6. G. L. Fleming, R. N. Haszeldine, and A. E. Tipping, J. Chem. Soc. Perkin Trans. 1, 1973, 574.
7. J. M. Teddev, J. C. Walton, and K. D. R. Winton, J. Chem. Soc. Faraday Trans. 1, 68, 1866 (1972).
8. W. B. Smith and H. G. Gilde, J. Am. Chem. Soc., 81, 5325 (1959).
9. W. R. Hashek and W. C. Smith, J. Am. Chem. Soc., 82, 544 (1960).
10. M. Hauptschein, M. Braid, and F. E. Fawlor, J. Am. Chem. Soc., 80, 846 (1958).
11. N. B. Kaz'mina, G. S. Krasnikova, É. P. Lur'e, E. L. Mysov, and L. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 2525.
12. Dictionary of Organic Compounds [Russian translation], Vol. 2, IL (1949), p. 90.

REACTION RATE OF α-OXIDES WITH ALIPHATIC AMINES

I. I. Mutin, Kh. A. Arutyunyan, S. P. Davtyan, and B. A. Rozenberg

UDC 541.127:547.422:547.233

Information exists in the literature that the reactions of α-oxides with amines are both first and second order in amine [1-4]. It seemed of interest to ascertain the reason for the contradictory literature data on the reaction rate of α-oxides with amines in the absence of proton-donor compounds. For this purpose we studied the reaction rate of phenyl glycidyl ether (PGE) with n-butylamine (BA) employing the isothermal calorimetry method [5]. The employed reactants and solvent (cyclohexane) were subjected to precision purification as described in [4]. The heat effect of the reaction, determined calorimetrically [1], is 103 ± 3 kJ/mole of PGE. The initial reaction rate was determined with an accuracy of ± 0.10.

The reaction of PGE with BA has an autocatalytic character (Fig. 1). Independent of the ratio of the initial concentrations of the reactants the PGE conversion reaches 1.00, which is due to the ability of the formed tertiary amine to polymerize the α-oxide.

An analysis of the data on the initial reaction rates (v_0) (Table 1) shows that the formal order of the reaction in amine depends on the temperature. Thus, at 285, 301, 315, and 331°K the order of the reaction in BA is respectively 1.8, 1.6, 1.4, and 1.2. Such a relation between the reaction order and the temperature can be explained by the fact that the aliphatic amine reacts with the epoxide group by a complex mechanism in two steps, which respectively have a first and second reaction order in amine

$$A_1 + E \xrightarrow{k_{11}} A_2$$
$$2A_1 + E \xrightarrow{k_{12}} A_2 + A_1 \qquad (1)$$

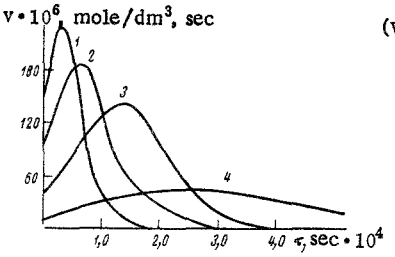

Fig. 1

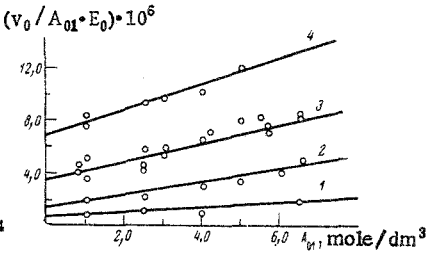

Fig. 2

Fig. 1. Reaction rate of PGE with BA as a function of time at 315°K: E_0 = 2.5 mole/dm^3, A_{01}: 1) 6.5; 2) 5.8; 3) 4.0; 4) 0.84 mole/dm^3.

Fig. 2. Reduced reaction rate as a function of initial concentration of BA at E_0 = 2.5 mole/dm^3. T, °K: 1) 285; 2) 301; 3) 315; 4) 331.

Division of Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2828-2829, December, 1977. Original article submitted May 27, 1977.

TABLE 1. Dependence of v_0 on Initial Concentrations of PGE and BA at Various Temperatures

$[PGE]_0$	$[BA]_0$	$v_0 \cdot 10^6$, mole/dm³·sec			
mole/dm³		285 K	301 K	315 K	331 K
2,5	1,0	1,54	4,86	8,90	19,0
2,5	2,5	6,85	13,1	34,1	58,0
2,5	3,0	–	–	43,0	72,0
2,5	4,0	9,00	31,1	65,2	103
2,5	5,0	–	40,8	99,0	150
2,5	6,5	30,2	81,1	140	–
6,5	1,0	–	–	32,5	–
5,4	2,5	–	–	77,5	–
4,2	4,1	–	–	125	–
3,2	5,5	–	–	141	–

TABLE 2. Kinetic Parameters of Reaction of PGE with BA

Parameter	Temperature, °K				E, kJ/mole	k_0
	285	301	315	331		
$k_{11} \cdot 10^6$, dm³/mole·sec	0,39±0,05	1,1±0,1	3,3±0,4	6,5±0,7	42±10	21±10
$k_{12} \cdot 10^6$, dm⁶/mole²·sec	0,21±0,02	0,54±0,06	0,86±0,09	1,0±0,1	26±6	0,014±0,007
r	0,906	0,942	0,954	0,985		

*Remarks. E is the activation energy, k_0 is the preexponential factor, and r is the correlation coefficient.

where A_1, A_2, and E are respectively the concentration of the primary and secondary amines and epoxide groups.

In harmony with scheme (1)

$$v_0/A_{01}E_0 = k_{11} + k_{12}A_{01} \quad (2)$$

where A_{01} and E_0 are the initial concentrations of BA and PGE.

As can be seen from Fig. 2, the experimental data, obtained at various temperatures, are described well by Eq. (2). A quite marked difference is observed in the activation energy values for k_{11} and k_{12} (Table 2). The dependence of the reaction order on the temperature can be explained by specifically this difference. Actually, from the data given in [1, 2], and also on the basis of our experiments, it follows that at 343°K and higher the reaction is first order in amine. At low temperatures the step that has a second order of reaction in amine becomes the determining step. It should be mentioned that the obtained values of the constants are effective, since the presence of such complexes as $(A_1 \cdot A_1)$, $(A_1 \cdot E)$ is not taken into account.

CONCLUSIONS

Butylamine reacts with phenyl glycidyl ether by a mechanism that can be depicted as two processes that proceed in parallel, with a first and second order of reaction in amine. The ratio between the reaction routes depends on the temperature.

LITERATURE CITED

1. K. Horie, H. Hiura, M. Savada, J. Mita, and M. Kambe, J. Polym. Sci. A-1, 8, 1357 (1970).
2. H. Tiltscher, Angew. Makromol. Chem., 25, 1 (1972).
3. N. L. Lebedev and M. M. Smirnova, Kinet. Katal., 6, 457 (1965).
4. Kh. A. Arutyunyan, A. O. Tonoyan, S. P. Davtyan, B. A. Rozenberg, and N. S. Enikolopyan, Dokl. Akad. Nauk SSSR, 214, 832 (1974).
5. E. Calvet and H. Prat (editors), Recent Progress in Microcalorimetry, Pergamon (1963).