KINETIC SALT EFFECTS IN THE HYDROLYSIS OF ETHYL MALONATE, METHYL GLUTARATE AND ETHYL ADIPATE SEMIESTERS

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A study is made on the kinetic salt effect on the reaction of hydrolysis of several charged esters in alkaline media. The results are interpreted on the basis of the coulombic interaction, the "salting in" of hydroxide ion and a third component depending on size of the substrate.

Salt effects on saponification of ionic esters were first studied by Nielsen[1]. Other authors have also been interested in this subject[2-4]. Recently Holba et al.[5-16] have studied in more detail salt and medium effects on several reactions of this kind. However, none of these studies provide data on kinetic salt effects in concentrated solutions of supporting electrolytes, a subject of great interest to the authors[17]. On the other hand, in a study of the fading of bromophenol blue[18], one of the present authors observed an abnormal kinetic salt effect, that is, a decrease in the reaction rate with increase in the salt concentration, in a reaction where two ions of the same charge sign participate in the rate determining step. This abnormal behaviour could be associated with the participation of the OH^- ion, which in concentrated solutions of salts shows a decrease in its activity coefficient, due most likely to a local hydrolysis[19]. However, this effect is probably not the only one causing the abnormal behaviour, because in the case of the other reactions, in which the OH^- participates, a normal trend is observed[20], even in concentrated solutions of supporting electrolytes. For this reason we suppose that the size of the substrate that undergoes a nucleophilic attack by OH^- could also be a cause for the abnormal behaviour. The study of dicarboxylic acid esters offers an opportunity to test this supposition, by changing systematically the size of the substrate. Finally, kinetic salt effects on ester (and amide) hydrolysis with a second carboxylic group are of interest in relation with some enzyme mechanisms[21].

EXPERIMENTAL

The monoethyl malonate was prepared by the Nielsen method[1] from AnalaR grade Merck chemicals. Monoethyl adipate and monomethyl glutarate were prepared *in situ* by mixing

solutions of their monoesters (Aldrich) with solutions containing potassium hydroxide at double the concentration of those of the esters. The supporting electrolytes (Merck) are shown in Table I. The kinetics of the reaction was carried out as described in the literature[19]. All kinetic runs were performed at $25 \cdot 0 \pm 0 \cdot 1°C$. All the data in Table I are the results of at least three experiments.

DISCUSSION

The results in Table I seem to be in agreement with the hypothesis presented in the introduction, that is, the size of the ester is apparently related to the "normal" or "abnormal" salt effect. So, in the malonate case a positive salt effect is observed, whereas in the other cases salt effects are negative or absent.

As the chemical processes are the same in all three cases, it seems reasonalbe to suppose that the size factor is operative as previously supposed[18]. Also, since the coulombic effect increases the rate of reaction, the fact that the salt effect is non-existent or negative for the adipic and glutaric esters suggests that the overall salt effect is dependent on more than one factor. These factors should be dependent on the nature and concentration of the salt in the reaction medium. In the case of the salts where a negative salt effect is observed, the rate-decreasing factor should dominate in all the concentration range for the two greater substrates. In the malonate case the opposite is true.

As the abnormal salt effect is observed only when one of the reactants is OH^-, it seems interesting to consider the changes in its activity coefficient in the electrolyte solutions used in this work. These activity coefficients were obtained in a previous paper[19]. It is important to underline that the values of γ_{OH^-} in the paper refer to a $0 \cdot 25 \ mol \ l^{-1}$ solution, instead of the normal (infinitely dilute solution) reference state. Taking into account that the activity coefficients at the above-mentioned $(0 \cdot 25 \ mol \ l^{-1})$ concentration are similar in the presence of different electrolytes and the probable error in liquid junction, this change in reference state seems rather unimportant.

In Table II we give $\log k - \log \gamma_{OH^-}$. The meaning of these data is clearer if, according to Brönsted's relation, we put,

$$\log k = \log k_0 + \log \frac{\gamma_{OH^-} \gamma_{ester}}{\gamma_{AC}}, \qquad (1)$$

or

$$\log k = \log k_0 + \log \gamma_{OH^-} + \log \frac{\gamma_{ester}}{\gamma_{AC}}. \qquad (2)$$

Therefore,

$$\log k_{corr}^T = \log k - \log \gamma_{OH^-} = \log k_0 + \log \frac{\gamma_{ester}}{\gamma_{AC}}. \qquad (3)$$

TABLE I

Dependence of rate constant $k \cdot 10^2 (dm^3 mol^{-1} s^{-1})$ on the ionic strength for the basic hydrolysis of the monoesters of malonic, glutaric, and adipic acid

Electrolyte	Concentration, mol dm^{-3}							
	1·0	1·5	2·0	2·3	2·7	3·0	4·0	5·0
monoethyl malonate								
LiNO$_3$	4·25 ± 0·08	—	5·16 ± 0·05	—	—	5·91 ± 0·18	7·00 ± 0·13	7·71 ± 0·10
NaNO$_3$	3·23 ± 0·06	—	3·70 ± 0·13	—	—	4·36 ± 0·08	4·63 ± 0·13	5·20 ± 0·08
KNO$_3$	2·78 ± 0·03	2·95 ± 0·06	2·95 ± 0·06	3·40 ± 0·05	3·18 ± 0·06	—	—	—
NaCl	3·75 ± 0·06	—	4·28 ± 0·15	—	—	4·70 ± 0·08	5·45 ± 0·11	6·33 ± 0·11
monomethyl glutarate								
LiNO$_3$	7·16 ± 0·16	—	6·75 ± 0·26	—	—	6·11 ± 0·10	4·81 ± 0·13	3·75 ± 0·13
NaNO$_3$	9·08 ± 0·30	—	8·78 ± 0·15	—	—	8·35 ± 0·31	9·15 ± 0·23	8·81 ± 0·26
KNO$_3$	8·05 ± 0·20	—	7·71 ± 0·46	—	7·91 ± 0·30	—	—	—
NaCl	8·85 ± 0·23	—	9·18 ± 0·26	—	—	9·45 ± 0·23	8·45 ± 0·25	7·93 ± 0·25
NaClO$_4$	7·78 ± 0·13	—	6·93 ± 0·16	—	—	6·10 ± 0·20	4·86 ± 0·06	5·05 ± 0·03
monoethyl adipate								
LiNO$_3$	4·73 ± 0·08	—	3·75 ± 0·05	—	—	3·30 ± 0·08	2·68 ± 0·01	2·30 ± 0·03
NaNO$_3$	4·68 ± 0·10	—	4·36 ± 0·08	—	—	4·18 ± 0·08	3·88 ± 0·05	4·33 ± 0·11
KNO$_3$	5·13 ± 0·11	—	4·80 ± 0·06	—	5·03 ± 0·11	—	—	—
NaCl	5·43 ± 0·08	—	5·28 ± 0·10	—	—	4·98 ± 0·05	4·58 ± 0·06	4·20 ± 0·06
NaClO$_4$	4·21 ± 0·06	—	3·25 ± 0·05	—	—	2·53 ± 0·03	2·15 ± 0·05	1·83 ± 0·03

Supposing now that coulombic and non-coulombic effects are additive, it is possible to write:

$$\log k_{corr}^T = \log k - \log \gamma_{OH^-} = \log k_0 + \log \left(\frac{\gamma_{ester}}{\gamma_{AC}}\right)_{coul} + \log \left(\frac{\gamma_{ester}}{\gamma_{AC}}\right)_{non\text{-}coul} . \qquad (4)$$

As can be seen from Table II, the general trend for these γ_{OH^-} corrected rate constants increases with increasing salt concentration, except for KNO_3, where the relative error for γ_{OH^-} is greater. So, it can be concluded that the coulombic interactions increase the rate of reaction, in the three cases, and this rate is decreased by the effect of the electrolytes on γ_{OH^-}.

Finally, it is interesting to discuss the effect of the substrate size. As can be seen from data in Table II, except for KNO_3, the increase in the γ_{OH^-} corrected rate constant is greater for the malonate ester. The cause of this can be seen from the

TABLE II

Dependence of corrected rate constant $(\log k_{corr}^T) . 10^3$ on the ionic strenght for basic hydrolysis of the monoesters of malonic, glutaric, and adipic acid

Electrolyte	Concentration, mol dm^{-3}							
	1·0	1·5	2·0	2·3	2·7	3·0	4·0	5·0
			monoethyl malonate					
LiNO$_3$	−972	—	−487	—	—	−128	245	487
NaNO$_3$	−1 391	—	−1 232	—	—	−1 161	−1 034	−984
KNO$_3$	−1 656	−1 630	−1 730	−1 269	−1 698	—	—	—
NaCl	−1 326	—	−1 169	—	—	−1 128	−964	−899
			monomethyl glutarate					
LiNO$_3$	−745	—	−371	—	—	−114	82	174
NaNO$_3$	−942	—	−857	—	—	−878	−739	−755
KNO$_3$	−1 194	—	−1 213	—	−1 302	—	—	—
NaCl	−953	—	−837	—	—	−825	−773	−801
NaClO$_4$	−809	—	−760	—	—	−715	−713	−597
			monoethyl adipate					
LiNO$_3$	−925	—	−626	—	—	−381	−172	−38
NaNO$_3$	−1 230	—	−1 161	—	—	−1 179	−1 111	−1 064
KNO$_3$	−1 390	—	−1 519	—	−1 498	—	—	—
NaCl	−1 165	—	−1 077	—	—	−1 103	−1 039	−1 077
NaClO$_4$	−1 076	—	−1 088	—	—	−1 097	−1 067	−1 038

right-hand side of expression (4). Two terms contribute to the constant, (i) coulombic which must be similar for all three substrates because they have the same charge and because coulombic interactions tend to be nearly constant in concentrated solutions of electrolytes[22-23] and (ii) non-coulombic. In the authors' opinion this second factor is the cause of the size effect. An explanation for this could be that the relative salting in ester and transition state, caused by electrolytes, decreases with increasing size of the ester, because the differences between transition state and ester are slight when the size of the latter increases. In other words the transition state and the ester are more alike, in this sense, the greater the ester is.

REFERENCES

1. Nielsen R. F.: J. Am. Chem. Soc. *58*, 206 (1936).
2. Hoppé J. I., Prue J. E.: J. Chem. Soc. *1957*, 1775.
3. Indelli A., Nolan G., Amis E. S.: J. Am. Chem. Soc. *82*, 3237 (1960).
4. Indelli A.: Trans. Faraday Soc. *59*, 1827 (1963).
5. Holba V., Rievaj M.: This Journal *37*, 2841 (1972).
6. Holba V., Rievaj M.: This Journal *38*, 3283 (1973).
7. Holba V., Benko J.: Z. Phys. Chem. (Leipzig) *258*, 1088 (1977).
8. Holba V., Benko J., Okalová K.: This Journal *43*, 1581 (1978).
9. Benko J., Holba V.: This Journal *43*, 193 (1978).
10. Holba V.: Chem. Zvesti. *33*, 323 (1979).
11. Holba V., Benko J., Kozanková J.: This Journal *45*, 255 (1980).
12. Benko J., Holba V.: This Journal *45*, 1485 (1980).
13. Holba V., Benko J.: This Journal *45*, 2873 (1980).
14. Holba V., Benko J., Komadel P.: Z. Phys. Chem. (Leipzig) *262*, 445 (1981).
15. Komadel P., Holba V., Truchlík Š. jr: This Journal *48*, 1305 (1983).
16. Komadel P., Holba V.: Chem. Zvesti *38*, 151 (1984).
17. Sánchez Burgos F., Bertrán Rusca J., Carmona Guzmán M. C.: Rev. Inorg. Chem., in press.
18. Rodríguez Velasco J., Sánchez-Burgos F., Carmona Guzmán M. C., Hidalgo Toledo J.: An. Quim. *80*, 173 (1984).
19. Harned H. S., Owen B. B.: *The Physical Chemistry of Electrolytic Solutions*, p. 514. Reinhold, New York 1958.
20. Maraver J. J., Tejera J. I., Rodríguez Velasco J., Sánchez Burgos F., Dobarganes E.: An. Quim. *79*, 542 (1983).
21. Fije T. H., Przystas T. J., Lum Squillacok V.: J. Am. Chem. Soc. *101*, 3017 (1979).
22. Bruhn H., Nigam S., Holzwarth J. F.: Faraday Discuss. Chem. Soc., *74*, 129 (1982).
23. Dung M. H., Kozak J. J.: J. Chem. Phys., *76*, 982 (1982).