. It can be seen that the reaction rate increases with increasing acidity (angular coefficient being about unity), reaches a maximum, and again decreases. The rate maximum of the acid-catalyzed hydrolysis of several benzohydroxamic acids was observed by other authors, too³. Our results are interpreted by a reaction sequence starting with a rapid reversible proton-transfer to the substrate (Eq. (F)).



The conjugated acid is formulated with protonated oxygen atom, but the tautomer with the protonated nitrogen atom must be considered, too. As it was found¹⁵ that hydrolysis of amides proceeds by two competitive reactions, *i.e.* nucleophilic attack of the both forms protonated at oxygen and nitrogen, we admit this possibility for the hydrolysis of benzohydroxamic acids, too, the respective transition states being formulated as *X* and *XI*. From Figs 3 and 4 it can be seen that the



hydrolysis rate maximum of benzohydroxamic and 3-nitrobenzohydroxamic acids is reached at $H_0 - 2$ and -3 , respectively, the half-neutralization value of benzohydroxamic acid was found³ at $H_0 - 1.93$ at 25°C . We presume that also at 70 resp. 80°C the half-neutralization value will not be very different and that the reaction rate decrease at higher acidities (where the substrate is mainly present in its protonated form) is caused by decreasing activity of the nucleophile (water molecules). 3-Nitrobenzohydroxamic acid behaves similarly, and being less basic it has its rate maximum shifted towards more acidic region.

The Hammett correlation of acid-catalyzed hydrolysis rate constants of *m*- and *p*-substituted benzohydroxamic acids in 59.2% HClO_4 ($H_0 - 5.06$) at 80°C (Table I) gives Eq. (7).

$$\log k = 0.85\sigma + 0.73 \quad (r = 0.998; \quad s = 0.018; \quad n = 9) \quad (7)$$

Electron-withdrawing substituents accelerate the reaction as it is usual with reactions involving the rate-determining attack of nucleophile on substrate. The reaction constant found ($\rho = 0.85$) is almost the same as that (0.83) found³ at lower acidity and lower temperature 50.3°C (the 1. order rate constants were transformed into specific rate coefficients of the hydrolysis of the protonated substrate by using the half-neutralization values). The reaction constant found does not much differ from that of the rate-determining step of acid-catalyzed hydrolysis of amides¹⁶. The hydrolysis of the same series of substituted benzohydroxamic acids was studied also in 10.1% HClO_4 medium at 80°C . The rate constants found ($k_{\text{obs}} \cdot 10^4, \text{s}^{-1}$) are given in Table I. From the results it follows that polar effects do not practically affect the observed reaction rate. If the hydrolysis rate of the substituted benzohydroxamic acids is compared at the same low concentration of acid catalyst, the effect of substituents will influence both the protonation equilibrium and the rate-limiting reaction step. The Hammett equation can be modified for this case into Eq. (8) or (9).

$$\log (k/k_0)_{\text{obs}} = \log (k/k_0)_2 - \log (K/K_0)_{\text{BH}^+/\text{B}} \quad (8)$$

$$\rho_{\text{obs}} = \rho_2 - \rho_{\text{BH}^+/\text{B}} \quad (9)$$

On the basis of literature data³ and our values¹⁷ the value of the reaction constant of the protonation equilibrium of the substituted benzohydroxamic acids can be estimated ($\rho_{\text{BH}^+/\text{B}} \approx +0.8$). Practically the same value was found for the rate-limiting step of hydrolysis ($\rho_2 = +0.85$). It is obvious that the both effects cancel each other, and polar effects of substituents will not be significant for the observed reaction rate constant at low acidities.

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