

CHROM. 4547

A gas chromatographic study of the kinetics of the uncatalysed esterification of acetic acid by ethanol

The esterification of acetic acid by ethanol has been a widely studied reaction since the time of BERTHELOT AND ST. GILLES who first determined the equilibrium constant for the reaction¹. The reaction had been studied in the vapour phase catalysed by a large variety of substances, both inorganic²⁻⁶ and synthetic resins⁷⁻¹⁰. The reaction has been studied in the liquid phase but also catalysed by either salts¹¹ or hydrogen ions¹². Thus all the earlier results refer to the catalysed esterification, and no data are available for the kinetics of the uncatalysed reaction. In the absence of a catalyst, the reaction proceeds extremely slowly, and the amounts of products formed at any time are too small for analysis by conventional methods. We have, however, studied this reaction successfully by vapour-phase chromatography.

Since this reaction is susceptible to heterogeneous catalysis, both in the vapour and liquid phases, the possibility of wall catalysis in the present work was also examined. For this purpose the reaction was studied in the presence of added finely divided wall material and the rate compared with that in the absence of such wall material.

Experimental

A Beckman gas chromatograph GC-2 was used in these experiments. Nitrogen was the carrier gas at an inlet pressure of 2 kg/cm² and a flow rate of 40 ml/min. The column was a 2 m long copper tube of 6 mm I.D., packed with 40-60 mesh firebrick loaded with 2% glycerol. The detector was a thermal conductivity cell with a filament current at 150 mA. The temperature of the column and detector was 70°. The chromatogram was recorded on a Bristol Dynamaster recorder with a sensitivity of 1 mV for full-scale deflection.

The instrument was calibrated by injecting known amounts of pure ethyl acetate and water and by noting heights and areas of the peaks of the chromatogram.

Equimolar quantities of purified ethanol and acetic acid were mixed together and 1 ml of the mixture was placed in each glass tube, which was sealed off and kept in a thermostat maintained at the desired temperature. After every hour, one tube was taken out, cooled rapidly and cut open. 50 μ l of the liquid were injected into the column and the chromatogram was obtained. Each sample was analysed twice.

The study was carried out at 60, 65, 70, 75, 80 and 85°. The data for the measurement at 60°, which are typical of the several measurements made, are given in Table I and Fig. 1.

In order to look into the possibility of wall catalysis in this reaction, equal amounts of the reaction mixture were taken in two Pyrex bottles with well-fitting ground-glass stoppers. Into one a quantity of clean glass wool was introduced. The two bottles were maintained at the same temperature, and the kinetics of the reaction in the two cases were studied. The results are given in Table I and Fig. 1.

Results and discussion

From the calibration data for ethyl acetate and its peak height in the chromato-

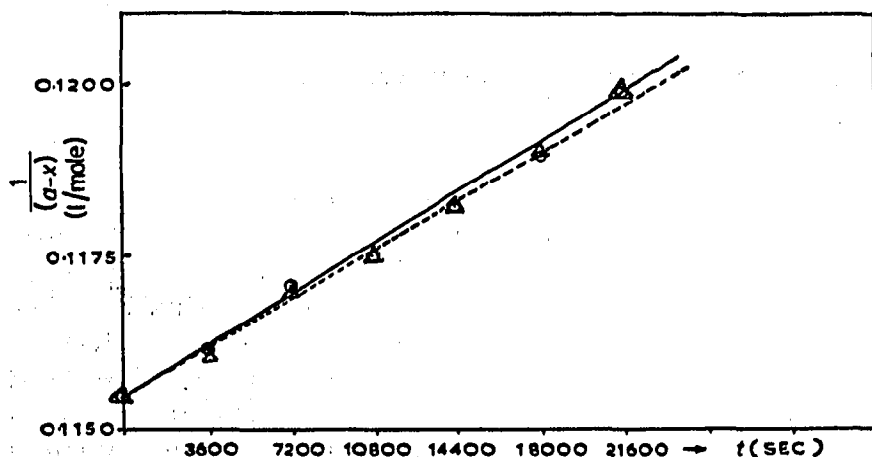


Fig. 1. Kinetics of the uncatalysed esterification of acetic acid by ethanol (*cf.* Table I). Temperature 60°. ○—○, without glass wool; △---△, with glass wool.

gram, the amount of it formed ($y \mu\text{l}$) at any stage of the reaction could be calculated. During calibration it was observed that the peak for ethyl acetate was sharp and that the peak height was proportional to the quantity of ester injected. The peak for water, however, was broad and the calibration, therefore, was less accurate. Hence for

TABLE I

KINETICS OF THE UNCATALYSED ESTERIFICATION OF ACETIC ACID BY ETHANOL (*cf.* Fig. 1)

Temperature: 60°. Initial concentration (a): acetic acid = 8.66 moles/l; ethanol = 8.66 moles/l. Calibration of the chromatogram: 19 divisions for 1 μl of ethyl acetate (attenuator = 10). Specific reaction rate calculated graphically: without glass wool = 2.02×10^{-7} l/mole·sec; with glass wool = 2.00×10^{-7} l/mole·sec.

Time (sec)	Peak height for ethyl acetate (No. of divisions)	Amount of ethyl acetate formed (y) (μl)	Concentration of ethyl acetate (x) (moles/l)	$(a-x)$ (moles/l)	$1/(a-x)$ (l/mole)
<i>Without glass wool</i>					
0	0	0	0	8.66	0.1155
3 600	6	0.32	0.06	8.60	0.1163
7 200	11	0.58	0.12	8.54	0.1171
10 800	14	0.74	0.15	8.51	0.1175
14 400	18	0.95	0.19	8.47	0.1184
18 000	23	1.21	0.24	8.42	0.1189
21 600	29	1.53	0.31	8.35	0.1198
<i>With glass wool</i>					
0	0	0	0	8.66	0.1155
3 600	5	0.26	0.05	8.61	0.1162
7 200	10	0.52	0.11	8.55	0.1170
10 800	14	0.74	0.15	8.51	0.1175
14 400	18	0.95	0.19	8.47	0.1184
18 000	24	1.26	0.26	8.40	0.1190
21 600	28	1.50	0.31	8.35	0.1198

purposes of computing the progress of the reaction with time, the peak heights for ethyl acetate were used.

Since 50 μ l of the reaction mixture were injected every time, from the amount of ethyl acetate formed at any time (y) its concentration x could be calculated from the relation.

$$x = (yd/50 M) 10^3 \text{ moles/l}$$

where d is the density of ethyl acetate (0.90 g/ml) and M is its molecular weight (88.1). The decrease in concentration of ethanol or acetic acid was also x . The density of the equimolar mixture of the reactants was found to be 0.92 g/ml. Hence the volume of the mixture containing a mole each of the reactant is 115.5 ml. Therefore the initial concentration (a) of each reactant is 8.66 moles/l.

If the reaction is of the second order, then the specific reaction rate k_1 would be related to $(a-x)$ by the expression:

$$1/(a-x) = k_1 t + 1/a$$

where t is the time. The plot of $1/(a-x)$ against t was found in the present instance to be a straight line; hence the reaction is concluded to be of the second order.

TABLE II

KINETICS OF THE UNCATALYSED ESTERIFICATION OF ACETIC ACID BY ETHANOL

$T(^{\circ}K)$	k_1 (l/mole · sec · 10 ⁻⁷)	$k_2 = k_1/K$ (l/mole · sec · 10 ⁻⁸)
333	2.02	5.05
338	2.78	6.95
343	4.37	10.93
348	5.11	12.78
353	6.96	17.40
358	7.50	18.75

The specific reaction rates at various temperatures are given in Table II. The activation energy E was determined from the slope of the linear plot of $\log k_1$ versus $1/T$ and was found to be 14 300 cal/mole. From the energy of activation, the frequency factor A_1 was calculated from the expression,

$$k_1 = A_1 e^{-E/RT}$$

from which $A_1 = 4.85 \times 10^2$ l/mole · sec. From the above data the entropy of activation ΔS_1^* was calculated from the relation,

$$A_1 = (kT/h) e^{\Delta S_1^*/R}$$

where h is the Planck's constant and k is the Boltzmann constant. Substituting for these constants we obtain,

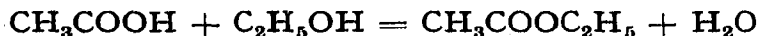
$$\Delta S_1^* = -46.0 \text{ cal/}^{\circ}\text{C.}$$

The kinetic data with and without finely divided wall material, presented in

Table I and Fig. 1 show that the two specific reaction rates are virtually the same, namely 2.0×10^{-7} and 2.02×10^{-7} l/mole·sec, respectively, indicating the absence of any wall catalysis.

From the data for the specific rate for the esterification reaction, it is possible to predict the kinetics of the reverse reaction in the absence of added catalysis.

The equilibrium constant K for the reaction,



is known to be 4.0. Further, this equilibrium constant is virtually unchanged over a range of temperatures, suggesting a small or nearly zero heat of reaction. At equilibrium we have, $K = k_1/k_2$ where k_1 and k_2 are the rate constants for the forward and the reverse reactions, respectively. The rate constants k_1 at various temperatures now having been determined, it is possible to calculate the corresponding values of k_2 at these temperatures. The values are given in Table II. Since the heat of reaction is nearly zero, the energy of activation of the forward and reverse reactions should be nearly the same. We have taken it to be the same as that of the forward reaction. On this basis we have calculated the frequency factor A_2 and the entropy of activation ΔS_2^* for the reverse reaction to be

$$A_2 = 1.23 \times 10^8 \text{ l/mole} \cdot \text{sec}$$

and $\Delta S_2^* = -49.0 \text{ cal/}^\circ\text{C}$, respectively.

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