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Kinetic Investigation of the Reaction between Propylene Oxide and Acetic Acid

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The rate of the reaction between propylene oxide and acetic acid was found to be first order in propylene oxide concentration, while the partial reaction order for acetic acid varied with the composition of the reaction mixture between 2.0 and 2.6. Different alkali-metal acetate catalysts were investigated as well as the temperature dependence of the ' non-catalysed ' and ' catalysed ' reactions. Our results suggest that protonated propylene oxide formed in the pre-equilibrium and the hydrogen-bonded acetic acid–propylene oxide complex react with acetate ion or with acetic acid.

The reaction between propylene oxide and acetic acid, which produces propylene glycol monoacetate by nucleophilic addition, is partly understood as so far only a few authors have dealt with the elucidation of its kinetics and mechanism.[1-3] Several basic questions remained unanswered, *e.g.* the relation between the change in composition of the mixture and the values of partial kinetic orders, the mechanism of the reaction, and the nature of the reaction catalysed by alkali-metal acetates. The investigation of the reaction between propylene oxide and acetic acid enables the ring-opening addition reactions between carboxylic acids and oxirans to be studied,[4-8] and gives information on important industrial reactions, such as the ' one-step ' production of propylene glycol monoacetate from propylene and acetic acid by catalytic acetoxylation.[9,10]

Results

(1) *Kinetic Investigation of the Reaction between Propylene Oxide and Acetic Acid.*—The reaction is apparently first order in propylene oxide as found similarly by Isaacs and Schmitt.[1-3] For an acetic acid : propylene oxide molar ratio n° of 7 even at high conversion (*i.e.* 80%) no great deviations were found in the kinetic curve, but in mixtures of high propylene oxide concentration (*i.e.* n° 1) and high conversions the curve showed deviation from that for first-order kinetics. The value of the rate constant (k_1) changed with the composition of the mixture. From this fact it may be concluded that the reaction is not of first, but of a higher order with more complicated molecularity (see Figure 1). Thus, the rate of the reaction cannot be described by equation (1) which contains whole number exponents of the concentrations (see Table). The rate

$$r_e^\circ = k\,(C_A^\circ)^\alpha (C_B^\circ)^\beta \qquad (1)$$

constants obtained from the graphs and the initial rate obtained from k_1 determined over small concentration ranges ($r^\circ = k_1 C_B^\circ$) show good agreement in Figure 1 (therefore for simplicity the reaction rate was determined by the use of k_1 values).

A more general equation describing the rate of the propylene oxide–acetic acid reaction for a solvent-free medium was sought after. For such an equation an exact knowledge of the kinetic partial order of the reactants is required. Since it was expected that associated states would play an important role in the reaction, we tried to choose a solvent which behaves like an inert diluting material. Benzene, chlorobenzene, carbon tetrachloride, and other solvents with small dielectric constants and low affinity to hydrogen bond interaction influence the acetic acid dimer–monomer equilibrium the least.[11-18]

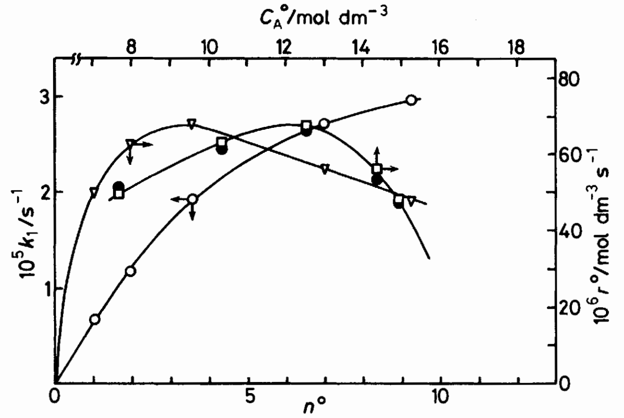

Figure 1. Dependence of the reaction rate and k_1 on the composition of the mixture at 50 °C: □, calculated from k_1; ●, obtained by differentiation of the plot

Figure 2 shows that the value of α changed with the mixture composition; at higher acetic acid concentrations α is 2.6, while at n° 1 it is 2.0. In the experimental range it was independent of temperature.

For the propylene oxide partial order determination changes in mixture composition (*i.e.* the chlorobenzene : propylene oxide ratio) affected the reaction only to a small degree. This is verified by the propylene oxide partial order (β 1.0) measured in chlorobenzene solution (see Figure 3).

Tetrahydrofuran, which has electron-donating character, interacts with acetic acid and so cannot be considered as inert as chlorobenzene as the β value of 0.9 shows.

The Table shows that the overall rate constants calculated at different mixture compositions based on α 2.6 and β 1.0 do not depend on the mixture composition. The solvent-free propylene oxide–acetic acid reaction may well be described by the partial orders obtained from the reaction in chlorobenzene (*i.e.* chlorobenzene solvent does not cause strong solvent–reactant interactions).

We suggest equation (2) for the initial rate of the propylene oxide–acetic acid reaction.

$$r = k(C_A^\circ)^{2.6}(C_B^\circ) \text{ for } n^\circ \geqslant 2 \qquad (2)$$

(2) *Investigation of the Reaction between Propylene Oxide and Acetic Acid in the Presence of Alkali-metal Acetates.*—In agreement with published data,[16] it was found that alkali-

Determination of partial kinetic reaction orders of the acetic acid–propylene oxide reaction at 50 °C by the differential method

Experiment	Acetic acid–propylene oxide concentration		Initial rate *	Rate constants k			
	$C_A°$/mol dm^{-3}	$C_B°$/mol dm^{-3}	$10^6\ r_e°$/ mol dm^{-3} s^{-1}	$\frac{10^6\ r_e°}{C_A°C_B°}$ (dm^3 mol^{-1} s^{-1})	$\frac{10^6\ r_e°}{C_A°(C_B°)^2}$ (dm^6 mol^{-2} s^{-1})	$\frac{10^6\ r_e°}{(C_A°)^2C_B°}$ (dm^6 mol^{-2} s^{-1})	$\frac{10^6\ r_e°}{(C_A°)^{2.6}C_B°}$ (dm$^{7.8}$ mol$^{-2.6}$ s^{-1})
1	7.68	7.43	50.5	0.885	0.119	0.115	0.0339
2	10.32	5.30	61.2	1.119	0.211	0.108	0.0267
3	12.52	3.53	66.0	1.493	0.423	0.119	0.0262
4	14.30	2.10	50.3	1.675	0.798	0.117	0.0237
5	14.36	2.06	52.8	1.785	0.866	0.124	0.0251
6	14.91	1.61	47.0	1.987	1.234	0.131	0.0260

* Extrapolated to time 0.

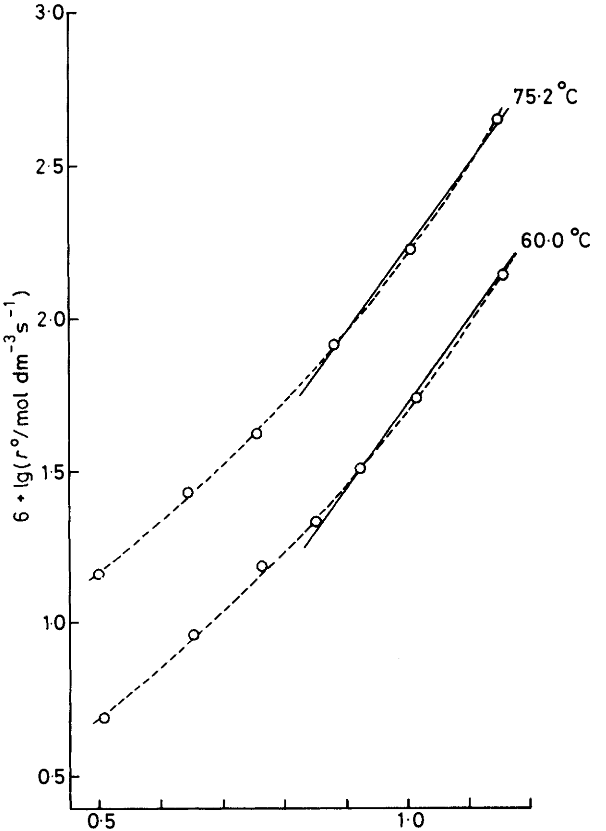

Figure 2. Determination of the reaction order for acetic acid at 60 and 75.2 °C, using chlorobenzene as solvent: $C_B°$ 2.0 mol dm^{-3}

metal acetates increase the rate of the reaction. The conversion of propylene oxide can be described by a first-order rate equation to a good approximation. Figure 4 shows the dependence of the initial rates on catalyst concentration. It can be seen that after an initial period the rate increases linearly with increasing catalyst concentration, and the reaction rate is also affected by the quality of alkali-metal acetate. Similar behaviour may be observed in the case of a molar ratio $n°$ of 1. At higher catalyst concentrations, however, there is a deviation from linearity. Presumably there is a decrease in the electrolytic dissociation of the catalyst in the case of $n°$ 1 (see Figure 5).

The dependence of the initial rate of the addition reaction catalysed by potassium acetate on the concentration of the catalyst and on the reaction temperature has been examined (see Figure 6). From the temperature dependence of the reaction rate for ' non-catalytic ' processes the following activation energy value (at $n°$ 7) was obtained: E_a 79.5 ± 3.9 kJ mol^{-1}, in good agreement with the literature value [2] 77.4 ± 3.8 kJ mol^{-1}. The linear slopes in Figure 6 are characteristic of the temperature dependence of the ' catalytic ' process. The activation energy calculated from the Arrhenius plot is in good agreement with that of the ' non-catalytic ' process.

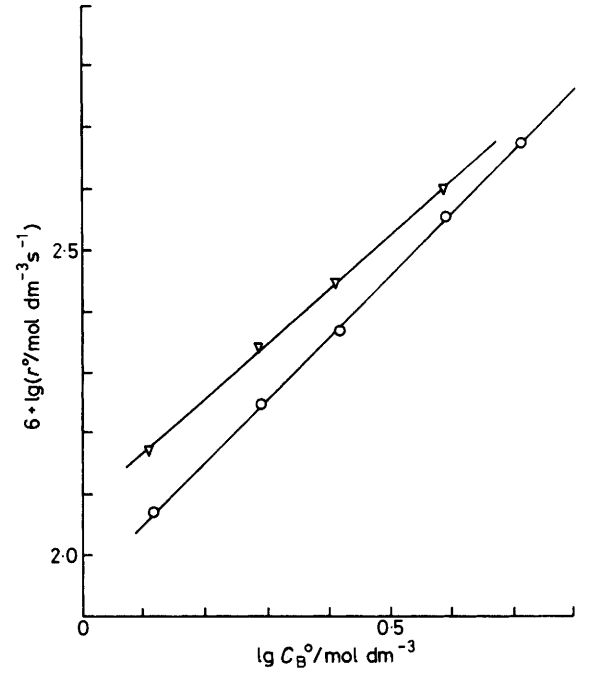

Figure 3. Determination of the reaction order for propylene oxide at 74.8 °C: ○, with chlorobenzene; ▽, with tetrahydrofuran; $C_A°$ 10.0 mol dm^{-3}

Discussion

The reaction of acetic acid with propylene oxide is a complex process of consecutive reaction steps, consisting of two bimolecular main steps. At first the oxiran (B:) becomes activated (protonated) by a solvated or a free proton (A_iH) or by acetic acid (A_2H) producing a hydrogen bond [reaction (3)]. Then the complex formed gives the product on reaction with a nucleophile (Nu_1 = acetic acid, Nu_2 = acetate anion) by a slower, rate-determining step (4). K_i is the pre-equilibrium

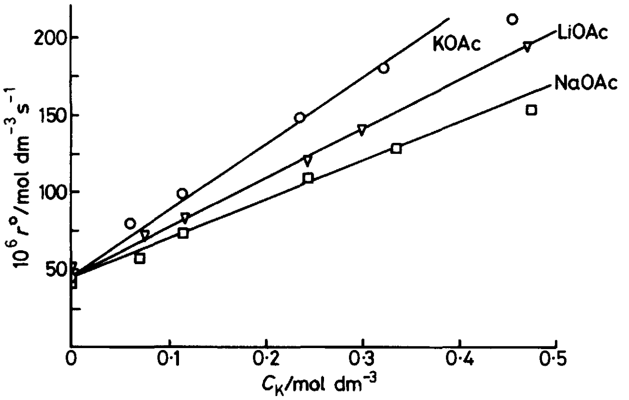

Figure 4. Effect of the amount of alkali-metal acetate catalyst on the rate of the propylene oxide–acetic acid reaction at 50 °C and n° 7

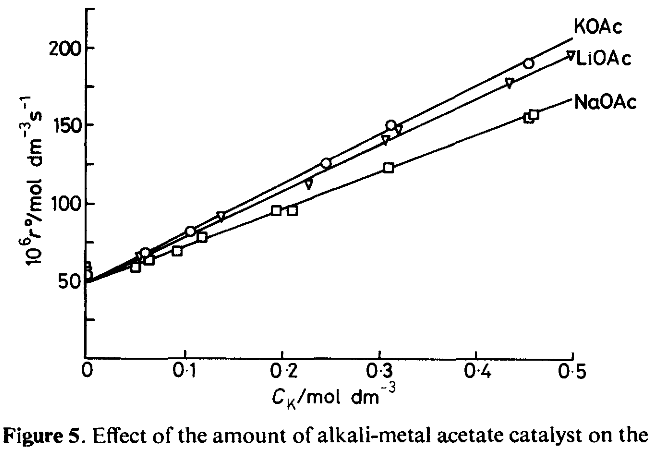

Figure 5. Effect of the amount of alkali-metal acetate catalyst on the rate of the propylene oxide–acetic acid reaction at 50 °C and n° 1

$$\mathrm{B\!:} + \mathrm{A_iH} \underset{}{\overset{K_i}{\rightleftharpoons}} \mathrm{A_iH\!:\!B} \qquad (3)$$

$$\mathrm{A_iH\!:\!B} + \mathrm{Nu}_j \xrightarrow{k_{i,j}} \mathrm{BHNu}_j + \mathrm{A}_i \qquad (4)$$

constant of the protonation and $k_{i,j}$ the rate constant of the partial process (4).

In the case of low conversion and at $n^\circ \geqslant 2$ the glycol monoacetate product (as $\mathrm{Nu_3}$) can be neglected because of its small concentration and slight nucleophility,[17] and the overall reaction rate (r) can be given by equation (5).

$$r = [\mathrm{B\!:}](k_{11}K_1[\mathrm{A_1H}][\mathrm{Nu_1}] + k_{21}K_2[\mathrm{A_2H}][\mathrm{Nu_1}] + k_{12}K_1[\mathrm{A_1H}][\mathrm{Nu_2}] + k_{22}K_2[\mathrm{A_2H}][\mathrm{Nu_2}]) \qquad (5)$$

The concentrations of the reactants ($\mathrm{A_iH}$) and (Nu_j) in equation (5) are simultaneously influenced by several factors. The acid in acetic acid–solvent systems is present as monomer, dimer, and oligomer forms.[11-15] The ratio of these forms depends on the solvent and on the concentration of the acid which is also influenced by the electrolytic dissociation process. The reaction rate depends on the concentration of acetic acid in a complicated manner, for the composition of the mixture influences the pre-equilibrium; with an increase in the dielectric constant of the mixture the stability of the $\mathrm{A_iH\!:\!B}$ transition complex decreases.[18,19] It is not surprising that the overall experimental partial reaction order (α) is a fraction, which makes possible the simultaneous occurrence of a number of steps.

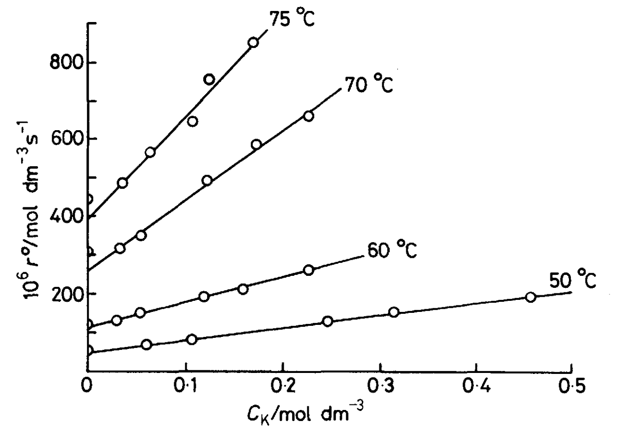

Figure 6. Dependence of the rate of the propylene oxide–acetic acid reaction catalysed by potassium acetate on the amount of catalyst at different temperatures and n° 7

Because of the complicated nature of the reaction, the validation of equation (5) requires further study.

Experimental

Kinetic investigations were carried out by dilatometry. Conversion values (X) were determined from the volume contraction values (ΔV) by relationship (6) where $m_B{}^\circ$ is the initial weight of propylene oxide in the dilatometer.

$$X(\%) = 100\,\mathrm{D_T}\Delta V(m^\circ_B)^{-1} \qquad (6)$$

For the calculation of the dilatometric constant (D_T), the densities in equations (7)—(9) were used[20] where d_A, d_B, and d_C are the densities of acetic acid, propylene oxide, and glycol monoacetate, respectively.

$$d_{A,T} = 1.0721 - 0.001\,12T,\ 15\ ^\circ\mathrm{C} \leqslant T \leqslant 115\ ^\circ\mathrm{C} \qquad (7)$$

$$d_{B,T} = 0.8552 - 0.001\,32T,\ 0\ ^\circ\mathrm{C} \leqslant T \leqslant 90\ ^\circ\mathrm{C} \qquad (8)$$

$$d_{C,T} = 1.0679 - 0.001\,00T,\ 40\ ^\circ\mathrm{C} \leqslant T \leqslant 90\ ^\circ\mathrm{C} \qquad (9)$$

Equations (8) and (9) were determined by a dilatometer[21] of calibrated volume. The temperature dependence of D_T is given by equation (10).

$$D_T = 4.365 - 0.03\ T^{0.864} \qquad (10)$$

The value of D_T was also determined experimentally in the case of 100% conversion. At lower temperatures (50—60 °C) and with high n° values the experimentally determined and calculated D_T values were equal to within 1%; at higher temperatures (80 °C or above) however, experimental values *ca.* 10% higher than those calculated were obtained. In g.l.c. analysis, propylene glycol diacetate and oxypropylated products of high molecular weight were found. In the formation of these substances, the role of transacylation processes[22] cannot be excluded.

Materials were Fluka puriss grade. Propylene glycol monoacetate was prepared in an autoclave.[16]

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