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NOTE CONCERNING THE KINETICS OF HYDROLYSIS OF SCHIFF BASES OBTAINED FROM SALICYLALDEHYDES

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I have read with interest the paper of Hoffmann and coworkers on the kinetic of hydrolysis of substituted salicylideneanilines[1], and I would like to make the following comments.

In a previous paper[2] we have reported the results of a study on the hydrolysis of hydroxy and methoxy derivatives of N-benzylidene-2-aminopropane. The experimental rate constants for the *ortho* and *para* hydroxy derivatives have been shown to be a function of true rate and equilibrium constants (Eq. (*1*)) corresponding to the mechanism given in Scheme 1.

$$k_{obs} = \frac{k_1 k_4 [H^+] + k_2 k_4 \cdot 10^{14} + k_3 k_4 K_1 [^-OH]}{\{K_1 + [H^+] + K_1 K_2 / [H^+]\} \{k_{-1}[H^+] + k_{-2} + k_{-3}[^-OH] + k_4\}} . \qquad (1)$$

Thus, one has to take into account the existence of a tautomeric equilibrium with an equilibrium constant K_T. The relations (2) between the different equilibrium constants are:

$$K_T = [S]/[T], \quad K_{SH^+} = [S][H^+]/[SH^+], \quad K_{TH^+} = [T][H^+]/[SH^+],$$

$$K_T = K_{SH^+}/K_{TH^+} . \qquad (2)$$
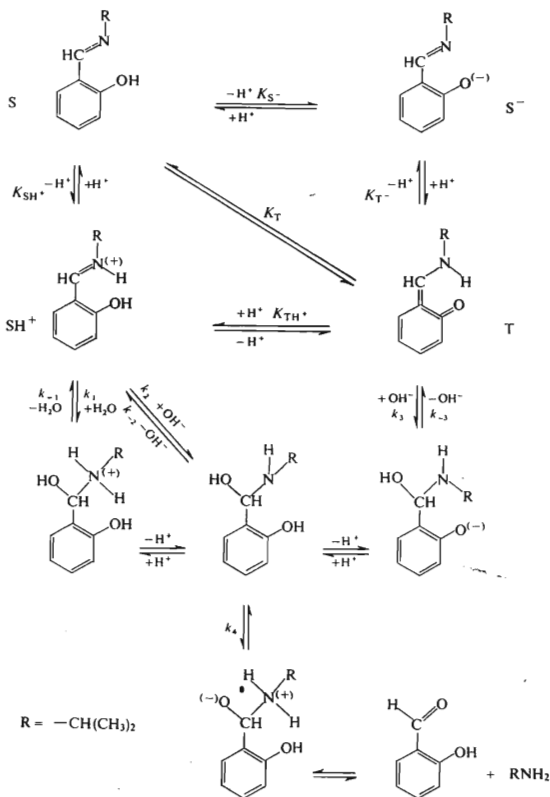
SCHEME 1

The observed acidity constant for the conjugate acid of the Schiff base is related to the real constants by the relation (3):

$$K_1 = ([T] + [S]) [H^+]/[SH^+] = K_{SH^+} + K_{TH^+} = K_{SH^+}(1 + 1/K_T).$$ (3)

Similarly, for the apparent ionisation of the phenolic hydroxyl one obtains Eq. (4):

$$1/K_2 = 1/K_{S^-} + 1K_{T^-}.$$ (4)

The same tautomeric equilibrium exists for the salicylideneanilines derivatives. This equilibrium has been spectroscopically observed by many authors (ref.[3]). More recently Bidegaray and Viovy[4] have reported a semi-quantitative study on this equilibrium. Accordingly, the experimental results of Hoffman and coworkers[1] must be reexamined in the light of the influence of this tautomeric equilibrium. Comparing the shape of the curve of the logarithms of experimental rate constants *versus* pH values obtained by these authors to that obtained for the corresponding N-salicylidene-2-aminopropanes[2], one may conclude that the experimental rate constants are also a complex function of the real rate and equilibrium constants. Even if at the pH of interest some terms may be neglected, it remains that one has to take into account at least one of the two acid-base dissociation constants. These, as shown by Eqs (*3*) and (*4*) are sums of real constants. Furthermore, the tautomeric equilibrium, involving two reaction centers in the same ring, could be a complex function of Hammett's σ constants. Hence, one should not expect that the apparent rate constants should give a straight line when plotted in a Hammett relation. And the fact that there is no linear relation should not be interpreted without further analysis as the consequence of a change in mechanism. For the same reasons, the ϱ value obtained for the dissociation constants of the conjugate acids of substituted benzylideneanilines is not immediately comparable to that expected for salicylidene compounds.

In my opinion the main conclusion of the very good experimental results of Hoffman and coworkers[1] is that the main effect of the *ortho*-hydroxy group is to slow down the reaction rate at pH's between 8 and 9. There is no internal catalysis by the ionized hydroxy group, since the specific rate is even greater at acidic pH's than at alkaline ones.

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