Table III

Species	Mole % present — pH 8.00	pH 11.55
Anilic acid	3.5	90.2
Anil	94.8	9.3
Aniline	0.0	0.0

system largely precipitated from the solution, the value shown representing the sum of the amounts extracted from the solution phase and that in the precipitate. These results suggest that tetramethylsuccinanilic acid is unstable in aqueous solution, the amide hydrolyzing to yield protonated aniline in acidic solutions and forming the imide in neutral solutions. Only under highly alkaline conditions such that the effective concentration of the free acid is very low will the anilic acid be expected to be moderately stable, slow hydrolysis to dianion, however, probably taking place.

Although the preceding data have been limited to hydrolysis of anilides there appears to be no reason to feel that essentially similar situation does not exist for other amides. Comparable data for unsubstituted succinamic acid are shown in Figure 4 and for succinylamphetamine in Figure 5. In the latter instance the rate was followed by extraction of the amine formed, the rate at pH 2.5 being also checked polarimetrically. These compounds appear to cleave in essentially the same way and at rates roughly within the same order of magnitude as succinanilic acid.

Discussion

Because of the magnitude of the catalytic effect produced by favorably located carboxyl group in promoting amide formation and hydrolysis it is certainly attractive to consider the possibility of similar mechanism being directly or indirectly responsible for the catalytic properties of enzymes. The ease with which normally resistant amides can be cleaved under extremely mild conditions under the influence of favorably located carboxyl is suggestive. Enzymes behave as they do presumably because of their highly efficient structural organization. It does not require too great a stretch of imagination to picture one or more free carboxyls in these biocatalysts operating from sterically favorable position on peptide linkages.

Kinetics of Hydrolysis of Hydroxy and Methoxy Derivatives of N-Benzylidene-2-aminopropane

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Contribution from the Departments of Physics and Chemistry, Lovanium University of Leopoldville, Leopoldville, Congo. *Received April 6, 1966*

Abstract: The kinetics of hydrolysis of *o*-, *m*-, and *p*-hydroxy-N-benzylidene-2-aminopropane, and of their methoxy analogs, has been investigated in the pH range from 0 to 14, at 30°, by means of ultraviolet spectrophotometry. Dissociation constants have been determined. The pH–rate profile is very similar to ones previously reported for similar compounds, except for a different behavior of the *o*- and *p*-hydroxy derivatives in the pH region where they predominantly exist as free bases, as well as for the three hydroxy compounds when they are converted into the anionic form. The pK_1 values for the addition of a proton to the *o*-hydroxy and *p*-hydroxy derivatives are very different from the corresponding values for the methoxy analogs, while the pK_1 of *m*-hydroxy and *m*-methoxy are identical. The pK_2 value for the formation of the anion of the *p*-hydroxy derivative is inconsistent with pK values of phenol derivatives, while the *m*-hydroxy compound seems to be normal in that respect. The possibility of a tautomeric equilibrium in strongly polar solvents is suggested by examination of the ultraviolet absorption spectra. This hypothesis allows a coherent interpretation of the totality of the kinetic data.

The hydrolysis reaction of Schiff bases has been extensively studied, especially as regards to the effect of substitution on the benzylidene ring in the case of alkyl aromatic molecules.[1-8] We have been led to investigate the effect of hydroxy substituents in a systematic study of stability of chelating compounds.[9-11] In order to help in the elucidation of some singularities observed in the spectral and kinetic behavior of the *o*- and *p*-hydroxy-N-benzylidene-2-aminopropanes, we have compared them to their methoxy analogs.

Experimental Section

Kinetic measurements were carried out spectrophotometrically with a Perkin-Elmer 350 spectrophotometer equipped with a cell holder thermostated at 30 ± 0.1°. In all kinetic runs, ionic strength was maintained at 0.10 by addition of KCl. Acetate, phosphate, borate, and carbonate buffers were used in their appropriate pH range.[12] All reactions were conducted in doubly distilled water containing 2% Spectrograde methanol for solublity. Spectra were scanned continuously from 400 to 200 mμ (or part of this range) at fixed time intervals (0.5 to 5 min), and the zero-time

(1) A. V. Willi, *Helv. Chim. Acta*, 39, 1193 (1956).
(2) W. P. Jencks, *J. Am. Chem. Soc.*, 81, 475 (1959).
(3) B. M. Anderson and W. P. Jencks, *ibid.*, 82, 1773 (1960).
(4) E. H. Cordes and W. P. Jencks, *ibid.*, 84, 832 (1962).
(5) R. L. Reeves, *ibid.*, 84, 3332 (1962).
(6) R. L. Reeves and W. F. Smith, *ibid.*, 85, 724 (1963).
(7) E. H. Cordes and W. P. Jencks, *ibid.*, 85, 2843 (1963).
(8) K. Koehler, W. Sandstrom, and E. H. Cordes, *ibid.*, 86, 2413 (1964).
(9) P. Teyssie and J. J. Charette, *Spectrochim. Acta*, 19, 1407 (1963).
(10) J. Charette, G. Faltlhansl, and P. Teyssie, *ibid.*, 20, 597 (1964).
(11) J. Charette, C. Decoene, G. Faltlhansl, and P. Teyssie, *Bull. Soc. Chim. Belges*, 74, 518 (1965).

(12) R. G. Bates, "Determination of pH, Theory and Practice," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 121, 157–163.

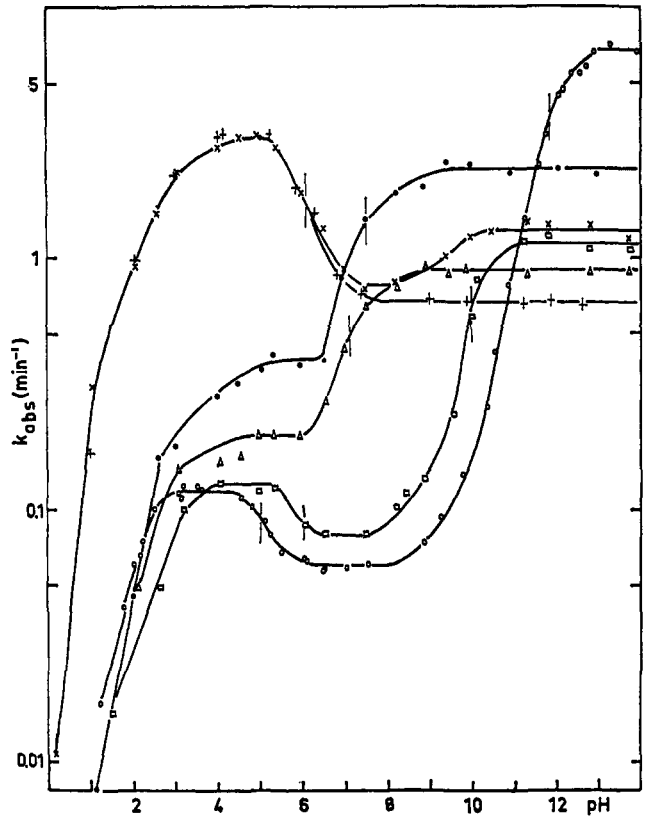


Figure 1. First-order rate constants for the hydrolysis of N-(X)-benzylidene-2-aminopropane at 30° and ionic strength 0.10 plotted against pH. X = *o*-hydroxy, ○; *m*-hydroxy, ×; *p*-hydroxy, □; *o*-methoxy, ●; *m*-methoxy, +; *p*-methoxy, △. Solid line curve for the *p*-hydroxy compound has been recalculated from eq 8.

spectra were obtained by extrapolation. Plots of absorbance *vs.* time were also recorded at fixed wavelengths where the absorptivity of the Schiff base was large, and the one of the parent aldehyde was small.

The pH values were measured in the reaction medium, at the temperature of the kinetic runs, with a glass electrode G 202C and a Radiometer PHM 22 pH meter. All measurements were made with freshly prepared buffers and stock solution of Schiff base in methanol.

Infrared spectra were recorded on a Perkin-Elmer 112G spectrophotometer.

The Schiff bases were prepared by condensation of commercially available isopropylamine with the appropriate aldehyde, following known procedures.[18] However, for the hydroxy derivatives, sodium sulfate was used instead of potassium hydroxide for final drying and distillation. All compounds were purified by distillation under reduced pressure, except the *p*-hydroxy derivative which was recrystallized from benzene. Elemental analysis and azomethine stretching frequencies for the substituted benzylidene-2-aminopropanes are as follows. *Anal.* Calcd for *o*-OH: C, 73.6; H, 8.02; N, 8.59 (1634 cm^{-1}). Found: C, 72.37; H, 7.81; N, 9.07. Calcd for *o*-OCH_3: C, 74.6; H, 8.52; N, 7.92 (1638 cm^{-1}). Found: C, 75.24; H, 8.52; N, 8.27. Calcd for *m*-OH: C, 73.6; H, 8.02; N, 8.59 (1644 cm^{-1}). Found: C, 73.34; H, 8.02; N, 8.39. Calcd for *m*-OCH_3: C, 74.6; H, 8.52; N, 7.92 (1644 cm^{-1}). Found: C, 73.7; H, 8.47; N, 7.96. Calcd for *p*-OH: C, 73.6; H, 8.02; N, 8.59 (1641 cm^{-1}). Found: C, 73.57; H, 8.03; N, 8.77. Calcd for *p*-OCH_3: C, 74.6; H, 8.52; N, 7.92 (1642 cm^{-1}). Found: C, 74.06; H, 8.52; N, 8.18.

Analysis of the product was made at the conclusion of each kinetic run by recording a complete spectrum. In all cases, it was quantitatively identical with the one of the parent aldehyde, obtained in similar solvent conditions with authentic samples.

(13) K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Am. Chem. Soc.*, **66**, 82 (1944).

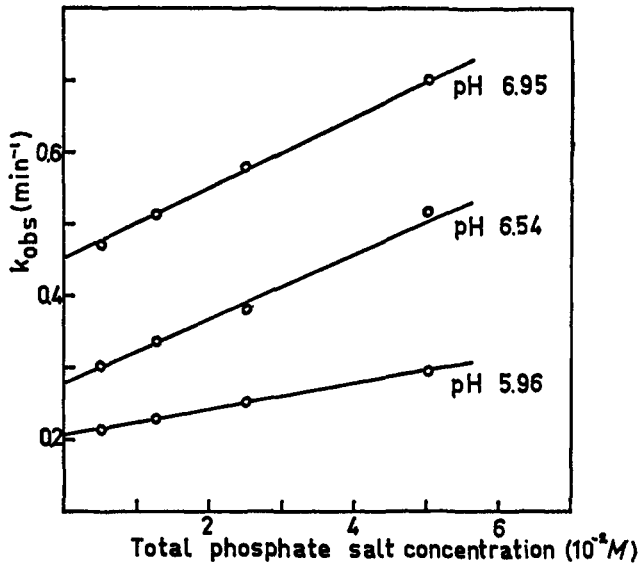


Figure 2. First-order rate constants for the hydrolysis of N-*p*-methoxybenzylidene-2-aminopropane plotted against the total concentration of phosphate buffer at several pH values, at 30° and ionic strength 0.10.

Dissociation constants for proton addition to the free base, S, and to its anion, S^-, are defined by the following equations. They

$$SH^+ \overset{K_1}{\rightleftharpoons} S + H^+ \quad (1)$$

$$S \overset{K_2}{\rightleftharpoons} S^- + H^+ \quad (2)$$

were determined from the change in the absorption curves with pH. Absorbance at the appropriate wavelength was recorded at a series of pH values over the range of dissociation, and extrapolated to zero time. If A represents the absorbance of the solution, and A_b, the one of the free Schiff base, a plot of A *vs.* $(A_b - A)/[H^+]$ gives K_1, while a plot of A *vs.* $(A_b - A)[H^+]$ gives K_2. Where possible, measurements were performed at various wavelengths. Given values of pK values (see Table I) are reliable to within 0.05 pK units.

Table I. Dissociation Constants of Substituted Benzylidene-2-aminopropanes and Rate Constants for the Hydrolysis of the Same Schiff Bases, at 30° and Ionic Strength 0.01[a]

Substituent	pK_1	pK_2	k_1, min^{-1}	k_2, M^{-1} min^{-1}	k_3, M^{-1} min^{-1}
o-OH	4.95	11.9	0.125	7.2×10^7	800
m-OH	6.1	9.3	3	6.2×10^7	(66,000)[b]
p-OH	6.0	10	0.12	8.2×10^6	11,400
o-OCH_3	7.5	...	0.39	6.8×10^6	...
m-OCH_3	6.05	...	3.1	5.9×10^7	...
p-OCH_3	7.1	...	0.2	6.2×10^6	...

[a] The symbols K_1, K_2, k_1, k_2, and k_3 are defined, respectively, by eq 1–4 and 7, in the text. [b] This value is $k_3' = K_3 k_3$.

Results

No induction period has been detected for any reaction. The continuous spectra show sharp isosbestic points at all pH values, indicating that there is no accumulation of intermediate products between the Schiff base and the aldehyde resulting from its hydrolysis.

The variation of the apparent first-order rate constant with respect to pH is depicted in Figure 1. All rate constants are extrapolated to zero buffer concentration. Buffer catalysis is very important in some cases, as shown by an example in Figure 2.

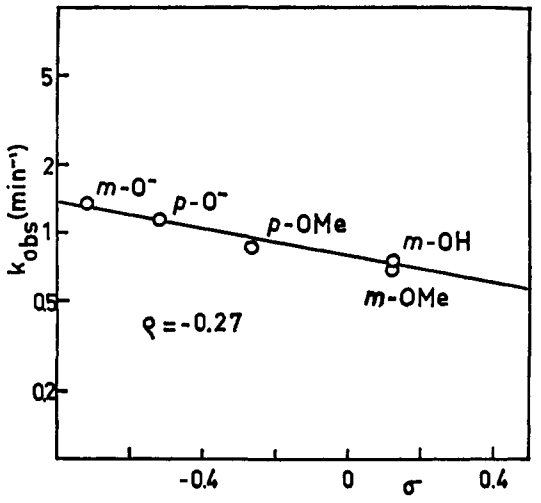


Figure 3. First-order rate constants for the hydrolysis of substituted N-benzylidene-2-aminopropanes at 30° plotted against the σ-substituent constants. For m-O$^-$, p-O$^-$, m-OCH$_3$, and p-OCH$_3$, rate constants at pH 14 have been used; for m-OH, rate constant at pH 8.

For methoxy derivatives, the shape of our curves is identical with the one observed by Cordes and Jencks[7] with similar compounds. But the three hydroxy derivatives exhibit a definite increase of the rate at alkaline pH values. This increase is very large for the o-hydroxy where the rate of hydrolysis at pH 14 is 110 times that at pH 7; it is still great for the p-hydroxy (14 times), and becomes small for the m-hydroxy (twice). In all three cases, the midpoint in the break of the kinetic curve coincides with the pK_2 value as determined by changes in the absorption curves. For all compounds, the pK_1 values obtained from spectroscopic and kinetic data agree fairly well (to within 0.1 pK unit).

The plot of the pK_1 values against the σ-substituent values[14] for m-OH, m-OCH$_3$, and p-OCH$_3$ gives the same slope ($\rho = -2.4$) as the one obtained from the values of Cordes and Jencks[7] for the conjugated acids of substituted benzylidene-1,1-dimethylethylamines. However, the pK_1 of the p-hydroxy derivative does not at all fit into this correlation line, being too small by an amount of 1.3 pK units. The value of pK_1 of the o-hydroxy derivatives also seems abnormally low (4.95) when compared to its methoxy analog (7.5).

The same anomalous behavior of the p-hydroxy compound appears if one tries to determine the σ-substituent values of the N-isopropylazomethinic groups in a series of substituted phenols.[15] While the m-C=NCH-(CH$_3$)$_2$ gives a reasonable value ($\sigma = 0.27$) for its electron-withdrawing power, the pK_2 of the p-hydroxy-N-benzylidene-2-aminopropane places it in a position that would give an electron-donating power ($\sigma = -0.06$) to a p-isopropylazomethinic group (plot not shown).

In the pH region where the substrates exist predominantly as free bases, the apparent rate constants of o- and p-hydroxy compounds are abnormally low when compared to their methoxy analogs. On the other hand, if the apparent rate constants of p-hydroxy and m-hydroxy compounds are taken at pH 14, they correlate nicely with the ones of the p- and m-methoxy derivatives in their pH-independent region, as well as with the one of the m-hydroxy derivative at pH 8 (see Figure 3). The slope of the correlation line gives $\rho = -0.27$, in good accord with the value -0.29 recalculated from the data of Cordes and Jencks.[7]

Discussion

The p-, o-, and m-methoxy and m-hydroxy derivatives of N-benzylidene-2-aminopropane exhibit a kinetic behavior entirely similar to the one observed by Cordes and Jencks[7] for related Schiff bases, except for a slight acceleration by anionization of the m-hydroxy compound. This seems to indicate that their hydrolysis reaction follows the mechanism proposed by Cordes and Jencks, the steps being formulated as

$$SH^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + H^+ \quad (3)$$

$$SH^+ + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \quad (4)$$

$$X \xrightarrow{k_4} \text{products} \quad (5)$$

where X is the carbinolamine intermediate.

The observed first-order rate constants k_1 for the attack of water on the conjugated acid, as well as the calculated second-order rate constants k_2 for the attack of hydroxyl ion on the conjugated acid, are correlated by the σ-substituent constants with ρ values of 2.44 and 1.78, respectively (plot not shown). These values agree fairly well with the ones derived from the data of Cordes and Jencks, 2.50 and 1.83.

The first difference to explain is the apparent anomalous behavior of the o- and p-hydroxy-N-benzylidene-2-aminopropanes in the region of neutral pH: the apparent first-order rate constant of the p-hydroxy compound at pH 7 is $^1/_{10}$ as large as the one of the p-methoxy; for the o-hydroxy and o-methoxy, the factor is $^1/_{40}$. On the other hand, the m-hydroxy and m-methoxy derivatives have the same rate constant at pH 7. This anomaly of o- and p-hydroxy compounds is restricted to the neutral pH zone: all six compounds behave very similarly in acidic and alkaline media. In this neutral region, the rate-determining step is the addition of hydroxyl ion to the protonated Schiff base (eq 4), this being indicated by the fact that the reaction rate is pH independent. Accordingly, the observed rate constant, k_{obsd}, is related to the second-order rate constant k_2 and to the dissociation constant K_1 by eq 6.

$$k_{obsd} = \frac{k_2[OH^-]}{1 + \frac{K_1}{[H^+]}} \quad (6)$$

The values of k_2 calculated from this equation are very similar for the p-hydroxy and p-methoxy derivatives (see Table I); the values for the o-hydroxy and o-methoxy compounds still differ by a factor 10 which could be attributed to steric effects. In conclusion, we may state that the above-mentioned anomaly in the values of the apparent rate constants of hydrolysis of o- and

(14) Normal σ values are used throughout this work, as σ^+ values for m-OH, m-O$^-$, and p-O$^-$ were not available. They are taken from J. Clark and D. D. Perrin, *Quart. Rev.* (London), 18, 295 (1964). They have been used to replot the data of Cordes and Jencks[7] for comparison purpose.

(15) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London, 1962, p 130.

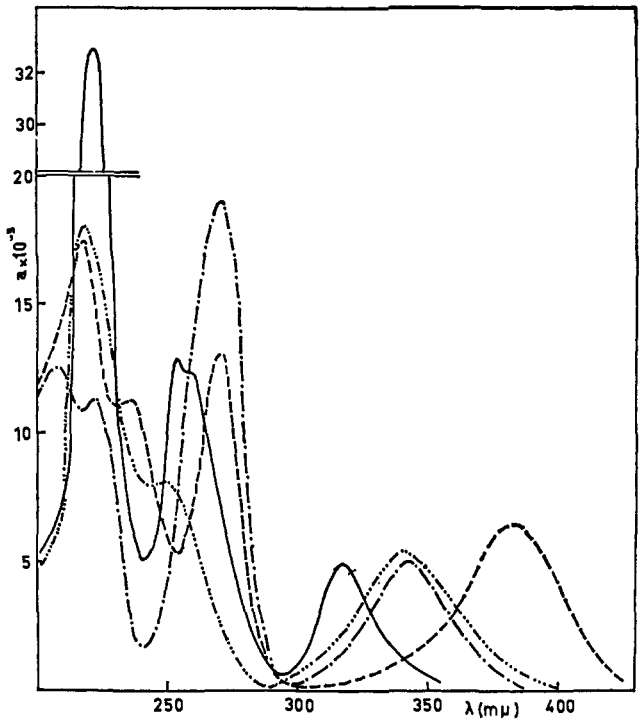


Figure 4. Ultraviolet spectra of N-(X)-benzylidene-2-aminopropane (X = *o*-OH). Solvents: cyclohexane (———); water, pH 2 (-·-·-·-); water, pH 14 (—···—); water, pH 7 (- - - -).

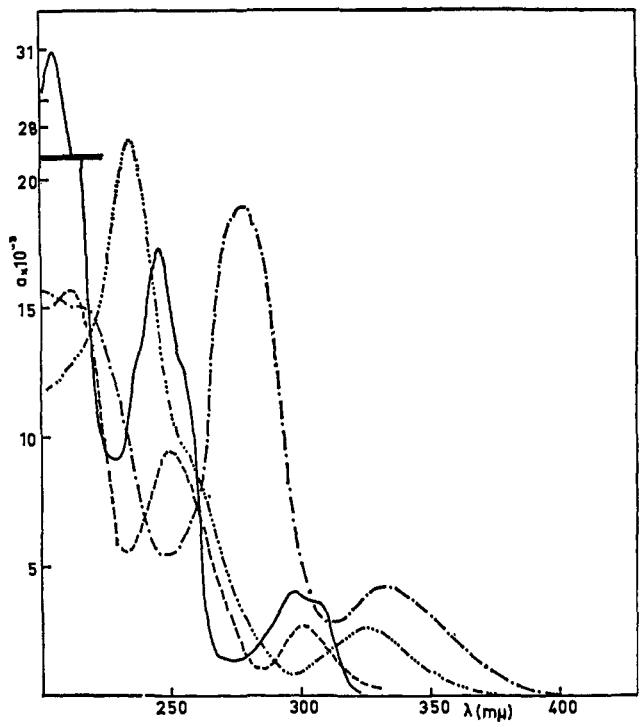
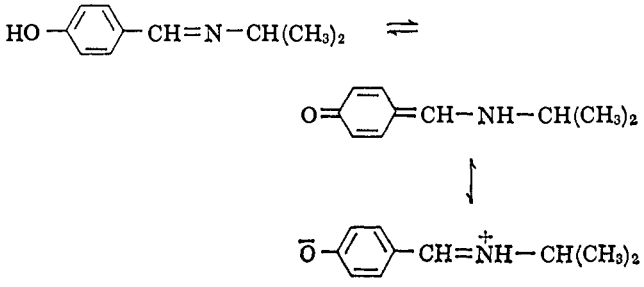


Figure 5. Ultraviolet spectra of N-(X)-benzylidene-2-aminopropanes (X = *m*-OH). Solvents: cyclohexane (———); water, pH 2 (-·-·-·-); water, pH 14 (—···—); water, pH 7.5 (- - - -).

p-hydroxy-N-benzylidene-2-aminopropane is entirely due to the anomaly in their acid dissociation constants.

The surprisingly large difference between these dissociation constants K_1 of *p*-hydroxy and *p*-methoxy-N-benzylidene-2-aminopropanes could tentatively be explained by strong intermolecular bonding, leading to dimeric association of the *p*-hydroxy compound. This dimerization is indeed clearly borne out by infrared results. At the low concentration (10^{-4} *M*) used for ultraviolet measurements, however, this association is negligibly small. And, on the other hand, the same dimerization has been detected for the *m*-hydroxy compound whose pK_1 is entirely normal.

Another alternative seems to be the existence of a tautomeric equilibrium between enolimine and ketoamine forms, in strongly polar solvents



the ketoamine being stabilized by the strong resonance between its neutral and zwitterionic structures. The same tautomeric equilibrium is conceivable for the *o*-hydroxy, but not for the *m*-hydroxy derivative.

This hypothesis would explain the anomaly observed in the acid dissociation constants; it will also help to justify the striking regularities observed in the hydrolysis reaction at alkaline pH, as will be dealt with below. Let us first examine if the hypothesis of tautomeric equilibrium is consistent with ultraviolet data (see Figures 4–9). The most revealing feature, as far as tautomerism is concerned, is the presence or absence of a shift in the position of the band around 255 mμ (and 300 mμ for some compounds) in inert solvents, while going to polar solvents. Large shifts have been

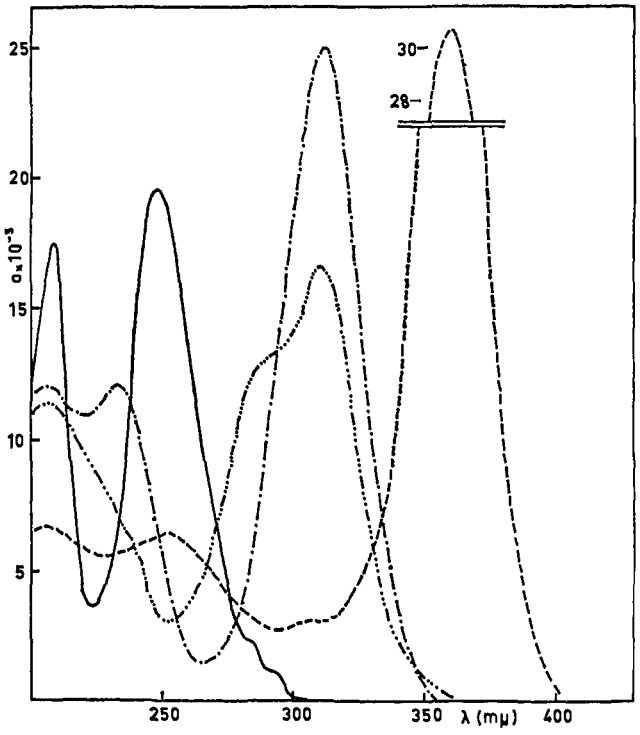


Figure 6. Ultraviolet spectra of N-(X)-benzylidene-2-aminopropanes (X = *p*-OH). Solvents: cyclohexane (———); water, pH 2 (-·-·-·-); water, pH 14 (—···—); water, pH 9 (- - - -).

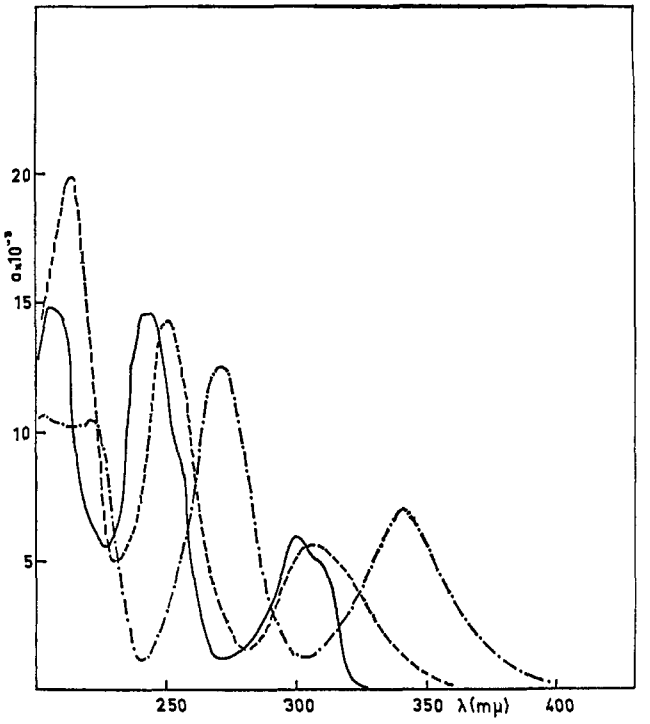


Figure 7. Ultraviolet spectra of N-(X)-benzylidene-2-aminopropanes (X = o-CH_3). Solvents: cyclohexane (———); water, pH 2 (-·-·-·); water, pH 12 (- - - -).

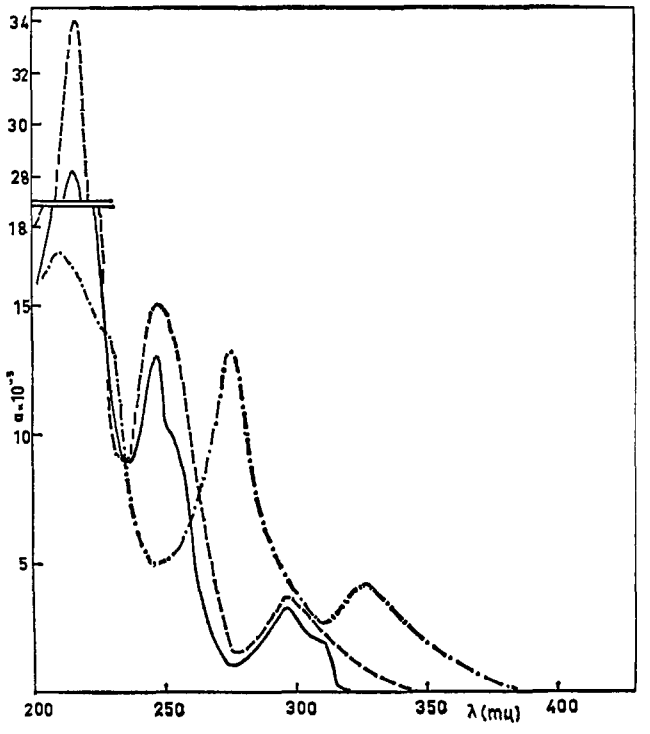


Figure 8. Ultraviolet spectra of N-(X)-benzylidene-2-aminopropanes (X = m-OCH_3). Solvents: cyclohexane (———); water, pH 2 (-·-·-·); water, pH 7.5 (- - - -).

connected with the formation of the ketamine form;[16] this is indeed the case for the o- and p-hydroxy derivatives. The first product has absorption bands at 252 and 318 mμ in cyclohexane, which shift at 272 and

(16) K. K. Chatterjee and B. E. Douglas, *Spectrochim. Acta*, 21, 1625 (1965).

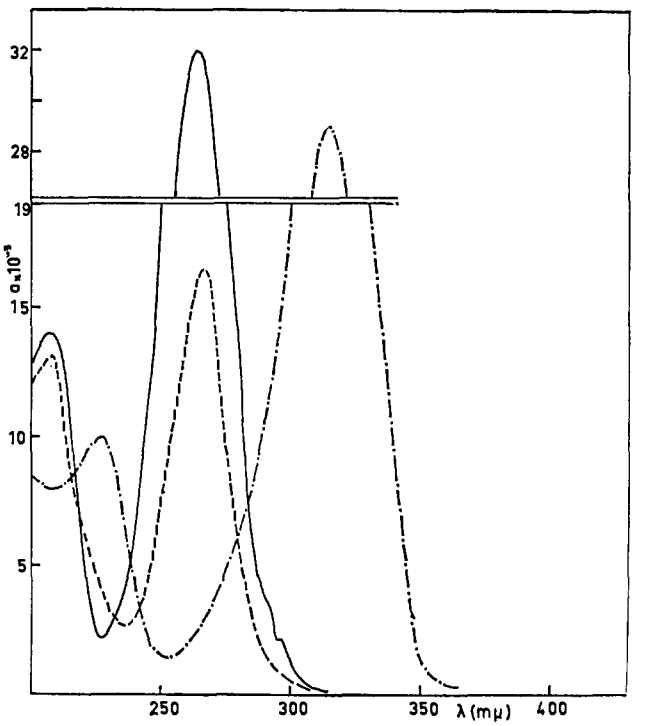
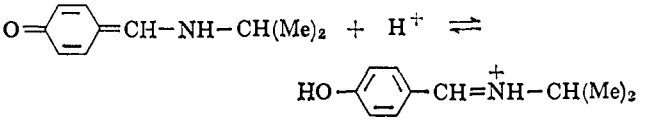


Figure 9. Ultraviolet spectra of N-(X)-benzylidene-2-aminopropanes (X = p-OCH_3). Solvents: cyclohexane (———); water, pH 2 (-·-·-·); water, pH 10 (- - - -).

385 mμ in water; the p-hydroxy has a band at 248 mμ in cyclohexane and at 360 mμ in water. On the contrary, the m-hydroxy and the three methoxy compounds exhibit only small shifts which may be explained by solvent effects.

In addition, it should be emphasized that the ketamine form of the hydroxy compounds has a conjugated acid having the same structure as the conjugated acid of the methoxy analogs, as in clearly indicated by the similarity

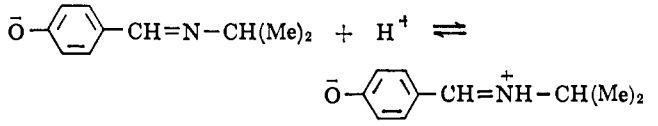


of their ultraviolet spectra at pH 2 (see Figures 4–9). This explains why the hydrolysis of the fully protonated forms of the p-hydroxy and p-methoxy derivatives have the same rate constants k_1 (see Figure 1, at pH 4). This also explains the regularities exhibited by the calculated rate constants k_2. And all this provides an independent confirmation of the mechanism of hydrolysis proposed by Cordes and Jencks for these two pH regions. Now, the great advantage of the tautomerism hypothesis is that it requires no distinct mechanism for the hydrolysis in strongly alkaline media. The fact that the mechanism must be similar (attack of OH^- on the protonated substrate) in alkaline and neutral pH values is borne out by the existence of two remarkable regularities in the kinetic data: (1) the rate of hydrolysis at pH 14 is of the same order of magnitude for the six compounds (see Figure 1); (2) the observed rate constants for m-OH, m-O^-, m-OCH_3, p-O^-, and p-OCH_3 are perfectly correlated by the σ-substituent constants, with the same ρ value as the one found with substituted (other than hydroxy) benzylidene-1,1-dimethylethylamines (see Figure 3).

If we accordingly assume a single mechanism for the whole 7–14 pH range, the rate constants are related by the following equation

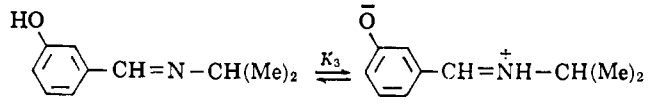
$$k_{obsd}[S_0] = k_2[SH^+][OH^-] + k_3[S][OH^-] \quad (7a)$$

with $[S_0] = [S] + [SH^+] + [S^-]$, for the *o*- and *p*-hydroxy compounds, where the protonated form of the anion is identical with the zwitterion, *i.e.*, with the ketoamine tautomer.



This is not the case with the *m*-hydroxy derivative, where the equilibrium constant for the formation of the zwitterion should be introduced.

$$k_{obsd}[S_0] = k_2[SH^+][OH^-] + k_3K_3[S][OH^-] \quad (7b)$$



As K_3 is unknown, an apparent constant $k_3' = k_3K_3$ will be obtained for the *m*-hydroxy derivative. The values of the rate constants calculated by use of eq 7 are given in Table I.

In conclusion, it appears from our results that hydroxy derivatives of N-benzylidene-2-aminopropane are similar to other derivatives in their kinetic behavior during the hydrolysis reaction, in the full 0–14 pH range. The hypothesis of an internal catalysis by O^- in the *ortho* position[17,18] is not consistent with our results. Indeed, at pH 14, *o*-O^- and *o*-OCH_3 derivatives have rates of the same order of magnitude, as is also the case with the *meta* and *para* derivatives.

As our results show that no accumulation of intermediate occurs at any pH value, we may apply the steady-state approximation to the concentration of the carbinolamine intermediate. This leads to the formula

$$k_{obsd} = \frac{k_1k_4[H^+] + k_2k_4 10^{-14} + k_3k_4K_1[OH^-]}{\{K_1 + [H^+] + K_1K_2/[H^+]\}\{k_{-1}[H^+] + k_{-2} + k_{-3}[OH^-] + k_4\}} \quad (8)$$

Moreover, individual values of some real rate constants may be calculated from the horizontal parts of the kinetic curves in Figure 1. This allows us to recalculate the apparent rate constant over the whole pH range—this has been made for the *p*-hydroxy compound in Figure 1—and to note the excellent agreement between the theoretical and the empirical curves.

Acknowledgment. One of us (J. J. C.) is indebted to Industrial Distributors (1946), Johannesburg, for financial support.

(17) R. L. Reeves, *J. Org. Chem.*, 30, 3129 (1965).
(18) T. C. French, D. S. Auld, and T. C. Bruice, *Biochemistry*, 4, 77 (1965).

Kinetic Studies of Hydrogen Exchange in Dialkylanilines. II

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Abstract: Further kinetic and thermodynamic parameters for hydrogen exchange in substituted dialkylanilines are reported. Qualitative discussion of the reactive species is followed by consideration of the dependence of rate constant on acidity and solvent composition in relation to possible reaction mechanisms. The evidence supports an A-SE2 mechanism, in which exchange occurs on the basic form of the dialkylaniline molecule. A linear relationship between *external* activation enthalpy and entropy is observed.

The kinetic data reported in the previous paper[2] suggested that the exchange reaction is a typical electrophilic substitution occurring only in acid solution. The influence of substituents was shown to follow the Hammett $\rho\sigma$ relationship, giving particularly good linearity when using the electrophilic substituent constants σ^+. In this paper we report the final measurements from this phase of the work and consider possible reaction mechanisms which are consistent with the observations.

Analysis of the kinetic data from variously substituted dialkylanilines has led to the development of a satisfactory relationship between activation entropy and enthalpy, in which a clear distinction has been made between the internal and external components. This relationship not only serves to complement the Hammett $\rho\sigma$ relationship previously established for exchange in this system,[2] but also provides data to support the concept of separability of internal and external entropy and enthalpy effects.[3]

The effect of changing acidity on the reaction rate has been studied, and the application of the Hammett acidity function considered.[4] The role of acidity functions in determination of reaction mechanism in

(1) Material taken from a thesis by I. Lee submitted in partial fulfillment of the Ph.D. degree.
(2) B. B. P. Tice, I. Lee, and F. H. Kendall, *J. Am. Chem. Soc.*, 85, 329 (1963).
(3) (a) L. G. Hepler, *ibid.*, 85, 3089 (1963); (b) K. J. Laidler, *Trans. Faraday Soc.*, 55, 1725 (1959); (c) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 323 (1964).
(4) L. P. Hammett, *Chem. Rev.*, 16, 67 (1935).