ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL ACETATES CATALYZED BY QUATERNARY AMMONIUM SALTS

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Alkaline hydrolysis of the phenyl acetates $CH_3COOC_6H_4X$ (X = 4-NO_2, 3-NO_2, 3-Cl, H, 4-CH_3, 3-CH_3, and 4-OCH_3) in the presence of hexadecyltris(2-hydroxyethyl)ammonium chloride, bis(2-hydroxyethyl)hexadecyl(methyl)ammonium bromide, and hexadecyltrimethylammonium bromide has been studied. Comparison of the rates of the hydrolysis for the above tenzides showed that the most efficient catalyst is the hexadecyltris(2-hydroxyethyl)ammonium chloride. In all cases, the rate data correlated well with structure effects by the Hammett equation.

The effect of micelles on the rate of chemical reactions has been frequently studied on example of alkaline hydrolysis of organic esters[1,2]. For this purpose, the esters of the acids with 4-nitrophenol (4-nitrophenyl acetate, diphenyl(4-nitrophenyl) phosphate etc.) were preferred because of the easy detection of the coloured 4-nitrophenoxide ion formed by hydrolysis. Fundamental works on the effect of quaternary ammonium salts on basic hydrolysis of substituted phenyl acetates are cited in numerous studies (cf. refs[3,4]). The catalytic action of the micelles of alkyltrimethylammonium salts has been attributed to the reduction of the energy of the negatively charged transition state of the ester located most likely in the Stern layer by the positively charged surface of micelle[5]. The different course of the hydrolysis has been observed in the presence of hydroxyalkylammonium salts[6] in that the tenzide hydroxy group and not the hydroxide ion acts as the nucleophilic agent. Such a conclusion has been arrived at by Martinek and coworkers[6] on the basis of the study of basic hydrolysis of 4-nitrophenyl heptanoate in the presence of cationic micelles of diethyl(2-hydroxyethyl)octadecylammonium bromide as an example of the so called functionalized tenzides.

The aim of the present work was to compare the catalytic behaviour of the so far not investigated hydroxyalkylated tenzide, hexadecyltris(2-hydroxyethyl)ammonium chloride (*I*) with the less hydroxyalkylated analogue (bis(2-hydroxyethyl)hexadecyl(methyl)ammonium bromide (*II*)) and a related commercial tenzide (hexadecyltrimethylammonium bromide (*III*)). For this purpose, the alkaline hydrolysis of the series of substituted phenyl acetates of the type $CH_3COOC_6H_4X$ (X = 4-NO_2, 3-NO_2, 3-Cl, H, 4-CH_3, 3-CH_3, and 4-OCH_3) was chosen as a model reaction.

EXPERIMENTAL

Chemicals

The phenyl acetates were prepared by reported procedures[7 – 12] and their physical data (m.p. resp. b.p.) agreed with those reported. The purity of the esters was checked by HPLC. The hydroxyalkylated ammonium bromide *II* was produced by the Research Institute for Fats, Division Rakovník and was recrystallized twice from acetone prior to using. The tenzide *III* was commercial sample.

Hexadecyltris(2-hydroxyethyl)ammonium chloride was prepared by the following two-step synthesis (compare with that reported by Ralston and coworkers[13]). Bis(2-hydroxyethyl)hexadecylamine prepared by reported procedure[14] (89% yield, b.p. 200 °C/660 Pa, for $C_{20}H_{43}NO_2$ (329.6) calculated: 72.95% C, 13.01% H, 4.25% N; found: 72.86% C, 13.01% H, 4.32% N) was placed (70 g, 0.21 mol) in a flask and 2-chloroethanol (50 cm^3, 0.75 mol) was added. The reaction mixture was refluxed for 20 h. Then, the excess 2-chloroethanol was distilled off, the product was washed with acetone and recrystallized thrice from the same solvent. The procedure afforded a total of 28.5 g of hexadecyltris-(2-hydroxyethyl)ammonium chloride (33% yield) as fine white tabular crystals melting at 92.5 – 93.5 °C. For $C_{22}H_{48}NO_3Cl$ (410.1) calculated: 64.44% C, 11.80% H, 8.65% Cl, 3.42% N, 11.69% O; found: 64.37% C, 11.86% H, 8.70% Cl, 3.39% N, 11.68% O. The two-phase titration of the product with sodium dodecyl sulfate solution showed that the sample contains 98.6% of the quaternary ammonium salt.

Determination of critical micellar concentration. The measurement for the tenzides *I* – *III* was made by using the solubilization method[15] on Sudan I under the following conditions: borate buffer of pH 9.00 (ionic strength μ = 0.092 mol dm^{-3}) at 20 °C for ammonium salts *I* and *II* and borate buffer of pH 10.00 (ionic strength μ = 0.047 mol dm^{-3}) at 20 °C for the ammonium bromide *III*.

Rate Measurements

Rate of the reaction was measured in a thermostatted cell (20 °C) of Specord M-40 (Zeiss, Jena) spectrophotometer, using the borate buffer of pH 10.00 or of pH 9.00 (see the preceeding paragraph) prepared in a deionized redistilled water. The pH value of the buffer was checked by digital pH-meter OP-208 (Radelkis, Hungary), using a combined glass electrode OP 0808 (Radelkis, Hungary). The calibration buffers were a phosphate buffer of pH 7.00 and a borate buffer of pH 9.00. The phenyl acetates were dissolved in methanol in such weight amounts (tens of milligrams to 50 cm^3) that ensured the maximum of absorbance not exceeding the value of 1. Hydrolysis was carried out in a 2 cm quartz cell which was filled with 5 cm^3 of the tenzide solution in the appropriate buffer. The reaction was started by injecting 0.05 cm^3 of the methanolic ester solution to the solution placed in the cell. The time from the injection and mixing of the substrate up to the first measured value of absorbance in the programme "cycle" of the spectrophotometer was measured by a stop watch and added to the time values of the cycles. The measurements were made at the wavelength corresponding to the maximal absorbance of the substituted phenolate formed (402 nm for 4-nitrophenyl acetate, 398 nm for the 3-nitro derivative, and 280 – 292 nm for the other esters).

The first order rate constants k (in s^{-1}) of the hydrolysis were calculated from the relation $A_{t_i} = A_{\infty} - (A_{\infty} - A_0)\exp^{-kt_i}$ (A_0 is the absorbance in time t_0, A_{t_i} is the absorbance in time t_i, and A_{∞} is that in infinite time). The error was max. 5% in the whole region of the measurements.

RESULTS AND DISCUSSION

The critical micellar concentration (in mol dm^{-3}) of the ammonium salts *I* – *III* determined by the solubilization method[15] was as follows: $5.9 \cdot 10^{-4}$ for *I*, $4.4 \cdot 10^{-4}$ for *II*, and $4.7 \cdot 10^{-4}$ for *III*. However, these values hold only for the borate buffers used (see Experimental) and correspond to measurement conditions. This follows from the fact that even small changes in the above conditions (e.g. a different procedure in buffer preparation) affect markedly the value of critical micellar concentration. The data obtained above were therefore used for estimating the concentration of the tenzides for their testing as catalysts of basic hydrolysis of the substituted phenyl acetates.

In order to quantify the catalytic effect of the tenzides studied, the rate of the hydrolysis of phenyl acetates in the buffers as such had to be determined. The results show that the hydrolysis proceeds as pseudo-first order reaction, and the rate data obtained for the series of the acetates can be well correlated with their structure by the Hammett equation (σ constants taken from ref.[16]):

$$\log k = -(4.54 \pm 0.04) + (0.97 \pm 0.02)\,\sigma \text{ for pH 9.00 and}$$
$$\log k = -(3.74 \pm 0.03) + (0.98 \pm 0.02)\,\sigma \text{ for pH 10.00.}$$

The dependence of the rate constant of the hydrolysis of 4-nitrophenyl acetate on tenzides concentration is presented in Fig. 1 as an example. A similar course was observed for 3-nitro, 3-chloro, 3-methyl, and 4-methyl derivatives. As shown in the figure, the hydrolysis proceeds at the fastest rate with tenzide *I* and it is slowest with tenzide *III*. The hydrolysis of 4-methoxyphenyl acetate shows the reverse sequence at tenzide concentrations about 10^{-3} mol dm^{-3} (Fig. 2).

The hydrolysis was measured at two pH levels: at pH 10.00 for the commercial quaternary salt *III* and at pH 9.00 for the tenzides *I* and *II*. The efficiency of the latter compounds is documented by the fact that at ten times lower concentration of OH^- ions (i.e. at pH 9), the hydrolysis in the presence of *I* and *II* is faster than that with *III* (carried out at pH 10). At the same time the rate in the presence of *I* is about 2.4 times faster compared to the hydrolysis in the presence of *II*. As the hydrolysis rate constant vs tenzide concentration dependence passes through a maximum, further discussion is based on the values of the rate constants at this maximum (k_{max} in s^{-1}). The maximum thus mentioned is located for all the tenzides studied in the narrow concentration region of ca $1 \cdot 10^{-2}$ mol dm^{-3}. The efficiency of the tenzides can be characterized by the ratio of k_{max} to the rate constant of hydrolysis in the absence of tenzide in the same buffer, k (see discussion above). Furthermore, the effect of the ammonium salt *I* when compared to the tenzide *II* can be then expressed by the $k(I)_{max}$ to $k(II)_{max}$ ratio (designated as k_a in Table I). Relevant data are summarized in Table I.

TABLE I
k_{max} to k ratios for the hydrolysis of the phenyl acetates $CH_3COOC_6H_4X$ in the presence and absence of quaternary salts *I* – *III* and k_a ($k(I)_{max}/k(II)_{max}$) values

X	k_{max}/k			k_a
	III	*II*	*I*	
4-NO_2	8.9	11.9	29.2	2.5
3-NO_2	5.5	9.3	16.3	1.8
3-Cl	6.0	9.7	23.0	2.4
H	1.7	1.6	4.3	2.7
3-CH_3	1.6	2.5	6.0	2.4
4-CH_3	2.4	2.8	7.8	2.8
4-OCH_3	2.6	1.8	3.8	2.1

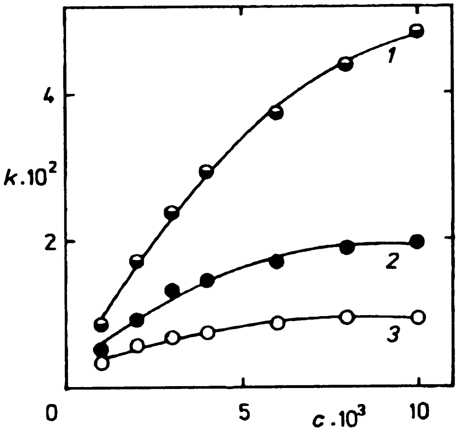

FIG. 1
Dependence of rate constants k (s^{-1}) of hydrolysis of 4-nitrophenyl acetate on concentration c (mol dm^{-3}) of hexadecyltris(2-hydroxyethyl)ammonium chloride (*1*) (pH 9.00, μ = 0.092 mol dm^{-3}), bis(2-hydroxyethyl)hexadecyl(methyl)ammonium bromide (*2*) and hexadecyltrimethylammonium bromide (*3*) (both at pH 10.00, μ = 0.092 mol dm^{-3})

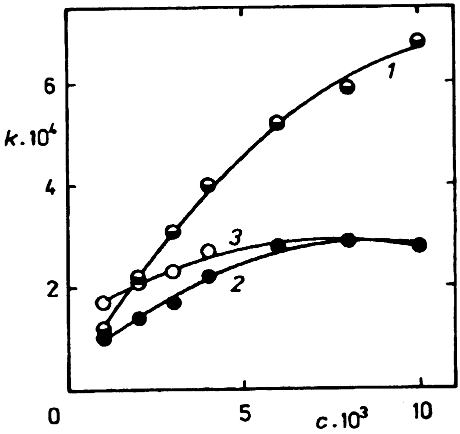

FIG. 2
Dependence of rate constants k (s^{-1}) of hydrolysis of 4-methoxyphenyl acetate on concentration c (mol dm^{-3}) of tenzides *I* – *III* (for designation of curves and hydrolysis conditions see Fig. 1)

Similarly to the hydrolysis in buffers as such, also in the presence of all the tenzides studied, the effect of the ester structure on the hydrolysis rate can be well described by the Hammett equations (the correlation coefficients being higher than 0.985):

$$\log k_{max} = -(3.30 \pm 0.02) + (1.51 \pm 0.02)\,\sigma \text{ for } \mathit{III}$$
$$\log k_{max} = -(3.09 \pm 0.03) + (1.76 \pm 0.01)\,\sigma \text{ for } \mathit{II}$$
$$\log k_{max} = -(2.79 \pm 0.02) + (1.78 \pm 0.01)\,\sigma \text{ for } \mathit{I}\,.$$

This proves that structure changes do not alter the mechanism of the reaction. The very similar ρ values for the quaternary salts *I* and *II* demonstrate that we deal here with same hydrolytic processes which proceed most likely as already proposed by Martinek and coworkers[6]. The additional 2-hydroxyethyl group in tenzide *I* thus exerts effect only on the rate of the hydrolysis.

REFERENCES

1. Gould E. S.: *Mechanism and Structure in Organic Chemistry*. Holt, New York 1959.
2. Ingold C. K.: *Structure and Mechanism in Organic Chemistry*. Cornell University Press, Ithaca, New York 1969.
3. Romsted L. R., Cordes E. H.: J. Am. Chem. Soc. *90*, 4404 (1968).
4. Mayer G.: Tetrahedron Lett. *1972*, 4581.
5. Mayer G.: C. R. Acad. Sci. *276*, 1599 (1973).
6. Martinek K., Levashow A. V., Berezin I. V.: Tetrahedron Lett. *1975*, 1275.
7. Kaufman A.: Ber. Dtsch. Chem. Ges. *42*, 3482 (1919).
8. Arball F.: J. Chem. Soc. *125*, 811 (1924).
9. Wohlleben W. J.: Ber. Dtsch. Chem. Ges. *42*, 4369 (1909).
10. Chattaway F. D.: J. Chem. Soc. *1931*, 2495.
11. Claus A., Hirsch J.: J. Pract. Chem. *42*, 62 (1889).
12. Klemenc A.: Monatsh. Chem. *35*, 90 (1914).
13. Ralston A. W., Eggenberger D. N., Harwood H. J., Du Brow P. L.: J. Am. Chem. Soc. *69*, 2096 (1947).
14. Wilson E., Tischler M.: J. Am. Chem. Soc. *73*, 3635 (1951).
15. Kulič J., Vitáček T.: Sb. Ved. Pr., Vys. Sk. Chem. Technol., Pardubice *49*, 369 (1986).
16. Exner O.: *Korelační vztahy v organické chemii*, p. 75. SNTL, Praha 1981.

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