

## High Pressure Kinetics of Alkaline Ester Hydrolysis

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Kinetic measurements of the hydrolysis of a series of aliphatic esters are described. The hydrolysis catalyzed by hydroxyl ions has been followed at various temperatures and pressures. From the measurement of velocity constants at different temperatures the activation energy has been determined. The results are of the same magnitude, around 56 kJ/mol, as earlier findings.

From the determination of velocity constants at various pressures up to 8000 atm the activation volume, which in the transition state theory is the difference between the partial molar volumes of the activated complex and the reactants, has been calculated. The values of  $\Delta V^{\ddagger}$  found are about  $-6.0$  ml/mol at  $20^{\circ}\text{C}$  for all of the investigated esters.

Measurements at various pressures for the same ester at two temperatures result in roughly the same values for  $\Delta V^{\ddagger}$  showing that the activation volume is independent of temperature in the range examined.

The hydrolysis of esters of the lower fatty acids catalyzed by hydrogen ions and by hydroxyl ions has been extensively examined in the past. From kinetic measurements at constant pressure and variable temperature, the activation energy is known for a number of esters.

Only a few investigations have dealt with the hydrolysis at constant temperature and variable pressure, which allows calculation of the activation volume  $\Delta V^{\ddagger}$ . Bogojawlensky and Tammann<sup>1</sup> have determined the velocity constants for the acid hydrolysis of methyl acetate at 1 and 500 atm, from which the activation volume may be calculated to be  $-8.3$  ml/mol. Using the same method, Osborne and Whalley<sup>2</sup> calculated the value for methyl acetate as  $-9.1$  ml/mol and for ethyl acetate as  $-9.3$  ml/mol. Laidler and Chen<sup>3</sup> hydrolyzed the two esters in alkaline solution at  $25^{\circ}\text{C}$  and at pressure up to 800 atm and found activation volumes of  $-9.93$  ml/mol for methyl acetate and  $-8.77$  ml/mol for ethyl acetate, respectively, apparently based on volume concentrations at atmospheric pressure.

The present paper describes a series of kinetic measurements performed on the alkaline hydrolysis of a number of esters at various pressures up to 8000 atm.

## EXPERIMENTAL

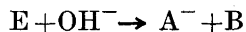
The experiments were carried out in a 10 000 atm apparatus designed to follow reaction kinetics continuously by conductivity measurements. The apparatus consists of a pressure generator with a Bourdon manometer, a reaction chamber with electrodes allowing conductivity measurements, and an electrical circuit for measuring the conductivity. In a preceding paper a detailed description of the equipment and of a series of control measurements of temperature, pressure and conductivity in the reaction chamber has been given.

In the present investigation the conductivity was measured with a Radiometer conductivity meter type CDM 2 connected with a network that permitted continuous recording. The meter output current, which is proportional to the conductivity, was fed to a recorder through an electric circuit designed so that the change in conductivity corresponding to completion of the chemical reaction would produce a deviation of one or two recorder spans. In this way the conductivity, and hence the degree of advancement of the chemical reaction, could be conveniently recorded as a function of time. The setup was checked by replacing the conductivity cell with decade resistors, and the linearity was better than 0.5 %.

All esters were FLUKA products of at least 99 % purity. Before an experiment, the ester was diluted with twice-distilled water to  $2 \times 10^{-2}$  mol/l or  $10^{-2}$  mol/l according to solubility. The solution was thermostatted and 50 ml taken out, to which were added 10 ml or 5 ml of  $10^{-1}$  mol/l NaOH, also thermostatted. The relative concentration error was in all cases smaller than  $1/10^3$ . The time for start of the reaction was noted, and about 3 ml of the mixture were transferred to the high pressure cell. The latter was then connected to the pressure generator and immersed in a thermostat regulated to  $\pm 0.05^\circ\text{C}$ , after which the pressure was raised to the desired value. This would typically take about 30 s; the time was again noted, and recording of the conductivity started. The reaction was normally completed in one or two hours.

## THEORY

The relationship between kinetics and conductivity may be described as follows. Let the reaction be symbolized by:



in which HA is the organic acid and B the alcohol composing the ester E. The specific conductance  $\kappa$  of the reaction mixture may be considered as the sum of the contributions of the various ionic species of concentration  $c_i$ :  $\kappa = \sum_i \Lambda_i c_i$ . In the first approximation the molar conductances  $\Lambda_i$  may be assumed to be constant, since the total number of ions remains constant. If  $\kappa_0$  denotes the specific conductance due to ions not taking part in the reaction, then the total conductivity  $\kappa$  may be written

$$\begin{aligned} \kappa &= \kappa_0 + \Lambda_{\text{OH}^-} c_{\text{OH}^-} + \Lambda_{\text{A}^-} c_{\text{A}^-} \\ &= \kappa_0 + \Lambda_{\text{OH}^-} (C - c) + \Lambda_{\text{A}^-} c \\ &= p + q (C - c) \end{aligned}$$

where  $C$  is the initial concentration of E or  $\text{OH}^-$ , whichever is the smaller, and  $c = c_{\text{A}^-}$ . There is thus a linear relationship between conductance and reactant or product concentration.

Strictly speaking, the molar conductances are not constant but depend on composition, and a better approximation would presumably be to calculate the  $\Lambda$ -values for NaOH and NaA from the Onsager equation and to suppose

the conductances to be additive. This results in a relationship that is not exactly linear; but numerical calculation shows that deviation from linearity amounts in the worst case to 1 % of the total change in conductivity, or to an error of 1 % in the concentration values. Because of this, and since the justification for using the Onsager equation is questionable, the simple linearity has been assumed to be valid. The assumption is supported by the fact that concentrations calculated in this way fit very nicely with kinetic theory.

The kinetics of the reactions examined are known to be of the second order at room temperature and atmospheric pressure. Supposing that this is equally so in the present case, and that the initial concentrations of E and OH<sup>-</sup> have the same value  $C$ , the rate equation is:

$$dc/dt = k (C-c)^2$$

that is,

$$kt = \frac{1}{C-c} - \frac{1}{C}$$

If the linear relation between  $\kappa$  and  $c$  is inserted in this equation, and the constants are replaced by  $\kappa$  values at  $t=0$  and  $t=\infty$ , the following expression may be obtained:

$$\kappa(t) = \kappa(\infty) + \frac{1}{kC} \frac{\kappa(0) - \kappa(t)}{t}$$

This expression is useful when the last, rather than the first, measurements of a run are reliable. Numerical calculation of the factor  $(kC)^{-1}$  was made on a computer as follows. First, the parameters of a straight line giving the best fit to 30–40 points are determined by the method of least squares, using the experimental value of  $\kappa(0)$ . Since this latter value is somewhat uncertain the time axis is later shifted by various amounts to obtain the best possible fit, again using the least squares principle.

Knowing the value of the product  $kC$ , it is still necessary to determine  $C$  in order to obtain the rate constant  $k$ . For experiments carried out at atmospheric pressure, the initial concentration  $C$  is calculated directly from known volumes and concentrations of the solutions that are mixed at  $t=0$ . For high pressure experiments, the same method is applied, and the concentration of the reactants is then calculated for the moment the pressure is raised from 1 atm to the pressure chosen for the experiment. The subsequent phase is thus considered as a separate reaction starting at the moment of transition and with a mixture of the calculated concentration. The correct value of  $k$  still cannot be found until the relevant initial concentration, valid at high pressure, has been computed from the 1 atm value. This is done using the data of Bridgman<sup>4</sup> for the relative volume of water at high pressures. The calculations were all included in the computer program.

When the rate constant  $k$  has been determined for a given reaction at various temperatures and pressures, two parameters of the absolute rate theory may be calculated. According to transition state theory, the activation enthalpy  $\Delta H^\ddagger$  is given by the equation

$$\frac{\partial \ln k}{\partial(1/T)} = - \frac{\Delta H^{\ddagger}}{R} - T$$

and similarly the activation volume  $\Delta V^{\ddagger}$  may be found from

$$\frac{\partial \ln k}{\partial P} = - \frac{\Delta V^{\ddagger}}{RT}$$

The latter is the molar volume of the activated complex less the sum of the molar volumes of the reactants, referred to the standard states of the components.

## RESULTS

*Reactions at atmospheric pressure.* Although most of the reactions have been examined at 1 atm by other authors (*cf. e.g.* Refs. 5, 6), it was judged necessary to repeat them with the method described, partly to ensure consistency with high pressure results, and with results found by other authors, but also to provide the necessary corrections for the high pressure results since reactions were started at low pressure in these cases.

The results are summarized in Table 1. The values at 25°C were obtained before all refinements had been made and so are less precise than the rest. For each reaction, the rate constant was measured at two temperatures in order that errors due to temperature fluctuation might be estimated. The activation energy calculated from these values is tabulated in the last column. The agreement with results of other authors<sup>5,6</sup> is, in most cases, better than 1–2 % for the  $k$ -values.

Table 1. Rate constants of alkaline hydrolysis of esters at atmospheric pressure.

Ester	$k$ at 20.0°C l mol <sup>-1</sup> min <sup>-1</sup>	$k$ at 25.0°C l mol <sup>-1</sup> min <sup>-1</sup>	$k$ at 30.0°C l mol <sup>-1</sup> min <sup>-1</sup>	$\Delta H^{\ddagger}$ kJ mol <sup>-1</sup>
Methyl acetate	8.04–8.14		15.9 – 16.0	48.5 ± 0.7
Ethyl acetate	4.83–4.86	6.62–6.65	9.04 – 9.04	43.9 ± 0.2
sec. Propyl acetate	1.28–1.29	1.58–1.72	3.37 – 3.42	69.8 ± 0.8
Butyl acetate	4.02–4.08		7.34 – 7.47	42.6 ± 1.1
Amyl acetate	3.62–3.63		6.77 – 6.86	44.6 ± 0.6
Isopentyl acetate	3.14–3.20		6.40 – 6.57	51.1 ± 1.5

*Reactions at high pressure.* Preliminary investigations have shown, and later measurements have confirmed that in the conditions investigated all of the reactions examined conform to second order kinetics theory. An example is shown in Fig. 1 in which  $\kappa(t)$  is plotted against  $(\kappa(0) - \kappa(t))/t$  for the amyl acetate reaction at 20.0°C and 4000 atm. The points are seen to fit satisfactorily to the theoretical straight line; no other simple kinetic scheme would fit the data equally well.

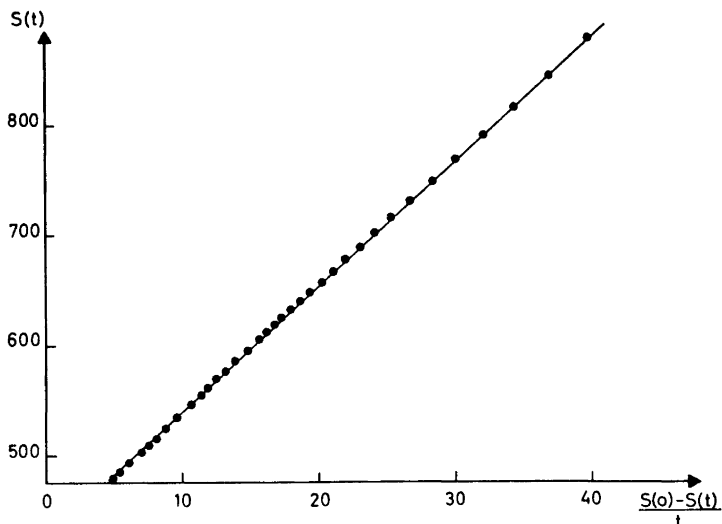


Fig. 1. Plot of  $S(t)$  vs.  $(S(t)-S(0))/t$  where  $S(t)$  is a recorder reading that depends linearly on the specific conductivity  $\kappa$  of the reaction mixture at the time  $t$ .

Kinetic measurements have been performed on hydrolysis reactions of the six esters mentioned in Table 1, in most cases at 20.0°C, and at pressures between 2000 and 8000 atm. The results are collected in Table 2 where  $t_0' - t_0$

Table 2. Rate constants of alkaline hydrolysis of esters at high pressure.

Ester	Temperature °C	Pressure atm	$t_0' - t_0$ min	Rate constant $k$ l mol <sup>-1</sup> min <sup>-1</sup>
Ethyl acetate	20	5000	4	15.9 ± 0.1
Ethyl acetate	20	8000	5	31.0 ± 0.5
Ethyl acetate	30	5000	4	31.5
Ethyl acetate	30	8000	4	70.5 ± 4.0
Butyl acetate	20	2000	3	6.1 ± 0.1
Butyl acetate	20	5000	3	14.1
Butyl acetate	20	8000	4	25.7
Isobutyl acetate	20	2000	3	5.7
Isobutyl acetate	20	5000	3	12.3
Isobutyl acetate	20	8000	4	28.3
sec-Propyl acetate	20	2000	3	2.08
sec-Propyl acetate	20	5000	4	5.2
sec-Propyl acetate	20	8000	4	11.4
Amyl acetate	20	2000	3	6.0
Amyl acetate	20	4000	3	9.5
Amyl acetate	20	6000	4	14.3
Amyl acetate	20	8000	3	25.2

indicates the time elapsed between the mixing of the components at one atmosphere and the achievement of the high pressure, and  $k$  is the rate constant at the indicated pressure and temperature.

The results are displayed graphically in Fig. 2, which depicts curves of  $\ln k$  against pressure for the six esters. The points fit straight lines, showing

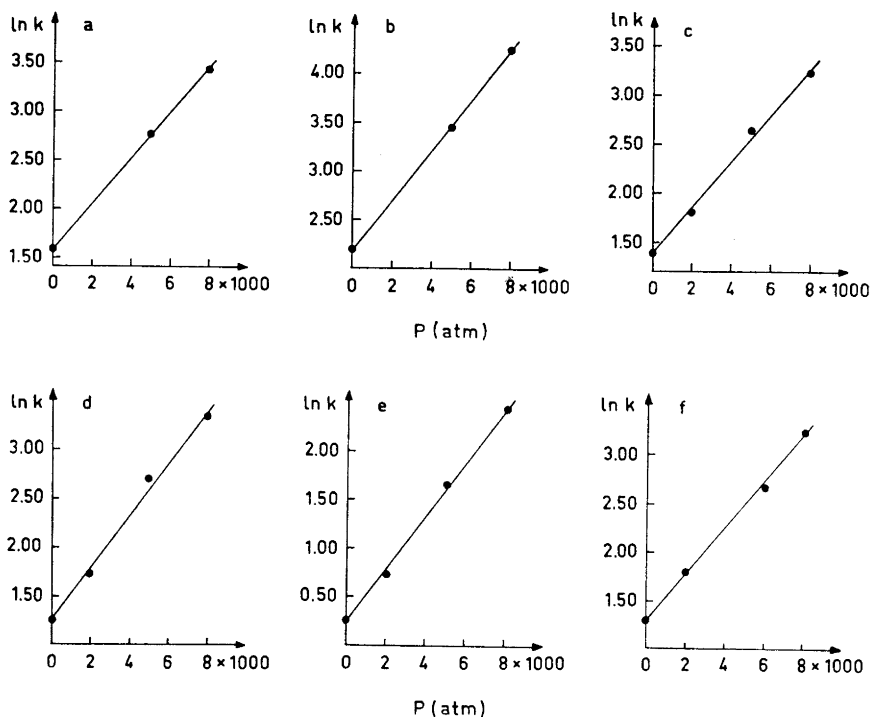


Fig. 2. Plots of the natural logarithm of the rate constant  $k$  against the pressure  $P$  at constant temperature.

a) ethyl acetate at 20°C; b) ethyl acetate at 30°C; c) butyl acetate at 20°C; d) isobutyl acetate at 20°C; e) *sec*-propyl acetate at 20°C; f) amyl acetate at 20°C.

Table 3. Activation volumes of esters.

Ester	Temperature °C	$\Delta V^\ddagger$ ml mol <sup>-1</sup>
Ethyl acetate	20	-5.6
Ethyl acetate	30	-6.4
<i>sec</i> -Propyl acetate	20	-6.6
Butyl acetate	20	-5.6
Isobutyl acetate	20	-6.3
Amyl acetate	20	-5.8

that within the experimental error, the activation volume is pressure independent, in contrast to what is generally found.<sup>7</sup> In all cases,  $k$  is increased by a factor of about 6 when the pressure is raised from 1 to 8000 atm.

Finally, Table 3 contains the activation volumes for the six ester reactions as calculated from the rate constant values. It is apparent that the activation volume has not only the same sign but also same magnitude, about  $-6$  ml per mole, in all cases. These independent measurements thus support each other if, as is likely, the mechanism is the same in all six cases.

In the case of ethyl acetate, high pressure measurements have been performed at two temperatures. These allow determination of the energy of activation at 1, 5000, and 8000 atm as  $43.9 \pm 0.2$ ,  $48 \pm 3$ , and  $58 \pm 5$  kJ mol<sup>-1</sup>, respectively. Because of high reaction rates, the latter values are somewhat uncertain, but the energy of activation appears to rise with increasing pressure.

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#### REFERENCES

1. Bogojawlensky, A. and Tamman, G. *Z. physik. Chem. (Leipzig)* **23** (1897) 13.
2. Osborne, A. R. and Whalley, E. *Can. J. Chem.* **39** (1961) 1094.
3. Laidler, K. J. and Chen, D. *Trans. Faraday Soc.* **54** (1958) 1026.
4. Bridgman, P. W. *The Physics of High Pressure*, G. Bell and Sons, London 1958, p. 130.
5. Olsson, H. *Z. physik. Chem. (Leipzig)* **118** (1925) 107; **125** (1927) 243.
6. Salmi, E. J. and Leimu, R. *Suomen Kemistilehti B* **20** (1947) 43.
7. Hamann, S. D. *Ann. Rev. Phys. Chem.* **15** (1964) 351.

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