KINETICS AND MECHANISM OF HYDROLYSIS OF 3'- AND 4'-SUBSTITUTED BENZYLIDENE-2-HYDROXY-5-METHYLANILINES

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The dependence of hydrolysis rate of six benzylidene-2-hydroxy-5-methylaniline derivatives on pH resp. H_0 has been measured. In the diluted sulphuric acid medium a linear dependence of the experimental rate constant on H_0 has been found, the slope being 1·52. The log k_{exp} values read at H_0 −3·5 correlated with the substituent constants according to the Yukawa-Tsuno equation, the constants ϱ and r being 1·79 and 0·60, respectively. The water-catalyzed decomposition of the protonated carbinolamine into products is rate-determining for all the derivatives in this medium. In buffer media the formation of the intermediate becomes rate-limiting for some derivatives. The log k_{exp} values measured in those pH regions where the protonated Schiff's base reacted with water or OH^- ion and the neutral base reacted with OH^- ion were correlated with the σ constants calculated from the Yukawa–Tsuno equation. In all the cases the correlation found showed a break caused by a change in the rate-limiting step of the reaction. The values of the dissociation constants of the neutral Schiff's bases were determined by direct measurements of spectra and correlated with the σ constants. From the pH dependence of log k_{exp} of the 3'-nitro derivative determined by the stopped-flow method the pK_a value of this protonated base has been estimated.

In the foregoing papers[1-3] the hydrolysis kinetics was studied of the Schiff's bases substituted at the aniline nucleus and having a relatively strong intramolecular hydrogen bond in the neutral molecule. The formation and decomposition of the intermediate are the rate-determining steps of the hydrolysis of the derivatives substituted by σ-positive and σ-negative substituents, respectively, in buffer solutions. The rate of decomposition of the protonated carbinolamine into products decreased with decreasing concentration of the basic buffer component and water, so that in diluted sulphuric acid media this step becomes rate-limiting for all the derivatives.

The aim of the present work was to study the influence of acidity of medium and of the substituents in the benzylidene nucleus on the hydrolysis rate of 3'- and 4'-substituted benzylidene-2-hydroxy-5-methylanilines.

EXPERIMENTAL

Preparation of anils. All the anils were prepared by mixing the methanolic solutions of equimolecular amounts of 3-amino-4-hydroxytoluene and the respective aldehyde[4]. The resulting mixtures were boiled for a short time, and the Schiff's bases formed were collected by suction and recrystallized from methanol[4,5]. 4′-Methylbenzylidene-2-hydroxy-5-methylaniline (yellow crystals melting at 84—84·2°C) was obtained in a similar way; for $C_{15}H_{15}NO$ (225·3) calculated: 79·97% C, 6·71% H, 6·22% N; found: 79·75% C, 6·53% H, 6·09% N.

Kinetic measurements were carried out similarly as in the previous reports[1-3] in aqueous-ethanolic medium (22% by vol. ethanol), diluted sulphuric acid, diluted hydrochloric acid, chloroacetate, acetate, phosphate and carbonate buffers and in a mixture sodium hydroxide–potassium chloride. The constant ionic strength 0·100 was maintained by addition of potassium chloride up to pH 1·18, further, the ionic strength increased with increasing acid concentration. A small amount of ascorbic acid ($0·5—1·0 . 10^{-3}$ mol/l) was added into the buffer before the hydrolyses in neutral and alkaline media in order to prevent the undesirable subsequent reaction of the 3-amino-4-hydroxytoluene formed by hydrolysis.

In diluted sulphuric acid (H_0 −2 to −4) and in media of pH > 5 the hydrolysis was so slow at 22°C that it could be followed spectrophotometrically by means of the Unicam SP-800 apparatus and 4 cm cells[1-3]. In media of pH 5 to 0 the velocity was measured by the stopped-flow method using a Durrum Stopped-Flow Spectrophotometer Model D 110. The stock solution of the Schiff's base in absolute ethanol was prepared as it is described in ref.[3], and it was diluted just before the measurement with water to give 44% by vol ethanol containing a small amount of phosphate buffer of pH about 8. During the proper measurement this solution was mixed with the same volume of aqueous buffer in the mixing chamber of the apparatus thermostated at 22°C. The Schiff's base concentration in the reaction medium was about $1—2 . 10^{-5}$ mol/l. The sulphuric acid concentration was determined by titration with sodium hydroxide; pH of the solution was measured by means of a pHM 4c apparatus (Radiometer, Copenhagen).

RESULTS AND DISCUSSION

The reaction studied takes a pseudomonomolecular course in all the cases, and it is 1. order in the Schiff's base. The time dependence of the extinction logarithm was linear up to at least 70% of the reaction.

Influence of Basicity of Medium on Hydrolysis Rate

Acid-base reactions of this type of Schiff's bases can be represented by the following Scheme 1.

The pH resp. H_0 dependences of logarithm of experimental rate constants of hydrolyses of three benzylidene-2-hydroxy-5-methylaniline derivatives (4′-methoxy, 3′-nitro, and the unsubstituted derivative) are given in Fig. 1. The H_0 acidity function of the system water–sulphuric acid was used as in the ref.[3], in order to enable the mutual comparison of reactivities of individual derivatives. Of course, the other less frequent acidity functions could serve the same purpose, too.

During hydrolysis in aqueous buffers the value of experimental rate constant depends only on pH, and it is independent of buffer concentration. At pH < 7 the
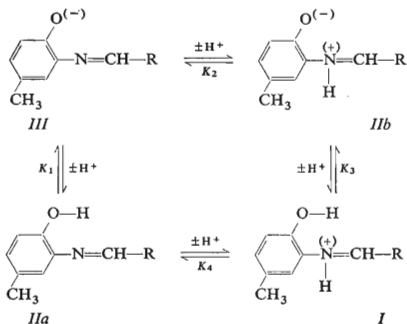
SCHEME 1

protonated Schiff's base reacts with water so that the hydrolysis rate is directly proportional to the concentration of this form. At a pH about $1·5$ the reaction rate reaches its maximum value, because practically all the Schiff's base is in its protonated form, and the water activity equals unity. In the pH range $8-9·5$ the reaction of the protonated form with OH^- ions predominates, and the experimental rate constant is independent of the acidity of medium. At higher pH values the neutral Schiff's base dissociates to a gradually increasing extent, which makes itself felt (in the case of the 3'-nitro derivative) by a decrease of the hydrolysis rate. With increasing pH the experimental rate constant becomes again pH-independent, because the
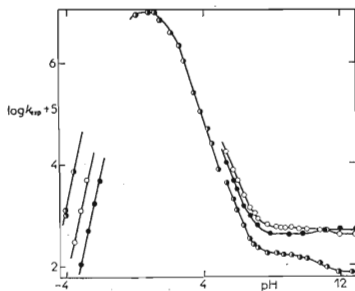

FIG. 1

pH resp. H_0 Dependence of Hydrolysis Rates of Benzylidene-2-hydroxy-5-methylanilines

4'-Methoxy (●), unsubstituted (○) and 3'-nitro derivative (◑). The rate constants are given in s^{-1}.

reaction of neutral form of the Schiff's base with OH^- ions becomes increasingly significant kinetically. This decrease diminishes with increasing σ value of the substituent down to the 4'-methoxy derivative where, on the contrary, a slight increase of the dependence again begins (Fig. 1), because here the reaction of the neutral Schiff's base with OH^- ion makes itself felt kinetically sooner than its dissociation.

In the medium of diluted sulphuric acid the reaction rate strongly decreases with increasing $-H_0$ value, the angular coefficient being 1·59. The decomposition of the protonated carbinolamine is rate-determining in this medium (as it was the case with hydrolysis of p-trimethylamoniumbenzylidene-p'-hydroxyanilinium chloride[6] and N-(5-methylsalicylidene)anilines[3]), so that water acts both as a nucleophile and base, binding the proton of the OH group of the carbinolamine (Scheme 2).

$R = \underset{}{\underbrace{}}\!\!-X$, $X =$ H, 4'-CH_3, 4'-OCH_3, 3'-Cl, 3'-NO_2, 4'-NO_2
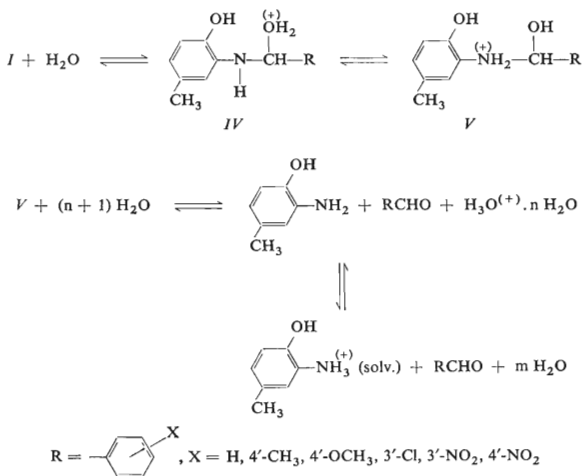
SCHEME 2

The logarithms of the experimental rate constants read at H_0 $-3\cdot5$ were correlated with the substituent constants according to the Yukawa–Tsuno equation[7] (Eq. (1)).

$$\log k = -2\cdot39 + 1\cdot79 \left(\sigma + 0\cdot60\,\Delta\sigma^+\right) \tag{1}$$

The value $r = 0\cdot60$ points at the mesomeric effect of methyl and methoxy groups being more significant in the initial state than in the activated complex.

Reaction of Unprotonated Schiff's Base with OH⁻ *Ion*

At pH > 12 the hydrolysis rate is pH-independent, as almost all the substrate is present in the form of anion; consequently, the concentration of neutral Schiff's base reacting with OH⁻ ion is directly proportional to the proton concentration. The experimental rate constant is defined by Eq. (2)

$$k_{exp} = k_{OH} \cdot K_w / K_2 , \qquad (2)$$

where K_w and K_2 are the dissociation constants of water and the reacting tautomer of the Schiff's base, respectively, and k_{OH} is the rate constant of the proper reaction with OH⁻ ion. Log k_{exp} values (Table I) were correlated with the Hammett σ constants (Fig. 2, curve a) except for 4′-methyl- and 4′-methoxy derivatives, where the σ constants calculated from Eq. (1) were used. We supposed that these constants would better reflect the influence of the substituent on both the proper reaction and antecedent equilibrium. The dependence shows a break (which decidedly is not caused by the σ constants used) characteristic for cases in which a change of substituents causes a change in the rate-limiting reaction step[8]. The experimental ϱ constants have the values 0 and −1 in the left (derivatives with σ-negative substituents) and right parts of the correlation, respectively, and they are given by the difference of ϱ constants of the proper reaction and that of the antecedent equilibrium. Electron-withdrawing substituents enable the proper reaction with OH⁻ ion and, hence, the ϱ constant of this step must have a positive value. As the ϱ_{exp} equals −1, the ϱ constant of dissociation must be greater than unity. The values of logarithms of dissociation constants (dissociation of neutral Schiff's base) determined by direct measurement

TABLE I
Measured Values of log k_{exp} of Hydrolysis of Benzylidene-2-hydroxy-5-methylanilines Used in Hammett Correlations

The rate constants are given in s⁻¹.

Derivative		log k_{exp} + 5 in the region of pH		
		12[a]	8–9·5[b]	6[c]
H	(1)	2·60	2·72	3·69
4′-CH₃	(2)	2·71	2·74	3·66
4′-OCH₃	(3)	2·70	2·63	3·46
3′-Cl	(4)	2·20	2·45	3·42
3′-NO₂	(5)	1·86	2·22	3·09
4′-NO₂	(6)	1·80	2·15	3·04

The rate constants is defined [a] by Eq. (2), [b] by Eq. (3), [c] by Eq. (5).

correlated with the σ constants, the value of ϱ being 0·35 (substituent and log K_a are given: 4′-OCH$_3$ −10·92, 4′-CH$_3$ −10·84, H −10·81, 3′-Cl −10·67, 3′-NO$_2$ −10·57, 4′-NO$_2$ −10·52).

Protonation of the anion *III* gives two tautomers *IIa* and *IIb*, the latter being more stable thermodynamically and present in a far grater amount; therefore, the measured values of K_a and ϱ correspond practically to the dissociation constants of the tautomer *IIb* to give the respective anion (K_1). From the influence of substituents on the overall reaction and from the above discussion it follows that the second tautomer *IIb* is the main reacting species during hydrolysis; it is present in a far smaller amount, but it is far more reactive, because the N=C bond is more strongly polarized. In contrast to the first tautomer *IIa*, the proton is split off from the nitrogen atom of the tautomer *IIb* and, therefore, the ϱ value will be relatively high. By this condition is fulfilled the ϱ value of the antecedent equilibrium must be greater than unity. The mesomeric effects of 4′-methoxy and 4′-methyl groups will be more significant with the tautomer *IIb* than with *IIa*, which was the reason for our presumption that
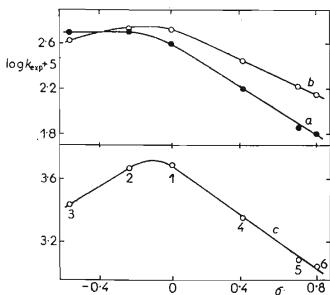

FIG. 2

Hammett Correlation of Experimental Rate Constants (s^{-1}) of Hydrolysis of Benzylidene-2-hydroxy-5-methylanilines in Alkaline (*a*), Neutral (*b*) and Acid (*c*) Media (pH 6)

The exalted σ value −0·24 was used for the 4′-methyl derivative, and the value −0·57 calculated from Eq. (2) was used for 4′-methoxy derivative. The ϱ values read from the graph are for the left and right part of the correlation, respectively: curve *a* $\varrho \approx 0$, −1·0; *b* $\varrho \approx 0·4$, −0·7; *c* $\varrho \approx 0·60$, −0·80.
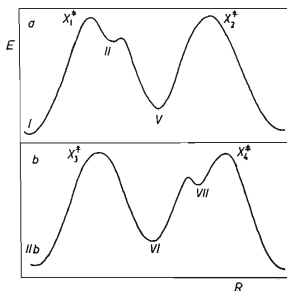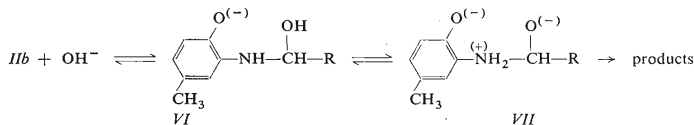
FIG. 3

Presumed Dependence of Energy (*E*) on Reaction Coordinate (*R*) for Reaction of Protonated Schiff's Base with Water (*a*) or Its Neutral Form with OH$^-$ Ion (*b*)

it would be better to use the same σ constants for the dissociation constants as for the proper reaction (see above). The whole reaction mechanism can be expressed by the following scheme:

SCHEME 3

The rate-determining step may consist either in formation or in decomposition of the intermediate *VI* depending on the nature of the substituent. In order to be able to find which step is rate-determining for a certain substituent, it is necessary to consider the influence of the substituent on individual steps and have at least an approximative knowledge about the relative energies of the activated complexes and intermediates. A rough estimate of the dependence of energy on the reaction coordinate of the proper reaction is given in Fig. 3. The energy difference between the intermediate *VI* and the activated complex $X_3^{\ddagger}$ as well as that between *VII* and $X_4^{\ddagger}$ increase with increasing positive value of σ constant. As the reverse decomposition into the starting substances is far more energy-demanding than the transformation into products, it is very probable that the influence of the substituent on the first step will be greater, too, so that the energy difference between the intermediate *VI* and the activated complex $X_3^{\ddagger}$ will increase faster with increasing value of the σ constants, and the first step will become rate-limiting.

Reaction of Protonated Schiff's Base with OH^- *Ion*

This reaction predominates in the pH range $8-9.5$ (Fig. 1). As in the foregoing case the experimental rate constant is defined by Eq. (3), where K_4 means the constant of dissociation of the

$$k_{exp} = k_{OH}^+ \cdot K_w / K_4 \qquad (3)$$

protonated Schiff's base into the tautomer *IIa* (Scheme 1), and k_{OH}^+ stands for the rate constant of the reaction of the protonated form with OH^- ion. The correlation of log k_{exp} (Table I) with the same substituent constants as those used in the foregoing case shows again a break, the respective ϱ values being about $+0.4$ and -0.7 (Fig. 2, curve *b*). The mechanism of the proper reaction is analogous to that of the reaction of the neutral Schiff's base with OH^- ion (Scheme 3), the only difference being the presence of *ortho* —$O^{(-)}$ group instead of the *ortho* —OH group in the aniline nucleus. Therefore, the overall interpretation of the reaction and substituent influence on the change of the rate-determining step is analogous, too.

There were serious objections[9] raised against the interpretation of the break

in the Hammett dependence of the hydrolysis of Schiff's bases as being caused by the change in the rate-determining step. The breaks found were explained by that the concentration of the second tautomer *IIb* increased with decreasing σ constant value to such an extent, that the dependence of logarithms of dissociation constants of the protonated Schiff's bases on the σ constants was not linear and, hence, the dependence of log k_{exp} *vs* σ could not be linear either[9]. The following are the reasons for our interpretation of the break as being caused by a change in the rate-limiting step: *1)* The overall reaction mechanism as well as the dependence of the rate constants on the substituents are analogous to those of the reaction of neutral Schiff's base with OH⁻ ion, and it is, therefore, logical that also the interpretation will be similar in this case. *2)* If such a great break as that found in the present case were caused by a change in the tautomers ratio, the respective tautomer *IIb* should predominate with 4'-methoxy derivative. In correlation of pK_a *vs* σ constants, however, this should necessarily lead to a marked increase in the dissociation constant of the 4'-methoxy derivative (by more than a unit — roughly estimated) as compared to the unsubstituted derivative; in fact, the difference found is only about 0·1. *3)* The spectra of the tautomers *IIb* must be very different from those of tautomers *IIa*, and they will show similar characteristics to those of the protonated Schiff's bases[10]. The concentration of the form *IIb* rapidly decreases with decreasing dielectric constant of the medium. When measuring the spectra of the individual derivatives, we have found that all the spectra have similar character, and even in the case of 4'-methoxy derivative the character of spectrum is very much different from those of the protonated Schiff's bases. There was practically no change in spectrum of the 4'-methoxy derivative when going from 22% ethanolic medium to absolute alcohol. From the dissociation constants measured and from the spectra it is obvious that the concentration of the tautomer *IIb* must be very small even with the 4'-methoxy derivative and, hence, the break found cannot be explained by an enormous concentration increase of this tautomer. Therefore, the change of the rate-limiting step remains as the only acceptable explanation of the break in the correlation of log k_{exp} *vs* σ constants.

In both the cases (*i.e.* the reactions of the protonated and non-protonated forms with OH⁻ ions) the experimental ϱ constant is given by a difference of ϱ of the proper reaction and that of the dissociation equilibrium. When appreciating the relative effects of the substituents on the dissociation constants K_2 and K_4 (Scheme 2) we considered the equilibria

$$III + H^+ \xrightleftharpoons{K_1^{-1}} IIa$$

$$IIb + H^+ \xrightleftharpoons{K_3^{-1}} I$$
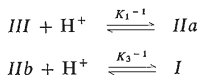
As the protonation takes place at oxygen in the both cases, the constants are small (the value $\varrho = 0.35$ was found for the correlation of log K_1 with the σ constants) and,

hence, also their differences must be very small, and they hardly will be greater than ± 0.1. As the protonation equilibria in Scheme 2 form a closed cycle, the differences of ϱ constants of the two remaining equilibria must be also small. Further we suppose that the ϱ constant of the proper reaction of the protonated Schiff's base with OH^- ions has a slightly higher value than that for the same reaction of the non-protonated anil. This statement may seem surprising at first, because the protonated form is much more reactive and should be, therefore, less selective. In both the neutral and protonated Schiff's base a partial shift of electrons towards azomethine nitrogen atom occurs, and thus a partial positive charge at the benzylidene nucleus is formed, which can be represented by individual resonance structures. In neutral Schiff's base this electron shift results in separation of opposite charges $(Eq. (A))$, whereas energetically advantageous charge diffusion occurs in the protonated form, so that the partial positive charges at the benzylidene nucleus are substantially greater in this case.

$$IIb \quad \longleftrightarrow \quad \text{[structure VIII]} \quad \longleftrightarrow \quad etc. \qquad (A)$$

VIII
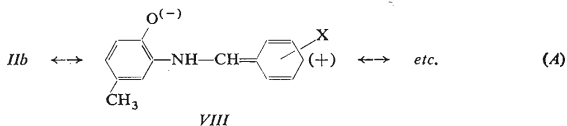
This electron shift does not practically take place in the addition products in the both cases, and the only difference in the polarity of benzene nucleus is due to different inductive effects of $-O^{(-)}$ resp. $-OH$ groups at aniline nucleus. The polarity change of the nucleus carrying the substituent is substantially greater during formation of the adduct from the protonated form than during that from the neutral form and, therefore, also the effect of the substituents on this reaction will be greater. In the activated complexes these polarity changes are only partial and, hence, the effects of the substituents will not make themselves felt to the full extent. The value of the difference in the ϱ constants (deduced on the basis of experimental data) of the proper reaction of the protonated and neutral forms of the Schiff's base with OH^- ion, *viz.* 0.3 ± 0.1, agrees with this theoretical consideration.

Reaction of Protonated Schiff's Base with Water

In media having pH < 7 the reaction of the protonated Schiff's base with water takes place predominantly (Fig. 1). Its concentration is directly proportional to the proton concentration and overall substrate concentration in this region, so that the experimental rate constant is defined by Eq. (4). The hydrolysis mechanism is the same in this region as it is for the

$$k_{exp} = k_{H_2O}^+ [H^+]/K_{SH_2} \qquad (4)$$

reaction in diluted sulphuric acid (Scheme 2) except for the fact that here the antecedent acid–base equilibrium makes itself felt, too. There is, however, a difference in comparing the influence of substituents on the reaction rate, as there can be seen a break in correlation of log k_{exp} (Table I) vs σ constants (Fig. 2, curve c), which suggests that the formation of the protonated carbinolamine is rate-limiting with some derivatives (the values of the experimental ϱ constant $+0.6$ and -0.8). In sulphuric acid the water activity is decreased and, therefore, the energy of the activated complex X_2^* (Fig. 3a) is increased to such an extent that the decomposition of the intermediate V becomes rate-limiting for all the derivatives. An analogous change in the Hammett correlation was observed during hydrolysis of salicylideneanilines, too[3].

On the basis of both the influence of substituents on the individual reaction steps and the dependence of energy on the reaction coordinate (Fig. 3a) we suppose that the formation of the protonated carbinolamine and its decomposition into products are the rate-limiting steps for the derivatives with σ-negative and σ-positive substituents, respectively. As in the reaction with OH^- ion, the activation energy of decomposition of the intermediate into products or starting substances increases with increasing value of σ constant. Whereas in the reaction with OH^- ion the activation energy of the decomposition of the intermediate VI into product is by about 10 kcal higher than that of the decomposition of the intermediate VII into products (this energy difference corresponds to the estimated energy of a proton-transfer from neutral OH to neutral NH group), in the reaction of the protonated anil with water, on the contrary, the activation energy of this step (decomposition of IV into the starting substances) is lower by about 10 kcal for similar reasons. As the interactions of both the protonated azomethine group and carbonyl group with substituents are comparable, it is logical to presume that the relative influence of substituent on the decomposition of the intermediate in the both directions will be opposite, if the energy situation of the reaction is reversed.

The value 1.79 was found for the ϱ constant of the reaction of the protonated Schiff's base with water in diluted sulphuric acid. As the slopes of the dependences log k_{exp} vs H_0 are the same for all the derivatives (Fig. 1), the ratios of rate constants and, hence, the ϱ constants are independent of the medium, too (in the sulphuric acid concentration range investigated). The difference between this value and the experimental value $\varrho = -0.80$ (Fig. 2) found for the derivatives with σ-positive substituents where the decomposition of the intermediate into products is rate-limiting, too, gives directly the value of the ϱ constant of the dissociation of the protonated benzylidene-2-hydroxy-5-methylaniline derivatives: $\varrho_{K_4} = 2.59$. From the ϱ_{K_4} value found and from the value of the dissociation constant of 3'-nitro derivative (log $K_4 = -2.00$) determined from the kinetic data it is possible to calculate the dissociation constants of the other derivatives of these Schiff's bases.

*Quantitative Influence of Substituents on Individual Reaction Steps*

From the calculated value ϱ_{K_4} and experimental ϱ constant $+0.60$ resp. -0.80 (Fig. 2, curve c) of the hydrolysis of derivatives with σ-negative resp. positive substituents we can calculate $\varrho = 3.19$ for the first rate-limiting step (*i.e.* the formation of the inter-

mediate *III* by reaction of the protonated anil with water) resp. $\varrho = 1.79$ for the second rate-limiting step. As the substituent effect acts only slightly (small ϱ) in the reverse reaction, *i.e.* splitting off of water from the protonated carbinolamine, the ϱ constant of the equilibrium $I + H_2O \rightleftharpoons V$ will be about $+3.5$. This estimate seems to be quite reasonable. The value $\varrho_{K_4} = 2.59$ was found for dissociation of the proton-ated Schiff's base. The polar effects of substituents are substantially more significat in the protonated anil than in neutral Schiff's base. However, when the protonated carbinolamine *III* is formed, the positive charge of the nitrogen atom is separated from the benzene nucleus carrying the substituent by a single bond (only inductive effects are possible), and it can thus be expected, that the possibility of formation of a partial positive charge on the nucleus carrying the substituent will be still smaller than that in the case of the non-protonated Schiff's base. Therefore, also the ϱ con-stant of the above mentioned equilibrium will be greater than that of the dissociation of the protonated anil.

If we use the value $\varrho = 2.59$ for the dissociation of the tautomer *IIb* into the respective anion, we get the ϱ values $+1.59$ and $+2.59$ for the reaction of the neutral Schiff's base with OH^- ion having the rate-limiting first and second step, respectively.

In the reaction of the protonated Schiff's base with OH^- ions the calculated values of ϱ constants are $+1.89$ and $+2.99$ for the first and second rate-limiting step, respectively. The ϱ value of the equilibrium $I + OH^- \rightleftharpoons$ intermediate will be sub-stantially greater here $(4-4.5)$ than in the reaction of the protonated Schiff's base with water, because the carbinolamine being formed has no charge at the nitrogen atom (a still greater polarity change).

The ϱ values of the correlations of the hydrolysis rate constants of such derivatives where the second step is rate-limiting increase from $+1.79$ (reaction of the protonated anil with water) to $+2.99$ (reaction of the same form with OH^- ion). The difference in the ϱ constants can be explained by the overall distribution of charges in the res-pective activated complexes. In the first case the OH group of the carbinolamine acts as a nucleophile; the C—N bond is considerably split in the activated complex
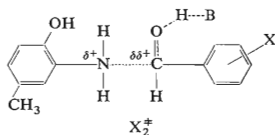
$X_2^{\ddagger}$ and, hence, the partial positive charge is formed at the carbon atom of the alde-hyde being formed. In the second case the negatively charged oxygen atom acts as a very strong nucleophile and the activated complex $X_4^{\ddagger}$ is very close to the inter-mediate in its energy and structure (the Hammond postulate). A slight positive charge is created at the carbon atom of the aldehyde being formed, and the overall

polarity change is substantially greater in this case, the ϱ value being consequently greater, too.

REFERENCES

1. Hoffmann J., Klicnar J., Štěrba V., Večeřa M.: This Journal *35*, 1387 (1970).
2. Hoffmann J., Klicnar J., Štěrba V.: This Journal *36*, 4057 (1971).
3. Hoffmann J., Štěrba V.: This Journal *38*, 2091 (1973).
4. Klicnar J., Kristek F., Bekárek V., Večeřa M.: This Journal *34*, 553 (1969).
5. Kristek F., Klicnar J., Vetešník P.: This Journal *36*, 3608 (1971).
6. Cordes E. H., Jencks W.: J. Am. Chem. Soc. *84*, 832 (1962).
7. Yukawa Y., Tsuno Y., Sawada M.: Bull. Chem. Soc. Japan *32*, 965 (1959).
8. Jencks W. P. in the book: *Progress in Physical Organic Chemistry* (S. G. Cohen, A. Streitwieser jr, R. W. Taft, Eds), Vol. 2. Interscience, New York 1964.
9. de Hoffmann E.: This Journal *36*, 4115 (1971).
10. Bidegaray J. P., Viovy R.: J. Chim. Phys. *66*, 1479 (1969).

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