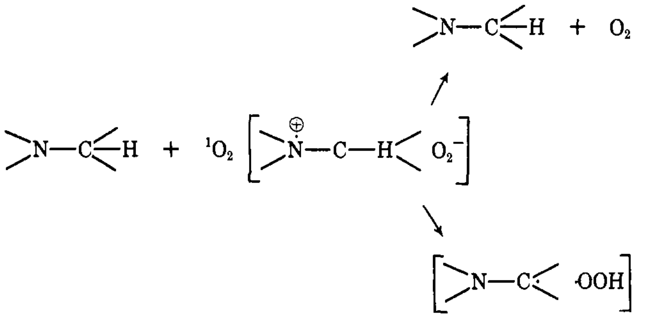
ethylamine toward singlet oxygen by a minimum of one order of magnitude. Ogryzlo and Tang were unable to detect any reaction of triethylamine with singlet oxygen even after more than 100 deactivating collisions per amine molecule. In contrast, in pyridine solution one amine molecule is destroyed per nine deactivating collisions. This difference may result from the longer lifetime of the amine radical cation in solution, allowing proton transfer to O_2^- to occur in competition with back transfer of an electron from O_2^- to the amine radical cation.



The fact that proton transfer does not occur from $DABCO^{\cdot+}$ suggests that the amine radical must gain some stabilization from resonance structures of the type $>\cdot N{=}C<$. Such contributions to a resonance hybrid cannot occur with the rigid, bicyclic amine.

Experimental Section

A. Materials. Pyridine was Eastman grade, used without further purification. Rose Bengal (Eastman grade, C.I. 45440, 84% dye content) was purified by dissolving 2 g in the minimum amount of 0.14 *M* NH_4OH, and passing this over a 2 × 20 in. bed of Sephadex G-25 Fine (Pharmacia Fine Chemicals, Inc.) using water as eluent. Several bands were obtained, the main one being collected and acidified with dilute HCl, and the Rose Bengal free acid collected by filtration. After drying, a 1.14×10^{-4} *M* solution in pyridine had a λ_{max} at 573 nm with D_{573} 1.13, D_{546} 0.35, both for 1-mm layers. The dye does not follow Beer's law, the D_{max} shifting hypso- and hyperchromically upon dilution. 2-Methyl-2-pentene was Phillips Petroleum Company pure grade, 99 mol % minimum. This was passed over a short column of aluminum oxide (Woelm Neutral) prior to use. Triethylamine was Eastman grade, once distilled.

B. Measurements. The reactions were followed by measuring the rate of oxygen consumption in a constant pressure, automatic recording gasometer apparatus. This apparatus is basically a hybrid of two that are described in the literature.[16,17] The absorption cell was similar to the one described by Mahoney, *et al.*,[16] and the physical arrangement of the gasometer itself was similar to that of Traylor and Russell.[17] Pressure differentials were detected by a Schaevitz P476-A10 pressure transducer (0–10 in. of water), which was attached to the gasometer *via* small-diameter, stainless steel tubing with Swagelok fittings (Teflon front ferrules). The signal from the transducer activated a Harvard infusion–withdrawal pump. This pumped mercury into a gas buret attached to the gasometer until the null point of the transducer was reached. The pump displacement was converted to a voltage change by appropriate gearing of the pump to a Helipot linear potentiometer. Output from the potentiometer was fed into a 10-mV span strip chart recorder, equipped with chart speeds of 2, 5, 8, and 20 in./hr (Varian Associates Model G11A). Rates as low as 10^{-7} *M* sec^{-1} can be measured on a 10-ml sample.

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Kinetics of the Formation of Imines from Isobutyraldehyde and Primary Aliphatic Amines with Polar Substituents[1]

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 18, 1971*

Abstract: The kinetics of the reaction of isobutyraldehyde with *n*-propylamine, 3-methoxypropylamine, 2-methoxyethylamine, 2,2-dimethoxyethylamine, and 2,2,2-trifluoroethylamine to give the corresponding imines have been studied by stopped-flow spectrophotometry in aqueous solution at pH's around the pK_a of the conjugate acids of the amines and higher at 35°. The formation of the intermediate carbinolamines was too fast to follow; the equilibrium constant K_{ca} for carbinolamine formation was found to be decreased somewhat by electron-withdrawing and bulky substituents. The overall second-order rate constants for imine formation were found to be independent of the pH above about pH 10 and proportional to the hydrogen-ion concentration below about pH 9 in the cases where rate measurements could be made at this low a pH. The second-order rate constants for the uncatalyzed reaction were greatly decreased by electron-withdrawing substituents but were relatively insensitive to the differences in steric effects among the amines studied.

Previous studies have shown that the α-hydrogen exchange reactions of aldehydes and ketones may be catalyzed by a mixture of a primary amine salt and a base.[2–5] The primary amine salt transforms the carbonyl compound partially to an equilibrium mixture of an imine and an iminium ion, whose α-hydrogen atoms are much more acidic than those of the carbonyl

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(1) (a) This investigation was supported in part by Public Health Service Grant No. AM 10378 from the National Institute of Arthritis and Metabolic Diseases. (b) Abstracted largely from the Ph.D. Dissertation of F. A. Via, The Ohio State University, 1970.

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Table I. Rate and Equilibrium Constants for the Reaction of Primary Amines with Isobutyraldehyde in Water at 35° [a]

Amine	K_{ca}, M^{-1}	K_{lc}, M^{-1}	K_{im},[b] M^{-1}	k_0K_{ca}, M^{-1} sec^{-1}	$10^{-8}k_hK_{ca}$, M^{-2} sec^{-1}	pK_a[c]
$MeNH_2$[d]	8.5 ± 0.5		118	53	27	10.31
n-$PrNH_2$	5.1 ± 0.9	103 ± 1	101	50		10.21
$MeO(CH_2)_3NH_2$	3.0 ± 0.8	75 ± 3	89	20		9.83
$MeO(CH_2)_2NH_2$	2.4 ± 0.4	54 ± 3	52	5.2	~23	9.09
$(MeO)_2CHCH_2NH_2$	1.1 ± 0.2	27 ± 2	30	1.06	7.5	8.35
$F_3CCH_2NH_2$	0.24 ± 0.04	5.4 ± 0.5	6.0	0.0049	0.29	5.22

[a] All ± figures are standard deviations. [b] Calculated from the value of K_{ic}' reported earlier[9] and the value of K_{ca} determined in the present work. [c] Data from ref 9. [d] Data from ref 10.

compound; the base removes these acidic hydrogen atoms. Certain compounds with a primary amino group and another basic functional group in the same molecule are capable of acting as bifunctional catalysts.[6,7] In order to obtain a better understanding of such processes equilibrium constants for the formation of a number of imines from isobutyraldehyde have been determined[8,9] and the kinetics of the formation[10] and hydrolysis[11] of N-methylisobutyraldimine studied. Although the establishment of equilibrium between the carbonyl compound and the corresponding iminium ion is ordinarily rapid relative to the subsequent removal of α-hydrogen,[12] if the hydrogen removal process becomes efficient enough iminium ion formation may become rate controlling.[7] For this reason we need to understand the effect of structure on reactivity in the formation of simple aliphatic imines and have studied the kinetics of the formation of imines from isobutyraldehyde and amines of the type RCH_2NH_2, where large changes in the polar properties of R were made but where the effective bulk of R was not changed greatly. Similarities to the results that have been observed in the formation of other types of compounds with carbon–nitrogen double bonds[13] are expected.

Results

Our stopped-flow measurements on the reaction of isobutyraldehyde with amines in aqueous solution at 35° were interpreted in terms of the following reaction mechanism, in which the abbreviations to be used for several of the species involved are written below the species. In the reactions in which water appears, its essentially constant concentration will be absorbed into the appropriate rate or equilibrium constants. The absorbance at 285 nm, largely due to the aldehyde, underwent a small but significant decrease that was too fast to follow; it then decreased more slowly and became constant within a minute or so. As in the case of the reaction of methylamine, it was assumed that the initial rapid decrease was due to establishment of equilibrium with the carbinolamine (Ca) and the larger but slower decrease was due to establishment of equilibrium with the imine. The hydration equilibrium governed by K_h (whose value is 0.429 under our conditions) complicates each of the processes. As with methylamine, values of K_{ca} were calculated from transmittance values extrapolated to zero time. In order to learn the effect of aldehyde hydration on such measurements, we calculated rate constants for hydration from the value for the uncatalyzed reaction,[10] the catalytic constants for hydroxide and hydrogen ions,[10] and the estimated catalytic constant for the amine present. The estimates were based on the catalytic constants for N-methylmorpholine and a Brønsted β of 0.5 (which is within 0.05 of the values for the hydration of several aldehydes and ketones,[14] including isobutyraldehyde at 0°[15]). There seems to be no significant probability that general acid catalysis could be important under any of the conditions we used. From the rate constants for hydration it could be calculated that in some runs the hydration equilibrium was essentially established before the time of the first measurements that were used in the calculations; in other runs aldehyde hydration had not progressed significantly (from its extent in the absence of amine) up to the time of the last of the measurements that were used. The differences in the methods used for calculating K_{ca} in these two different types of runs are obvious. In the few cases in which the hydration rate was intermediate between the two extremes referred to, no value of K_{ca} was calculated. In all cases the carbinolamine was assumed to be too weakly basic to exist in its protonated form to a very large extent under the conditions (pH never more than 0.6 below the pK of the ammonium ion present and usually considerably higher). Data on other carbinolamines show that α-hydroxy substituents lower the basicity of the amines by around 2 pK units.[16] Values of K_{ca} and standard deviations are listed in Table I.

$$\underset{\text{Al}}{i\text{-PrCHO}} + H_2O \overset{K_h}{\rightleftharpoons} \underset{\text{Ah}}{i\text{-PrCH(OH)}_2}$$

$$i\text{-PrCHO} + \underset{\text{Am}}{RCH_2NH_2} \overset{K_{ca}}{\rightleftharpoons} \underset{\text{Ca}}{i\text{-PrCH(OH)NHCH}_2\text{R}}$$

$$i\text{-PrCH(OH)NHCH}_2\text{R} \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} \underset{\text{Im}}{i\text{-PrCH=NCH}_2\text{R}} + H_2O$$

Equilibrium constants for the formation of carbinolamine plus imine based on total aldehyde concentration (including hydrate) were reported earlier[9] and will be

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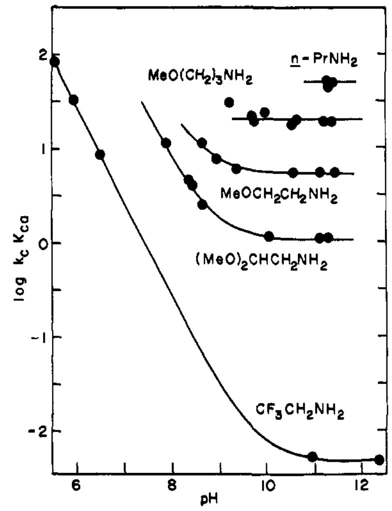

Figure 1. Plot of second-order rate constants for imine formation *vs.* pH.

denoted K_{ic}' here. Values of K_{ic}' calculated from the

$$K_{ic}' = \frac{([\mathrm{Ca}] + [\mathrm{Im}])[\mathrm{H_2O}]}{([\mathrm{Al}] + [\mathrm{Ah}])[\mathrm{Am}]}$$

equilibrium absorbance values observed after several minutes ranged from 0.2 to 19% lower than those reported earlier. Division of K_{ic}' by [H$_2$O] and multiplication by $1 + K_h$ gives K_{ic}. Since the values of K_{ic}'

$$K_{ic} = \frac{[\mathrm{Ca}] + [\mathrm{Im}]}{[\mathrm{Al}][\mathrm{Am}]}$$

reported earlier were determined using a more accurate spectrophotometer and in most cases checked by pH measurements, they are believed to be more reliable and were used in the calculation of our kinetic results and also in the calculation of the values of K_{im}, the equilibrium constant for imine formation, listed in Table I.

$$K_{im} = \frac{[\mathrm{Im}]}{[\mathrm{Al}][\mathrm{Am}]}$$

The kinetics of imine formation may be treated by assuming that the changes in pH (found experimentally to be less than 0.3) during individual kinetic runs were negligible, that negligible concentrations of protonated carbinolamine and iminium ion were present, and that equilibrium between the aldehyde and its hydrate was established rapidly relative to the rate of imine formation. This yields kinetic eq 1, which was derived previously[10,17]

$$k_c t = \left(\frac{2K_{im}}{K_{ic}} - \frac{\beta}{\alpha}\right) \ln \frac{K_{ic}\gamma a_0 + \alpha}{K_{ic}\gamma a + \alpha} + \frac{\beta}{\alpha} \ln \frac{a_0}{a} \qquad (1)$$

where

$$\alpha = \sqrt{(\delta K_{ic} + \gamma)^2 + 4K_{ic}\gamma[\mathrm{Al}]_0}$$

$$\beta = \frac{K_{im}}{K_{ca}}\left[\gamma + \delta K_{ca} + \frac{K_{ca}(\alpha - \delta K_{ic} - \gamma)}{K_{ic}}\right]$$

$a = [\mathrm{Al}] - [\mathrm{Al}]_e$, $[\mathrm{Al}]_e = [\mathrm{Al}]$ at equilibrium, $a_0 = a$ when $t = 0$, $[\mathrm{Al}]_0 = [\mathrm{Al}] + [\mathrm{Ah}] + [\mathrm{Ca}] + [\mathrm{Im}]$, $\gamma = 1 + K_h$, $\delta = [\mathrm{Am}] - [\mathrm{Al}] - [\mathrm{Ah}]$, and t = time. Equation 1 was used in all cases in which the first-order rate constant for approach to equilibrium in hydration was more than five times as large as the rate constant for approach to equilibrium in imine formation (*e.g.*, in all runs made above pH 10). When imine formation was more than five times as fast as hydration (*e.g.*, in all runs made below pH 7), the equation was modified in accordance with the assumption that there was no net hydration of aldehyde or dehydration of aldehyde hydrate during the formation of imine. This modification consists of setting γ equal to 1.0, setting δ equal to $[\mathrm{Am}] - [\mathrm{Al}]$, and using as $[\mathrm{Al}]_e$ the concentration of aldehyde that would be present if carbinolamine and imine formation were at equilibrium but the concentration of aldehyde hydrate had not changed since the solutions were mixed. When neither hydration nor imine formation could be considered to be fast relative to the other, the rate constant was calculated in each of the two possible ways and the two values (which differed by about 15%, with the rapid-hydration rate constant being larger) were averaged.

The largest uncertainties in the values of k_c obtained arise from uncertainties in the values of K_{ca} used in the calculations. If the value of K_{ca} in a given calculation of k_c is replaced by a value half as large, the resulting value of k_c will be about twice as large. That is, the magnitude of the product k_cK_{ca} is relatively independent of the value of K_{ca} used in the calculation (if this value is not too large). This product is simply the second-order rate constant for the reaction of amine with aldehyde to give imine *via* carbinolamine, which could have been calculated from a much simpler equation if the values of K_{ca} had been small enough that the steady-state assumption could have been made for the carbinolamines. Kinetic runs were made over a range of pH's, but it was not possible to go to pH's much below the pK of the conjugate acid of the amine being studied because in more acidic solutions the amount of imine (and carbinolamine) formed at equilibrium was too small to bring about a reliably measurable change in the concentration of aldehyde present. The dependence of the value of k_cK_{ca} on the pH for the amines studied is illustrated by the plots of log k_cK_{ca} *vs.* pH in Figure 1.

Discussion

A plot of log K_{ca} *vs.* the pK_a values[9] for the conjugate acids of the amines used (the solid circles in Figure 2) shows that equilibrium constants for addition of amines to isobutyraldehyde tend to increase with increasing basicity of the amines. To the extent to which the basicity of the amines, all of the form RCH$_2$NH$_2$, is governed solely by polar effects, the sizable deviations from linearity in the plot show that nonpolar substituent effects are also important. The direction and magnitude of the deviations suggest that bulky R groups decrease the size of K_{ca}. This suggestion is supported by use of a linear free-energy relationship of the form shown in eq 2, where P is a polar reaction constant, S is a steric reaction constant, E_s is the Taft steric substituent constant,[18] and B is the intercept.

$$\log K_{ca} = P\mathrm{p}K_a + SE_s + B \qquad (2)$$

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[17] To correct two typographical errors in this derivation,[10] in both eq 23 and 25 the "2" in the numerator should be replaced by "($K_{ca} + K_{im}$)."

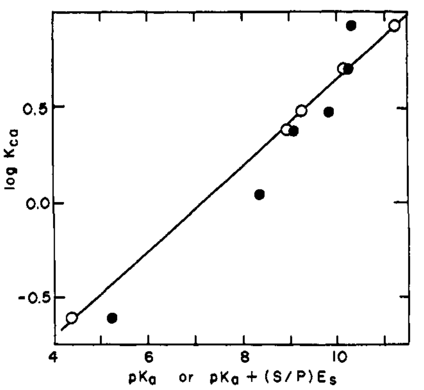

Figure 2. Plots of log K_{ca} *vs.* pK (solid circles) and log K_{ca} *vs.* pK_a + $(S/P)E_S$ (open circles).

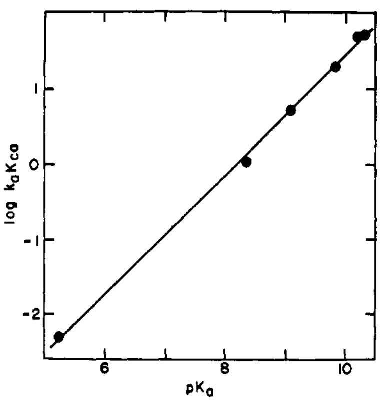

Figure 3. Plot of the logarithm of the second-order rate constants for uncatalyzed imine formation *vs.* pK_a for the conjugate acid of the amine.

A least-squares treatment for the five RCH_2NH_2's for which Taft lists an E_s value for R gave values of 0.227, 0.168, and -1.615 for P, S, and B, respectively, from which the five values of log K_{ca} may be calculated with a standard deviation of 0.02, which is smaller than the average experimental uncertainty. The improvement in the correlation brought about by the inclusion of steric effects may be seen in the plot of log K_{ca} *vs.* pK_a + $(S/P)E_s$ shown by the open circles in Figure 2. For 2,2-dimethoxyethylamine, for which no E_s value was available, an E_s value of -1.41 would be required to make the point fit exactly on the line. This would correspond to the dimethoxymethyl group having the largest effective bulk of any of the six R groups under consideration, which certainly seems plausible. This observation of significant steric effects on the addition of amines, all of the type RCH_2NH_2 with no really bulky R groups, is in agreement with the observations of Jencks and coworkers that steric effects on equilibrium constants for additions to aldehydes tend to be rather large.[16,19]

The polar effects on addition to isobutyraldehyde that we have observed are somewhat larger than those observed by Jencks and coworkers.[16,19] Assuming that steric effects are the same for piperidine, morpholine, piperazine, and piperazinium ions and plotting the data for addition of these amines to formaldehyde, pyridine-4-carboxaldehyde, and *p*-chlorobenzaldehyde by use of eq 2 gives P values around 0.1, rather smaller than the value we have obtained. An even smaller value would be obtained in plotting the equilibrium constants for addition of substituted dinitromethanes to formaldehyde (which vary by less than threefold) against the acidity constants (which vary by more than 10^{11}-fold).[20] On the other hand, data on addition of ethanol and trifluoroethanol to pyridine-4-carboxaldehyde[19] suggest the operation of a significant polar factor. The reasons for these differences in polar effects on various kinds of carbonyl addition reactions are not clear.

Figure 1 shows that all the amines studied give values of k_cK_{ca} that are essentially independent of acidity above pH 10. Increases in k_cK_{ca} with increasing acidity are observed for the amines upon which measurements were made below pH 9. Systematic searches for general acid and general base catalysis were not made, but least-squares fits[21] of the experimental values of k_cK_{ca} to eq 3, in which general catalysis is neglected, gave

$$k_cK_{ca} = k_hK_{ca}[H^+] + k_0K_{ca} \qquad (3)$$

values of k_hK_{ca} and k_0K_{ca} from which the experimental values could be calculated with standard deviations of 4.6, 6.7, and 3.8% for 2,2,2-trifluoroethylamine, 2,2-dimethoxyethylamine, and 2-methoxyethylamine, respectively. These deviations are probably in the vicinity of the uncertainty in the experimental values of k_cK_{ca}. Furthermore, a least-squares fit of the data to eq 4, which allows for general acid catalysis, gave a negative value of $k_{BH}K_{ca}$ in the case of trifluoroethylamine and was incapable of reducing the standard deviation by as much as one-fourth in the cases of 2,2-dimethoxyethylamine and 2-methoxyethylamine. It was therefore concluded that general catalysis had not been established and the values of k_hK_{ca} and k_0K_{ca} listed in Table I are those calculated from eq 3, which also defines the lines drawn in Figure 1. Values of k_hK_{ca} are listed only for those amines for which the value of k_cK_{ca} at least doubled on going to more acidic solutions. The values of k_hK_{ca} obtained in the pH range 9–10, where the change in mechanism of dehydration of the carbinolamine occurs, are of reduced reliability in many cases because the rate of aldehyde hydration was comparable to that of imine formation and because the amine was so highly protonated that the extent of imine formation at equilibrium was relatively small.

$$k_cK_{ca} = k_hK_{ca}[H^+] + k_{BH}K_{ca}[RCH_2NH_3^+] + k_0K_{ca} \qquad (4)$$

A plot of log k_0K_{ca} *vs.* pK_a for the conjugate acid of the amine (Figure 3) shows a good correlation (least-squares slope 0.80). The strong tendency of electron-withdrawing substituents to decrease k_0K_{ca} was expected, because although K_{ca} is not highly sensitive to polar substituent effects the uncatalyzed dehydration of the carbinolamine, whose rate constant is k_0, is believed to involve a rate-controlling ionization to hydroxide and iminium ions. To the extent to which there were

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(21) In the least-squares treatments it was the sum of the squares of the fractional deviations (|obsd − calcd|/obsd) that was minimized.

$$i\text{-PrCH(OH)NHCH}_2\text{R} \xrightarrow{k_0} i\text{-PrCH}{=}\overset{+}{\text{N}}\text{HCH}_2\text{R} + \text{OH}^-$$

significant steric effects on K_{ca} but only very small steric effects on k_0K_{ca}, it follows that the steric strains introduced by the addition of the amines to isobutyraldehyde have been largely relieved in the transition state for loss of hydroxide ions from the adducts.

With only three reliable values of k_hK_{ca} (the maximum amount of acid catalysis observed with 2-methoxyethylamine being barely enough to double the reaction rate) little can be said about the probable importance of steric effects, but the monotonic increase of k_hK_{ca} with increasing pK_a shows that the overall process of acid-catalyzed imine formation is slowed by electron-withdrawing substituents, whose effect is seen to be much smaller than in the case of the uncatalyzed reaction. It is not surprising to find the more facile acid-catalyzed reaction (the values of k_h are around $10^8 M^{-1}$ sec^{-1}) to be a more nearly random process than the uncatalyzed reaction.

From the fact that log k_0K_{ca} and log k_hK_{ca} both increase with increasing pK_a, but with proportionality constants (*e.g.*, P in eq 2) less than 1.0, it follows that the most rapid imine formation at a given pH will take place with an amine whose conjugate acid has a pK_a in the vicinity of the given pH. The less basic amines are less reactive and the more basic amines exist to too great an extent in their protonated forms.

Experimental Section

Reagents. Gas–liquid partition chromatography showed that the 2,2,2-trifluoroethylamine was about 96% pure and that the other amines were more than 99% pure.

Kinetic Runs. Stopped-flow spectrophotometric measurements were made as described previously.[10] Each of the values of K_{ca} and K_{ic} listed in Table I is the average of 10–56 individual determinations. Each of the values of k_cK_{ca} plotted in Figure 1 is the average of the values obtained in 4–8 runs. In no set of runs was the standard deviation greater than 17%; in the average set it was 7%. The total concentration of isobutyraldehyde used ranged from 0.018 to 0.040 *M*. The total concentration of amine (including ammonium ion) ranged from 0.02 to 0.17 *M* (the higher concentrations being used in some of the runs in the more acidic solutions) except in the case of trifluoroethylamine where concentrations around 0.38 *M* were used because of the small values of K_{ca} and K_{ic}. The initial pH's of the reaction mixtures (after establishment of the carbinolamine equilibrium) were calculated from the pK_a values of Table I. These pK_a values refer to zero ionic strength but to a reaction whose equilibrium constant is independent of the ionic strength, according to the limiting form of the Debye–Hückel equation. The ionic strength in the reaction with propylamine was increased from 0.005 to 0.05, 0.31, and 0.41 *M* by added sodium chloride with an accompanying overall increase in reaction rate of about 10%. The ionic strength in the other runs, due almost entirely to the perchlorate of the amine being studied, ranged up to as much as 0.17 *M* in the more acidic solutions.

The Kinetics of Iodination of Propiolic Acid

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Contribution from the Marion Edwards Park Laboratory,
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Abstract: The kinetics of the addition of iodine to propiolic acid and its anion were studied in water in the presence of iodide ion at varying pH and salt concentrations. The rate of the reaction can be represented by the rate law $-d(I_2)_T/dt = k_2(A)(I_2) + k_3(A)(I_2)(I^-)$, where A is the substrate and $(I_2)_T$ the total titratable iodine. The products of the reaction are *trans*-2,3-diiodoacrylic acid and a substance related to pyruvic acid. The amount of the latter depends on the iodide ion concentration. The first term in the rate equation corresponds to an electrophilic attack by iodine molecules. There are several mechanistic interpretations for the second term. The most attractive interpretation for this term involves a termolecular, but not synchronous, attack of iodine and iodide ion on the triple bond, with the nucleophile initiating the reaction on the free acid and the electrophile the reaction on the anion.

The kinetics of iodination of sodium phenylpropiolate are characterized by a three-term rate equation in which the three terms correspond, respectively, to an iodide ion catalyzed termolecular reaction of iodine, a reaction of free iodine, and one which possibly involves the hydrated iodine cation.[2] We now report the results of a study of the iodination of propiolic acid, $HC{\equiv}C{-}COOH$, and its sodium salt. As before, reaction was conducted in water and in the presence of iodide ion, at varying pH and salt concentrations.

Results

Under all conditions which were investigated, the rate is given by $-d(I_2)_T/dt = k_{obsd}(A)(I_2)_T$, where $(I_2)_T$ is the total titratable iodine, (A) the concentration of the acid or anion, and k_{obsd} is the observed second-order rate constant. The constant k_{obsd} remains constant over a fourfold variation in the concentrations of either of the reactants. The reaction has a strong dependence on salts, which accelerate the rate in all cases.

The Effect of Iodide Ion. The effect of iodide ion on the rate of iodination of the acid was studied in five sets of runs, in which the concentration of iodine was held constant, but in which the iodine to iodide

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[1] Taken in part from the Ph.D. Dissertation of E. Mauger, Bryn Mawr College, May, 1970; United States Steel Fellow in Chemistry, 1967–1968; National Science Foundation Trainee, 1968–1970.

[2] M. H. Wilson and E. Berliner, *J. Amer. Chem. Soc.*, 93, 208 (1971).