NEGATIVE TEMPERATURE COEFFICIENT PHENOMENON IN EXCHANGE REACTIONS BETWEEN ALKENE OXIDES AND ALKYL-β-HYDROXYALKYL SULFIDES

É. F. Brin, V. V. Vints, and A. D. Malievskii UDC 541.12.036:542.91:547, 422:547,279.1

There is a series of chemical reactions that proceed faster at lower temperatures (negative temperature coefficient) [1]. Some of them have been investigated quite thoroughly. The formation of reactive molecular donor-acceptor complexes as intermediate compounds is a necessary condition for these reactions, but not the only condition.

This paper reports a study of the forward exchange reaction in the alkene oxide-alkyl- β -hydroxyalkyl sulfide system:

$$R^{1}CH-CH_{2}+S$$

$$CH_{2}CH(R^{3})OH$$

$$R^{2}$$

$$R^{3}$$

$$CH_{2}CH(R^{3})OH$$

$$CH_{2}CH(R^{1})OH$$

$$(1)$$

over a wide temperature range. It was shown in [2] that in concentrated solutions of alkyl- β -hydroxyalkyl sulfides at 150°C, the forward reaction is basically due to two bimolecular reactions: an interaction of the sulfide monomer with an H-complex (I) formed from the alkene oxide and the alkyl- β -hydroxyalkyl sulfide and an interaction of two H-complexes



It is assumed that a sulfonium salt (II) and a bipolar ion (II') are intermediate products of exchange reaction (1), and the unique composition of reaction products (3) and (4) is determined by the decomposition of the ion:

$$\begin{bmatrix} CH_{2}CH(R^{1})OH \\ R^{2}S \\ CH_{2}CH(R^{3})OH \end{bmatrix} \xrightarrow{OCH(R^{3})CH_{2}SR^{2} \rightarrow R^{2}S \\ -R^{2}SCH_{2}CH(R^{3})OH \\ CH_{2}CH(R^{3})OH \\ -R^{2}SCH_{2}CH(R^{3})OH \\ CH_{2}CH(R^{3})O \\ CH_{2}CH(R^{3})OH \\ CH_{2}CH(R^{3})O \\ CH_{2}CH(R^{3})OH \\ CH_{2$$

Reactions (3) and (4) are the rate-limiting steps in the process.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 51-57, January, 1985. Original article submitted July 18, 1983.



Fig. 1. Temperature dependence of the initial reaction rate in the system propylene oxide—octyl- β -hydroxyethyl sulfide: 1) for $[A]_0 = 0.55$ and $[B]_0 = 2.5$ moles/liter, solvent: monochloro-benzene; 2) the same system, ac nting only for the k_1 , k_2 , and k_3 pat

An unexpected finding was the fact that the initial rate W_0 of the forward reaction in the propylene oxide—octyl- β -hydroxyethyl sulfide system as a function of temperature shows extremes between 60 and 110°C, with a maximum at 90°C (under comparable conditions: $[A]_0 =$ 0.55 mole/liter, $[B]_0 = 2.5$ moles/liter, solvent: monochlorobenzene) (Fig. 1, curve 1). As Fig. 1 indicates, the reaction rate rises as the temperature is lowered between 90 and 110°C.

In order to estimate the contribution of steps (3) and (4) to the overall rate of the process between 60 and 110°C, we studied the reaction in this system quantitatively between 130 and 160°C, where the reaction rate has an Arrhenius temperature dependence. The values of k_2 and k_3 were calculated at 130, 140, and 160°C from the reaction rate equation:

$$W_{0}' = k_{1}K_{e}[A] [B] + k_{2}K_{e}[A]^{2} [B] + k_{3}K_{e}^{2}[A]^{2} [B]^{2}$$
(1)

as we had done earlier in [2] for 150°C; [A] and [B] are the concentrations of free hydroxyethyl sulfide and propylene oxide, respectively. When $[A]_0 \ge 0.4$ mole/liter and $[B]_0 \gg [A]_0$, we may assume that $[B] \approx [B]_0$ and $[A] \approx [A] - [I]$; then Eq. (I) becomes:

$$k_{2} + k_{3}K_{e} [B]_{0} = \frac{W_{0}'(1 + K_{e} [B]_{0})^{2}}{K_{e}[A]_{0}^{2}[B]_{0}} - \frac{k_{1}(1 + K_{e}[B]_{0})}{[A]_{0}} = Y$$
(II)

where k_1 is the constant for the monomolecular transformation of H-complex (I) and K_e is the equilibrium constant for the formation of H-complex (I) [3]. The dependence of Y on [B] is used to determine the values of k_2 and k_3 (Fig. 2 and Table 1). The constants can be determined to an accuracy of $\sim 20\%$. From the values of the rate constants obtained for 130, 140, and 160°C in this work and for 150°C in [2] we derived the following values: $k_2 = 2.37 \times 10^5 \exp(-19350/\text{RT})$ and $k_3 = 8.2 \times 10^3 \exp(-17820/\text{RT})$.

We used the kinetic characteristics that we found for the reaction in this system to estimate the constants K_d and the enthalpy change for the dimerization of $octyl-\beta-hydroxyethyl$ K_d sulfide (2 monomers \rightleftharpoons dimers), which are needed to calculate the concentrations of the reactant molecules between 60 and 110°C. K_d was determined from a material balance equation as follows:

$$2K_{\rm d}K_{\rm e}[{\rm A}]^3 + (2K_{\rm d} + K_{\rm e})[{\rm A}]^2 + (1 + K_{\rm e}[{\rm B}]_0 - K_{\rm e}[{\rm A}]_0)[{\rm A}] - [{\rm A}]_0 = 0$$
(III)

Values of [A] were found for (III) from Eq. (I) transformed by substituting $[B]_0/(1 + K_e[A])$ for [B]. The estimate was made with high concentrations of A₀ and concentrations of B₀ that where comparable to or less than that of A₀. Table 1 lists the results of these calculations.

TABLE 1. Values of the Rate Constants k_2 and k_3 for Reactions (3) and (4) in the System Propylene Oxide-Octyl- β -Hydroxyethyl Sulfide and Values of the Dimerization Constant for Octyl- β -Hydroxyethyl Sulfide (solvent: monochlorobenzene)

т., ℃	h₂·10 ⁵	A3+106		K _d , liters/mole	
	liters/n	nole •sec	Т., °С		
130	0,65	1,98 2,97	25 140	86,4	
150 162	2,20 4,15	4,71 7,70	150 162	3,05 2,46	



Fig. 2. Y as a function of $[B]_{\circ}$ for the reaction of the system propylene oxide—octyl- β -hydroxyethyl sulfide; $[A] \ge 0.4$ mole/liter; $[B]_{\circ} \gg$ $[A]_{\circ}$; 140°C; solvent: monochlorobenzene.

From the value of K_d obtained for several temperatures by calculation from the kinetic data and also by a spectroscopic method for 25°C ($K_d = 86.4$ liters/mole), we found $-\Delta H$ to be 6.7 kcal/mole. The hydrogen bonds in the alcohols have strengths between 3 and 10 kcal/mole [4].

Values of W₀' for 60 and 120°C that account for steps (3) and (4) were calculated from Eqs. (I) and (III). The calculated initial rate W₀' accounting for these steps turned out for the 60 to 120°C interval to be 50% of the overall reaction rate W₀ for 120°C, 10% for 110°C, and ≤ 1 to 2.5% for 60 to 95°C (see Fig. 1, curve 2), i.e., steps (3) and (4) cannot explain the trend of W₀ as a function of t in this interval.

It was also shown that chlorobenzene, used as a solvent, is inert in this process. Replacing it with benzene, a chlorobenzene-decane mixture (1:1, since hydroxyethyl sulfide has a limited solubility in pure decane), and acetonitrile, made no significant changes in W_0 as a function of t in spite of the differences in these compounds' properties, such as dielectric permeability (Table 2). At the same time, we found marked changes in W_0 for protondonor solvents, which may participate directly in one of the steps of the process between 60 and 110°C. Since the composition of the products does not change over the entire temperature range, we must assume that the sulfonium salt (II) and the bipolar ion (II') are formed at the final step of the reaction, as they are between 130 and 160°C. Apparently then, W_0 shows extremes as a function of t as a result of the participation of a new active species in the reaction that is different from those that take part in steps (3) and (4). This species may be the complex (III) formed by the reaction of the H-complex (I) with octyl- β hydroxyethyl sulfide (ROH):

 $\begin{array}{c} M_{e}CH-CH_{2} & + ROH \xrightarrow{k_{4}} M_{e}CH-CH_{2} \\ O \cdots HOCH_{2}CH_{2}SC_{e}H_{17} \\ (I) & (III) & HOCH_{2}CH_{2}SC_{e}H_{17} \\ HOR \end{array}$ (6)

TABLE 2.		Initial	Reac	tion	Rates	in	the
Propylen	е	Oxide-Oc	ctyl-	-β-Hyd	lroxye	thyl	Sulfide
System a	t	90.5°C t	with	Diffe	erent	Solv	ents

[A]。 [B]。 moles/liter		W₀·10 ⁶ , moles/liter-sec	Solvent
0,545 * 0,566 † 0,572 0,550 0,490 0,420 ‡ 0,520 *89°. †92.5°. ‡96°.	2,22 2,22 2,12 2,39 2,28 2,28 3,58	2,0 2,0 2,17 1,9 1,62 8,0 37,5	PhCl PhCl C_6H_6 PhCl - decane (1:1) MeCN EtOH EtOH - H ₂ O (1:1)

The formation of associates of three molecules, including alcohol molecules, is not rate [5-7]. It is suggested that the reactivity of complex (III) is higher than that of H-complex (I) in nucleophilic reactions. If that is the case, it must be assumed that the proton on the OH group of fragment "a" migrates to the oxygen of the oxide ring, as observed in protondonor systems such as Et₃N [8]. Therefore, the role of fragment "a" in the first step is one of activation of the oxide ring. In deciding on a mechanism for the reaction between 60 and 110°C, we also considered the fact that the ratio $(W_0 - W_0')/[A]^2[B] = K_{ef}$ is constant over a wide range of initial Ao and Bo concentrations at a given temperature (Table 3), where [A] and [B] are the calculated concentrations of the free hydroxyethyl sulfide monomer and propylene oxide, respectively. When [A] and [B] were calculated by material balance equation (III), it was assumed that the concentration of complex (III) was not high and could be neglected. The assumption that K_{ef} is constant is apparently supported by the fact that it is a combination of constants that do not include concentrations. Then the formation of the reaction products may be represented as the result of an intramolecular nucleophilic attack by the S atom of sulfide complex (III) at the C-O bond of the epoxy group through the sulfonium salt (II) and the bipolar ion (II'):



The active centers of the molecules should be nearby and oriented in the most favorable manner for the reaction to take place. The probability of so specific an orientation drops as the temperature rises. The rate constant k_s of reaction (7) may be represented as follows:

$$k_5 = P(T) A e^{-E_b/RT}$$
(IV)

where A is a preexponential factor and P(T) is a probability factor that depends on temperature. The latter reflects the fraction of the molecules oriented in the proper direction for the reaction.

The following steps must be added to the general scheme of the process over a wide temperature range (60 to 160°C) in addition to the reactions described earlier in [2]:

$$A + (I) \xrightarrow{\kappa_4} (III) \tag{8}$$

$$k \qquad (III) \xrightarrow{\kappa_b} \text{Reaction products} \tag{9}$$

(III) \rightarrow Decomposition without formation of products (10)

B 60	[A] ₀	[B]。	[A]	[B]	W ₀ • 10 ⁶	Wo' . 107	K _{ef} ×10 ⁴ ,
т., чс	moles/liter				moles	/liter • sec	liter ² /mole ² . sec
67 75	0,486 0,469 0,519 1,015 1,177 1,490 0,520 4,045	6,480 8,330 9,070 0,624 0,333 0,437 8,520	0,022 0,017 0,017 0,129 0,148 0,167 0,020	6,036 7,890 8,580 0,435 0,223 0,281 8,023	0,25 0,19 0,23 0,60 0,34 0,65	0,06 0,06 0,07 0,03 0,02 0,03 0,03	0,84 0,83 0,89 0,83 0,69 0,83 Mean 0,82±0,04 1,16
	1,015 1,119 0,550 0,534 0,551	0,624 0,437 2,510 3,750 5,350	0,143 0,186 0,057 0,041 0,032	0,429 0,275 2,125 3,315 4,863	0,76 0,88 0,70 0,60 0,59	0,06 0,06 0,10 0,12 0,14	0,86 0,92 0,99 1,03 1,19 Mean 1,03±0,10
82	0,517 0,552 0,441 0,540 1,177	2,280 4,760 7,690 6,890 0,333	0,061 0,035 0,186 0,026 0,175	1,920 4,310 7,280 6,390 0,217	0,86 0,73 0,34 0,65 0,75	0,16 0,21 0,16 0,23 0,06	1,20 1,36 1,29 1,51 1,12 Mean 1,30±0,08
90,5	0,533 0,577 0,804 0,660	4,520 4,520 4,110 4,360	0,040 0,043 0,066 0,051	4,060 4,030 3,470 3,810	1,53 1,83 4,25 2,30	0,40 0,46 0,81 0,58	2,29 2,36 2,76 2,24 Mean 2,37±0,16
95	0,687 1,205 0,790 0,536 0,515	2,440 0,203 6,950 2,750 3,700	0,086 0,218 0,042 0,063 0,048	1,981 0,128 6,240 2,353 3,276	2,56 1,17 2,78 1,62 1,59	0,69 0,14 1,20 0,52 0,47	1,70 1,90 2,38 1,69 2,07 Mean 1,95±0,22
110	0,532 0,749 0,981 1,351 1,686 2,178	2,420 2,330 2,330 2,360 0,265 0,458	0,076 0,107 0,136 0,179 0,297 0,336	2,047 1,834 1,756 1,651 0,149 0,254	0,71 1,60 2,53 4,00 0,84 1,94	1,30 2,30 3,20 5,00 0,69 1,60	0,50 0,65 0,68 0,66 0,59 0,62 Mean 0,616±0,05

TABLE 3. K_{ef} for the Reaction of the Propylene Oxide-Octyl- β -Hydroxyethyl Sulfide System between 67 and 110°C

The reaction rate is determined at low temperatures by the expression W_0 " = $k_5[(III)]$, in which the concentration of complex (III) is determined by assuming steady-state conditions. Step (10), which has the rate constant k_6 , includes decomposition of complex (III) without the formation of the reaction products (including decomposition to form the original components). The overall expression for the reaction rate, accounting for all possible reaction routes, would be:

$$W_{0} = \frac{k_{4}K_{e}[A]^{2}[B]}{1 + \frac{k_{6}}{k_{5}}} + k_{1}K_{e}[A][B] + k_{2}K_{e}[A]^{2}[B] + k_{3}K_{e}^{2}[A]^{2}[B]^{2}$$
(V)

We ran this equation on a computer and the $W_{0 \text{ calc}}$ vs t function that we found describes the experimental points satisfactorily with the following values $k_4 = 3.32 \times 10^7 \exp(-9542/T)$ and $k_6/k_5 = 8.76 \times 10^{23} \exp(-20080/T)$. The temperature dependence of the reaction rate between 60 and 110°C is essentially determined by the first term of Eq. (V). From Eq. (V), $K_{ef} = k_4 K_e/(1 + k_6/k_5)$, where the numerator increases exponentially. Between 60 and 90°C, the denominator increases slowly (from 1.02 to 1.9) and the change in K_{ef} is determined by the increase in the numerator, the reaction rate rising in the process. A further rise in temperature results in a sharp increase in the denominator (from 4.7 to 2 $\cdot 10^3$ between 100 and 150°C) and K_{ef} decreases, lowering the reaction rate. The contribution of W_0 " to the overall reaction rate for 150°C ([A]₀ = 0.55 and [B]₀ = 2.5 moles/liter) is a total of only 2.7%, i.e., Eq. (9) practically disappears as a reaction path at high temperatures and the major contribution to the formation of the reaction products is through Eqs. (3) and (4).

The system propylene oxide-octyl- β -hydroxyethyl sulfide is not the only one that shows minima and maxima in the reaction-rate-temperature curve. Such a trend is typical for the butylene oxide-octyl-B-hydroxyethyl sulfide system as well, where the initial reaction rate has a sharp maximum at 86°C as a function of temperature.

EXPERIMENTAL

The tests were performed as described in [2]. The following constants were used in the calculations: $K_e = 0.147 \exp(1076/T)$ liters/mole; $k_d = 1.02 \times 10^{-3} \exp(3384/T)$ liters/mole, $k_1 = 1.52 \times 10^9 \exp(-14850/T) \sec^{-1} [3]; k_2 = 2.37 \times 10^5 \exp(-9770/T)$ liters/mole·sec; $k_3 = 1.52 \times 10^9 \exp(-14850/T)$ 8.2 × 10³ exp(-9000/T) liters/mole·sec. The computations were performed on a BESM-6 computer by minimizing the sum of the squares of the differences between the theoretical and experimental values of the variable in question by the method given in [9]. The experimental function is described to an accuracy of at least 20%, which agrees closely with experimental error.

CONCLUSIONS

The temperature dependence of the initial rate of the exchange reaction in the propylene $oxide-octyl-\beta-hydroxyethyl$ sulfide system shows a maximum and a minimum between 60 and 110°C, the maximum at 90°C. This behavior may be explained by the participation in the reaction of an associate that is formed from a molecule of propylene oxide and two molecules of hydroxyethyl sulfide. Computer calculations have been made for this scheme of the reaction over a wide temperature range.

LITERATURE CITED

- 1. G. B. Sergeev, in: Problems in Chemical Kinetics [in Russian], Nauka, Moscow (1979), p. 312.
- 2. A. D. Malievskii and V. V. Vints, Izv. Akad. Nauk SSSR, Ser. Khim., 2702 (1977).
- 3. A. D. Malievskii, V. V. Vints, and N. M. Émanuél', Dokl. Akad. Nauk SSSR, 223, 1180 (1975).
- 4.
- A. Singh and C. N. R. Rao, J. Phys. Chem., <u>71</u>, 1074 (1967).
 A. I. Brodskii, V. D. Pokhodenko, and V. S. Kuts, Usp. Khim., <u>39</u>, 753 (1970). 5.
- V. F. Shvets and D. N. Tsivinskii, Kinet. Katal., 22, 1192 (1981). 6.
- 7. I. P. Gragerov, V. K. Pogorelyi, and I. F. Franchuk, The Hydrogen Bond and Rapid Proton Exchange [in Russian], Naukova Dumka, Kiev (1978), p. 135.
- N. S. Golubev, G. S. Denisov, and V. M. Shraiber, in: The Hydrogen Bond [in Russian], 8. Nauka, Moscow (1981), p. 246.
- É. F. Brin and B. V. Pavlov, Kinet. Katal., <u>16</u>, 232 (1975). 9.