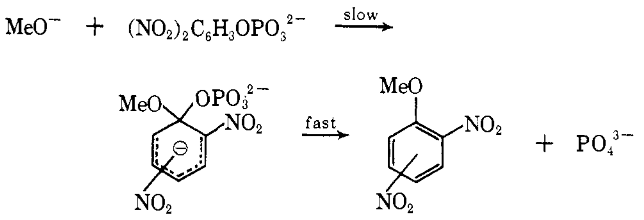
For example, we cannot distinguish between a positive salt effect of the methoxide ion upon dianion solvolysis and attack of methoxide ion upon the phosphorus atom. This problem cannot be avoided by working at constant ionic strength, because kinetic salt effects depend upon the nature of the electrolyte.

Reactions of the dianions with alkoxide ion gives considerable amounts of ethers by nucleophilic attack upon the phenyl group, even though the phosphate trianion should be a poor leaving group. However, nucleophilic attack upon a phenyl group is generally insensitive to the nature of the leaving group[25] suggesting the reaction below.



The 2,4- and 2,6-dinitrophenyl phosphates differ considerably in their reactions with methoxide ion, because with the 2,6 compound ether is the major product, suggesting that the second nitro group assists nucleophilic attack upon the phenyl group, as is found in other aromatic nucleophilic substitutions. The electronic effect of the nitro groups should be greatest when they are in the *ortho* positions. So far as attack upon phosphorus is concerned electronic effects should be less, and steric effects more, important. There is much more phosphorus–oxygen fission in the alkaline methanolysis of the 2,4- than the 2,6-dinitrophenyl phosphate (Tables XII and XIII).

The Temperature Dependence of the Hydrolysis of a Series of Substituted Benzylidene-1,1-dimethylethylamines[1]

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Abstract: Activation parameters have been determined for the hydrolysis of a series of benzylidene-1,1-dimethylethylamines in aqueous solutions under conditions of pH in which (a) attack of hydroxide ion on the protonated substrates is rate determining, (b) attack of water on the protonated substrates is rate determining, and (c) decomposition of the carbinolamine intermediates is rate determining. In basic solution, condition a above, enthalpies and entropies of activation, calculated from first-order, pH-independent rate constants, vary in a random fashion as the nature of the polar substituent in the benzaldehyde moiety is varied, although the free energies of activation are nearly independent of this parameter. At slightly acidic values of pH, condition b above, values of $\Delta H^{\ddagger}$ near 13 kcal/mole and of $\Delta S^{\ddagger}$ near -30 eu were obtained. These values may vary somewhat with the nature of the polar substituent although definite trends have not been established. In 0.1 *M* HCl, condition c above, values of $\Delta H^{\ddagger}$ increase regularly with increasing electron-donating power of the polar substituent; those for $\Delta S^{\ddagger}$ are independent of the nature of the polar substituent.

The kinetics of hydrolysis of Schiff bases derived from both aromatic and aliphatic amines has received considerable attention during the last few years.[3–13] Conclusions regarding reaction pathways and transition state structures drawn from these studies have been corroborated and complemented by investigation of the reverse reaction, the addition of nitrogen nucleophilic reagents to carbonyl compounds.[3,5,12,14–16] As a result, certain aspects of these reactions, including the effect of structure on reactivity and the effect of pH on rate, seem to be clearly understood. Other aspects, such as the precise transition-state structure for those reactions involving general acid–base catalysis, are less clearly resolved.[9,12,14,17–19] One noticeable gap in information regarding these reactions, and one that might on closing shed light on unresolved issues, is the lack of activation parameters for the various steps in the reaction sequence. In the few cases in which activation parameters have been measured, it is frequently unclear which step in the over-all process is rate determining under the reaction conditions employed. This manuscript reports a study of the temperature depen-

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(2) Career Development Awardee of the National Institute of Health.

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dence of the rates of hydrolysis of several structurally related Schiff bases.

The substrates chosen for study are a series of benzylidene-1,1-dimethylethylamines substituted in the benzaldehyde moiety. These are suitable compounds for study since a previous investigation has established the principal features of the hydrolytic processes.[7] Furthermore, the rates of hydrolysis are such that, in each case, the reactions may be followed by conventional techniques over the pH range of 1 to 14. Thus, the system is flexible in that the activation parameters may be evaluated as a function of several variables.

Experimental Section

Materials. Schiff bases employed were synthesized from *t*-butylamine and the appropriate benzaldehydes as previously described.[7] All other reagents, with the exception of inorganic salts, were purified by redistillation or recrystallization prior to use. Solutions of Schiff bases were prepared in ethanol just prior to use in kinetic studies.

Kinetic measurements were made spectrophotometrically with the aid of a Zeiss PMQ II spectrophotometer equipped with a cell holder through which water from a thermostated bath was continuously circulated. Details of the measurements have been described previously.[7] Temperature was maintained with the aid of a Bronwill thermostated heater and circulator. Temperatures were measured using a calibrated Beckman thermometer. On repeated occasions, temperatures were measured in the reaction vessels within the cell housing of the spectrophotometer. These temperatures were ordinarily within ±0.05° of the value for the water bath. All reactions were carried out at an ionic strength of 0.50, maintained through the addition of KCl. Reactions were run in aqueous solutions containing 3% ethanol. Activation parameters were obtained from Arrhenius plots and the appropriate ancillary equations. Slopes of all Arrhenius plots were obtained by unweighted least-squares analysis.

Measurements of pH were performed with the aid of a Radiometer 4c pH meter equipped with a glass electrode. All measurements of pH were conducted at the temperature appropriate to the particular experiment through the use of a thermostated water bath with which the solution was equilibrated prior to and during the measurement.

Results

Ready comprehension of the data presented below requires some familiarity with the nature of the pH-rate profiles for hydrolysis of benzylidene-1,1-dimethylethylamines. To this end, such profiles for the compounds substituted with the *p*-methyl and *p*-nitro groups are provided in Figure 1. This figure has been constructed from data obtained in an earlier study of Schiff base hydrolysis.[7] The principal conclusions derived from this and related studies as they pertain to the pH-rate profiles are the following.[7,9] First, the pH-independent reactions observed under basic conditions reflect the rate-determining attack of hydroxide ion on the protonated substrates. Second, under more acidic conditions in which appreciable fractions of the Schiff bases are converted to the protonated form, the rate constants either increase or decrease depending on the nature of the polar substituent and, finally, reach new plateau values which reflect the rate of attack of water on the fully protonated substrates. Third, under still more acidic conditions, a transition in the rate-determining step occurs and decomposition of tetrahedral carbinolamine intermediates becomes a slow step. More complete explanations of the pH-rate behavior together with data for additional substrates are provided in ref 7 and 9.

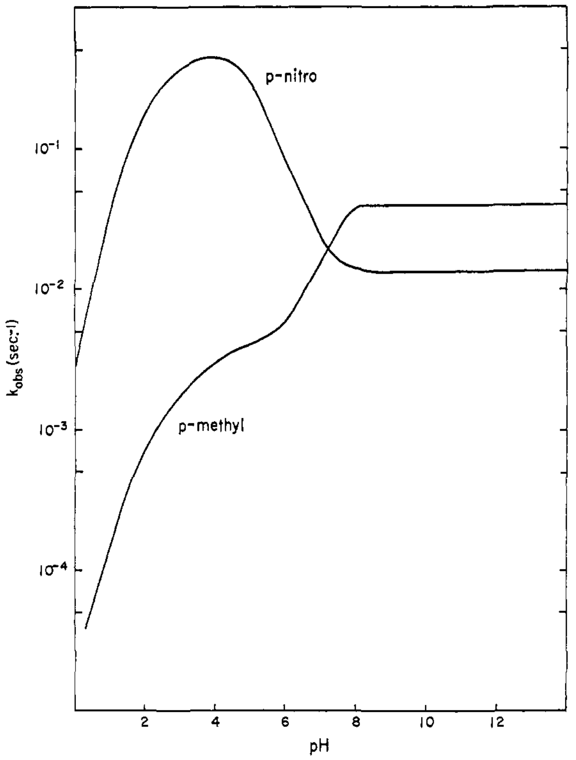
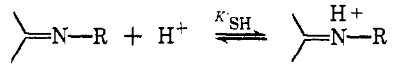
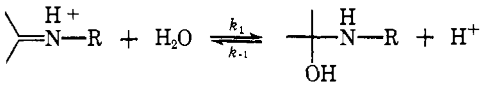


Figure 1. pH-rate profiles for the hydrolysis of *p*-methyl- and *p*-nitrobenzylidene-1,1-dimethylethylamines. Reference 7 should be consulted for details.

In light of the above comments, we may formulate the hydrolysis of benzylidene-1,1-dimethylethylamines in terms of the following series of reactions.


(1)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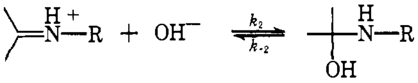
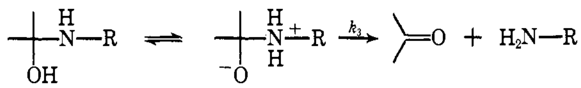

(3)


(4)

Employing the steady-state assumption for the concentration of the carbinolamine intermediates, we obtain the following rate expression for the over-all hydrolysis reaction[7]

$$k_{\text{obsd}} = \frac{k_1k_3(\text{H}^+) + K_\text{w}k_2k_3}{[(\text{H}^+) + K_{\text{SH}}][k_{-1}(\text{H}^+) + k_{-2} + k_3]} \tag{5}$$

in which K_w is the ionization constant for water and the remaining quantities are defined in eq 1-4.

In Table I, first-order rate constants for hydrolysis of a series of five substituted benzylidene-1,1-dimethylethylamines at each of four temperatures are collected. Each rate constant was determined in the presence of 0.05, 0.1, 0.2, and 0.5 *M* sodium hydroxide at a total ionic strength of 0.50 in order to ensure that the rate constants were, in fact, pH independent. The recorded values are the average of the four determina-

Table I. First-Order Rate Constants and Activation Parameters for Hydrolysis of a Series of Substituted Benzylidene-1,1-dimethylethylamines in Basic Aqueous Solution

Substituent	Temp, °K	k_{obsd},[a] sec^{-1}	$\Delta G^{\ddagger}$, kcal/mole	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
p-Nitro	298.11	0.00765	20.19	10.9	−31.2
	303.22	0.00995			
	308.24	0.0133			
	318.28	0.0243			
p-Chloro	298.17	0.0152	19.93	11.5	−28.4
	303.16	0.0207			
	308.24	0.0280			
	313.20	0.0385			
Unsubstituted	298.11	0.0217	19.72	10.4	−31.3
	303.22	0.0292			
	308.24	0.0385			
	313.20	0.0509			
p-Methyl	293.11	0.0179			
	298.16	0.022	19.72	8.8	−36.6
	303.16	0.0297			
	308.24	0.0371			
p-Methoxy	293.11	0.0161			
	298.12	0.0220	19.72	10.6	−30.7
	303.14	0.0308			
	308.24	0.0388			

[a] Measured in 0.05, 0.1, 0.2, and 0.5 *M* NaOH. Recorded values are averages of the four determinations.

tions. The extreme values did not deviate from the mean by more than 5% in any case. The values at 298° are in good agreement with those obtained previously.[7] Plots of the logarithms of the first-order rate constants against the reciprocal of the absolute temperature yield satisfactory straight lines from which activation energies are evaluated: slope = $-E_a/2.3RT$. Employing these values and the following expressions, activation parameters were calculated and have been included in Table I: $\Delta H^{\ddagger} = E_a - RT$, $k_r = (kT/h)\exp(-\Delta G^{\ddagger}RT)$, $\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T$.[20] The values of $\Delta G^{\ddagger}$ are largely independent of the nature of the polar substituent reflecting the compensation of polar effects on the preequilibrium protonation and on attack of hydroxide ion.[7] On the other hand, values of $\Delta H^{\ddagger}$, accurate to 0.5 kcal/mole, and $\Delta S^{\ddagger}$, accurate to 1.5 eu, exhibit random variation with the nature of the polar substituent.

Returning to eq 5, we note that under conditions in which the concentration of the hydrated proton is vanishingly small, the first-order rate constant is given by

$$k_{obsd} = k_2 \frac{K_w}{K_{SH}} \frac{k_3}{(k_{-2} + k_3)} = k_2 \frac{K_w}{K_{SH}} \qquad (6)$$

Hence, the observed activation energy for a reaction in basic solution is, in fact, a function of the activation energy for the actual second-order reaction and the standard enthalpy changes for the associated equilibria. If the latter values are assumed to be independent of temperature over the range studied, we obtain: $E_{obsd} = E_2 + \Delta H^{\circ}_w - \Delta H^{\circ}_{SH}$. Hence, if the latter two quantities were known, the activation parameters for the attack of hydroxide ion on the protonated substrates could be evaluated. This has been accomplished for the case of *p*-methylbenzylidene-1,1-dimethylethylamine. Values of K_{SH} for the conjugate acid of this substrate have been evaluated at several temperatures by spectrophotometric titration and from kinetic data as previously described.[7] Values of K_w have been calculated from the expression:[21] $\log K_w = -4470.99/T + 6.0875 - 0.01706T$. The calculated values together with those obtained for the second-order rate constants are collected in Table II. The second-order rate constants are substantially independent of temperature; an Arrhenius plot suggests an activation energy in the vicinity of 1 kcal/mole. The derived values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are included in Table II.

Table II. Activation Parameters for the Reaction of Hydroxide Ion with *p*-Methylbenzylidene-1,1-dimethylethylamine

Temp, °K	k_{obsd},[a] sec^{-1}	K_{diss},[b] M	K_w,[c] M^2	k_2,[d] M^{-1} sec^{-1}	$\Delta G^{\ddagger}$, kcal/mole	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
293.11	1.79×10^{-2}	3.16×10^{-8}	6.6×10^{-15}	8.58×10^{4}	10.7	0.4	−34.5
298.16	2.22×10^{-2}	3.98×10^{-6}	1.0×10^{-14}	8.85×10^{4}			
303.16	2.97×10^{-2}	4.47×10^{-8}	1.44×10^{-14}	9.25×10^{4}			
308.24	3.71×10^{-2}	5.02×10^{-8}	2.04×10^{-14}	9.15×10^{4}			

[a] The observed rate constant for the pH-independent reaction under basic conditions. [b] The dissociation constant of the conjugate acid of the Schiff base. [c] The dissociation constant of water. See text for method of calculation. [d] The second-order rate constant for attack of hydroxide ion on the protonated substrate: $k_2 = k_{obsd}K_{diss}/K_w$.

Under conditions sufficiently acidic to convert the Schiff bases to their conjugate acids, $(H^+) \gg K_{SH}$, there is a narrow region of pH in which $k_1k_3(H^+) \gg K_wk_2k_3$ and $(k_{-2} + k_3) > k_{-1}(H^+)$. In this range of pH, eq 5 reduces to $k_{obsd} = k_1$; that is, the rate constants for the pH-independent reaction observed under slightly acidic conditions (Figure 1) are simply those for the attack of water on the protonated substrates. Thus, division of the observed rate constants by the molar concentration of water, 55, yields the appropriate second-order rate constants. Such rate constants for the hydrolysis of four substituted benzylidene-1,1-dimethylethylamines at each of three temperatures are collected in Table III. As may be appreciated from examination of Figure 1, the narrowness of the pH region in which the rate constants are really pH independent introduces considerable difficulty into their accurate evaluation. The rate constants in Table III were estimated from plots of first-order rate constants against pH over the pH range 4–9.5. Thirteen measurements were made for each compound at each temperature. In all cases, the pH was maintained by the use of dilute borate, phosphate, or acetate buffers. Values of rate constants obtained at 298° are in good agreement with those previously obtained.[7] Satisfactory Arrhenius plots were obtained from which

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(20) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961.

(21) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958.

activation parameters, included in Table III, were calculated as indicated above. While the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are probably reasonably accurate, the difficulty in determining the rate constants introduces sufficient uncertainty into these values to preclude identification of trends in these parameters as the nature of the polar substituent is varied.

Table III. Second-Order Rate Constants and Activation Parameters for Hydrolysis of a Series of Substituted Benzylidene-1,1-dimethylethylamines under Conditions in Which Attack of Water on the Protonated Substrates is Rate Determining

Substituent	Temp, °K	k_2,[a] M^{-1} sec^{-1}	$\Delta G^{\ddagger}$, kcal/mole	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
p-Chloro	293.44	0.00020	22.2	12.9	−31.2
	303.21	0.00041			
	313.42	0.00082			
Unsubstituted	293.45	0.000091			
	298.15[b]	0.000125	22.8	13.6	−30.9
	308.23	0.000275			
p-Methyl	293.44	0.0000255	23.3	13.4	−33.2
	303.21	0.000056			
	313.42	0.00011			
p-Methoxy	298.15[b]	0.0000087	24.3	16.6	−25.8
	308.23	0.0000225			
	318.26	0.000051			

[a] $k_2 = k_{\text{obsd}}/55$. [b] From ref 7.

Under still more acidic conditions, in which carbinolamine decomposition becomes rate determining, eq 5 reduces to $k_{\text{obsd}} = k_1k_3/k_{-1}(\text{H}^+)$; thus, the observed rate constants become inversely proportional to the concentration of the hydrated proton (Figure 1). Rearranging this equation and realizing that the addition of water is a preequilibrium reaction at these values of pH, we may write

$$k_{\text{obsd}}(\text{H}^+) = K_{\text{hyd}}k_3 \tag{7}$$

in which K_{hyd} is the equilibrium constant for the hydration of the protonated Schiff base: $K_{\text{hyd}} = k_1/k_{-1} = (\text{X})(\text{H}^+)/(\text{SH}^+)$. In Table IV, values of the right-hand side of eq 7 are collected for a series of four substituted benzylidene-1,1-dimethylethylamines at four temperatures. All of the observed rate constants were measured in the presence of 0.1 *M* HCl except those for the *p*-nitro derivative, which were measured in 0.5 *M* HCl. In each case, satisfactory Arrhenius plots were obtained from which activation energies were calculated. From eq 7, it is clear that $E_{\text{obsd}} = E_3 + \Delta H^{\circ}{}_{\text{hyd}}$. The remaining activation parameters were calculated as indicated above and are included in Table IV. Values of $\Delta H^{\ddagger}$ are considered to be accurate to ±1 kcal/mole and values of $\Delta S^{\ddagger}$ to ±2 eu.

Table IV. Rate Constants and Activation Parameters for Hydrolysis of a Series of Substituted Benzylidene-1,1-dimethylethylamines in 0.1 *M* HCl[a]

Substituent	Temp, °K	k_2, M sec^{-1}	$\Delta G^{\ddagger}$, kcal/mole	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
p-Nitro	298.17	0.0405	21.1	15.5	−18.8
	302.76	0.0600			
	308.14	0.1011			
	313.32	0.140			
p-Chloro	298.13	0.00699	23.1	15.7	−24.8
	302.78	0.0109			
	313.15	0.0272			
	323.08	0.0540			
Unsubstituted	298.13	0.00270	23.7	17.5	−20.8
	302.78	0.00412			
	313.15	0.0110			
	323.08	0.0264			
p-Methyl	298.13	0.000757	24.4	18.2	−20.8
	302.78	0.00136			
	313.15	0.00350			
	323.08	0.00848			

[a] Rate constants measured in 0.5 *M* HCl.

Discussion

Activation parameters calculated from first-order rate constants for the hydrolysis of substituted benzylidene-1,1-dimethylethylamines under basic conditions, in which attack of hydroxide ion on the protonated substrates is the rate-determining step, vary randomly with the nature of the polar substituent. Thus, the opposing effects of such substituents on preequilibrium protonation and on attack of hydroxide, which account for the lack of dependence of the observed rate constants on the Hammett σ values,[7] must have both enthalpic and entropic components. Naively, one might have expected the effects to be largely enthalpic in origin. Actually, most of the possible patterns of variation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with the nature of the polar substituent for reactions involving hydroxide ion as nucleophilic reagent have been observed. For example, Tommila, *et al.*, have demonstrated that the rate-promoting effect of electron-withdrawing polar substituents on the alkaline hydrolysis of ethyl benzoates in 60% aqueous acetone is almost entirely the result of lowered activation energies.[22] Tommila and Hinshelwood have made similar observations for the alkaline hydrolysis of substituted phenyl acetates in the same solvent.[23] In contrast, Bruice and Benkovic find that the effect of polar substituents on the latter reaction in water is largely due to changes in the entropies of activation.[24] Finally, as in the case studied here, the activation parameters vary randomly with the nature of the polar substituent for the reaction of substituted phenyl acetates with imidazole.[25]

The observed activation parameters for the hydrolytic reactions under basic conditions contain contributions from both the standard thermodynamic values for the preequilibrium protonation and from the activation parameters for the actual attack of hydroxide ion. In the case of *p*-methylbenzylidene-1,1-dimethylethylamine hydrolysis these have been sorted out as described in the Results (Table II). The value of $\Delta S^{\ddagger}$ for the attack of hydroxide ion on the protonated substrate (−35 eu) is consistent with other values for bimolecular reactions involving this nucleophilic reagent. For example, the alkaline hydrolysis of phenyl acetates, alkyl acetates, and alkylamides exhibits $\Delta S^{\ddagger}$ values in the range −20 to −34 eu.[24,26] On the other hand, the very small value of $\Delta H^{\ddagger}$ for this reaction, ~1 kcal/mole, is a good deal smaller than those observed for the latter reactions. This may reflect the existence of a favorable energy term arising from electrostatic

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(22) E. Tommila, A. Nurro, R. Murén, S. Merenheimo, and E. Vuorinen, *Suomen Kemistilehti*, 32B, 115 (1959).

(23) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

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(26) K. J. Laidler and D. Chen, *Trans. Faraday Soc.*, **54**, 1026 (1958).

interactions in the transition state between the oppositely charged species.

Measurement of the dissociation constants for the conjugate acid of *p*-methylbenzylidene-1,1-dimethylethylamine as a function of temperature (Table II) permits an approximate evaluation of the standard enthalpy and entropy changes for this reaction. A value for ΔH° of 5–6 kcal/mole and for ΔS° of -15 eu has been obtained. These values fall in the range typically noted for dissociation of ammonium ions in water.[27] In addition, the value for ΔH°, but not that for ΔS°, is close to those measured for the association of benzylideneanilines with *p*-nitrophenol in carbon tetrachloride.[28]

Activation parameters for the attack of water on the protonated Schiff bases (Table III) have not been determined with sufficient accuracy to permit identification of trends with change in the nature of the polar substituent. The values, taken as a group, are comparable in magnitude with those previously obtained by Willi and Robertson for the acid-catalyzed hydrolysis of benzylideneanilines in 50% aqueous methanol[29] and by Geisler, *et al.*, for the hydrolysis of benzylideneaminooctanes in acidic aqueous dioxane.[30] The nature of the rate-determining step in the latter studies is uncertain. Activation parameters have also been measured for the hydrolysis of cyclohexanone oxime in acid[31] and for two 2-hydroxybenzylideneanilines[32] although uncertainties concerning reaction conditions make comparison with results obtained in this study difficult. Comparison of the activation parameters for the attack of water and hydroxide ion on the conjugate acid of *p*-methylbenzylidene-1,1-dimethylethylamine suggests that the greater facility of the latter reaction is due almost entirely to a more favorable enthalpy of activation. Activation parameters for the attack of water on the protonated Schiff bases are also comparable with those typical of related reactions at the acyl level of oxidation, including the reaction of water with acetylimidazolium ion.[33] These values are, in contrast, rather different from those for attack of water on protonated ethylenimines.[34]

In the region of rate-determining carbinolamine dehydration, the effect of polar substituents on Schiff base reactivity is largely reflected in changes in the values for the enthalpy of activation (Table IV). Within the limits of uncertainty, this series of reactions appears to be isoentropic. It is of interest to compare this observation with related findings concerning reactions of substrates at the acyl level of oxidation in which tetrahedral intermediate decomposition is also rate determining. For example, DeWolfe and Augustine have established that the effect of polar substituents on the rate of hydrolysis of ethyl benzimidates under acidic conditions is reflected almost entirely in changes in the entropies of activation.[35] Thus this reaction series appears to be isoenthalpic, in marked contrast to the case investigated in this study. Yet another type of behavior has been established for the alkaline hydrolysis of a series of substituted benzamides.[36] In this case, the effect of polar substituents is reflected in changes in both the enthalpies and the entropies of activation.

The data indicated above, both from this and earlier work, indicate the complexity of the effects of modest structural alterations on reactivity. Thus, examination of the thermodynamic basis of the effect of polar substituents on reactivity within a series of related reactions has revealed almost every conceivable pattern. At the moment, we can advance no convincing explanations for the divergent behavior patterns observed.

As noted above, the activation parameters observed for the hydrolysis of Schiff bases under conditions of rate-determining carbinolamine decomposition involve contributions both from the preequilibrium hydration and the unimolecular decomposition. Particular attention is focused on the entropy of activation for the decomposition of the hydrate since such values may be employed as an indication of mechanism.[27] From eq 7, it follows that $\Delta S^{\neq}{}_{\text{obsd}} = \Delta S^\circ{}_{\text{hyd}} + \Delta S^{\neq}{}_3$. The entropy change accompanying hydration may be roughly estimated from those for the hydration of acetaldehyde,[37] $\Delta S^\circ{}_{\text{aldehyde}} = -16.4$ eu, and for the ionization of secondary ammonium ions in water,[27] ΔS° -10 eu, since $K_{\text{hyd}} = (\text{X})(\text{H}^+)/(\text{SH}^+) = K_{\text{ion}} \cdot (\text{XH}^+)/(\text{SH}^+)$, in which K_{ion} is the dissociation constant for the conjugate acid of the carbinolamine intermediate (X). Assuming that the effect of temperature on the equilibrium $\text{SH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{XH}^+$ is similar to that for the hydration of acetaldehyde, we obtain $\Delta S^\circ{}_{\text{hyd}} = \Delta S^\circ{}_{\text{ion}} + \Delta S^\circ{}_{\text{aldehyde}} \simeq -26$ eu. Since this value is about the same as that observed for the Schiff base hydrolyses (Table IV), it follows that the entropy of activation of the unimolecular decomposition reaction is near zero, a conclusion fully consistent with previously observed behavior.[27]

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