

REACTIONS OF AMINES WITH EPOXY GROUP. III.*
 CALCULATION OF REACTION RATE CONSTANTS
 OF AROMATIC DIAMINES WITH *p*-TOLYL GLYCIDYL ETHER

J. EICHLER and I. DOBÁŠ

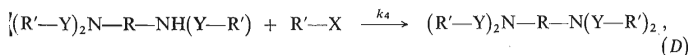
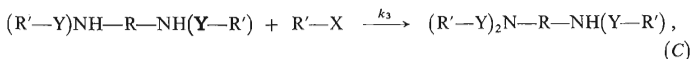
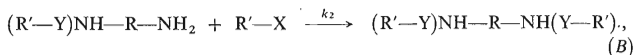
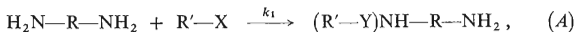
Research Institute of Synthetic Resins and Lacquers, 532 07 Pardubice

Received January 19th, 1973

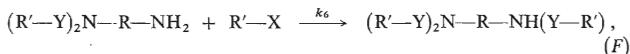
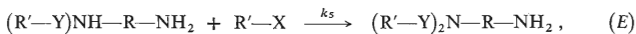
The present paper gives a calculation of rate constants $k_1 - k_4$ of a system of consecutive competitive reactions of aromatic diamines $H_2N-C_6H_4-X-C_6H_4-NH_2$ and 1,4-diaminobenzene with *p*-tolyl glycidyl ether. The described procedure enables the rate constant calculation from time dependence of epoxide group decrease. A presumption has been adopted in the calculation that the reaction rates ratio k_1/k_2 of the reaction of primary amino-hydrogen atoms is approximately equal to that of secondary hydrogen atoms, and its validity has been verified experimentally.

Reactions of substituted anilines and N,N'-disubstituted aromatic diamines with *p*-tolyl glycidyl ether were described in the foregoing reports^{1,2}. It is known^{3,4} and follows from our results that both the primary and secondary amino-hydrogen atoms react with epoxide groups, hence consecutive competitive reactions take place. Methods are given in literature for calculation of two^{5,6} and three^{7,8} consecutive competitive reactions from a known course of decrease of a component consumed in all the reaction steps (*i.e.* epoxide compound in our case).

The present work deals with calculation method of rate constants of primary and secondary amino-hydrogen atoms for the reaction of aromatic diamines with epoxide group of *p*-tolyl glycidyl ether. Eqs (A)–(F) can be written for this reaction.



* Part II: This Journal 38, 3279 (1973).

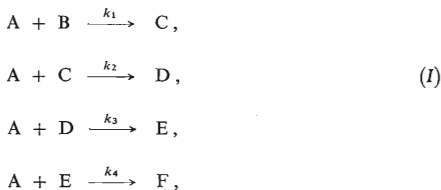


where $-X$ means $\overline{CH-O-CH_2}$ and $-Y$ means $-CH(OH)-CH_2-$.

The following diamines were chosen for the proper kinetic study: 1,4-diaminobenzene, benzidine, 4,4'-diaminodiphenylmethane, and 4,4'-diaminodiphenyl sulphone. *p*-Tolyl glycidyl ether was used as the model epoxide compound.

From Eqs (A)–(F) it is obvious that the reaction of diamines with epoxide group represents a system of consecutive competitive reactions having six rate constants altogether. In the work¹ concerned with the reaction kinetics of substituted anilines and *p*-tolyl glycidyl ether we found that the reaction rate constants ratio of the primary and secondary amino-hydrogen atoms was within 3.5–4.5 for these compounds. From the results of the present work and from those of kinetic measurements of reactions between *N,N'*-disubstituted aromatic diamines and *p*-tolyl glycidyl ether² we conclude that, after the reaction of one primary amino-hydrogen atom, the secondary hydrogen atom of the diamine investigated will be about three times less reactive towards epoxide group than the primary hydrogen atom of the remaining free amino group. Hence, the intermediate of the reaction (E) will be formed to about three times smaller extent than that of reaction (B). With respect to this fact and to that the reactivity of the second amino group is not substantially influenced by the substitution of the first one (as it follows from kinetic measurements of *N,N'*-disubstituted diamines with *p*-tolyl glycidyl ether²), the constants k_5 and k_6 have been omitted in the calculation. The system of the consecutive competitive reactions will be, therefore, solved only for the constants $k_1 - k_4$ whereby the calculation will be simplified.

Thus, the following scheme (I) can be written for the reaction of diamine and glycidyl ether:



where A means *p*-tolyl glycidyl ether, B stands for the starting diamine, C, D, E are reaction intermediates, and F is the final reaction product. The reaction scheme (I)

is described by a system of consecutive equations. If a new time variable λ is defined by equation $\lambda = \int_0^t [A] dt$ where $[A]$ is molar concentration of the component A, the equation set can be transformed into a set of equations of the first order and solved by gradual integrations of equations for $[B]$, $[C]$, $[D]$, $[E]$, $[F]$ and $[A]$. If $[A] = [A_0]$, $[B] = [B_0]$, and $[C] = [D] = [E] = [F] = 0$ for $\lambda = 0$, then the solution of the equation system is obtained in the form:

$$\begin{aligned} \frac{[A]}{[B_0]} = & \left(1 + \frac{k_1}{k_2 - k_1} \left(1 + \frac{k_3}{k_3 - k_1} \left(1 + \frac{k_4}{k_4 - k_1} \right) \right) \right) e^{-k_1\lambda} - \\ & - \frac{k_1}{k_2 - k_1} \left(1 + \frac{k_3}{k_3 - k_2} \left(1 + \frac{k_4}{k_4 - k_2} \right) \right) e^{-k_2\lambda} + \\ & + \frac{k_1 k_2}{(k_3 - k_1)(k_3 - k_2)} \left(1 + \frac{k_4}{k_4 - k_3} \right) e^{-k_3\lambda} - \\ & - \frac{k_1 k_2 k_3}{(k_4 - k_1)(k_4 - k_2)(k_4 - k_3)} e^{-k_4\lambda} \end{aligned} \quad (1.1)$$

$$[B] = [B_0] e^{-k_1\lambda} \quad (1.2)$$

$$[C] = [B_0] \frac{k_1}{k_2 - k_1} (e^{-k_1\lambda} - e^{-k_2\lambda}) \quad (1.3)$$

$$\begin{aligned} [D] = k_1 k_2 [B_0] & \left(\frac{e^{-k_1\lambda}}{(k_2 - k_1)(k_3 - k_1)} - \frac{e^{-k_2\lambda}}{(k_2 - k_1)(k_3 - k_2)} + \right. \\ & \left. + \frac{e^{-k_3\lambda}}{(k_3 - k_2)(k_3 - k_1)} \right) \end{aligned} \quad (1.4)$$

$$[E] = k_1 k_2 k_3 [B_0] \sum_{i=1}^4 (e^{-k_i\lambda} / \prod_{j \neq i}^4 (k_j - k_i)) \quad (1.5)$$

$$[F] = [B_0] \sum_{i=1}^4 (1 - e^{-k_i\lambda}) \prod_{j \neq i}^4 (k_j / (k_j - k_i)) \quad (1.6)$$

Now, the rate constants $k_1 - k_4$ of the studied system of consecutive competitive reactions can be calculated from the known time course of the epoxide compound concentration. For the calculation the both iteration methods by Svrbely and Blauer^{7,8} were modified. Neither of these methods, however, gave satisfactory convergence due to considerable numerical errors in calculation of the variable λ (these

are, in turn, caused by the numerical error of the used integration method and proportional to the reaction time in which λ was determined (see definition of λ) in the case of the first iteration method, and, in the case of the second one, due to the rapidly increasing error of determination of auxiliary variables of the type of integrals $\int_0^\lambda A^{(n)} d\lambda$, where $A^{(n)} = \int_0^\lambda A^{(n-1)} d\lambda$ for $n = 2, 3, 4$; $A^{(1)} = \int_0^\lambda [A] d\lambda$. The iteration cycle either diverged or resulted in a too high value of the sum of squares of deviations between the measured and calculated curves of $[A]$ decrease, or it even gave negative values of some reaction rate constants. Application of other iteration methods (e.g. gradient method or the Gramm-Schmidt orthogonalization method) also failed in finding the constants $k_1 - k_4$ due to complexity of the expression (1.1) for calculation of $[A]$. All the methods mentioned are too sensitive to both the choice of initial values of $k_1^0 - k_4^0$ and accuracy of the value of the variable λ resp. $A^{(n)}$. In order that these difficulties might be circumvented, we used a rate constant calculation method which made use of the properties of solution of a system of differential equations by the Picard method of gradual approximations⁹.

Let us have a system of ordinary differential equations

$$dy/dt = f(y, k) \quad (2.1)$$

the initial conditions being $y_0 = Y$, and $f(y, k)$ being a continuous function fulfilling the Lipschitz condition in the range \bar{R} . If a sequence of gradual approximations is constructed in such a way that Eqs (2.2) are fulfilled:

$$y_0(k, t) = Y$$

$$y_n(k, t) = Y + \int_0^t f(y_{n-1}(k, \tau), k) d\tau \quad (2.2)$$

then the sequence of the stepwise approximations converges uniformly to the solution of the problem¹⁰:

$$y(k, t) = \lim_{n \rightarrow \infty} y_n(k, t). \quad (2.3)$$

Now, if this procedure is applied to the system of differential equations for calculation of the molar concentrations of components A - F and limited to only the fourth approximation, the solution is obtained for the component A in the following form:

$$[A_4] = [A_0] - tk_1[A_0]^2/4 - \frac{t^2}{2} (k_1[A_0] \alpha_1/4 + [A_0] (k_1\beta_1 + k_2\gamma_1)) -$$

$$- \frac{t^3}{3} (k_1[A_0] \alpha_2/4 + \alpha_1(k_1\beta_1 + k_2\gamma_1) + [A_0] (k_1\beta_2 + k_2\gamma_2 + k_3\delta_2)) -$$

$$\begin{aligned}
& - \frac{t^4}{4} (k_1[A_0] \alpha_3/4 + \alpha_2(k_1\beta_1 + k_2\gamma_1) + \alpha_1(k_1\beta_2 + k_2\gamma_2 + k_3\delta_2) + \\
& \quad + [A_0] (k_1\beta_3 + k_2\gamma_3 + k_3\delta_3 + k_4\varepsilon_3)) + \\
& \quad + \text{members of higher degrees up to } t^{50}, \tag{3}
\end{aligned}$$

where $\alpha_1 = \beta_1 = -\gamma_1 = a_1 = b_1 = -c_1 = -k_1[A_0]^2/4$,

$$\alpha_2 = -\frac{1}{2}[A_0] (k_1b_1 + k_2c_1 + k_1a_1/4),$$

$$\alpha_3 = -\frac{1}{3}(k_1a_2[A_0]/4 + [A_0] (k_1b_1 + k_2c_2 + k_3d_2) + a_1(k_1b_1 + k_2c_1)),$$

$$\beta_2 = \frac{1}{2}k_1[A_0] (b_1 + a_1/4),$$

$$\beta_3 = \frac{1}{3}k_1([A_0] (b_2 + a_2)/4 + a_1b_1),$$

$$\gamma_2 = \frac{1}{2}[A_0] (k_1(b_1 + a_1/4) - k_2c_1),$$

$$\gamma_3 = \frac{1}{3}(k_1a_2[A_0]/4 + [A_0] (k_1b_2 - k_2c_2) + a_1(k_1b_1 - k_2c_1)),$$

$$\delta_2 = \frac{1}{2}k_2c_1[A_0],$$

$$\delta_3 = \frac{1}{3}(k_2(a_1c_1 + [A_0]c_2) - k_3[A_0]d_2),$$

$$\varepsilon_3 = \frac{1}{3}k_3[A_0]d_2,$$

where $a_2 = \frac{1}{32}k_1[A_0]^3 (5k_1 - 4k_2)$, $a_3 = -\frac{1}{48}k_1^2[A_0]^4 (k_1 - k_2)$,

$$b_2 = \frac{5}{32}k_1^2[A_0]^3, \quad b_3 = -\frac{1}{48}k_1^3[A_0]^4,$$

$$c_2 = \frac{1}{32}k_1[A_0]^3 (5k_1 + 4k_2), \quad c_3 = \frac{1}{48}k_1^2[A_0]^4 (k_1 + k_2),$$

$$d_2 = \frac{1}{8}k_1k_2[A_0]^3, \quad d_3 = -\frac{1}{48}k_1^2k_2[A_0]^4.$$

The solutions for the components [B], [C], [D], [E], [F] have similar forms. As it can be seen from Eqs (3), the solution of [A] was obtained in a form of a power series in time, the coefficients of the individual powers of t being the functions of the studied rate constants $k_1 - k_4$. The obtained solution (3) is very advantageous in its form, since the coefficients of the first four powers of time involve all the studied rate constants in such a way that each increase of the power by unity results in acceding of a further rate constant. The coefficients of the higher powers of time are merely functions of $[A_0]$ and $k_1 - k_4$. Now, if the experimental time course of the component [A] is described by a polynomial P

$$[A] = \sum_{i=0}^n P_i t^i \tag{4}$$

and the coefficients P_i of individual powers of time compared to those of Eq. (3) corresponding to the same powers of time, a system of non-linear equations is obtained for the studied rate constants, the solution of which gives the rate constants $k_1 - k_4$ in the following forms:

$$\begin{aligned} k_1 &= -4P_1/[A_0]^2, \quad k_2 = -8P_2/k_1[A_0]^3 + 5k_1/4, \\ k_3 &= -\frac{3P_3 + \alpha_1(k_1\beta_1 + k_2\gamma_1) + k_1[A_0]\alpha_2/4 + [A_0](k_1\beta_2 + k_2\gamma_2)}{[A_0]\delta_2}, \\ k_4 &= -\frac{1}{[A_0]\varepsilon_3}(4P_4 + \alpha_2(k_1\beta_1 + k_2\gamma_1) + \alpha_1(k_1\beta_2 + k_2\gamma_2 + k_3\delta_2)) - \\ &\quad - (k_1\beta_3 + k_2\gamma_3 + k_3\delta_3)/\varepsilon_3. \end{aligned} \quad (5)$$

The development coefficients P_i , $i = 0, \dots$ of the polynomial P (Eq. (4)) can be obtained by the least squares method¹¹⁻¹³. The polynomial thus obtained need not cross the origin $(0, [A_0])$, *i.e.* the course of $[A]$ expressed in this way need not fulfil the initial condition. To ensure its fulfilling, it is required that $[A_0] = P_0$ for $t = 0$. For this condition the equation can be written in the matrix form:

$$\mathbf{Q} \cdot \mathbf{P} = \mathbf{Z}, \quad (6)$$

where $\mathbf{Q} = |1 \ 0 \ \dots \ 0|$, $\mathbf{P}^T = |P_0, P_1, \dots, P_n|$, $\mathbf{Z} = [A_0]$ are the respective matrices. The transformed coefficients \mathbf{R} (fulfilling the condition $[A_0] = P_0$ for $t = 0$) of the polynomial \mathbf{P} can be calculated from Eq. (7) (refs¹¹⁻¹³).

$$\mathbf{R}^T = \mathbf{P}^T + (\mathbf{Z}^T - \mathbf{P}^T \cdot \mathbf{Q}^T) \cdot (\mathbf{Q} \cdot \mathbf{B}^{-1} \cdot \mathbf{Q}^T)^{-1} \cdot \mathbf{Q} \cdot \mathbf{B}^{-1} \quad (7)$$

where \mathbf{T} denotes the transposed matrices, \mathbf{B} is the matrix of the system of normal equations $\mathbf{B} \cdot \mathbf{P} = \mathbf{d}$. If the indicated matrix operations are carried out, the elements of the vector of transformed coefficients \mathbf{R} can be written in the form:

$$R_i = P_i + \frac{[A_0] - P_0}{B_{00}^{-1}} \cdot B_{0i}, \quad i = 0, \dots, n. \quad (8)$$

For the calculation of rate constants $k_1 - k_4$ the coefficients $P_1 - P_4$ of Eqs (5) are substituted by the coefficients $R_1 - R_4$ calculated from Eq. (8). For the described method of the calculation of the rate constants $k_1 - k_4$ a program was devised for use with the computer IBM/360-40.

During numerical approximation of the component $[A]$ by the polynomial R ,

the signs of the development coefficients of the polynomial R oscillate, the ratio $|a_i/a_{i-1}|$ being smaller than 0.2 for most of the studied cases. As it can be seen from Eq. (5), for determination of all the four rate constants it is necessary to approximate $[A]$ by a polynomial of at least fourth degree. At the same time it is obvious that the rate constant k_1 will be determined relatively most accurately, its error estimate being proportional to that of the coefficient R_1 . The error estimates of determination of rate constants $k_2 - k_4$ are not so simply connected with those of determination of the coefficients $P_2 - P_4$; the present paper does not deal with them.

EXPERIMENTAL

4,4'-Diaminodiphenyl sulphone. 287 g (1 mol) 4,4'-dichlorodiphenyl sulphone, 1500 g (22 mol) 25% aqueous ammonia and 10 g (0.16 mol) copper powder were heated at 210°C in an autoclave 24 h. After cooling the substance was collected by suction, dissolved in 10% hydrochloric acid and, after filtration, precipitated with 10% sodium hydroxide up to pH about 4. Crystallization from ethanol gave 213 g (86%) product melting at 176–177°C (ref.¹⁴ gives 176°C).

Thin-layer chromatography was carried out using the plates Silufol UV₂₅₄ and the solvent system benzene-methanol 8 : 2. After drying the chromatogram, the spots of amines were made visible by spraying with 1% ethanolic solution of *p*-dimethylaminobenzaldehyde acidified with hydrochloric acid or by spraying with acetone solution of *p*-nitrobenzenediazonium fluoroborate.

Paper chromatography in polar and non-polar solvent system was used. In the former case Whatman paper No 2 was impregnated with 30% solution of dimethylformamide in benzene, and descendent elution with the organic layer of the mixture 1-butanol-acetic acid-water 4 : 1 : 5 was adopted; in the latter case Whatman paper No 3 was impregnated with 20% ethanolic formamide, and benzene was used for descendent elution. Detection was the same as with the thin-layer chromatography. The reagents used were found to be pure by both the methods.

Kinetic measurements were carried out in 99.9% ethanol at 60°C, the concentrations of amines and *p*-tolyl glycidyl ether being 0.025–0.1 and 0.1–0.4 mol/l, respectively (stoichiometric ratio of amine to epoxide compound was maintained in all experiments). Detailed description of experiments is given in ref.¹. The reaction of 1,4-diaminobenzene with *p*-tolyl glycidyl ether was carried out under nitrogen gas, for otherwise the reaction mixture turned dark during measurement probably due to oxidation of the amine.

RESULTS AND DISCUSSION

1,4-Diaminobenzene, benzidine, 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenyl sulphone were chosen for kinetic measurements of reactions of aromatic diamines with *p*-tolyl glycidyl ether. The distance of the both amino groups of these compounds is presumed to be large enough to minimize the steric influence of the substituent of the reacted amino group on the remaining free amino group. With this presumption the rate constants ratio of the reactions of the both primary hydrogen atoms of amino groups with epoxide group should be equal to that of reaction of secondary hydrogen atoms, because the steric hindrance will be the same at the secondary hydrogen atoms of the both amino groups. The value of this ratio was

determined in previous work² for the reactions of *p*-tolyl glycidyl ether with N,N'-dimethyl and N,N'-diethyl derivatives of the same aromatic diamines as those used in the present work. The reactivity ratio of the both amino groups towards epoxide group was found to be similar for all the amines studied, being within 1.3–1.6.

The rate constants $k_1 - k_4$ were calculated by the above mentioned method, and by introduction into Eq. (1) time-concentration dependences of the components A – F obtained. The curve of concentration decrease of epoxide groups [A] with time agreed with the experimental curve up to 30–40% of the reaction only. Graphical representation of the reaction of benzidine and *p*-tolyl glycidyl ether is given in Fig. 1. From the difference between the experimental and calculated curves and from the formal expression of reactants it can be concluded that the accuracy of the rate constants calculation decreases from k_1 to k_4 .

By comparison of the rate constant k_1 calculated by the described method with those obtained from angular coefficients of tangents to the curves of concentration decrease of primary diamine or epoxide groups it was found that these values are, within experimental error, quite equivalent (Table I). Also the values of k_1/k_2 were, within experimental error, equivalent with those of N,N'-disubstituted diamines, therefore it can be concluded that the above mentioned method should give the correct k_2 value, too. Thus mainly the constants k_3 and k_4 are subject to error. The agreement between calculation and experiment was not improved even when approximating the curve [A] by polynomials of higher degrees ($n > 12$), nor by use of an alternative approximation method (other than the least squares method) of polynomial curve, e.g. application of the Stieffel algorithm^{11–13} or approximation with the use of the Chebyshev polynomials and reverse transformation of the found vector of coefficients of the base of orthogonal polynomials into a vector of development

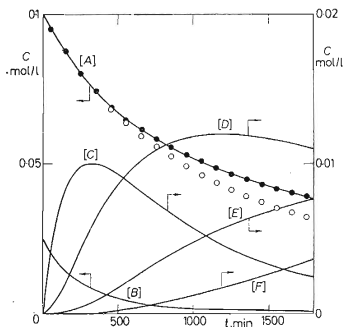


FIG. 1
Time-concentration Dependence of Reaction Components in Reaction of Benzidine with *p*-Tolyl Glycidyl Ether

● Experimental values, ○ calculated values before correction, — calculated values after correction. Left-hand side scale for A and B, right-hand side scale for C–F.

coefficients in the base of time powers¹⁵ or application of economization of the polynomial R by means of the Chebyshev polynomials^{11-13,15}. Therefore, an iteration cycle was inserted in the program for calculation of the constants after the block in which the rate constants are calculated according to Eqs (5); in this cycle the values of the rate constants k_3 and k_4 are gradually increased or decreased to obtain the minimum sum of squares of deviations between the experimental curve $[A]$ and the curve $[A]$ calculated by introduction of the rate constants into Eq. (1.1). In the iteration cycle the values of k_1 and k_2 were kept constant, and the initial value of k_3 was that calculated from Eq. (5). The constant k_4 was taken in each step of the iteration cycle in such a way that $k_1/k_2 = k_3/k_4$. By this modification a very good agreement was achieved between the experimentally found and calculated decreases of the component A (*p*-tolyl glycidyl ether) in the whole range studied *i.e.* up to 60–70% conversion. Both the calculated and experimental curves of epoxide compound decrease in the reaction of benzidine with *p*-tolyl glycidyl ether are given in Fig. 1 along with the calculated time dependences of concentrations of diamine B, intermediates C, D, E and the product F.

Fig. 1 shows a rapid concentration decrease of primary diamine B, a relatively rapid formation and an immediately following concentration decrease of inter-

TABLE I
Reaction Rate Constants $k \cdot 10^3$ ($l \text{ mol}^{-1} \text{ min}^{-1}$) of Aromatic Diamines with *p*-Tolyl Glycidyl Ether in Ethanol

Compound	c TGE ^a mol/l	k_1^b	k_1^c	k_1	k_2	k_3	k_4	k_1/k_2	$\sum d^2$
4,4'-Diamino- diphenyl- methane	0.4	42.7	43.7	43.8	34.8	12.9	10.3	1.26	$2.313 \cdot 10^{-3}$
	0.2	44.5	49.9	43.7	37.8	14.8	12.9	1.16	$4.052 \cdot 10^{-3}$
1,4-Diamino- benzene	0.2	120	114	151.5	125	53.7	44.3	1.22	$4.740 \cdot 10^{-3}$
	0.1	136	—	155	128	55.8	46.1	1.22	$3.600 \cdot 10^{-4}$
	0.05	163	—	158	129	58.9	48.2	1.23	$1.336 \cdot 10^{-4}$
Benzidine	0.2	38.3	—	38.7	30.1	11.7	9.1	1.29	$3.515 \cdot 10^{-5}$
	0.2	43.7	—	38.5	30.7	11.0	8.76	1.26	$1.824 \cdot 10^{-4}$
	0.1	38.0	—	39.1	31.6	12.0	10.0	1.24	$3.949 \cdot 10^{-4}$
4,4'-Diamino- diphenyl sulphone	0.4	1.54	1.42	1.24	0.844	0.637	0.434	1.47	$1.570 \cdot 10^{-4}$
	0.4	1.33	—	1.30	0.795	0.769	0.470	1.63	$2.088 \cdot 10^{-4}$

^a Concentration of *p*-tolyl glycidyl ether in the reaction mixture; ^b the rate constant was calculated from angular coefficient of the curve of decrease of epoxide groups at a time 0; ^c the rate constant was calculated from angular coefficient of the curve of primary amine decrease at a time 0.

mediate C. The intermediates D and E and the product F are formed far more slowly as it could be expected. If the experimental curve of the decrease of A is compared to that calculated without correction, it can be seen that the systematic deviation becomes apparent first at that time when the components D and E begin to make themselves felt in the reaction, their course being (according to Eq. (1)) dependent on the rate constant values k_3 and k_4 , whereas the course of the components B and C depends only on the rate constants k_1 and k_2 .

Good reproducibility of the rate constants $k_1 - k_4$ of reaction of aromatic diamines with *p*-tolyl glycidyl ether, calculated by the described method, can be seen in Table I. The values of rate constants ratios k_1/k_2 are comparable with the corresponding values found for the reaction of N,N'-disubstituted aromatic diamines with *p*-tolyl glycidyl ether², which supports our presumption that the reactivity ratio of the both amino groups is not substantially influenced by substitution at the amino groups, and hence $k_1/k_2 \approx k_3/k_4$. Also the values of the rate constant ratio k_1/k_3 of the reaction of primary and secondary amino-hydrogen atoms are within 2.8 - 3.5 *i.e.* close to the values 3.5 - 4.5 found for the reactions of *ortho*, *meta*, and *para*-substituted anilines with *p*-tolyl glycidyl ether¹. The only exception is 4,4'-diaminodiphenylsulphone, where the ratio was found to be lower. However, the values of the rate constants k_3 and k_4 for the reaction of this compound with *p*-tolyl glycidyl ether are subject to the largest error, because the kinetics was measured only up to 50% conversion, the reaction being very slow.

The authors are indebted to PhMr J. Mašeš for carrying out the paper-chromatographic analyses.

REFERENCES

1. Dobáš I., Eichler J.: This Journal 38, 2602 (1973).
2. Dobáš I., Eichler J.: This Journal 38, 3279 (1973).
3. Smith I. T.: Polymer 2, 95 (1961).
4. Lee H., Newille K.: *Handbook of Epoxy Resins*. McGraw-Hill, New York 1967.
5. Frost A. Schwemer W. C.: J. Am. Chem. Soc. 74, 1268 (1952).
6. Isaacs N. S., Parker R. E.: J. Chem. Soc. 1960, 3497.
7. Svirbely W. J., Blauer J. A.: J. Am. Chem. Soc. 83, 4115 (1961).
8. Svirbely W. J., Blauer J. A.: J. Am. Chem. Soc. 83, 4118 (1961).
9. *Přehled užité matematiky* (Rektorys K. Ed.), Chapter 22 and 25. Published by SNTL, Prague 1968.
10. Živný A., Kubín R., Zach P.: *Malé makromolekulární monografie*. Vol. 5, Chapter 4. Institute of Macromolecular Chemistry, Czechoslovak Academy of Science, Prague 1970.
11. Newhouse A.: CACM 1962, No 5, Alg. 91.
12. Hale R. P.: CACM 1963, No 4, Alg. 91.
13. Naur P.: CACM 1964, No 5, Alg. 91.
14. Ferry C. W., Bock J. S., Baltzly R.: *Org. Syn.*, Col. Vol. III, 239.
15. *Digital Computer Users' Handbook* (M. Klerer, G. A. Korn, Eds). McGraw-Hill, New York 1967.

Translated by J. Panchartek.