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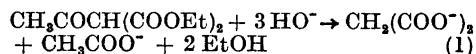
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The Alkaline Hydrolysis of Diethyl Acetomalonate

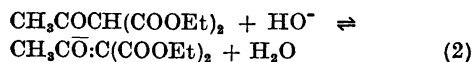
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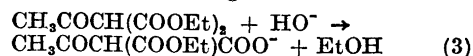
When diethyl acetomalonate is dissolved in an aqueous solution of a strong base it will react with 3 hydroxyl ions according to the scheme



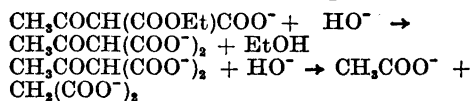
One hydroxyl ion disappears immediately, while the other two are consumed at a measurable rate which is proportional to the ester concentration but independent of the hydroxyl ion concentration. This experimental result is explained as follows. The keto-form of the diethyl ester is rapidly and nearly completely transformed into enolate ion by the balanced reaction



The rate-determining reaction is



It is followed by the two rapid reactions



The rate of reaction 3 will be proportional to the product of the hydroxyl ion concentration and the concentration of the keto-form of the diethyl ester, but since the latter, according to scheme 2, is inversely proportional to the hydroxyl ion concentration, the rate will be independent of the hydroxyl ion concentration and of first order with respect to the total concentration of diethyl acetomalonate (keto-form and enolate ion).

Diethyl acetomalonate was prepared according to Lund¹ and was distilled twice under reduced pressure in an all-glass apparatus fitted with a Widmer stillhead. The fraction used in the experiments distilled within less than 1°C. It was found that the ester could be titrated as a monobasic acid when thymolphthalein was used as indicator and a rather strongly blue colour was chosen as end-point. The average of several titrations was that 99.7% of the calculated amount of base was used. When the ester is dissolved in an excess of strong base, it will therefore be rapidly and nearly completely transformed into enolate ion by reaction 2.

To 60 ml of 0.2 N barium hydroxide in a glass-stoppered flask was added 0.8 g of the ester. The clear solution was left at room temperature. After half an hour the first crystals were noticed, and the next day a large crystalline precipitate had been formed. The crystals were isolated by suction, washed with ice-cold water, and air-dried to constant weight. It was shown that they did not contain carbonate, from which it is concluded that no decarboxylation takes place in the reaction. In order to show that the crystals consisted of barium malonate this substance was prepared by mixing solutions of malonic acid and barium acetate. The crystals obtained here were isolated and dried in the same way as before. Weighed amounts of the two preparations were transformed into carbonate by ignition in a platinum crucible, and the residues were weighed. On the assumption that one molecule of both substances gives one molecule of barium carbonate, it was found that the molecular weight of the substance prepared from diethyl acetomalonate was 254.5 while that of the salt prepared from malonic acid was 255.0 (calc.

for $\text{CH}_2(\text{COO})_2\text{Ba}\cdot\text{H}_2\text{O}$: 257.4). From acidimetric titration of the two residues was found 254.2 and 254.8, respectively. It is therefore concluded that the two substances are identical, and that malonate is formed as end-product in the alkaline hydrolysis of diethyl acetomalonate (scheme 1).

Measurements of the rate of hydrolysis of diethyl acetomalonate in solutions of sodium hydroxide were carried out at the two temperatures 25.0 and 37.0°C. A graduated flask filled to a little below the mark with sodium hydroxide solution was placed in a water thermostat. When temperature equilibrium was attained, a weighed-out amount of the ester was dissolved, and the flask was quickly filled to the mark with water of the proper temperature. At suitable time-intervals during the reaction, and after it had come to an end, samples of the solution were pipetted into an excess of 0.1 N hydrochloric acid; thymolphthalein was added, and the solutions were titrated back with 0.03 N sodium hydroxide to a rather strongly blue colour. When x denotes the concentration of titratable base, and c that of diethyl ester in the reacting solution at the time t after the start of the reaction, we have according to our assumptions that $x - x_\infty = 2c$ where subscript ∞ denotes final value. When $\log(x - x_\infty)$ was plotted against t , the points fell in all the experiments very close to straight lines showing that the first-order law holds for the reaction. The composition of the solutions examined, and the rate constants k (in sec^{-1}) found, are given in Table 1. The values of k increase slightly with increasing concentration of strong base in the original

Table 1. Rate of hydrolysis of diethyl acetomalonate (initially c_0 M) in solutions of sodium hydroxide (initially x_0 M). x_∞ is the final concentration of sodium hydroxide and k the rate constant in sec^{-1} .

c_0	x_0	x_∞	$\frac{x_0 - x_\infty}{c_0}$	$k \times 10^4$
<i>Temperature 25.0°C:</i>				
0.02012	0.0774	0.0169	3.01	1.070
0.03980	0.1351	0.0153	3.01	1.097
0.03990	0.1549	0.0352	3.00	1.110
0.04000	0.1852	0.0647	3.01	1.132
0.04042	0.1349*	0.0133	3.01	1.161
<i>Temperature 37.0°C:</i>				
0.01979	0.0770	0.0174	3.01	3.57
0.03983	0.1342	0.0145	3.01	3.73
0.03956	0.1539	0.0353	3.00	3.86
0.03952	0.1834	0.0647	3.00	3.93

* The solution contained in addition 0.300 M sodium chloride.

solution, and, as shown in one experiment, with addition of sodium chloride. It also appears from the table that the number of hydroxyl ions reacting per molecule of diethyl acetomalonate $(x_0 - x_\infty)/c_0$ is always 3 in agreement with scheme 1.

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