

## REACTION KINETICS OF AROMATIC DIAMINES WITH EPOXIDE COMPOUNDS\*

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Reaction rate constants of amino primary and secondary hydrogen atoms with epoxide group have been obtained from kinetic measurements of reactions of some aromatic diamines with *p*-tolyl glycidyl ether and 2,2-bis(4-(2,3-epoxypropoxy)phenyl)propane. The region has been established where the diffusion controlled reaction operates at the given temperature. Logarithms of the rate constants have been correlated with the indices of electron density at the amino groups obtained by quantum-chemical calculations and with  $pK_{a1}$  values of the diamines. Linear dependences have been obtained in all the cases studied.

Nucleophilic addition of polyamines to epoxide group represents an important chemical reaction used for hardening of epoxide resins. Epoxide group is attacked by the both hydrogen atoms of amino group, *i.e.* a competitive-consecutive reaction occurs which is autocatalyzed by the hydroxyl groups formed<sup>1</sup>. Reaction of diamines with diepoxide compounds is complicated by formation of space network. That is why this reaction was studied mostly with model systems<sup>1-4</sup>.

In the present work we have tried to measure the reaction kinetics of aromatic diamines with *p*-tolyl glycidyl ether and 2,2-bis(4-(2,3-epoxypropoxy)phenyl)propane (further only dian-bisglycidyl ether) without solvent. For analytic following of the reaction we have developed a new method consisting in simultaneous automatic measurements of concentration changes of epoxide groups, primary and secondary amino groups and hydroxyl groups in near infrared spectral region, which can be used for the cross-linked systems, too. We tried to distinguish between the reaction rate constants of the primary and secondary amino hydrogen atoms with epoxide group and determine the conversion degree up to which the reaction with dian-bisglycidyl ether is kinetically controlled. Next we carried out correlations of logarithms of the reaction rate constants with  $pK_{a1}$  values of the diamines and with the electron density values of amino groups calculated by the MO LCAO method in Hückel approximation<sup>5</sup> (HMO) and the SCF MO LCAO method in the Pariser-Parr-Pople approximation<sup>6,7</sup> (PPP).

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## EXPERIMENTAL

## Reagents

4,4'-Diaminodiphenylmethane, benzidine and 1,2-diaminobenzene were commercial reagents and were purified by crystallization. 4,4'-Diaminodiphenyl sulphide, 4,4'-diaminodiphenyl sulphoxide, 4,4'-diaminodiphenyl sulphone, and 4,4'-diaminodiphenyl oxide were synthesized by the methods described previously<sup>8</sup>. The purity of the diamines was checked by paper chromatography and thin-layer chromatography<sup>9</sup>. *p*-Tolyl glycidyl ether was prepared as in ref.<sup>10</sup>, its epoxide group and chlorine content being 99.5% and 0.04%, respectively. Dian-bisglycidyl ether was prepared in Spolek pro chemickou a hutní výrobu (Company for Chemical and Metallurgical Production), Ústí nad Labem. The epoxide group and chlorine content was 99.2% and 0.08%, respectively.

## Kinetic Measurements and Calculations

The kinetic measurements were carried out with the use of a Unicam SP-100 spectrophotometer at 80, 100 and 120°C using the stoichiometric ratio of the diamine and epoxide compounds. In near infrared region the extinction changes were measured at 4535 cm<sup>-1</sup> (epoxide group<sup>11,12</sup>), 6800 cm<sup>-1</sup> (hydroxy group<sup>13</sup>), 4950 cm<sup>-1</sup> (primary amino group<sup>13</sup>), and 6500 cm<sup>-1</sup> (sum of primary and secondary amino groups<sup>13</sup>). For quantitative evaluation of bands the method of basic line and the band at 5860 cm<sup>-1</sup> as internal standard (probably a harmonic vibration of CH bond of aromatic ring) were used. The mixture of the aromatic diamine and epoxide compound was heated in a test tube to the reaction temperature (in some cases to a higher temperature for a short time) and mixed until dissolution; from that moment time was counted. Then the liquid was transferred by means of a syringe into a 1 mm glass cell and placed in the thermostated cell compartment of the apparatus. At definite time intervals the spectral record was taken automatically in the region containing the absorption bands of the abovementioned functional groups.

From the time-concentration dependences measured for primary amino groups and epoxide groups and from mass balance it was possible to calculate the time-concentration dependence of secondary amino groups up to the moment of disappearance of the primary amino groups from the reaction mixture. From the extinction of the absorption band at 6500 cm<sup>-1</sup> belonging to the sum of primary and secondary amino groups we calculated the part due to secondary amines alone on the basis of the presumption that the intensity ratio of the bands at 4950 cm<sup>-1</sup> and 6500 cm<sup>-1</sup> for the primary amine remains constant during the reaction and can be determined at the beginning of the reaction (absence of secondary amines in the reaction mixtures). In this sense the following relations can be accepted:

$$E_{01}/E_{02} = K, \quad (1)$$

$$E_{t2} = E_{t1}/K, \quad (2)$$

$$E_{t3} = E_{t4} - E_{t2} = E_{t4} - E_{t1}/K, \quad (3)$$

where  $E_{01}$  and  $E_{t1}$  are extinctions of the band at 4950 cm<sup>-1</sup> due to the primary amine at the time 0 and  $t$ , respectively;  $E_{02}$  and  $E_{t2}$  are the portions of extinction of the band at 6500 cm<sup>-1</sup> due to pure primary amines at the time 0 and  $t$ , respectively;  $E_{t3}$  is the portion of extinction of the band at 6500 cm<sup>-1</sup> due to pure secondary amine at the time  $t$ ;  $E_{t4}$  is the extinction of the band

at  $6500\text{ cm}^{-1}$  due to the sum of primary and secondary amines at the time  $t$ ;  $K$  is the ratio of the extinctions of bands at  $4950\text{ cm}^{-1}$  and  $6500\text{ cm}^{-1}$  for the pure primary amine at the beginning of the reaction. The extinction values of secondary amino groups and the concentration values calculated from mass balance were plotted against time. From the lines obtained the calibration straight lines of concentration *vs* extinction were constructed, wherefrom we could read the concentration values of secondary amino groups in the whole reaction course measured. The tertiary amino concentrations were calculated from the mass balance. The obtained time dependences of concentrations of individual reactions components were plotted in a graph.

The system of two autocatalytic competitive-consecutive reactions can be described by differential equations (4) to (7),

$$-d[A]/dt = k_1 x[A][B] + k_2 x[A][C], \quad (4)$$

$$-d[B]/dt = k_1 x[A][B], \quad (5)$$

$$d[C]/dt = k_1 x[A][B] - k_2 x[A][C], \quad (6)$$

$$d[D]/dt = k_2 x[A][C], \quad (7)$$

where  $k_1$  and  $k_2$  are the reaction rate constants of primary resp. secondary hydrogen atoms of amino group with epoxide group,  $[A]$ ,  $[B]$ ,  $[C]$ , and  $[D]$  stand for concentrations of epoxide, primary amino, secondary and tertiary amino groups, respectively,  $x$  is the concentration of hydroxyl groups in the reaction mixture which is equal to concentration decrease of epoxide groups. The concentrations are given in mol/kg.

From Eqs (4) to (7) relations (8) to (11) were obtained for calculation of the rate constants  $k_1$  and  $k_2$  from the changes of the individual components; they all should give equivalent values of the rate constants.

$$k_{1a} = -\frac{d[B]}{dt} \cdot \frac{1}{Y}; \quad k_{2a} = \frac{d[D]}{dt} \cdot \frac{1}{Z}, \quad (8)$$

$$k_{1b} = \left( \frac{d[C]}{dt} - \frac{d[A]}{dt} \right) \frac{1}{2Y}; \quad k_{2b} = -\left( \frac{d[A]}{dt} + \frac{d[C]}{dt} \right) \frac{1}{2Z}, \quad (9)$$

$$k_{1c} = \left( \frac{d[C]}{dt} + \frac{d[D]}{dt} \right) \frac{1}{Y}; \quad k_{2c} = \left( \frac{d[B]}{dt} - \frac{d[A]}{dt} \right) \frac{1}{Z}, \quad (10)$$

$$k_{1d} = -\left( \frac{d[A]}{dt} + \frac{d[D]}{dt} \right) \frac{1}{Y}; \quad k_{2d} = -\left( \frac{d[B]}{dt} + \frac{d[C]}{dt} \right) \frac{1}{Z}. \quad (11)$$

Here  $Y = x[A][B]$  and  $Z = x[A][C]$ . One of the pairs of equations (8)–(11) is sufficient for calculation of  $k_1$  resp.  $k_2$ . Even though the input data are subject to experimental error (the accuracy of IR spectra measurements is within 3–5%, and it is further decreased by processing the experimental data with the use of calibration line and by readings from the graph; in addition to it, it can be presumed that the accuracy of determinations of individual components concentration changes will depend on the conversion degree), we take the suggested procedure

of calculation of the rate constants for sufficiently accurate. Derivations with respect to time were calculated from the time-concentration dependences with the use of the five-point formulas derived from Lagrange's interpolation polynomials for equidistant partition. Concentrations to be introduced into the formulas (8)-(11) were read from graphs. The calculations were carried out with an IBM 360/40 computer. In this way the rate constant values were obtained for the whole measured reaction course.

## RESULTS AND DISCUSSION

Aromatic diamines contain per molecule four amino hydrogen atoms capable of reacting with epoxide group. When studying the reaction kinetics of these diamines with 4-tolyl glycidyl ether in ethanolic solution we tried to differentiate between the rate constants of the four amino hydrogen atoms<sup>8,9</sup>. We found that the reactivities of the both primary hydrogen atoms were not very different even in the case of conjugated diamines. The reaction rates ratio was within 1.2-1.6. A quite analogous result was obtained in the study of reaction kinetics of N,N'-dialkyl derivatives of the same diamines with *p*-tolyl glycidyl ether<sup>14</sup>. In the present work, due to the autocatalytic reaction course, we have not been able to make use of the same calculation method as in the previous papers<sup>8,9,14</sup>. The analytic method chosen made it possible to follow only the sum of individual functional groups in the reaction mixture. Therefore the studied reaction was evaluated as a system of two competitive-consecutive reactions with the rate constants  $k_1$  and  $k_2$  belonging to the reaction of epoxide group with the primary and secondary amino hydrogen atoms, respectively.

The interpretation of the bands  $6500\text{ cm}^{-1}$  and  $4950\text{ cm}^{-1}$  was verified by measuring the spectra in the cases of 1,4-diaminobenzene and 4,4'-diaminodiphenylmethane and their N,N'-di- and N,N,N',N'-tetramethyl derivatives. For the case of determination of epoxide groups a comparison was carried out between the values obtained spectrophotometrically and those obtained titrimetrically<sup>10</sup> in the system *p*-tolyl glycidyl ether-4,4'-diaminodiphenylmethane. A relatively good agreement of the both determinations was obtained *viz.* the straight line % epoxy (spectr.) = = 0.9805% epoxy (titr.) + 1.8988;  $r = 0.9967$ .

The calculated rate constants are summarized in Tables I and II. Each measurement was repeated. The rate constant values are related to concentrations of the reactive groups. The kinetic measurements of reactions of diamines with *p*-tolyl glycidyl ether were carried out up to 70-80% conversion of epoxide groups and, in the case of reactions with dian-bisglycidyl ether, up to practical reaction stop. The rate constants  $k_1$  given in the Tables represent arithmetical mean of the values calculated within 10-60 (70)% conversion of primary amino groups, the constants  $k_2$  are the arithmetical mean of the values obtained in the range from about 10% conversion (to give tertiary amines) up to finishing of the respective experiment, or, in the case of reactions of diamines with dian-bisglycidyl ether, up to the region where the reac-

TABLE I  
Rate Constants  $k \cdot 10^3$  ( $\text{kg}^2 \text{mol}^{-2} \text{min}^{-1}$ ) of Reaction of Aromatic Diamines with *p*-Tolyl Glycidyl Ether at 80°C

Compound	$k_{1a}$	$k_{1b}$	$k_{1c}$	$k_{1d}$	$k_{2a}$	$k_{2b}$	$k_{2c}$	$k_{2d}$	$k_{1a}/k_{2a}$
4,4'-Diaminodiphenylmethane (I)	2.99	2.52	3.05	2.14	1.32	1.43	1.58	1.70	2.27
	4.05	3.87	3.41	3.92	1.36	1.36	1.41	1.36	2.97
1,2-Diaminobenzene (II)	2.29	2.20	2.40	—	0.703	0.424	—	0.658	3.26
	1.77	1.80	1.75	1.96	0.683	0.580	—	0.723	2.60
4,4'-Diaminodiphenyl sulphide (III)	2.11	1.94	1.93	1.96	0.710	0.714	0.70	0.726	2.97
	1.89	1.84	1.82	1.38	0.841	1.06	1.13	0.908	2.25
4,4'-Diaminodiphenyl sulphone (IV)	0.247	0.248	0.250	0.248	0.0634	0.0644	0.0677	0.0675	3.90
	0.273	0.282	0.279	0.293	0.0686	0.0672	—	—	3.97
4,4'-Diaminodiphenyl sulphoxide (V)	0.877	0.864	0.958	0.795	0.190	0.207	0.220	0.183	4.62
	0.839	0.882	0.865	0.899	0.148	0.162	0.181	0.144	5.65
Benzidine (VI)	1.90	—	—	—	—	—	—	—	—
4,4'-Diaminodiphenyl oxide (VII)	4.21	4.27	4.07	4.13	1.40	1.53	1.52	1.58	3.01
	4.42	4.41	4.50	4.32	2.28	2.49	2.22	2.35	1.95

tion was no more kinetically controlled, being diffusion-controlled due to cross-linking of the reaction product. This region made itself felt by a marked decrease of the rate constant  $k_2$ , and we have found it by plotting  $\log k_2$  against the conversion percentage relative to dian-bisglycidyl ether. A typical dependence is given in Fig. 1 for reaction of 4,4'-diaminodiphenyl sulphide with dian-bisglycidyl ether at 80°C. We have found that at 80°C the reaction is kinetically controlled up to 71–74% conversion (*i.e.* far behind the gelatination point) for all compounds of the series

TABLE II

Rate Constants  $k \cdot 10^3$  ( $\text{kg}^2 \text{mol}^{-2} \text{min}^{-1}$ ) of Reaction of Aromatic Diamines with Dian-bisglycidyl Ether

Compound	$k_{1a}$	$k_{1b}$	$k_{1c}$	$k_{1d}$	$k_{2a}$	$k_{2b}$	$k_{2c}$	$k_{2d}$	$k_{1a}/k_{2a}$	$T, ^\circ\text{C}$
I	2.14	2.07	1.77	—	0.777	0.633	0.802	—	2.76	60
	4.74	3.77	4.48	3.05	1.59	1.54	—	1.54	2.98	80
	4.25	3.66	3.87	3.40	1.83	2.02	2.42	1.73	2.32	80
II	2.98	3.09	3.07	3.15	0.633	0.665	0.664	0.627	4.71	80
	3.16	2.97	3.14	2.93	0.965	1.02	0.709	—	3.28	80
III	4.00	3.93	3.96	3.63	1.28	1.29	—	—	3.13	80
	3.34	3.22	3.10	3.34	1.16	1.04	1.14	1.17	2.88	80
	6.17	5.01	4.96	4.58	2.99	3.17	3.73	3.19	2.06	100
	6.01	5.68	5.96	5.40	2.32	3.17	3.33	2.46	2.59	100
	14.3	13.8	10.8	16.8	5.85	5.37	6.92	6.10	2.45	120
	17.6	19.9	—	18.1	7.34	9.63	—	7.94	2.40	120
IV	0.345	0.355	0.347	0.363	0.0754	0.0773	0.0780	0.0683	4.58	80
	0.375	0.365	0.380	0.378	0.0805	0.0800	0.0850	0.0750	4.65	80
IV	0.917	0.903	0.845	0.911	0.197	0.218	0.232	0.187	4.64	100
	1.25	1.25	1.25	1.33	0.220	0.224	0.270	0.183	5.68	100
	2.73	2.62	2.53	2.70	0.584	0.543	0.561	0.559	4.68	120
	3.07	3.61	3.47	3.76	0.829	0.867	—	—	3.71	120
V	1.18	1.21	1.23	1.22	0.175	0.179	0.206	0.179	6.74	80
	1.30	1.44	1.41	1.48	0.111	0.191	0.250	0.129	6.82	80
VI	6.99	6.16	7.12	5.74	2.77	3.01	—	2.56	2.52	80
	6.04	6.05	6.22	4.13	1.98	—	—	2.24	3.05	80
VII	11.2	9.99	9.19	10.6	2.05	1.70	1.92	—	5.46	80
	9.39	9.66	9.20	10.1	1.61	2.01	2.51	1.81	5.83	80

studied except for 1,2-diaminobenzene. The reactions of 4,4'-diaminodiphenyl sulphide and 4,4'-diaminodiphenyl sulphone with dian-bisglycidyl ether were carried out at 100°C and 120°C, too. In these cases the diffusion controlled region extended over 80% conversion relative to epoxide groups. Lowering of the reaction temperature down to 60°C did not cause any so marked change in the reaction of 4,4'-diaminodiphenylmethane with dian-bisglycidyl ether. The reaction was kinetically controlled up to 68% conversion.

The initial values of rate constants (up to about 10% conversion to primary amines) were not involved in calculation of the mean value, because much higher rate constants were found. We presume it to be caused by traces of humidity in the reaction mixture, the effect being gradually decreased as the concentration of hydroxyl groups increases in the reaction course. Accelerating influence of hydroxyl groups on the reaction of amines with epoxide group is considerable. *E.g.* the rate constants found for the reaction of diamines with *p*-tolyl glycidyl ether in ethanol<sup>8</sup> were higher than those for the reaction without solvent, the difference being in order of magnitude. This effect is probably also responsible for higher reactivity of dian-bisglycidyl ether as compared with *p*-tolyl glycidyl ether (Tables I and II), because a small amount of hydroxyl groups was found in dian-bisglycidyl ether.

The reaction rate constants ratio  $k_1 : k_2$  of the reactions of diamines with dian-bisglycidyl ether was found higher than that for *p*-tolyl glycidyl ether almost in all cases. We presume that the reason of this fact is in cross-linking of the product of the reaction with dian-bisglycidyl ether, *i.e.* lowered mobility of molecules in the reaction mixture at higher conversion.

We chose standard deviation as a criterion of accuracy, which was average  $\pm 20\%$  with  $k_{1a}$  to  $k_{1c}$ ,  $k_{2a}$  and  $k_{2b}$ , and  $\pm 25\%$  with  $k_{1d}$ ,  $k_{2c}$  and  $k_{2d}$  constants. From Tables I

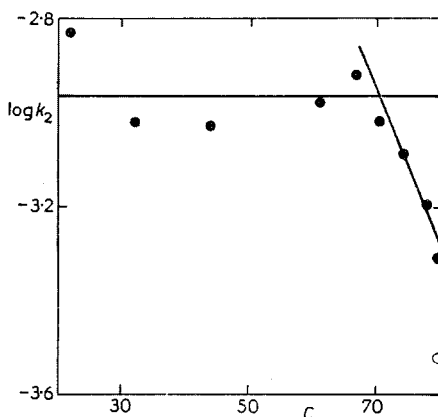


FIG. 1

Dependence of  $\log k_2$  on Conversion Degree of Epoxide Groups ( $C$ , %) for Reaction of 4,4'-Diaminodiphenyl Sulphide with Dian-bisglycidyl Ether

and II it is obvious that, except for  $k_{1d}$  and  $k_{2d}$  constants, a relatively good agreement was obtained between the individual rate constants calculated from various experimental curves according to Eqs (8) to (11).

For correlations of theoretical indices of electronic structure and chemical reactivity with logarithms of rate constants of the reactions studied we have used (as in the case of the reactions carried out in ethanol<sup>8</sup>) the electron density values at amino nitrogen atom which were calculated by HMO and SCF MO approximations. The parameters needed for calculations as well as the proper values of electron densities are given in the previous report<sup>8</sup>. We have obtained the linear dependences significant already when tested at 0.1% level of statistical significance. The both used quantum chemical methods gave approximatively the same scattering of points about the straight lines. This scattering is relatively large, however, we suppose that it does not exceed the usual limits of analogous quantum-chemical studies.

All the amines studied fulfil very well the linear dependence between  $\log k_1$  and  $pK_{a1}$  values. The scattering of points about the straight line is substantially lower than that in correlations with the electron density indices obtained by quantum-chemical calculations (as it was the case of substituted anilines<sup>10</sup> and aromatic diamines<sup>8</sup> with *p*-tolyl glycidyl ether in ethanol). Parameters of the found linear dependences are given in Table III. The  $pK_{a1}$  values used for correlation were given in the previous paper<sup>8</sup>.

On the basis of the results obtained it is supposed to be possible to estimate the reactivities of aromatic amines towards epoxide groups both from quantum-chemical

TABLE III

Parameters of Linear Dependences of Studied Correlations  $\log k_1(y)$  for Reaction of Aromatic Diamines with *p*-Tolyl Glycidyl Ether (*A*) and Dian-bisglycidyl Ether (*B*)

Value	Slope	Intercept	<i>R</i>	<i>s</i>
Reaction <i>A</i>				
$Q_{HMO}$	19.58	—36.39	0.9683	±0.664
$Q_{SCF}$	25.13	—45.49	0.9066	±0.436
$pK_{a(1)}$	0.378	— 4.45	0.9657	±0.099
Reaction <i>B</i>				
$Q_{HMO}$	22.90	—45.32	0.9044	±0.553
$Q_{SCF}$	32.42	—61.49	0.8738	±0.554
$pK_{a(1)}$	0.437	— 4.59	0.9697	±0.146



calculations and from correlations of logarithms of reaction rate constants with  $pK_a$  values of the amines. From the data given in Table III it is obvious that the best results were obtained from correlations  $\log k_1$  vs  $pK_{a1}$  values. Correlations of  $\log k_1$  with quantum-chemical data gave a substantially larger scattering of points about the straight lines. The accuracy of the both quantum-chemical methods used is approximately the same. Practical importance of the dependences found can be seen in the possibility of an approximative estimation of hardening time for various compositions of epoxide resins with amine hardeners.

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