

KINETICS OF REACTION OF 1-CHLORO-2,3-EPOXYPROPANE WITH LOW GLYCOLS

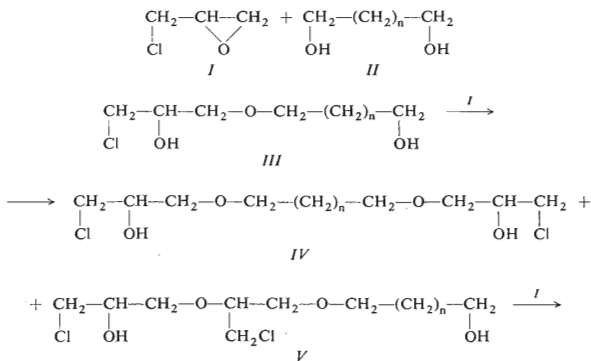
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Received February 9th, 1971

The reactions of 1-chloro-2,3-epoxypropane with 1,3-propanediol, 1,4-butanediol and 1,5-pentane-
diol, respectively, in the presence of boron fluoride diethyletherate catalyst are of the first order
with regard to 1-chloro-2,3-epoxypropane as well as to the catalyst; within the catalyst concentra-
tions ranging from 6–24 mmol/l the participation of the catalyst in the reaction is incomplete.
The reaction mechanism of studied reactions is similar to the S_N2 type judging from the activa-
tion entropy changes and from the influence of dielectric constant of reaction medium upon
the reaction.

1-Chloro-2,3-epoxypropane (*I*) reacts, in the presence of boron fluoride diethyletherate, with low
molecular glycols (*II*) forming linear ethers *i.e.* O-(3-chloro-2-hydroxypropyl) derivatives of gly-
cols (*III*)¹. The overall hydroxyl group content in the reaction mixture remains constant. The
hydroxyl groups of the primary adduct *III* (Scheme 1)² can compete with the initial glycol for
the monomer *I*. Polyethers *VI* and *VII* (ref.^{3,4}) are formed by polyaddition. It is assumed that
beside the above considered "normal" epoxy cycle opening⁵ also "abnormal" opening takes
place in a lesser extent thus leading to the 1-chloromethyl-2-hydroxyethyl hydroxyalkyl ethers
formation^{6–9}. These compounds, however, have not been isolated even in the simplest cases^{2,9–13}.



RESULTS AND DISCUSSION

The studied reactions of 1-chloro-2,3-epoxypropane (*I*) with glycols (*II*) represent systems where consecutive competing reactions take place. Not even 16-fold excess of 1,4-butanediol (*IIc*) with regard to *I* can preclude the consecutive addition of monomer *I*. This was confirmed by paper chromatography which revealed the presence of adduct *IVc* in the reaction mixture; when the ratio $[IIc]_0/[I] = 7$ the compound *VIII* can also be detected in the system. As these results have already been observed for the case of ethylene glycol², it is likely that the same applies to 1,3-propanediol and 1,5-pentanediol³. In the case of all three alkanediols the reaction rate obeys the equation

$$-d[I]/dt = k_1[I]. \quad (1)$$

The rate constant k_1 is directly proportional to the catalyst concentration $[C]$ within the concentration region ranging from $0.6 \cdot 10^{-2}$ to $2.4 \cdot 10^{-2} \text{ mol l}^{-1}$. The straight

TABLE I

Rate Constants of the Reaction of 1-Chloro-2,3-epoxypropane (*I*) with Alkanediols (*II*) Catalysed by Boron Fluoride Etherate (C)
Ratio $[II]_0/[I]_0 = 7$, 30°C.

$[C] \cdot 10^2$		$k_1 \cdot 10^3$ min^{-1}	$k'_2 \cdot 10^3$ $\text{mol}^{-1} \text{ s}^{-1}$	$k_2 \cdot 10^3$
mol l^{-1}	mol \%^a			
1,3-Propanediol, $q \cdot 10^2 = 0.350 \text{ mol l}^{-1}$				
0.848	0.5	3.28	6.45	10.98
1.190	0.7	5.03	7.04	9.98
1.708	1.0	8.79	8.58	10.79
2.400	1.4	13.12	9.11	10.67
1,4-Butanediol, $q \cdot 10^2 = 0.341 \text{ mol l}^{-1}$				
0.710	0.5	1.61	3.78	7.27
0.995	0.7	2.90	4.86	7.39
1.422	1.0	4.28	5.01	6.60
2.136	1.5	7.63	5.95	7.08
1,5-Pentanediol, $q \cdot 10^2 = 0.376 \text{ mol l}^{-1}$				
0.609	0.5	0.86	2.35	6.15
0.855	0.7	1.62	3.16	5.74
1.225	1.0	3.08	4.19	6.05
1.842	1.5	5.39	4.88	6.13

^a With regard to *I*.

lines expressing this relationship do not, however, go through the origin (Fig. 1). At the mentioned concentrations of $[C]$ the Eq. (1) can be substituted by the relationship²⁻¹³

$$-d[I]/dt = k_2[I]([C] - q), \quad (2a)$$

where k_2 is a rate constant with the dimension of the second order reaction (expressed in $\text{mol}^{-1} \text{l s}^{-1}$) and q is defined as a concentration of catalyst for $k_1 \rightarrow 0$ (extrapolation of k_1 vs $[C]$ at $k_1 = 0$). The experimental values of q obey the relationship $q = r[II]_0/[I]_0 + N$; by the least square method it was found that $r = -7.4 \cdot 10^{-5} \text{ mol l}^{-1}$ and $N = 0.4 \cdot 10^{-2} \text{ mol l}^{-1}$. According previous measurements² with ethylene glycol it was calculated that $r = -6 \cdot 10^{-5} \text{ mol l}^{-1}$ and $N = 0.3 \cdot 10^{-3} \text{ mol l}^{-1}$.

The difference between the constant k_2 defined by the equation (2a) and the corresponding values of constant k'_2 in the relationship

$$-d[I]/dt = k'_2[I][C], \quad (2b)$$

is apparent from Table I.

The reaction rate was followed for different initial molar ratios II and I ($[II]_0/[I]_0$ equal 7, 10, 13 and 16, respectively) and for various catalyst concentrations ranging from 0.5–1.5 mol. % with regard to I . The results (e.g. in the case of 1,5-pentanediol the average values of k_2 are calculated from 4–5 measurements $[II]_0/[I]_0$ being $6.02 \cdot 10^{-2}$, $4.52 \cdot 10^{-2}$, $5.34 \cdot 10^{-2}$ and $5.91 \cdot 10^{-1} \text{ l s}^{-1}$) are again in good agreement with the information obtained from studying reaction of I with ethylene

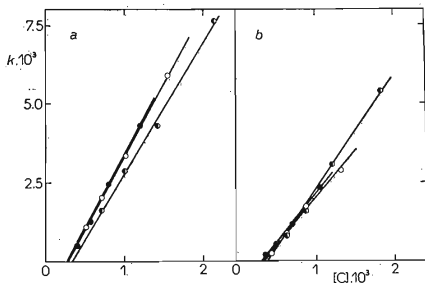


FIG. 1

The Influence of Catalyst Concentration ($[C]$, mol l^{-1}) upon the Rate Constant k_1 (min^{-1}) of the Reaction of I with 1,4-Butanediol IIc (a) or with 1,5-Pentanediol $IIId$ (b) at 30°

$[II]_0/[I]_0$: ● 7, ○ 10, ● 13.

glycol² and with low alcohols^{9,10}. It appears that the concentration of hydroxyl groups does not influence the rate of the studied reaction. The values of rate constants of primary and consecutive reactions must be very similar. If the consecutive reactions were faster than the primary initiation reaction then a marked change of the k_2 value have to appear when changing the $[II]_0/[I]_0$. Inversely, if the initiation reaction were faster than consecutive reactions then the presence of compound VIII could not be detected. If \bar{K} is taken as a ratio of rate constants of consecutive reactions (supposing they are all equal) to rate constants of initiation reactions then it is possible, using a mathematical model⁴, to calculate molar ratios of the first three addition steps. *E.g.* at $[II]_0/[I]_0 = 10$ and $\bar{K} = 0.1$ these values were calculated to be 9.9187 : 0.0534 : 0.0002, for $\bar{K} = 1$ only 8.0479 : 0.4569 : 0.0155 whereas for $\bar{K} = 10$ this ratio equals to 5.0283 : 1.6991 : 0.4107.

The values of overall activation energy and the frequency factor were calculated by the least square method employing kinetic data obtained from experiments carried out at 30–50°C, the ratio $[II]_0/[I]_0$ being 16 (Table II). The decrease of the reaction rate as well as the overall reaction rate and the frequency factor with the increasing length of the aliphatic chain of alkanediols is apparent. Almost identical are the activation entropy changes at 30°C, ΔS_{303}^\ddagger . This signifies that identical mechanisms are operative at a kinetically critical moment. Whereas typical S_N1 mechanism reactions¹⁷ exhibit at 24°C ΔS_{297}^\ddagger c. 7 e.u. and S_N2 mechanism reactions have $\Delta S_{297}^\ddagger = -22$ e.u., the values of ΔS_{303}^\ddagger observed by us suggest that hybrid form of both mechanisms, sometimes called "borderline S_N2 mechanism"^{5,10}, is operative in our case.

When examining the influence of the dielectric constant of environment upon the reaction rate the values^{18,19} of dielectric constants (D) were employed in the case of alkanediols *Ila–d*. To these results also the results obtained with ethylene glycol² were included. It was confirmed that the Kirkwood relationship²⁰

$$\log k_D = \log k - \text{const.} (D - 1)/(2D + 1) \quad (3)$$

holds here *i.e.* that in the case of polar molecules the reaction rate of similar reactions at given temperature or that of one reaction at different temperatures can be changed by changing the dielectric constant of the reaction medium. The straight line dependences of $\log k_2$ vs $(D + 1) : (2D + 1)$ corresponding to individual alkanediols intersect at one point which correspond to the reaction medium with $D = 61.6$ and $k_2 = 0.2 \cdot 10^{-3} \text{ mol}^{-1} \cdot \text{s}^{-1}$; It was calculated, using Arrhenius equation, that the intersection corresponds to the reaction rate at 1.2 K. Some authors^{10,21,22} employ another equation to express the relationship between the reaction rate and the dielectric constant,

$$\log k_2 = mD + p. \quad (4)$$

Sekiguchi and coworkers⁹ have found that the coefficients in Eq. (4) for low alcohols are not identical with those for 2-methoxyethanol. The same holds also for low molecular glycol homologues. Moreover, the value of m in this case increases with temperature (in the case of alcohols 0.053 at 20°C, 0.058 at 30°C and 0.051 at 40°C; in the case of alkanediols *Ila–d* 0.068 at 30°C,

0.071 at 35°, 0.085 at 40°C, 0.087 at 45°C and 0.103 at 50°C). Thus a mean value of m (0.083) was determined and this was used farther for calculations of isodielectric rate constant $k_{2,D}$ with the relative basis at 30°C employing the equation

$$k_{2,D}^t = k_2^t \text{antilog } m(D_{30} - D_t), \quad (4a)$$

where $k_{2,D}^t$ stands for a rate constant at $t^\circ\text{C}$ in a solvent whose dielectric constant corresponds to 30°C, k_2^t being a rate constant at $t^\circ\text{C}$ in a solvent with the dielectric constant D_t , the dielectric constant of solvent at temperature $t^\circ\text{C}$ is denoted as D_t . The values of isodielectric activation energies E_D and activation entropy changes $\Delta S_{303,D}^\ddagger$ were calculated us. γ values of $k_{2,D}$. In the case of alkanediols the values of E_D (Table II) vary more than those measured for methanol, ethanol, 1-propanol, 2-propanol and 1-butanol (19.3–20.0 kcal mol⁻¹)⁹ although these values are

TABLE II

Kinetic Parameters of the Reaction of 1-Chloro-2,3-epoxypropane (I) with Alkanediols (II)
The Ratio $[II]_0/[I]_0 = 16$.

t °C	k_2 10 ⁻³ mol ⁻¹ s ⁻¹	$k_{2,D}$	t °C	k_2 10 ⁻³ mol ⁻¹ s ⁻¹	$k_{2,D}$
1,2-Ethanediol			1,4-Butanediol		
30	49.2	49.2	30	10.2	10.2
35	70.6	85.5	35	13.9	16.5
40	123.8	184.96	40	17.0	23.9
45	179.0	329.9	45	23.2	38.8
50	304.0	678.5	50	27.9	54.4
1,3-Propanediol			1,5-Pentanediol		
30	15.7	15.7	30	5.9	5.9
35	20.4	24.7	35	7.3	8.5
40	28.3	40.6	40	8.8	11.7
45	35.3	61.5	45	13.0	19.8
50	48.7	100.7	50	14.9	26.0

Diol ^a	A mol ⁻¹ s ⁻¹	E kcal mol ⁻¹	E_D kcal mol ⁻¹	ΔS_{303}^\ddagger cal mol ⁻¹ K ⁻¹	$\Delta S_{303,D}^\ddagger$ cal mol ⁻¹ K ⁻¹
1,2-Ethanediol	5.2 · 10 ¹⁰	17.6	26.2	-15.9	-14.2
1,3-Propanediol	1.37 · 10 ⁶	11.0	18.4	-16.2	-15.4
1,4-Butanediol	4.31 · 10 ⁵	10.6	16.8	-16.4	-15.8
1,5-Pentanediol	4.22 · 10 ⁵	9.5	15.1	-16.6	-16.1

^a Temperature 30°C.

relatively closer than those of *E*. The values of $\Delta S_{303,D}^\ddagger$ have the same increasing tendency with increasing alkanediol chain length as the values of ΔS_{303}^\ddagger .

Beside the determination of activation entropy changes ΔS^\ddagger also the relationship

$$\log k_2 = a/D + b \quad (5)$$

was employed to elucidate the reaction mechanism. Individual alkanediols were compared at various temperatures; also the correlation of k_2 for various alkanediols at constant temperature is²³⁻²⁵ characteristic for given reaction mechanism. The straight lines, expressing the relationship of $\log k_2$ for individual examined alkanediols upon the dielectric constant changes with temperature, intercept at one point (Fig. 2), which corresponds to $k_2 = 0.5 \cdot 10^{-3} \text{ mol}^{-1} \text{ l s}^{-1}$, $D = 56.2$ and 1.4 K (according the Arrhenius equation). The positive value of the slope confirms, according Amis²³, that the transition complex of the studied reaction releases a proton. This is in agreement with the present hypothesis about the reaction mechanism of acid catalysed reaction of *I* with aliphatic hydroxy compounds^{5,9-11} (compare²⁶). The values of $\log k_2$ for ethyleneglycol cannot be fitted into the straight correlation lines at varying temperatures (Fig. 2 shows only 30 and 50°C lines). Thus if only the values for 1,3-propanediol, 1,4-butanediol and 1,5-pentanediol are considered then the negative values of slopes of correlation lines differ only very little within the region examined (-3.86 at 30° , -3.99 at 35° , -4.30 at 40° , -3.76 at 45° and -4.07 at 50°C) whereas in the case of five C_{1-4} alcohols methanol, ethanol, 1- and 2-propanol, 1-butanol the decreasing tendency is apparent¹¹: -30.2 at 20° , -26.7 at 30° and -22.6 at 40°C . Hiromi²⁴ has found the value of this correlation parameter to be -150 for typical S_N1 reactions and higher than 100 in the case of S_N2 reactions. The studied reaction thus does not proceed either *via* S_N1 or S_N2 mechanism. The longer is the carbon chain of the alkanediol the lesser is the temperature dependency of the dielec-

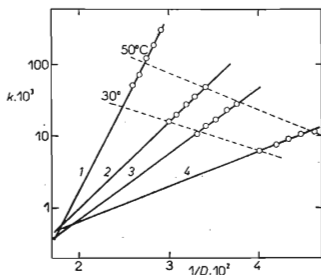


FIG. 2
The Change k_2 ($\text{mol}^{-1} \text{ l s}^{-1}$) with Changing the Dielectric Constant (D) at 30 to 50°C
1 1,2-Ethanediol, 2 1,3-propanediol, 3 1,4-butanediol, 4 1,5-pentanediol.

tric constant because of weaker intermolecular bonding. That is why the highest activation energy is measured in the case of ethylene glycol and then its value is asymptotically approaching the value corresponding to the indefinitely long carbon chain. Comparable reactivities are reached in the region round absolute zero where the mobility is lowered to a minimum.

Thus the glycols have stronger tendency to react with *I* via the S_N2 mechanism than the alcohols. Similar conclusion is reached when the $\Delta S_{303}^{\ddagger}$ values of alcohols and alkanediols are compared. Both cases can, however, be denoted according the accepted^{2,9-13} Parker and Isaacs notation⁵ as the borderline S_N2 mechanism.

Stimulating comments of Dr J. Kálal are greatly appreciated.

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¹Translated by J. Sedlář.