and 1 ml of hydrochloric acid. The resulting mixture was vigorously refluxed for 4 days with portions of HCl and amalgamated zinc being added every 6 h. After cooling, the reaction mixture was diluted with 40 ml of water and extracted with ether (6 × 25 ml). The combined ether extracts were washed several times with 5% aqueous sodium bicarbonate, then with saturated aqueous sodium chloride (2 × 25 ml), and finally dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a white solid which GLC analysis (10 ft × 0.25 in. DC-550 column, 200 °C) showed contained some unreacted starting material, a minor component which was not identified, and a major component with a relatively short retention time. Purification of the major product by GLC (above conditions) gave a white solid whose ir spectrum was identical with that of **27** obtained by procedure A.

C. Lithium (54 mg, 7.7 mmol) was added to a stirred solution of 19 mg (0.1 mmol) of a mixture of **21** and **22** in 2 ml of *tert*-butyl alcohol and 10 ml of dry tetrahydrofuran. The reaction mixture was stirred at room temperature for 3.5 h. Water (10 ml) was then added and stirring was continued for 30 min. The resulting solution was extracted with ether (3 × 40 ml) and the combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave a white solid which by GLC analysis (10 ft × 0.25 in. DC-550 column, 200 °C) contained a trace of starting material and a single major product. Purification of the product by GLC provided 3.5 mg of a white solid whose mass spectrum was identical with that of **27** obtained by procedure A.

Tricyclo[4.4.1.1^{3,9}]dodecane (3). A. A solution of 110 mg of **23** in 50 ml of ethanol was stirred at room temperature with 660 mg of 10% palladium on charcoal under an atmosphere of hydrogen for 24 h. The reaction mixture was filtered to remove the catalyst and the catalyst was washed several times with methanol. The filtrate and washings were combined and the methanol was removed by distillation to leave a solid residue which by GLC analysis (10 ft × 0.25 in. DC-550 column, 175 °C) contained a single component. Isolation of the product by GLC (above conditions) gave 47 mg of **3** as a white solid: ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 2.5–1.4 (br m); ^{13}C NMR δ_{Me_4Si} ($CDCl_3$) 44.65 (t), 40.99 (t), 36.62 (d), 34.35 (t), 32.57 (d), 31.76 (t), 31.06 (t), and 29.55 (d) in the ratio of 1:1:1:2:1:2:2:2, respectively; ν (CCl_4) 2910, 1450, 1260, 1200, 1140, 1110, and 1060 cm^{-1}.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.84; H, 12.09.

B. Hydrogenation of **27** under the conditions employed for **23** → **3**, followed by purification of the product by GLC, provided a white solid whose mass spectrum was identical with that of **3** obtained by procedure A.

C. A solution of 50 mg of **25–26**, 264 mg of potassium hydroxide, and 230 mg of 95% hydrazine in 1.5 ml of diethylene glycol was heated with stirring at 110 °C for 30 min, and then for 3 h at 180 °C. During this time, a white solid appeared on the water-cooled condenser. The system was cooled and the material on the condenser was dissolved in ether and then dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded 30 mg of a white solid which by GLC analysis (10 ft × 0.25 in. DC-550 column, 175 °C) was homogeneous. Isolation of the product by GLC gave a white solid whose ir spectrum was identical with that of **3** obtained by procedure A.

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Registry No.—**3**, 36071-59-7; **9**, 55638-05-6; **11**, 59839-97-3; **12**, 59839-98-4; **19**, 59839-99-5; **20**, 59840-00-5; **21**, 59840-01-6; **22**, 59840-02-7; **23**, 59840-03-8; **24**, 55638-10-3; **25**, 59840-04-9; **26**, 59840-05-0; **27**, 59840-06-1; **28**, 59840-07-2; **29**, 59840-08-3; phosphoryl chloride, 10025-87-3.

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Kinetics and Mechanism of Acidic and Alkaline Hydrolysis of Hindered *N*-Methylarylhydroxamic Acids

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Thg kinetics of acidic and basic catalyzed hydrolysis of ortho-substituted *N*-methylbenzohydroxamic acids have been investigated at moderate acidity and high basicity. The results are interpreted in terms of a bimolecular mechanism for acidic catalysis and as reaction of the hydroxamic acid conjugate base with water and hydroxide ion for basic catalysis in the catalytic range investigated. Specific salt effects are reported.

We have investigated the kinetics and mechanism of the acidic and basic catalyzed hydrolysis of hindered benzohydroxamic acids in order to learn the effect of this increased hindrance upon the mechanisms of the reactions, the range of catalyst concentration required, and the importance of salt effects at these higher concentrations. The increased hindrance is provided by use of ortho-substituted *N*-methylbenzohydroxamic acids in comparison to unsubstituted benzohydroxamic acid. Smith and Yates[1] have studied the acid-catalyzed hydrolysis of benzamide, *N*-methyl- and *N,N*-dimethylbenzamide and have inferred from their data that all three compounds probably do not react via the oxygen protonated form *or* that benzamide does hydrolyze via oxygen protonation while the other N-substituted compounds do not. McClelland's[2] recent report of small but detectable ^{18}O exchange for the acidic hydrolysis of benzamide supports the latter conclusion.

Our present results indicate that there is no mechanism change in the acid-catalyzed hydrolysis upon introduction of an *N*-methyl and ortho groups in hydroxamic acids. There appears to be a significant rate of reaction in the absence of added acid or alkali at high salt concentrations. Specific salt effects are also observed.

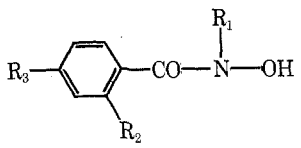
Acidic Catalysis. Equation 1 expresses the reaction under

Table I. Rate Data for Acid-Catalyzed Hydrolysis of 2- and 4-Methyl-*N*-methylbenzohydroxamic Acids

HCl, M	Temp, °C	$10^5 k$[a]
2-Methyl-*N*-methylbenzohydroxamic Acid		
0.149	90.0	1.48
0.150	90.0	1.33[b]
0.225	90.0	2.04
0.451	90.0	2.99
0.595	90.0	3.78
0.751	90.0	4.61
0.751	80.0	1.86
0.751	70.0	0.818
4-Methyl-*N*-methylbenzohydroxamic Acid		
0.225	84.0	29.0
0.225	71.7	10.8
0.225	61.1	4.16

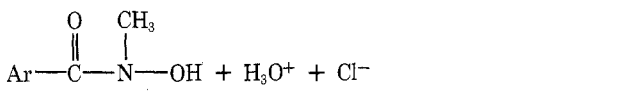
[a] Average pseudo-first-order rate constant, s^{-1}. Ionic strength maintained at 0.751 M with KCl except as noted. [b] Ionic strength maintained with CsCl.

Table II. Activation Parameters[a] for Acidic Hydrolysis of



R_1	R_2	R_3	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
CH_3	CH_3	H	20.8	−21.2
CH_3	H	CH_3	19.4	−17.8
H	H	H	19.4	−20.2[b]
H	H	H	20.2	−17.9[c]

[a] Calculated from second-order rate constants. [b] Calculated from data from ref 4 at two temperatures, HCl, ionic strength 0.577 M (KCl). [c] Reference 5, 1.00 M $HClO_4$.



$$\longrightarrow ArCO_2H + H_2\overset{+}{N}(CH_3)OH + Cl^- \quad (1)$$

acidic conditions. The reaction is cleanly pseudo-first-order in the presence of excess hydrochloric acid (Table I). A graph of the data for the *o*-methyl compound in Table I shows first-order dependence upon hydrochloric acid (extrapolation of the data outside the range studied is unwarranted owing to the specific salt effects discussed below). This dependence is similar to that observed for the hydrolysis of unsubstituted hydroxamic acids at comparable acidities.[3-5] Table II compares activation parameters for the compounds in Table I with those for the acid-catalyzed hydrolysis of benzohydroxamic acid under similar conditions.

These results are consistent with the acid-catalyzed bimolecular mechanism reported before for the unhindered RCONHOH compounds.[3-5] A tetrahedral intermediate likely is involved analogous to benzamide hydrolysis.[2,6] The activation parameters listed in Table II are in the usual range[1] for the bimolecular mechanism for amides. Furthermore, the enthalpy of activation is higher and the entropy of activation is more negative for the *o*-methyl-*N*-methylbenzohydroxamic acid hydrolysis than for the hydrolysis of the corresponding *p*-methyl compound. These results are consistent with the bimolecular mechanism with the more hindered compound exhibiting the higher enthalpy and lower entropy of activation.

A first-order reaction of 2-methyl-*N*-methylbenzohydroxamic acid occurs in the absence of added hydrochloric acid but in the presence of 0.751 M potassium chloride and is about 6% of the rate observed with 0.149 N hydrochloric acid at ionic strength 0.751 M.

Table III. Rate Data for Base-Catalyzed Hydrolysis of 2-Chloro-*N*-methylbenzohydroxamic Acid at 90.0 °C

NaOH, M	$10^6 k_{obsd}$[a]
7.31	2.57
6.58	2.28
5.47	1.89
4.40	1.44
3.23	0.92

[a] Average pseudo-first-order rate constant, s^{-1}. Ionic strength maintained at 7.31 M with NaCl.

Specific ion effects[7] as well as ionic strength effects on reaction rates are expected at moderate salt concentrations. Specific cation effects, outside experimental error, can be seen by comparing the first two entries in Table I. Nonlinear specific cation effects have been reported for the acidic hydrolysis of 4-nitroacetanilide.[8]

Basic Catalysis. Pseudo-first-order rates are observed according to the equation $-dS/dt = k_{obsd}S$, where S is the total stoichiometric amount of hydroxamic acid present at any time. The data for *N*-methyl-2-chlorobenzohydroxamic acid are in Table III. A graph of this data shows linear dependence of the pseudo-first-order rate constant upon hydroxide ion concentration (extrapolation of the data outside the range studied is unwarranted owing to specific ion effects—see below).

$$\underset{\mathbf{1}}{ArCON(CH_3)OH} + \bar{O}H \rightleftharpoons \underset{\mathbf{2}}{ArCON(CH_3)O^-} + H_2O \quad (2)$$

Under the strongly alkaline conditions used in the kinetic studies **1** will be almost completely converted into **2**. (The pK_a's of *N-tert*-butylbenzohydroxamic[9] and *N*-phenylbenzohydroxamic[10] acids are 10.1 and 9.15, respectively.) A reasonable mechanism consistent with the data is represented by eq 3–5.

$$1 + \bar{O}H \overset{K}{\rightleftharpoons} 2 + H_2O \quad (3)$$

$$2 + \bar{O}H \xrightarrow{k_2} \text{products} \quad (4)$$

$$2 + H_2O \xrightarrow{k_3} \text{products} \quad (5)$$

The linear dependence upon hydroxide concentration for *N*-methyl-2-chlorobenzohydroxamic acid is similar to the rate law obtained at high base strengths for hydrolysis of the unhindered benzohydroxamic acid.[4] Thus the mechanisms for hydrolysis of these compounds in strong base are probably similar. Tetrahedral intermediates presumably are involved as they are in alkaline hydrolyses of amides;[6,11] however, the kinetic results cannot distinguish between these possibilities.

Ahmad, Socha, and Vecera[12] have recently reported a study of the alkaline hydrolysis of benzohydroxamic acid over a wide hydroxide ion concentration range and have considered various mechanisms. They have incompletely and incorrectly graphed our earlier data[4] on the alkaline hydrolysis of benzohydroxamic acid and state that attack of hydroxide on the acid anion is insignificant. Our present and earlier work[4] demonstrates a positive slope for a graph of the pseudo-first-order constant vs. hydroxide concentration *in the range studied* as does Ahmad and co-worker's curve 2 of their own Figure 1 for benzohydroxamic acid. Mechanisms will of course vary as the hydroxide ion concentration range changes; however, for the hydroxide ion concentration ranges reported in our earlier work and herein the hydroxamic acids will exist as

Table IV. Rate Data for the Uncatalyzed Hydrolysis of 2-Chloro-*N*-methylbenzohydroxamic Acid in the Presence of Salts at 90.0 °C

Salt	Concn, M	$10^6 k_{obsd}$[a]
NaCl	3.00	1.11
NaCl	6.31	1.94
NaBr	6.31	1.33

[a] Average first-order rate constant, s^{-1}.

their conjugate bases and the rate laws are best interpreted according to the mechanism of eq 3–5 for that range.

Specific salt effects[7] are expected at the high concentrations employed to maintain constant ionic strength in the alkaline hydrolyses. These effects are illustrated in Table IV. Note that the rate constants reported in Table IV are for reactions in the absence of any added hydroxide. Direct comparison of the rate constants in Tables III and IV is not possible since in one case the reaction involves the hydroxamic acid reacting with water and in the other its conjugate base reacting with hydroxide ion or water. These two cases involve different charge types; however, at the concentrations of catalytic acid or base employed in this study, there will be specific salt effects for all charge types.

Experimental Section

The *N*-methylbenzohydroxamic acids were synthesized by adaptation of the method used by Ulrich and Sayigh[13] for the preparation of *N*-methylacetohydroxamic acid. ^{1}H NMR and ir spectra are consistent with the structures listed. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

N-Methyl-2-methylbenzohydroxamic acid, crystallized successively from benzene and carbon tetrachloride, had mp 120–121 °C. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.45; H, 6.72; N, 8.48. Found: C, 65.14; H, 6.48; N, 8.47.

N-Methyl-2-chlorobenzohydroxamic acid, crystallized as above, had mp 118–119 °C. Anal. Calcd for $C_8H_8ClNO_2$: C, 51.77; H, 4.34; N, 7.55. Found: C, 51.61; H, 4.38; N, 7.59.

N-Methyl-4-methylbenzohydroxamic acid had mp 119–120 °C dec (lit.[14] 122 °C).

Kinetic measurements were made by the spectrophotometric method reported previously[4] employing a Beckman DU spectrophotometer set at 520 nm for the 2-methyl- and 4-methyl-*N*-methylbenzohydroxamic acid runs and at 500 nm for the *N*-methyl-2-chlorobenzohydroxamic acid runs. The acidity of the $FeCl_3$ solution was adjusted as before[4] for the alkaline runs.

Pseudo-first-order rate constants were obtained from the slope of the appropriate graph[4] with numerical values computed by the method of least squares.

Each rate constant listed in Tables I, III, and IV is the average of two to five runs. Average deviation from the mean is less than 4.5%. Temperature control was ±0.1 °C. Initial hydroxamic acid concentrations were 0.01 M.

Registry No.—2-Methyl-*N*-methylbenzohydroxamic acid, 24962-87-6; 4-methyl-*N*-methylbenzohydroxamic acid, 1613-85-0; benzohydroxamic acid, 495-18-1; 2-chloro-*N*-methylbenzohydroxamic acid, 59686-63-4.

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Base-Catalyzed Hydration of α,β-Unsaturated Ketones

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Homologues of 3-buten-2-one hydrate in dilute aqueous base to produce aldols, which in some cases undergo retro aldol condensation under the hydration conditions. Hydration of 3-buten-2-one proceeds with rate-controlling attack of hydroxide ion on C_4, $k_{H_2O}/k_{D_2O} = 0.6$, $\Delta H^{\ddagger} = 13.6$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -30.1$ eu. Hydration of 4-methyl-3-penten-2-one is 10^{-2} as fast and proceeds via rate-controlling proton transfer from water to C_3 of the enolate ion formed by attack of hydroxide ion at C_4 of the substrate, $k_{H_2O}/k_{D_2O} = 1.1$, $\Delta H^{\ddagger} = 15.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -25.6$ eu. Rates of hydration, dehydration, and retroaldol condensation were competitive for 3-penten-2-one and were calculated to be 7.6×10^{-3}, 2.3×10^{-3}, and 1.6×10^{-4} M^{-1} s^{-1}, respectively, at 40 °C. Equilibrium ratios calculated for the dehydration of aldols, [alkenone]/[aldol], show that dehydration is thermodynamically unfavorable for aldol condensation products of aliphatic aldehydes and ketones; kinetic measurements show the rate of dehydration to be comparable to or faster than the aldol condensation in many of these cases. Thus self-condensation of acetone (using a Soxhlet extractor) leads to the aldol product rather than the dehydration product for thermodynamic rather than kinetic reasons.

The acid-catalyzed hydration of α,β-unsaturated carbonyl compounds has received considerable study in recent years.[1-5] For a variety of aliphatic 3-alken-2-ones the hydration proceeds via a 1,4 addition of water to the conjugated C=C–C=O system followed by rate-controlling proton transfer to the enol thus formed. The hydration is characterized by a large solvent isotope effect (indicative of a primary isotope effect) and a large negative entropy (indicative of the covalent binding of a solvent molecule to the substrate prior to the rate-controlling step). The change in rate with acidity shows the carbonyl group to be significantly protonated in acidities beyond 4–6 M $HClO_4$.[5] The pK_a's of several α,β-unsaturated compounds have been measured recently and found to be adequately described by the Bunnett–Olson treatment.[6]

Studies of base-catalyzed hydrations are rare; apparently there are only two previous reports of base-catalyzed additions of water to α,β-unsaturated carbonyl systems. Fedor[4] has