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Salt Effects in the Alkaline Hydrolysis of Potassium Ethyl Malonate

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The rate of the reaction of potassium ethyl malonate with sodium hydroxide has been measured at 25° in the presence of sodium and potassium salts with anions of different valences. The rate is not affected by the valence of the anion, and therefore not by the ionic strength, but only by the concentration of the cations. The agreement with previous measurements in the literature is good in the absence of added salts, but the difference reported between the effect of sodium and potassium salts disappears. The tetraethylammonium nitrate has a salt effect smaller than sodium or potassium chloride.

Introduction

Hoppé and Prue[1] have found that multivalent cations and thallous ions exert large, specific salt effects in the alkaline hydrolyses of potassium ethyl malonate and oxalate. Alkali cations instead give results which fit the equation[2]

$$\log k = \log k_0 + 2Az_1z_2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu \qquad (1)$$

where the value of A for water at 25° is 0.509.

The only investigation Hoppé and Prue made on the effect of the anion consisted in substituting, in one instance, barium nitrate for barium chloride, and no difference was found. We considered it interesting to study the effect of multivalent anions. to see whether the ionic strength or the cation concentration is the influential factor in determining the salt effect in the presence of alkali cations. Moreover, as tetraalkylammonium ions display an unusual behavior in the hydrolysis of trimetaphosphate[3] and in the reaction between persulfate and iodide,[4] we have studied the effect of the tetraethylammonium nitrate too.

Experimental

Potassium ethyl malonate was prepared and purified as described by Nielsen[5] and was found 98.9% pure by analysis. Sodium trimetaphosphate was prepared from monosodium orthophosphate, through the Graham salt,[6] and purified as described elsewhere.[7] Sodium triphosphate was prepared from sodium trimetaphosphate by alkaline hydration[8] and purified by repeated crystallizations from water–alcohol solutions.[9] Sodium tetrametaphosphate was prepared by hydration of αP_4O_{10}[10] and purified as described elsewhere.[11] Tetraethylammonium nitrate was prepared from the corresponding bromide and silver nitrate and crystallized twice from aqueous solutions. All other salts were C.P. grade and were not further purified. The solutions of sodium hydroxide were kept in polyethylene bottles equipped with a polyethylene tube, and the amounts required for the runs and the titrations were obtained by squeezing the bottles by means of a screw device. After withdrawing the solution, the end of the polyethylene tube was flame sealed.

Procedure.—A weighed amount of ester (0.5304 g., corresponding to 0.003082 mole) was dissolved in 500 ml. of water, containing eventually the added salt, and the solution was put in a stoppered 1,000 ml. polyethylene bottle, which was put in a water thermostat, together with a bottle containing the NaOH solution. After reaching thermal equilibrium, the bottle was flushed with CO_2-free air, and 100 ml. of 0.03082 M sodium hydroxide solution were added. The stopper was then replaced with another one carrying a polyethylene tube, of a convenient shape, to allow the withdrawing of samples by squeezing. The bottle next was fitted in a screw device contained in the thermostatic bath. The liquid contained in the tube was discarded each time, and samples of 50–100 ml. were collected periodically in weighed flasks containing a slight excess of potassium acid phthalate. The flasks were reweighed and the content backtitrated with standard NaOH, using a weight buret and thymol blue as an indicator. A current of CO_2-free air was passed through the flasks during the titrations. No correction was made for the difference from 1.00 of the specific gravity of the solutions. In the presence of $Na_5P_3O_{10}$ an excess of $Ba(NO_3)_2$ was added just before the titration to precipitate the buffering triphosphate ion as $Ba_5(P_3O_{10})_2$ and to obtain a sharp end-point. Six or seven samples were taken for every run, and the reciprocal of the concentration of the residual NaOH was plotted *versus* time. Fig. 1 shows the result for a typical run. Duplicate runs showed an agreement within 1 or 2%. The temperature was kept constant at 25.00 ± 0.02° and was measured with a Beckman thermometer matched against a N.B.S. thermometer.

The experimental results are reported in Table I, which gives the rate constants as $10^{+3}k$ (l. mol.$^{-1}$ sec.$^{-1}$). A run in the presence of 0.08 M NaCl gave a k value of 22.26×16^{-3} l.mole^{-1} sec.$^{-1}$.

Discussion

Table I shows that an increase in the ionic strength produced by an increase in the valence of the anion does not result in a corresponding increase in the rate. The equation 1 therefore is obeyed only if the added salt is a uniunivalent one. This is shown with more evidence by Fig. 2, where $\log k_0'$, defined as[2]

$$\log k_0' = \log k - 2Az_1z_2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (2)$$

is plotted against the ionic strength μ, for sodium chloride, sulfate, trimetaphosphate, triphosphate and potassium chloride. According to the simple electrostatic treatment, based on the Brönsted–Christiansen–Scatchard equation,[12] all points should fall on straight lines very close together, because the coefficient B of equation 1 should depend mainly on the nature of the ions of opposite sign to that of the reactants.[13] It can be seen that the lines are quite distinct and for sodium trimeta- and triphosphate show a clear curvature. For the latter the slope becomes so great that the value of the coefficient B in equation 1 eventually becomes the predominant factor in determining the salt effect. B instead is usually considered to be only a correction parameter, which takes in account all the individual causes of deviation from the limit-

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(1) Hoppé and J. E. Prue, *J. Chem. Soc.*, 1775 (1957).

(2) E. A. Guggenheim and J. E. Prue, "Physicochemical Calculations," North-Holland Publishing Co., Amsterdam, 1956, p. 466.

(3) A. Indelli, *Ann. Chim.* (*Rome*), **48**, 332 (1958).

(4) A. Indelli and J. E. Prue, *J. Chem. Soc.*, 107 (1959).

(5) R. F. Nielsen, THIS JOURNAL, **58**, 206 (1936).

(6) L. T. Jones, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 536 (1942).

(7) A. Indelli, *Ann. Chim.* (*Rome*), **43**, 845 (1953).

(8) E. Thilo and R. Rätz, *Z. anorg. Chem.*, **258**, 33 (1949).

(9) A. Indelli, *Ann. Chim.* (*Rome*), **46**, 367 (1956).

(10) R. N. Bell, L. F. Audrieth and O. E. Hill, *Ind. Eng. Chem.*, **44**, 568 (1952).

(11) A. Indelli, *Ann. Chim.* (*Rome*), **47**, 586 (1957).

(12) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, pp. 71 ff.

(13) E. A. Guggenheim and L. A. Wigeman, *Proc. Roy. Soc.* (*London*), **A203**, 17 (1950).

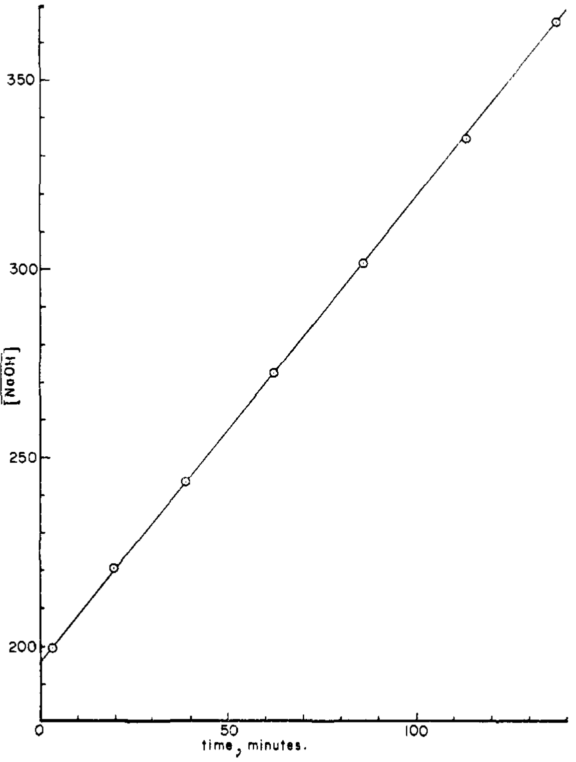

Fig. 1.—Second order plot in the presence of NaCl, 0.04 *M*.

ing law.[14] If the rate constants are compared at equal cation concentration, an agreement within 2 or 3% is observed in every case: this explains why it is not possible to detect any curvature in the second order plots, despite the increase in the ionic strength during the reaction.[1] The agreement of the present results with those obtained by Hoppé and Prue[1] in the absence of added salts is rather good (1.04 compared with 1.05), when the time is expressed in minutes, and the small difference probably can be accounted for by the fact that in the present experiments the reactant concentration was about one half of that used by Hoppé and Prue. The difference that Hoppé and Prue observed between potassium and sodium chloride, however, disappears in the present experiments. A change in the relative salt effect of different salts corresponding to a change in the reactant concentration has been observed in other cases.[15]

On the basis of the Mayer theory,[16] Scatchard[17] has proven that the equilibrium constant for a reaction between a bivalent and a univalent ion of the same sign, at appreciable concentration, depends more on the concentration of the ions of opposite sign than on the ionic strength. In this way an electrostatic interpretation could be given to the Olson and Simonson findings.[18] The present results show that the same must be true also for a reaction between two univalent ions of the same sign. At very low concentrations the Mayer theory coincides with the Debye–Hückel theory, and therefore a correlation with the ionic strength is to be expected. It is clear, however, that a much more refined experimental technique would be required to test such correlation. In fact the extent of the salt effect for the lowest concentration in the present work amounts to only a few per cent.

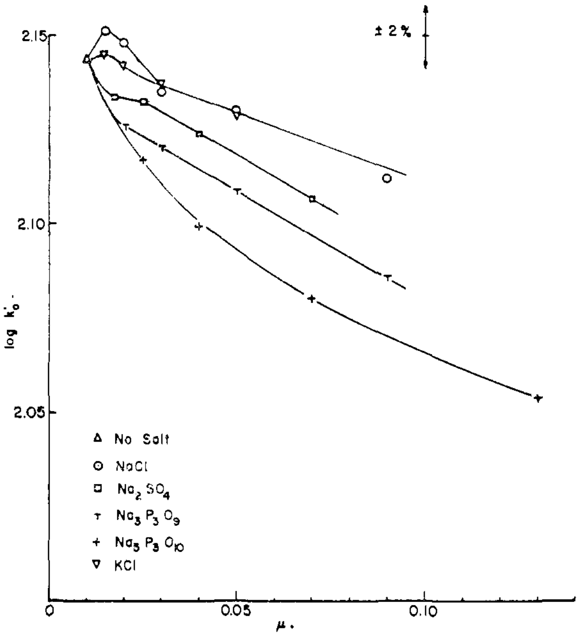

Fig. 2.—Log k_0' *versus* ionic strength.

TABLE I

SECOND ORDER RATE CONSTANTS, 10^3k (L. MOLE,$^{-1}$ SEC.$^{-1}$), FOR THE REACTION OF ALKALINE HYDROLYSIS OF POTASSIUM ETHYL MALONATE

$[KCO_2CH_2CO_2C_2H_5] = 5.137 \times 10^{-3}$; $[NaOH] = 5.137 \times 10^{-3}$; $10^3k = 17.28$ (l. mole^{-1} sec.$^{-1}$)

Added salt	Concn. equiv., l.$^{-1}$ 0.005	0.01	0.02	0.04	0.08
KCl	18.10	18.60	19.43	20.63	...
K_2SO_4	18.32	18.75	19.65	20.75	...
NaCl	18.35	18.83	19.32	20.70	22.26
Na_2SO_4	17.90	18.72	19.69	20.90	...
$Na_3P_3O_9$	17.88	18.68	19.75	20.95	...
$Na_4P_4O_{12}$	18.23	19.83	19.80	20.88	...
$Na_5P_3O_{10}$	18.05	18.60	19.65	21.07	...
$N(C_2H_5)_4NO_3$	...	...	18.97	19.75	...

The salt effect of the tetraethylammonium nitrate is somewhat less than that of the sodium and potassium chlorides. The difference, however, is not as large as it is in the alkaline hydration of trimetaphosphate[3] and in the reaction between persulfate and iodide.[4] The smaller charge on the activated complex that we have in this case could be the reason for the different behavior. More work seems to be required to draw more general conclusions regarding the salt effects of the tetraalkylammonium ions.

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(14) E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 543 (1934).

(15) A. Indelli, G. Nolan and E. S. Amis, THIS JOURNAL, **82**, 3233 (1960).

(16) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

(17) G. Scatchard, *Natl. Bur. Standards* (*U. S.*), Circ. No. **524**, 185 (1953).

(18) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).