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A NONLINEAR HAMMETT RELATIONSHIP AS EVIDENCE FOR A CHANGE-OVER IN MECHANISM IN THE ALKALINE HYDROLYSIS OF METHYL CARBANILATES

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A nonlinear Hammett relationship could be used as evidence for a change-over in mechanism in the alkaline hydrolysis of methyl carbanilates. The electron-withdrawing substituted compounds hydrolyse via an A-E pathway (ρ 1.06) whereas the hydrolysis of the electron-donating substituted compounds involves an E-A scheme.

The mechanism of the alkaline hydrolysis of carbamates with a labile proton on the atom α to the carbonyl function is usually difficult to characterize kinetically (1) as the two possible mechanisms - elimination-addition (E-A) and addition-elimination (A-E) - lead to the same type of rate equations :

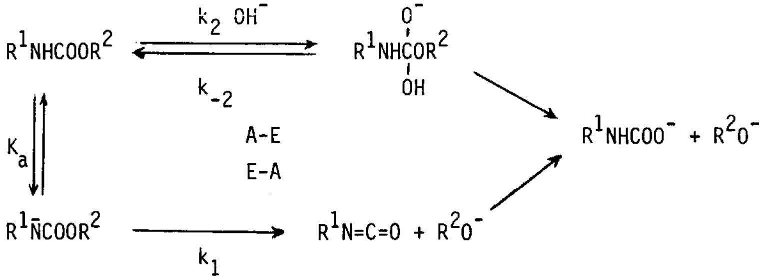
$$k_{obs} = k_1\ K_a/(K_a + a_H) \quad \text{for E-A} \quad [\text{eq. I}]$$

and $$k_{obs} = k_2\ K_w/\gamma\ (K_a + a_H) \quad \text{for A-E} \quad [\text{eq. II}]$$

When $a_H >> K_a$, these equations then become :

$$k_{obs} = k_1\ K_a/a_H \qquad [\text{eq. III}]$$

and $$k_{obs} = k_2\ [\text{OH}^-] \qquad [\text{eq. IV}]$$



Hammett and Brönsted linear relationships have been used successfully in the case of carbanilates (2,3), N-acetylcarbamates (4), and O-aryl-N-phenylthionocarbamates (5), so as to determine the reaction pathway actually involved. The Brönsted plot of the logarithm of the bimolecular rate constant k_{OH} against the pK_a of the leaving group reflected a change-over in the reaction mechanism, from E-A to A-E, in the case of N-(4-nitrophenyl) (3) and N-acetyl (4) carbamic acid esters, when the pK_a values of the leaving groups were above 13 and 10.5, respectively.

For a given leaving group, the mechanism involved only depends on the structure of the group attached to the nitrogen atom. Evidence could thus be given for an E-A mechanism in the hydrolysis of phenyl N-phenylcarbamates, irrespective of the nature of the substituent borne by the N-phenyl group (3). The methoxy leaving group is more nucleophilic than the phenoxy leaving group and should therefore disfavour the E-A mechanism in the hydrolysis of N-phenylcarbamates (1). A change-over in mechanism might then be observed. A series of variously m- or p-substituted methyl carbanilates was thus investigated so as to check the reliability of the above assumption.

RESULTS AND DISCUSSION

The alkaline hydrolysis of these carbanilates at 25°C was followed by means of u.v. spectrophotometry for hydroxide ion concentrations ranging from 0.005 to 1.0 N. The reactions were characterized by first-order kinetics with respect to the substrate. For each derivative investigated, the pseudo-first-order rate constants were proportional to the hydroxide ion concentration. The experimental data are in agreement with the rate equations III and IV ($a_H >> K_a$). The bimolecular rate constants $k_{OH} = k_{obs}/[OH^-]$ were obtained by linear regression ($r > 0.998$). The datum points of the Hammett plot are surrounded by circles whose radius is equal to the standard deviation on log k_{OH} (± 0.01 log unit).

The Hammett plot of log k_{OH} against σ is non-linear and can be divided into a straight line and a concave up curve.

The carbamates bearing electron-donating substituents [4-N Me$_2$, 4-NH$_2$, 4-MeO, 4-Me, and 3-Me] are on the curve, whereas the carbamates bearing electron-withdrawing substituents [3-MeO, 4-Cl, 3-Cl, 3-CF$_3$, 3,4-Cl$_2$ and 3-NO$_2$] are on a straight line whose equation is $\log k_{OH} = 1.06\ \sigma - 4.28$ [eq. V] (r 0.994, s 0.05). The datum point for the unsubstituted carbanilate is at the intersection of the straight line and of the curve.

The σ values used for most substituents were those of Mc Daniel and Brown (6) ; those for 4-NMe$_2$ and 3,4-Cl$_2$ (-0.60 and 0.525, respectively) were reported by Jaffe (7). For

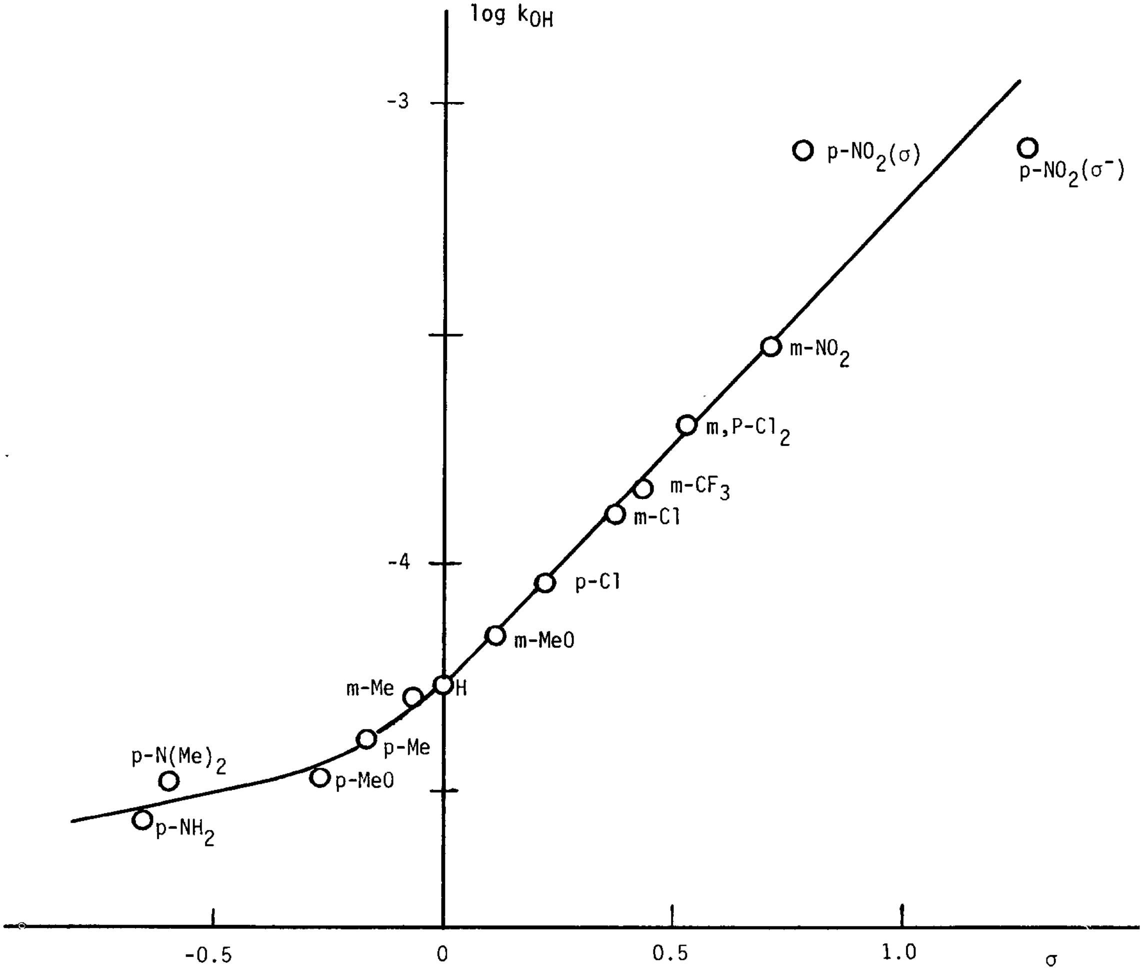


Figure - Plot of log k_{OH} against the σ values of the substituents of the N-phenyl group for the alkaline hydrolysis of methyl carbanilates at 25°C.

the 4-NO_2 substituent, the σ value (1.08) which best fits the straight line corresponding to the other electron-withdrawing substituents is intermediate between σ and σ^-. For this latter substituent, the degree of resonance interaction in the transition state calculated from the equation of Yukawa-Tsuno (8) was 0.60.

The shape of the plot of log k_{OH} against σ clearly suggests the occurrence of a change-over in mechanism depending on the nature of the substituents (9). As a matter of fact, a change in mechanism always causes the curve to be concave up while a change in rate-limiting step, with an otherwise constant mechanism, can cause the curve to be concave down (10, 11).

The data reported in the literature show that the straight line of slope 1.06 [eq. V] is in agreement with an A-E mechanism where hydroxide ion attack at the carbonyl group is the rate determining step. The sensitivity of such a reaction mechanism to substituent effects when a nitrogen or oxygen hereroatom is intercalated between the carbonyl and aromatic groups is usually reflected by a ρ value close to unity. Such is the case for the hydrolysis of two series of anilides $RCONR^1C_6H_4X$: R = Me, R^1 = H, $\rho = 1.00$ (12) ; and R = CF_3, R^1 = Me, $\rho = 1.18$ (13). For these anilides, the sequence between the reaction centre and the aromatic ring, which is the site of the substitution, is the same as that of methyl carbanilates (R = OMe, R^1 = H).

The same remark holds for the hydrolysis of aryl acetates and aryl benzoates $RCOOC_6H_4X$: R = Me, $\rho = 1.00$ (14) and R = C_6H_5, $\rho = 1.27$ (15).

The fact that the plot of log k_{OH} against σ is concave up for the electron-donating substituents can be interpreted in terms of a change-over in the reaction mechanism from A-E to E-A. For such a reaction, little information is provided by the literature. However, a ρ value of 0.64 was reported for the hydrolysis of phenyl N-(substituted phenyl) carbamates (3). The effect of the substituents on the reaction rate (see eq. III) is then the sum of opposite effects on K_a and k_1 : the acidity of a carbanilate bearing an electron-donating substituent is lower than that of the unsubstituted derivative whereas the decomposition rate of the anion is speeded up as a result of its destabilisation by the electron-donating group (16). The positive ρ value therefore suggests that the first effect is prevailing over the second one. For the substituted methyl carbanilates corresponding to the concave up curve, the decrease in the reaction sensitivity to the substituent effects is thus consistent with an E-A mechanism.

This investigation showed that the mechanism of the alkaline hydrolysis of methyl carbanilates markedly depends on the substituent of the N-phenyl group : a change-over in mechanism, from E-A to A-E, can be observed within the series as the σ value becomes positive. Moreover, the above data are in agreement with those of Williams who suggested an E-A scheme for methyl carbanilate (17), and with those of Hegarty who could show that methyl N-(4-nitrophenyl) carbamate hydrolysed via an A-E partway (3). For this latter derivative, the σ value of +1.08 accounts for the electron-withdrawing effect of the 4-NO_2 substituent on the lone pair of electrons of the nitrogen atom. The decrease in the electron density on the nitrogen atom therefore increases the electrophilic character of the carbonyl group which thus becomes more reactive towards the rate-determining hydroxide ion attack according to an A-E process. On the contrary, for an E-A process, the k_{OH} value for the hydrolysis of methyl N-(4-nitrophenyl) carbamate would be correlated to σ, as was the case for phenyl N-(4-nitrophenyl) carbamate (3).

The 3,4-Cl_2 substituent was selected for this investigation as the methyl ester of 3,4-dichlorocarbanilic acid (swep) exhibits a herbicidal activity (18). The above data clearly show that the alkaline hydrolysis of this derivative proceeds via an A-E pathway : the formation of 3,4-dichlorophenyl isocyanate, which is highly toxic to living organisms, can therefore be ruled out.

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