16). It is not possible in the present investigation to determine the relative extent to which each of these processes occurs. It is clear, however, that either mechanism for hydrogen abstraction from the solvent requires ethane and lithium *tert*-butoxide to be generated in equal amounts. Thus, the extent of hydrogen abstraction is given by the excess of ethane over ethylene, *i.e.*, 0.96 − 0.29 = 0.67 mmol. Subtraction of 0.67 mmol each of ethane and lithium *tert*-butoxide from the products in line 4 of Table IX, thus quantitatively accounts for the products of the reaction within the limits of experimental error. A similar analysis is equally applicable to other runs in Tables I and VII.

Physicochemical Properties of Schiff Bases. III.[1] Substituent Effects on the Kinetics of Hydrolysis of N-Salicylidene-2-aminopropane Derivatives

R. Herscovitch, J. J. Charette,*[2] and E. de Hoffmann

Contribution from the Department of Physics and Chemistry, National University, Kinshasa, Zaire, and the University of Louvain, Louvain-la-Neuve, Belgium. Received March 13, 1973

Abstract: The hydrolysis kinetics of five substituted N-salicylidene-2-aminopropanes has been studied between pH 0 and 14. Analysis of the observed rate constants as a function of pH leads to the following conclusions. The mechanism at acidic pH's is the same as that of the nonhydroxylic compounds. At neutral pH, the predominant reaction is the addition of water to the neutral quinoid tautomer. At alkaline pH's, the analysis of the substituent effects confirms that the rate-determining step is the addition of hydroxide ion to the neutral quinoid tautomer.

The mechanism of hydrolysis of Schiff bases derived from amines and aromatic aldehydes has been investigated by various authors.[3] These studies have established the existence of two rate-determining steps: formation of an amino alcohol intermediate, RCHOH-NHR', at neutral or alkaline pH's; decomposition of this intermediate at acidic pH's. The formation of the amino alcohol may occur through two different reactions: addition of water or addition of hydroxide ion to the protonated Schiff base. The presence in the benzylidene ring of hydroxy substituent in the ortho or para position with respect to the azomethine group introduces some modifications in this mechanism. According to Reeves[3c] who studied various derivatives of benzylideneaniline, the o-O⁻ substituent has an intramolecular catalytic effect on the formation of the intermediate. Hoffmann, *et al.*,[4] have investigated the hydrolysis of substituted salicylideneanilines. They reached the conclusion that more than one mechanism is at play, at pH 5.5 as well as at pH 12. However, their sole argument is that the observed constants do not follow a Hammett correlation.

In the preceding papers,[1] the influence of the tautomeric equilibrium between the phenolimine and the ketoamine forms has been investigated in the cases of o- and p-hydroxy-substituted benzylideneisopropylamines.
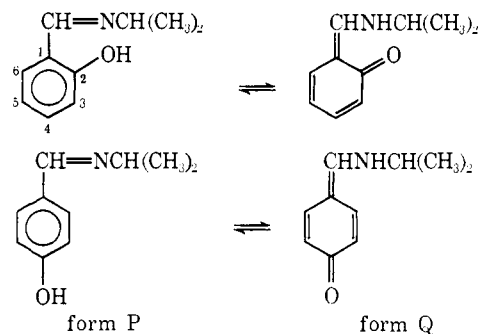
In part I[1a] it has been shown that this equilibrium

form P   form Q

introduces a new kinetically important reaction for the formation of the intermediate in alkaline media, the addition of hydroxide ion to the neutral ketoamine tautomer. The present study brings new evidence in favor of this latter mechanism. It also points out that a new mechanism occurs at neutral pH for the salicylidene derivatives, *i.e.*, the addition of water to the neutral ketoamine tautomer.

Experimental Section

Kinetic measurements were carried out at 30° and ionic strength 0.1 (between pH 1 and 13) as described in part I, except in the pH range between 12 and 14 where the rates of hydrolysis are too large and the variations of optical density between the Schiff bases and the corresponding aldehydes are too small. In this region, kinetic measurements were carried out with a Durrum D110 stopped flow spectrophotometer. pH values were measured as described in part I. The Schiff bases were prepared as described in part II. Commercially available isopropylamine, salicylaldehyde, and p-hydroxy-benzaldehyde were used to follow the kinetics of the formation reaction. The formation equilibrium constant, K_F, defined as K_F = [S]/[ald][am] where [S] = [P] + [Q], was determined for the salicylideneisopropylamine following the procedure of Green, *et al.*[5]

(1) (a) Part I: W. Bruyneel, J. J. Charette, and E. de Hoffmann, *J. Amer. Chem. Soc.*, **88**, 3808 (1966); (b) part II: R. Herscovitch, J. J. Charette, and F. de Hoffmann, *ibid.*, **95**, 5135 (1973).

(2) University of Louvain.

(3) (a) A. V. Willi, *Helv. Chim. Acta*, **39**, 1193 (1956); (b) E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.*, **84**, 832, 4319 (1962); (c) W. Reeves, *J. Org. Chem.*, **30**, 3129 (1965).

(4) J. Hoffmann, J. Klicnar, V. Sterba, and M. Vecera, *Collect. Czech. Chem. Commun.*, **35**, 1387 (1970).

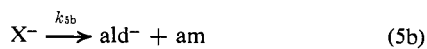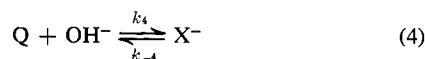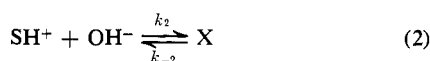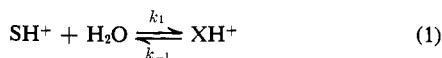(5) P. W. Green and P. W. Alexander, *Aust. J. Chem.*, **18**, 399 (1965).

Table I. Rate Constants for the Hydrolysis of N-Salicylidene-2-aminopropane Derivatives[a]

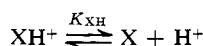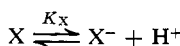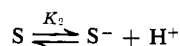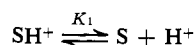| Substituent	Obsd (first order), min^{-1}				Calcd		
	1	2	3	4	5	6	7
H	0.014	0.13	0.060	7.2	2.5×10^{-3}	9.1×10^{-12}	1.4×10^{2}
4-NO$_2$	0.57	3.2	0.18	5.0	1.35×10^{-1}	6.3×10^{-10}	1.6×10^{2}
4-CH$_3$	0.006	0.04	0.021	4.8	8.5×10^{-4}	3.4×10^{-12}	2.0×10^{2}
5-NO$_2$	0.34	1.1	0.044	5.5	1.05×10^{-1}	5.1×10^{-10}	1.7×10^{2}
5-Cl	0.087	0.55	0.093	5.2	1.27×10^{-2}	5×10^{-11}	1.1×10^{2}
5-OCH$_3$	0.020	0.25	0.10	4.8	5.1×10^{-3}	1.3×10^{-11}	2.5×10^{2}

[a] 1, at pH 1.2. 2, at the maximum between pH 2 and 4. 3, at the neutral pH-independent rate, $k_{obsd} = k_3[H_2O]$. 4, at pH 14 5, for the attack of water on the conjugate acid of the Schiff base, k_1 (min^{-1}/mol^{-1} l.). 6, For the attack of hydroxyde ion on the neutral quinoid tautomer, $k_4 K_w$ (min^{-1} mol l.$^{-1}$). 7, k_{-1}'/k_{5a} (mol^{-1} l.).

At 30° and ionic strength 0.1, a value of 1.9×10^4 mol^{-1} l. was found for K_F, in good agreement with the one (5.62×10^4) observed by Green for N-salicylidene-n-butylamine.

Dissociation constants for proton addition to the free base S (K_1) and to its anion S$^-$ (K_2) were determined as described in part I, except for the 4-NO$_2$ derivative for which K_2 has been estimated from the plot of the observed rate constants against pH in the region between pH 7 and 14. This estimation is obtained from an analysis of the steady state rate equation for the hydrolysis reaction. 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. The hydrolysis reaction may be formulated as

$$SH^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XH^+ \qquad (1)$$

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

$$Q + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} X \qquad (3)$$

$$Q + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X^- \qquad (4)$$

$$X \overset{k_{5a}}{\longrightarrow} ald + am \qquad (5a)$$

$$X^- \overset{k_{5b}}{\longrightarrow} ald^- + am \qquad (5b)$$

$$XH^+ \overset{k_{5c}}{\longrightarrow} ald + amH^+ \qquad (5c)$$
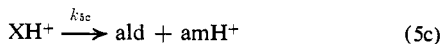
Dissociation constants are defined as

$$SH^+ \overset{K_1}{\rightleftharpoons} S + H^+$$

$$S \overset{K_2}{\rightleftharpoons} S^- + H^+$$

$$X \overset{K_X}{\rightleftharpoons} X^- + H^+$$

$$XH^+ \overset{K_{XH}}{\rightleftharpoons} X + H^+$$

X being the carbinolamine intermediate.

Reaction 5c is negligible, as may be seen from the absence of a leveling off at very low pH values, especially for the 4-CH$_3$ derivative for which the rate constant has been measured at pH 0.15 ($k_{obsd} = 3 \times 10^{-4}$ min^{-1}). Assuming further that [S] = [Q],[1b] the rate expression is

$$k_{obsd} =$$
$$\frac{\{k_1[H_2O][H^+] + k_2 K_w + k_4 K_1[OH^-] + k_3 K_1[H_2O]\}\{k_{5a} + (k_{5b}K_X/[H^+])\}}{\{K_1 + [H^+] + (K_1 K_2/[H^+])\}\{(k_{-1}[H^+]/K_{XH}) + k_{-2} + k_{-3} + (k_{-4}K_X/[H^+]) + k_{5a} + (k_{5b}K_X/[H^+])\}} \qquad (6)$$

In the acidic pH region where K_1 is small in respect to [H$^+$] and reactions 2, 3, 4, and 5b are negligible, the rate-determining step is the decomposition of the carbinolamine intermediate. Accordingly, eq 6 reduces to

$$k_{obsd} = k_1[H_2O]/[1 + (k_{-1}'[H^+]/k_{5a})] \qquad (7)$$

with $k_{-1}' = k_{-1}/K_{XH}$. In the pH region where H$^+$ is not greater than K_1, the rate-determining step is the formation of the intermediate so that the inverse reactions 1, 2, 3, and 4 are negligible with respect to 5a and 5b. Hence eq 6 reduces to

$$k_{obsd} =$$
$$\frac{k_1[H_2O][H^+] + k_2 K_w + k_4 K_1[OH^-] + k_3 K_1[H_2O]}{K_1 + [H^+] + (K_1 K_2/[H^+])} \qquad (8)$$

At neutral and alkaline pH's reaction 1 is negligible with respect to 2, 3, and 4 and eq 8 reduces to

$$k_{obsd} = \frac{(k_2 K_w/K_1) + k_4[OH] + k_3[H_2O]}{1 + (K_2/[H^+])} \qquad (9)$$

In the region around pH 7, the specific rate remains constant and the terms containing [OH] and [H$^+$] can be neglected; eq 9 reduces to

$$k_{obsd} = k_{(7)} = (k_2 K_w/K_1) + k_3[H_2O] \qquad (10)$$

If reaction 3 is negligible

$$k_{(7)} = k_2 K_w/K_1 \qquad (11)$$

whereas, if reaction 2 is negligible

$$k_{(7)} = k_3[H_2O] \qquad (12)$$

At pH 14, $k_{obsd} = k_{(14)}$ is at least 25 times greater than $k_{(7)}$. The latter is hence negligible in the expression of $k_{(14)}$ which may be written as

$$k_{(14)} = k_4 K_w/K_2 \qquad (13)$$

From eq 9, 10, and 13 it can be seen th at for $k_{obsd} = (k_{(7)} + k_{(14)})/2$ one obtains $K_2 = [H^+]$. The values of K_2 thus obtained agree with the ones deduced from the changes in the ultraviolet absorption curves with pH (part II). Equation 13 permits the evaluation of k_4.

In the region between neutral and acidic pH's, before the leveling off, eq 8 reduces to

$$k_{obsd} = \frac{k_1[H_2O][H^+] + k_2 K_w + k_3 K_1[H_2O]}{K_1 + [H^+]} \qquad (14)$$

Comparing eq 10 and 14 yields

$$k_{obsd} = \frac{k_1[H_2O][H^+] + K_1 k_{(7)}}{K_1 + [H^+]} \qquad (15)$$

k_1 is then evaluated from the measured k_{obsd} at several values of [H$^+$]. All the kinetically significant constants are given in Tables I and II. For the establishment of Hammett correlations, the Taft σ^0 value for p-CH$_3$ is often better than Brown–Okamoto[7] σ^+ owing to the strong ortho-resonance effect of OH. For comparison purposes slopes of correlation plots have been recalculated from Cordes and Jencks[3b] data after elimination of para-resonating substituents.

Results and Discussion

In Figure 1, the logarithms of the observed rate con-

(6) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(7) H. C. Brown and J. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).
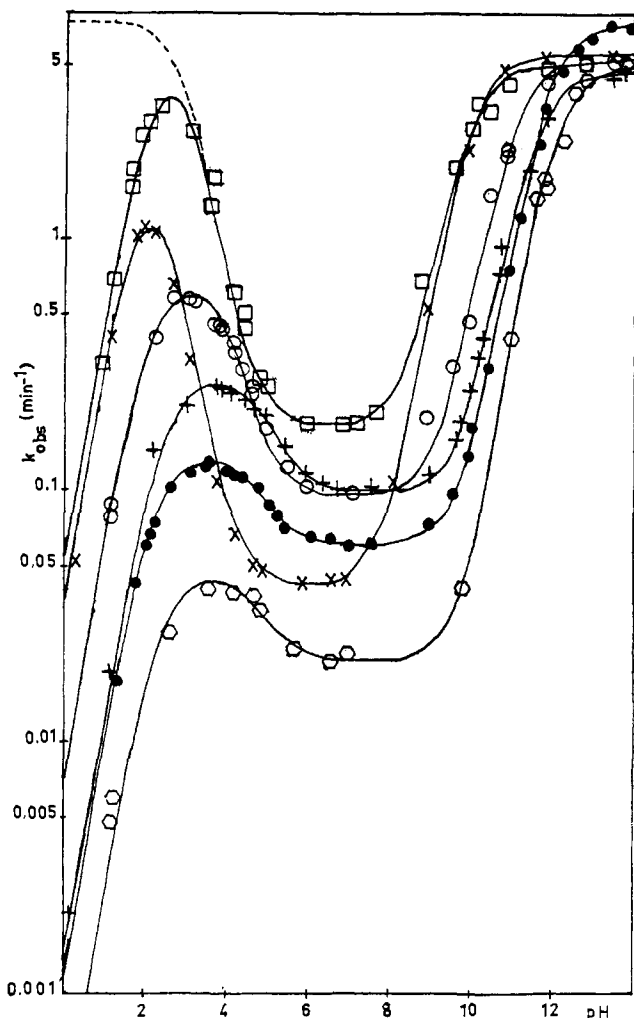
Figure 1. Logarithm of the first-order rate constants for the hydrolysis of substituted N-salicylidene-2-aminopropanes at 30° as a function of pH. Curves calculated from eq 6. Experimental points: (●) H; (□) 4-NO₂; (○) 4-CH₃; (X) 5-NO₂; (○) 5-Cl; (+) 5-OCH₃. The theoretical curve for the formation of the carbinolamine intermediate is indicated by a dashed line for the 4-NO₂ derivative.

Table II. Dissociation Constants of Substituted
N-Salicylidene-2-aminopropanes[1b]

| Substituent	pK_1	pK_2
H	4.70	11.90 (11.95)[b]
4-NO₂	2.93	(9.90)[b]
4-CH₃	4.74	12.16 (12.2)[b]
5-NO₂	2.0[a]	10.03 (10.0)[b]
5-Cl	4.05	11.02 (10.9)[b]
5-OCH₃	4.89	11.55 (11.6)[b]

[a] Value adjusted for best fit of the kinetic curve with experimental points. [b] Values given in parentheses were obtained from the kinetic curves.

stants for the hydrolysis of a series of substituted salicylidene-2-aminopropanes are plotted as a function of pH over the pH range 0–14. The curves drawn through the experimental points are calculated by use of eq 6. The rate constants have been extrapolated to zero buffer concentration for the borax/boric acid buffer. For the other buffers, it has been verified that, under the experimental conditions, the buffer concentration had no noticeable influence on the rate constants.

The kinetic behavior in the acidic region agrees with
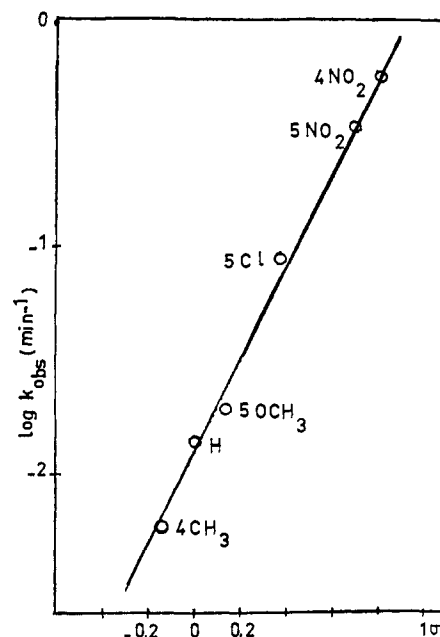
Figure 2. Logarithm of the first-order rate constants for the hydrolysis of substituted N-salicylidene-2-aminopropanes at pH 1.2, at 30°, plotted vs. σ°.
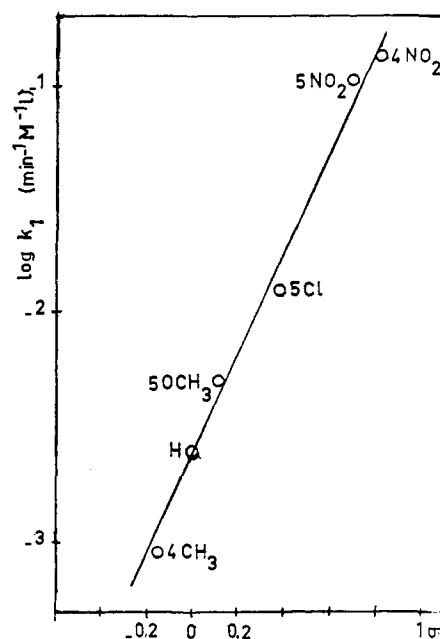
Figure 3. Logarithm of the calculated second-order rate constants for the attack of water on the conjugate acid of substituted N-salicylidene-2-aminopropanes, at 30°, plotted vs. σ°.

the mechanism proposed by Cordes and Jencks,[3b] i.e., the transition, with decreasing pH, from the formation of the carbinolamine intermediate to its decomposition, as the rate-determining step. At pH 1.2, the observed rate constants for substituted salicylidenes correlate with the σ^0 Taft constants with a ρ value of 2.0 which is similar to the one (2.36 at pH 1) obtained from Cordes and Jencks' data (see Figure 2).

Contrary to what has been observed with the benzylidene-*tert*-butylamines, the above mentioned transition occurs, in the cases of our products, before the protonation of the Schiff bases is completed. This fact
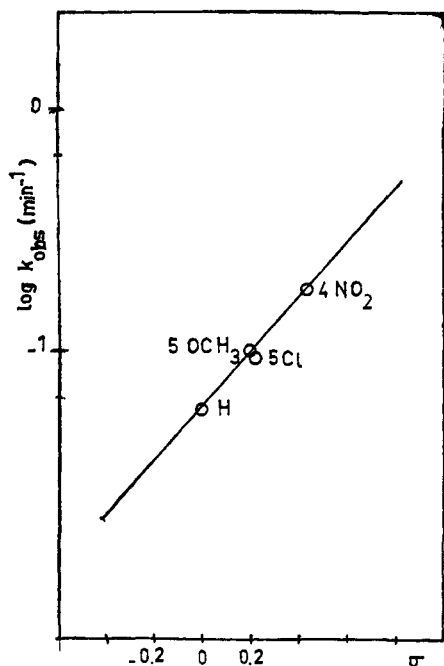
Figure 4. Logarithm of the first-order rate constants for the hydrolysis of substituted N-salicylidene-2-aminopropanes observed at neutral pH, at 30°, plotted $vs.$ $\sigma = \sigma_{CN} - 0.56\sigma_{CO}$, para-resonating substituents being omitted.

Figure 5. Logarithm of the rate constants k_4K_W for the attack of hydroxide ion on the quinoid tautomer of substituted N-salicylidene-2-aminopropanes, at 30°, plotted $vs.$ $\sigma°$.

is illustrated in Figure 1 where the theoretical curve calculated by eq 8 for the 4-NO_2 derivative, as an example, is indicated by a dashed line. Accordingly, the observed maximum rate constants are not correlated with σ values, while the second-order constants k_1, calculated according to eq 15, do obey the Hammett correlation with a slope (2.18) similar to the one (1.97) obtained from Cordes and Jencks' data (see Figure 3).

The invariance of the observed rate constant over more than one pH unit around pH 7 may be accounted for in two ways: reaction between the conjugate acid and hydroxide ion (eq 2), or reaction between a neutral form and water. Up to now, the first mechanism has been generally accepted. Accordingly, the second-order rate constant may be calculated by eq 11. However, the values thus obtained for k_2 present large anomalies. First, the calculated constant for N-salicylidene-2-aminopropane (7.2 × 10⁷) differs by one order of magnitude from the one of the methoxy analog (6.8 × 10⁶), while the corresponding para compounds have the same value of k_2.[1a] This difference can hardly be attributed to steric effects because they should produce at least the same difference in the k_1's. Second, one observes a large difference in the effects of substituents on k_2 between salicylidene ($\rho = 3.37$) and benzylidene ($\rho = 1.03$ from Cordes and Jencks' data) derivatives, the substituent effects on k_2 becoming larger than on k_1 for the salicylidenes. As a consequence, we must admit that the addition of water to the neutral Schiff base is the predominant mechanism in this pH range for the salicylidene derivatives. This new mechanism must be related to the presence of the Q tautomer in large excess (see part II). The predominance of reaction 3 in this case is corroborated by the relative magnitude of the terms in eq 10. By taking as a good approximation $k_2(o\text{-OH}) = k_2(o\text{-OCH}_3)$, the contribution of the first term is found to be only 8% for the
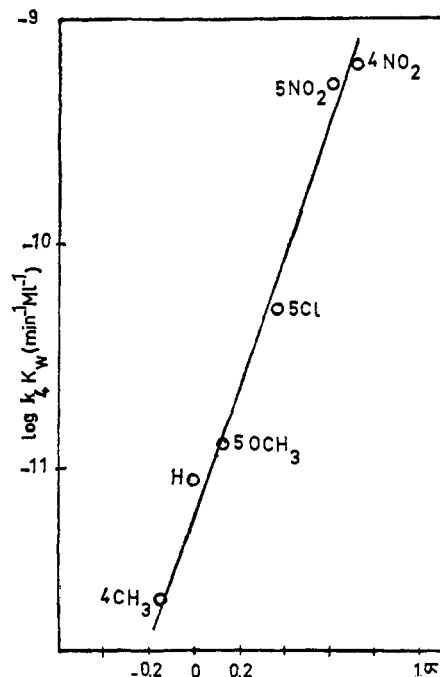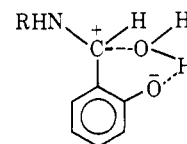
unsubstituted salicylidene. The values of k_3 calculated by eq 12 clearly show that the 4 and the 5 substituents have opposite influence on the reaction. This fact points to a two-center mechanism for the addition of water.

$$\text{RHN} \overset{+}{\diagdown} \underset{\underset{\displaystyle O'}{|}}{\overset{\displaystyle H}{\underset{|}{C}}} \text{---} O \diagdown \overset{\displaystyle H}{\underset{\displaystyle H}{\diagup}}$$

This reaction is kinetically possible in spite of the fact that the zwitterion exists chiefly in the intramolecular H-bond form. The specific rate for this reaction is $k_3 = 1.08 \times 10^{-3}$ min⁻¹ mol⁻¹ l. which is very low as compared, for example, to the k_2 value of the methoxy analog (6.8 × 10⁶). We believe that the value of k_3 for the benzylidene derivatives would be still lower, owing to the absence of the strongly dipolar structure of the Q form and of the favorable position of the reacting centers. Such a mechanism is of course not possible in the case of the p-hydroxybenzylidene. In order to take into account the opposite influence of the substituents on the reacting centers, the following Hammett-type equation has been devised: $\Delta \log k_3 = \rho(\sigma_{CN} - \alpha\sigma_{CO})$, where σ_{CN} is σ_p for a 4 substituent and σ_m for a 5 substituent, while σ_{CO} is σ_p for a 5 substituent and σ_m for a 4 substituent. With $\alpha = 0.56$ a good correlation was obtained as may be seen in Figure 4 ($\rho = 1.12$).

In the region of alkaline pH's, the observed rate constant increases until it reaches a constant value around pH 13–14. This behavior was explained[1a] by the increasing influence of a new mechanism, $i.e.$, the addition of hydroxide ion to the Q tautomer (eq 4). This new mechanism is here further confirmed by the study of the substituent effects. The substituents have opposite effects on the concentration of the neutral Q form and on the charge at the reaction site. Accord-

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Scheme I. R = CH(CH₃)₂
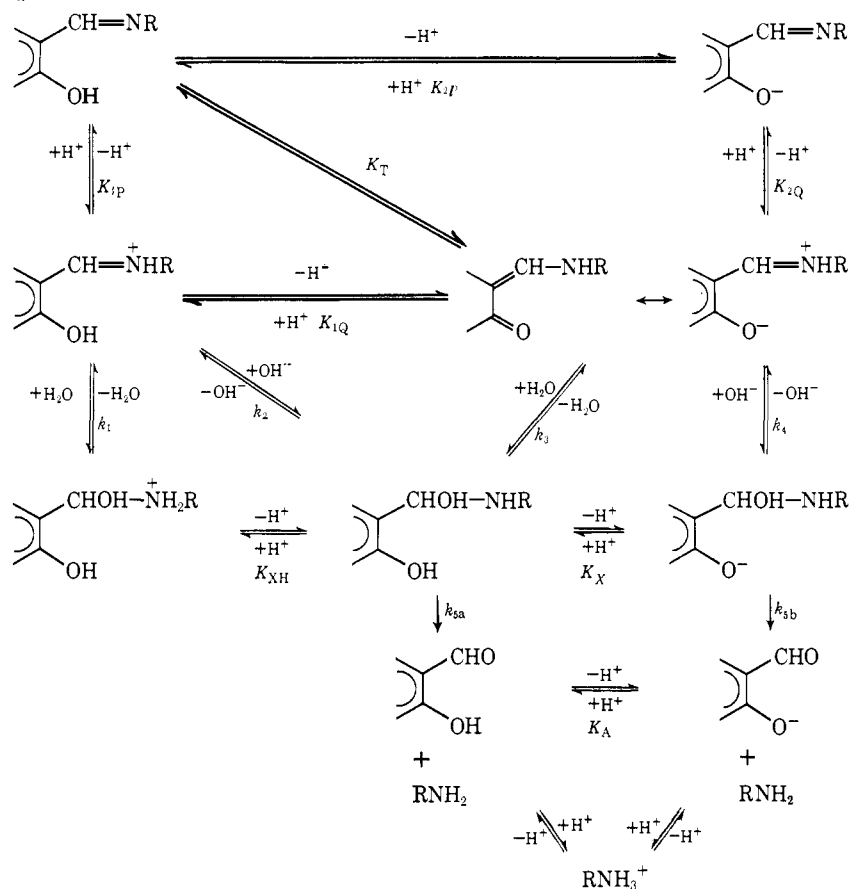
ingly, the k_{obsd} at pH 14 are expected to be rather insensitive to substituent effects, while the other a priori conceivable mechanism, addition of water to the ion of the Schiff base, would cause a strong influence of substituents on $k_{(14)}$. As a matter of fact, the observed values of $k_{(14)}$ are about the same for all the substituted

salicylidenes. If, however, reaction 4 is isolated, the calculated values of k_4 depend strongly on the σ's as may be seen in Figure 5 ($\rho = 2.85$).

All the kinetically important reactions, under the experimental conditions where hydrolysis was studied, are depicted in Scheme I.

Rates and Products of Addition of 4-Chlorobenzenesulfenyl Chloride to the *tert*-Butylethylenes[1]

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Contribution from the Department of Chemistry, University of Toronto, Toronto M5S 1A1, Canada. Received February 19, 1974

Abstract: The rates of addition of 4-chlorobenzenesulfenyl chloride to ethylene (1), *tert*-butylethylene (2), 1,1-di-*tert*-butylethylene (3), cis- (4) and *trans*-1,2-di-*tert*-butylethylene (5) and 1,1,2-tri-*tert*-butylethylene (6) have been measured in 1,1,2,2-tetrachloroethane at 25°. The relative rates of **1:2:3:4:5:6** are $1:1.5:4.9 \times 10^{-4}:13:8.2 \times 10^{-5}:1.3 \times 10^{-4}$. The rate difference of 1.6×10^5 between cis- and *trans*-1,2-di-*tert*-butylethylene is the largest yet reported for addition to a cis–trans pair of isomeric alkenes. All products are formed by stereospecific anti addition. The experimental results are interpreted in terms of rate-determining formation of episulfonium ion intermediates which are converted to products by displacement by chloride ion. The rate differences are primarily due to steric hindrance to the approach of the electrophile in the rate-determining transition state.

Alkenes substituted with bulky hydrocarbon groups are of considerable utility in both experimental and theoretical studies of the effects of structure on

(1) Reactions of Sulfenyl Chloride and Their Derivatives. XI. For Part X, see G. H. Schmid and D. G. Garratt, *Can. J. Chem.*, **52**, 1807 (1974).

chemical properties. The large substituents distort the ground-state geometries of the molecules, and thereby affect their reactivities relative to unstrained analogs. In addition the transition-state energies for reactions of alkenes are affected in two opposing ways by bulky substituents. On the one hand, significant repulsions