CORRELATION OF QUANTUM CHEMICAL AND KINETIC DATA OF REACTION OF AROMATIC DIAMINES WITH p-TOLYL GLYCIDYL ETHER*

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The reaction kinetics of diamines $I-X$ with p-tolyl glycidyl ether have been measured, and the respective rate constants $k_1 - k_4$ have been calculated by applying the Picard method of gradual approximations. The logarithms of the rate constants k_1 have been correlated with the electron density indices at amino nitrogen calculated by HMO and SCFMO methods and with the pK_a values of the amines determined potentiometrically.

It is known that the reaction of primary and secondary amines with epoxide group has a nucleophilic character[1]. In accordance with this fact the found Hammett reaction constants ϱ of e.g. the reaction of substituted N-methylanilines with phenyl glycidyl ether[2] and those of substituted benzylamines with epoxyethylbenzene[3] have negative values. It was also found that the reactivity of amines towards epoxide group increases with their basicity[4,5]. We arrived at the same conclusions when studying the kinetics of reactions of *ortho*, *meta* and *para* substituted anilines with p-tolyl glycidyl ether[6] where we found significant correlations between logarithms of rate constants and the quantum chemically calculated electron density indices at amino nitrogens, the Hammett σ constants, and pK_a values of the amines.

The aim of this work was to determine the possibilities of predicting of the reactivities towards epoxide group of the aromatic diamines of the type $H_2N-C_6H_4-X-$ $-C_6H_4-NH_2$ where $X = -CH_2-$ (*I*), $-SO_2-$ (*II*), $-O-$ (*III*), $-CH=CH-$ (*IV*), $-S-$ (*V*), $-SO-$ (*VI*), benzidine (*VII*), 3,7-diaminothioxanthene-S-dioxide (*VIII*), and 1,2- and 1,4-diaminobenzenes (*IX* and *X*). Therefore, the rate constants k_1 of the reactions of the mentioned diamines with p-tolyl glycidyl ether were correlated with the quantum chemically calculated electron density indices at amino nitrogen and with pK_a values of the amines.

EXPERIMENTAL

Reagents. 4,4'-Diaminodiphenylmethane (*I*), benzidine (*VII*), 1,2-diaminobenzene (*IX*) and 1,4-diaminobenzene (*X*) were commercial products and were purified by distillation or crystallization. 4,4'-Diaminodiphenyl sulphone (*II*) was prepared as in the previous paper[7] and crystal-

lized from ethanol; m.p. 176—177°C, ref.[8] 176°C. 4.4′-Diaminodiphenyl sulphide (*V*) was prepared by reaction of *p*-chloronitrobenzene with sodium sulphide and subsequent reduction of 4-amino-4′-nitrodiphenyl sulphide with tin and hydrochloric acid[9]; m.p. 107·5—109°C (from 50% aqueous ethanol), ref.[9] 108°C. 4,4′-Diaminodiphenyl sulphoxide (*VI*) was prepared by oxidation of 4,4′diaminodiphenyl sulphide with hydrogen peroxide[10] and crystallized from aqueous ethanol; m.p. 175—177°C, ref.[10] 175°C. 4,4′-Diaminodiphenyl ether (*III*) was prepared by reaction of 4-chloronitrobenzene with potassium *p*-nitrophenolate and reduction of the 4,4′-di-nitrodiphenyl ether formed with stannous chloride in methanolic hydrochloric acid[11]. Crystalization from ethanol gave a substance melting at 186—188°C, ref.[11] 185°C. 4,4′-Diamino-stilbene (*IV*) was prepared from 4-nitrotoluene by oxidation and subsequent reduction of 4,4′-di-nitrostilbene with stannous chloride[12]. It was purified by sublimation and crystallization from chlorobenzene and aqueous ethanol; m.p. 217—220°C, ref.[12] 217°C. 3,7-Diaminothioxanthene--S-dioxide (*VIII*) was prepared by reaction of 4,4′-diaminodiphenylmethane with 20% oleum[13] and crystallized from ethanol; m.p. 217—220°C, ref.[13] 217°C. Purity of the diamines was checked by thin-layer chromatography on Silufol UV$_{254}$ plates and by paper chromatography. The procedure and conditions are given in the previous report[7].

Kinetic measurements were carried out in 99·9% ethanol at 60°C; the concentrations of diamines and *p*-tolyl glycidyl ether were 0·0125—0·1 and 0·05—0·4 mol/l, respectively, their ratio being stoichiometric in each case[6]. The decrease of the epoxide group concentration was followed, and in some experiments also the decrease of concentration of primary aromatic diamine was measured in the reaction course by following the extinction at the absorption maximum of the anils formed by reaction of a sample of the reaction mixture with 4-dimethylaminobenzaldehyde[6]. The reactions of 1,2- and 1,4-diaminobenzenes and 4,4′-diaminodiphenyl sulphoxide with *p*-tolyl glycidyl ether were carried out under nitrogen, since otherwise the reaction mixture turned dark due to oxidation of the amines.

The rate constants k_1 to k_4 of the reaction of the aromatic diamines with *p*-tolyl glycidyl ether were calculated by application of the Picard method of gradual approximations; the procedure was described in our previous report[7]. For the sake of checking we computed the rate constants k_1 of several experiments from the angular coefficients of tangents to the curves of decrease of the primary diamine or *p*-tolyl glycidyl ether at a time 0. In the case of the reaction of 4,4′-diaminostilbene with *p*-tolyl glycidyl ether only the constant k_1 was calculated, because the reaction product separated from the reaction mixture and, therefore, the reactions were carried out only to low conversion. All the rate constants calculated are related to one molecule of diamine.

Dissociation constants. All the measurements were carried out under pure nitrogen at 25°C in a beaker with a tempering jacket connected with ultrathermostat. For pH measurements a compensation valve pH-meter PHK-1 (Mikrotechna), a glass electrode G 202 B (Radiometer) and a saturated calomel electrode KALC-4 (Laboratorní přístroje, Prag) were used. 0·02M-NaOH solution was prepared from carbonate-free sodium hydroxide; all the chemicals used were of p.a. purity grade, and only redistilled water was used. The measurements were carried out at constants ionic strength 0·1 (NaCl). The pH-meter was calibrated with standard buffers pH 4·01 and 6·98 (Ústav sér a očkovacích látek, Prague).

Each titration of a diamine hydrochloride with 0·02M-NaOH was repeated five times and plotted in a graph wherefrom the most probable pH value was read which was then used for the calculation of dissociation constants. The calculation was carried out with fulfilling the basic conditions (the condition of electroneutrality, concentration condition and expression of all the constants) from which Eq. (*1*) was derived for a dibasic base:

$$(K_{b1}K_w/[H^+]) (c - \alpha) + K_{b1}K_{b2}(2c - \alpha) = \alpha(K_w/[H^+])^2 \, , \qquad (1)$$

here $\alpha = (K_w/[H^+]) + a.c - [H^+]$, K_{b1}, K_{b2} are the basicity dissociation constants, c is the analytical concentration of acid, a stands for the molar ratio of the added acid and base, and K_w is the autoprotolytic constant of water. The dissociation constants K_{b1} and K_{b2} were obtained by solving graphically the Eq. (1) for individual points of the titration curve. In this way we obtained a system of straight lines which should theoretically cross in one point. In fact, they cross in a certain area. In Results we give the scattering of the values obtained as the area containing 95% of all the points of intersection of the straight lines of the graphical solution.

Quantum chemical calculations. The electron density Q at amino nitrogen was calculated with the use of simple MOLCAO method in the Hückel approximation (HMO) (ref.[14]) and alternatively with the use of MOLCAO method in Pariser–Parr–Pople approximation[15,16]. The Coulombic and exchange integrals were computed with the use of the following k_x and h_{xy} parameter values; k_x: —N(H$_2$), 1·5; =O, 1; —O—, 2; S, 0·5; h_{xy}: C—NH$_2$, 1; C=O, 0·8; C—O, 0·8; S—O, 0·5; C—S, 0·6. In the calculation of electron densities by the SCFMO method in PPP approximation the one-centre Coulombic integrals were approximated according to Pariser and Parr[16], the repulsion integrals between orbitals were calculated according to Mataga–Nishimoto formula[17]. The resonance integrals were calculated according to Wolfsberg and Helmholz[18], the value 0·39 being used for the constant k, and the overlap integrals were computed from tables of overlap integrals[19]. The values of the empiric parameters used are given in Table I.

TABLE I
Parameter Values Used in SCFMO Calculations

Atom (group)	I_μ, eV	$\gamma_{\mu\mu}$, eV	$\beta_{\mu c}$, eV	Z_μ	R_{cv}, Å
C	11·16	11·13	−2·318	1	1·39
NH$_2$[20]	22·6	14·45	−2·090	2	1·38
S[21,22,23]	12·86	9·52	−1·623	2	1·82
O[20]	17·3	14·0	−2·230	1	1·42

RESULTS AND DISCUSSION

The reaction of primary amines or diamines with epoxide group is a consecutive competitive reaction during which all the amino hydrogen can be displaced by the epoxide group. The tertiary amines are final products, being non-active for further reaction[24]. In this paper we have measured the reaction kinetics of aromatic diamines $I-X$ with epoxide group of *p*-tolyl glycidyl ether and calculated the rate constants of reactions of all the four amino hydrogens with epoxide group by applying the Picard method of gradual approximations. The rate constants $k_1 - k_4$ calculated by the abovementioned method and the rate constants k_1 calculated from slopes of tangents to the curves of concentration decrease of epoxide groups or aromatic

primary diamine at the time 0 are given in Table II. From the Table it can be seen that the both methods give consistent k_1 values. As it was the case with the reaction of substituted anilines with p-tolyl glycidyl ether[6], also here the rate constants slightly decrease with increasing concentration of the reaction components and,

TABLE II

Rate Constants $k . 10^3$ (l mol^{-1} min^{-1}) of Reaction of Aromatic Diamines with p-Tolyl Glycidyl Ether in 99·9% Ethanol at 60°C

Compounds	ε_{440}	c^a, mol/l	k_1^b	k_1^c	k_1	k_2	k_3	k_4	k_1/k_3
I	16 700	0·4	42·7	43·7	43·8	34·8	12·9	10·3	3·39
		0·2	44·5	49·9	43·7	38·9	14·5	12·9	3·02
II	8 320	0·4	1·54	1·42	1·24	0·84	0·64	0·43	1·95
		0·4	1·33	—	1·30	0·80	0·77	0·47	1·70
III	17 350	0·2	52·2	47·5	53·1	39·6	16·1	12·0	3·30
		0·2	47·9	—	46·9	40·7	18·4	16·0	2·55
IV	—	0·05	47·5	—	—	—	—	—	—
		0·05	54·6	—	—	—	—	—	—
		0·05	46·4	—	—	—	—	—	—
V	21 385	0·4	17·8	18·9	18·0	15·3	5·10	4·35	3·53
		0·2	23·5	—	22·2	16·3	4·79	3·53	4·64
		0·2	25·5	—	21·4	16·7	5·08	3·98	4·22
VI	10 440	0·4	2·91	2·78	2·91	2·31	0·94	0·75	3·08
		0·4	2·73	—	2·74	2·18	0·81	0·64	3·39
VII	—	0·2	38·3	—	38·7	30·1	11·7	9·10	3·31
		0·2	44·0	—	38·5	30·7	11·0	8·76	3·49
		0·1	37·4	—	39·2	32·8	12·9	10·8	3·04
		0·1	38·1	—	39·1	31·6	12·0	10·0	3·26
VIII	—	0·1	6·95	—	7·22	5·33	2·61	1·93	2·77
		0·1	6·65	—	7·13	5·59	2·66	2·09	2·68
IX	—	0·4	28·1	—	26·5	22·1	5·35	4·47	4·95
		0·2	35·6	—	32·6	27·0	6·52	5·40	5·00
		0·2	36·1	—	31·8	26·2	5·93	4·89	5·37
X	12 480	0·2	125	114	151·5	125	53·7	44·3	2·94
		0·1	136	—	155	128	55·8	46·1	2·78
		0·05	163	—	158	129	58·9	48·2	2·68

^{a} Concentration of p-tolyl glycidyl ether in the reaction mixture. ^{b} Calculated from the slope of the tangent to the curve of decrease of epoxide compound concentration. ^{c} Calculated from the slope of the tangent to the curve of the diamine concentration decrease.

TABLE III

Dissociation Constants of Aromatic Diamines and Respective Amino Nitrogen Electron Densities Calculated by HMO (Q_{HMO}) and SCFMO (Q_{SCFMO}) Approximation

Compound	$c . 10^4$, M	pKa_1	pKa_2	Q_{HMO}	Q_{SCFMO}
I	11·328	5·31 $\pm$ 0·03	4·45 $\pm$ 0·03	1·8916	1·8245
II	9·384	2·54 $\pm$ 0·15	1·45 $\pm$ 0·15	1·8296	1·7900
III	8·721	5·37 $\pm$ 0·03	4·26 $\pm$ 0·03	1·8820	1·8239
IV	—	5·2[a]	3·9[a]	1·8671	1·8220
V	12·372	4·55 $\pm$ 0·01	3·30 $\pm$ 0·05	1·8803	1·8181
VI	8·721	3·25 $\pm$ 0·04	1·94 $\pm$ 0·07	1·8527	1·8123
VII	12·500	4·93 $\pm$ 0·05	3·86 $\pm$ 0·05	1·8712	1·8274
VIII	8·854	3·15 $\pm$ 0·10	2·91 $\pm$ 0·07	—	—
IX	—	4·85[b]	0·67[b]	1·8831	1·8294
X	—	6·16[c]	2·89[c]	1·8852	1·8279

Taken from [a] ref.[26], [b] ref.[27,28], [c] ref.[29].

hence, the decreasing ethanol concentration in the reaction mixture. This finding agrees with the fact that the reactions of amines with epoxide group are accelerated by protic substances[25]. The rate constant ratio k_1/k_3 was found to be 2·7−4·6 for all the compounds measured except for 4,4'-diaminodiphenyl sulphone (II), where the ratio was found to be lower, and 1,2-diaminobenzene, where it was higher due probably to steric effects. The found value of the ratio k_1/k_3 approaches to the value 3·4−4·6 found for the ratio of the rate constants of the reaction of primary and secondary amino hydrogen atoms of the substituted anilines with epoxide group[6].

Table III gives the results of potentiometric determinations of concentration dissociation constants of the aromatic diamines. The potentiometric method proved to be more simple than the spectrophotometric one. The latter method meets with the difficulties connected with the experimental inaccessibility of the absorption spectrum of the monobasic cation BH⁺, and it must solve this problem by a time-consuming method of subsequent approximations. From the Table it can be seen that the accuracy of the pK_a determination is different for different diamines. The high precision of determination in the cases of diamines I, III, V and VII is given by relatively high solubilities of the bases in water, so that it was possible to use the whole titration curve for calculation. The lowest accuracy was attained with the compound II where the clear solution was formed only within $a = 1·16−2·00$, so that only few experimental points were available. The compound IV, being only slightly soluble, could not be determined at all. With the compounds VI and VIII it was possible to use the titration curve in the range $a = 0·8−2·00$. The values pK_{a1} 2·49

and 4·95 as well as those of pK_{a2} 1·30 and 3·85 were found in literature for the compounds *II* (ref.[30]) and *VII* (ref.[26]), respectively. From the Table it can be seen that our pK_{a1} and pK_{a2} values agree with the literature data within experimental error.

Except for 3,7-diaminothioxanthene-S-dioxide (*VIII*), all the compounds fulfil very well the statistically significant dependence $\log k_1 = 0.584\ pK_{a1} - 4.376$ ($r = 0.9966$, 0·1% level of statistical significance). We suppose that the deviation of the compound *VIII* is caused by that its structure differs from those of the remaining diamines of the series investigated. The found values of angular coefficient and intercept are close to the values 0·507 and −4·21, respectively, which were found for correlation of $\log k_1$ *vs* pK_a values of *ortho*, *meta* and *para* substituted anilines[6].

For the correlation of theoretical indices of electronic structure and chemical reactivity with the logarithms of the rate constants of reactions of aromatic diamines with *p*-tolyl glycidyl ether we have used the electron density values Q at amino nitrogen (Table III).

Fig. 1 gives the dependences of $\log k_1$ on the electron densities Q. The linear dependences are expressed by the following equations: $\log k_1 = 32.112\,Q_{HMO} - 61.693$ ($r = 0.8955$) and $\log k_1 = 47.030\,Q_{SCFMO} - 87.22$ ($r = 0.8852$) which both are significant already at 0·1% level of statistical significance. Scattering of the points of the former dependence is substantially greater than that of the correlation of $\log k_1$ *vs* pK_{a1} values of the aromatic diamines. With respect to the differences in skeletons of the individual diamines, the scattering does not deviate from the limits usual for
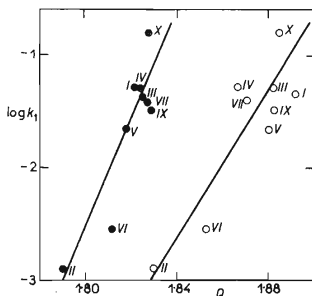

Fig. 1

Dependence of Logarithms of Rate Constants k_1 on Electron Densities of Amino Group of Aromatic Diamines Computed by Methods HMO (○) (Q_{HMO}) and SCFMO (●) (Q_{SCFMO})

such quantum chemical studies. In the second case the scattering is considerably less than that in the correlation of log k_1 *vs* Q_{HMO}, only the substances *VI* and *IX* being substantially deviated. The deviation of the substance *VI* can be caused by unsuitable choice of the parameters of the bridge atoms —SO— in the SCFMO calculation. Our calculation gave the same values of amino-nitrogen electron density for both the compounds *IX* and *X* (1,2- and 1,4-diaminobenzenes). Forshey and co-workers arrived at the same conclusion[31]. The relatively low value of the reaction rate constant k_1 of 1,2-diaminobenzene with *p*-tolyl glycidyl ether is probably caused by the steric effect of the amino group in *ortho* position to the reaction centre. The same conclusion was drawn also from our studies of substituent effects on the rate constant of the reaction of substituted anilines with *p*-tolyl glycidyl ether[6]. Logarithms of k_1 values of the reactions of *ortho* substituted anilines with *p*-tolyl glycidyl ether lay on a straight line different (having different slope) from that of *meta* and *para* substituted anilines. From the present and previous[6] results it can be stated that the SCF method reflects the influence of different skeletons on the reactivity of amino groups towards epoxide group better than the HMO method.

REFERENCES

1. Parker R. E., Isaacs N. S.: Chem. Rev. *59*, 737 (1959).
2. Sakai S., Sugiyama T., Ishliy I.: Kogyo Kagaku Zasshi *70*, 1521 (1967); Chem. Abstr. *68*, 104287 (1968).
3. Laird R. M., Parker R. E.: J. Chem. Soc. *1965*, 4784.
4. Kannebley G.: Kunststoffe *47*, 693 (1957).
5. Chapman N. R., Isaacs N. S., Parker R. E.: J. Chem. Soc. *1959*, 1925.
6. Dobáš I., Eichler J.: This Journal *38*, 2602 (1973).
7. Eichler J., Dobáš I.: This Journal *38*, 3461 (1973).
8. Ferry C. W., Bock J. S., Baltzly R.: Org. Syn. Col. Vol. III, p. 239.
9. Clemence L. W., Severac M., Moetsch J. C.: J. Am. Chem. Soc. *61*, 2763 (1939).
10. Gazdar M., Smiles S.: J. Chem. Soc. *93*, 1835 (1907).
11. Haussermann C., Teichmann H.: Ber. *29*, 1448 (1896).
12. Albert A., Mills J. A., Royer R.: J. Chem. Soc. *1947*, 1452.
13. Stein O.: Ber. *27*, 2806 (1894).
14. Streitwieser A. jr: *Molecular Orbital Theory of Organic Chemistry.* Wiley, New York 1962.
15. Pople J. A.: Trans. Faraday Soc. *49*, 1375 (1953).
16. Pariser R., Parr R. G.: J. Chem. Phys. *21*, 466, 767 (1953).
17. Mataga N., Nishimoto K.: Z. Physik. Chem. (Frankfurt) *13*, 140 (1957).
18. Wolfsberg M., Helmholz L.: J. Chem. Phys. *20*, 837 (1952).
19. Bacanov S. S., Zvjagina R. A.: *Integraly Perekryvanija i Problema Effektivnych Zarjadov*, Tom 1. Nauka, Moscow 1966.
20. Kysel' O., Zahradník R., Belluš D., Sticzay T.: This Journal *36*, 2867 (1971).
21. Hinze F., Jaffé H. H.: J. Am. Chem. Soc. *84*, 540 (1962).
22. Fabian J., Fabian K., Hartmann H.: Theor. Chim. Acta (Berlin) *12*, 319 (1968).

23. Fabian J., Menlhom A., Tröger G.: Theor. Chim. Acta (Berlin) *9*, 140 (1967).
24. Lee H., Newille K.: *Handbook of Epoxy Resins*. McGraw-Hill, New York 1967.
25. Smith I. T.: Polymer *2*, 95 (1961).
26. Hush N. S.: J. Chem. Soc. *1953*, 684.
27. Vetešnik P., Kaválek J., Beránek V.: This Journal *36*, 2486 (1971).
28. Kharkharova G. M.: Sbornik Statej Obšč. Chim. *2*, 1663 (1953); Chem. Abstr. *49*, 5340 (1955).
29. Willi A. V.: Z. Physik. Chem. N. F. *27*, 233 (1961).
30. Bell P. H., Roblin R. O.: J. Am. Chem. Soc. *64*, 2905 (1942).
31. Foshey D. R., Pukanic G. W., Wegener B. J. D., Greenshields J. B.: Theor. Chim. Acta (Berlin) *9*, 288 (1968).

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