REACTIONS OF AMINES WITH EPOXY GROUP. I.
CORRELATIONS OF QUANTUM CHEMICAL AND
KINETIC DATA ON REACTION OF SUBSTITUTED ANILINES
WITH p-TOLYL GLYCIDYL ETHER
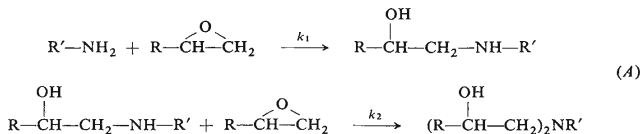
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Rate constants k_1 and k_2 of reaction of *ortho-*, *meta-*, and *para*-substituted anilines with *p*-tolyl glycidyl ether were measured and the indices of electronic structure and chemical reactivity of the anilines were calculated by HMO and SCFMO methods. Significant correlations were found of logarithms of the rate constants with calculated quantum chemical data, Hammett σ constants, and pK_B of the amines.

It is known that primary amines may react[1,2] with two epoxy groups according to scheme (A).

$$R'\text{—}NH_2 + R\text{—}\overset{O}{\overset{\diagup\diagdown}{CH\text{—}CH_2}} \xrightarrow{k_1} R\text{—}\overset{OH}{\overset{|}{CH}}\text{—}CH_2\text{—}NH\text{—}R'$$

$$R\text{—}\overset{OH}{\overset{|}{CH}}\text{—}CH_2\text{—}NH\text{—}R' + R\text{—}\overset{O}{\overset{\diagup\diagdown}{CH\text{—}CH_2}} \xrightarrow{k_2} (R\text{—}\overset{OH}{\overset{|}{CH}}\text{—}CH_2)_2NR'$$

$$(A)$$

As follows from the scheme we deal here with consecutive, competitive reaction. In harmony with the rate-accelerating effect of protic substances[1], the formed hydroxy groups were found to exert catalytic effect[3], which indicates autocatalytic course of the reaction. If the reaction is carried out in dilute solutions of hydroxylic solvents, *i.e.* if the concentration of hydroxyl groups is much higher than that of reacting substances, the reaction becomes pseudo-second order[1]. Tertiary amines may also react with epoxy groups[4], and that by a chain mechanism. As follows from hitherto studies the tertiary amines formed by the reaction of primary or secondary amines with epoxy group are no more active[2].

The main goal of this work was to find correlations of logarithms of rate constants of the reaction of substituted anilines with *p*-tolyl glycidyl ether with quantum chemical indices of the electronic structure of substituted anilines. Relationships between logarithms of the rate constants and Hammett σ constants and pK_A's of the amines

were also established. This work is thus connected with the study of reactivities of aromatic diamines with epoxy resins[5].

EXPERIMENTAL

Compounds used. Substituted anilines were in part commercial products and in part were synthetised by usual methods. They were purified by distillation or by crystallization. Their purity was checked by melting point, refractive index, and by gas chromatography carried out on Fractovap GV apparatus equipped with flame-ionization detector. The substances contained only trace amounts of impurities (less than 0·2%). *p*-Tolyl glycidyl ether was prepared by the reaction of *p*-cresol with 1-chloro-2,3-epoxypropane, using the procedure reported for the synthesis of *p*-tert-butyl phenyl glycidyl ether[6]. Threefold vacuum distillation afforded the product containing 98·8% of the theoretical amount of epoxy groups, n_D^{20} 1·5268, lit.[7] 1·5268. The ethanol used in kinetic measurements contained 0·1% of water.

Kinetic measurements. Kinetic measurements of the reaction of substituted anilines with *p*-tolyl glycidyl ether were carried out in 99·9% ethanol at 60°C, the concentration of amines being 0·1 and 0·2 gmol/l and that of *p*-tolyl glycidyl ether 0·2 and 0·4 gmol/l. Ethanolic solutions of *p*-tolyl glycidyl ether and the amine were mixed in volumetric flask at 60°C, then ethanol was added to the total volume of 100 ml, and after mixing the content was maintained at 60°C. Time was measured from the mixing of the reaction mixture. Depending on the concentration of reaction components, 2 or 5 ml-samples were taken off at fixed time intervals, added to 10 ml of acetone–water (1 : 1) mixture and 25 ml of 0·2м sodium thiosulphate solution in acetone–

TABLE I

Values of Constants k_x and h_{xy} Used in HMO Calculations[14]

Group	k_x	Bond	h_{xy}
—N(H₂)	1·5	C—NH₂	1(0·8)
≡N	0·5	C≡N	$\sqrt{2}$
—C(CH₃)[17,a]	2	C—CH₃	0·7
—OCH₃	2	C—OCH₃	0·8
—Cl[18,19]	1·9	C—Cl	0·4
—Br	1·4	C—Br	0·25
C(Br)	0·1	—	—
—I	1·4	C—I	0·3
C(I)	0·2	—	—
—F[19]	3·5	C—F	0·5
=O	1	C=O	0·8
—O—	2	C—O	0·8
N(O₂)[17]	2	C—N(O₂)	0·8
O(v NO₂)[17]	1	N—O	0·7

a Inductive model.

water (1 : 1) with several drops of phenolphthalein. The samples were set aside for at least 6 h and then titrated with standard acetic acid solution[8]. In order to verify whether the reaction proper is not accompanied by other reactions, in several runs the loss of the primary amine in the reaction mixture was also followed. In these cases 1 ml-samples were taken off and introduced to 50 ml-flask together with 10 ml of an ethanol–10M-HCl (9 : 1) mixture. After 2 h, the volume of the flask was made up by ethanol and after tenfold dilution with this solvent the extinction in absorption maxima of the corresponding anils (located in the 440–450 mm region) were measured with Optica Milano CF 4 NI spectrophotometer. With single anils, the validity of Lambert–Beer law was verified and extinction coefficients were calculated. The rate constants k_1 and k_2 of the reaction of substituted anilines with p-tolyl glycidyl ether were calculated by the "time ratio" method worked out by Frost and Schwemer[9,10], by two iteration methods worked out by Svirbely and Blauer[11,12] which we adapted for our purposes and designed the programs for ICL 4-50 and IBM 360/40 computers, and by graphical method described by Isaacs and Parker[13].

Calculation procedure. Quantum chemical indices of electronic structure and of chemical reactivity were calculated by simple MOLCAO method in Hückel approximation[14] (HMO) and by SCF MOLCAO method in Pariser–Parr–Pople (PPP) approximation[15,16]. The values of parameters k_x and h_{cx} adopted in calculation of coulombic and exchange integrals by HMO method are listed in Table I.

On calculating electronic structure by semiempirical SCF MO method in PPP approximation[15,16], one-centre coulombic integrals $\gamma_{\mu\nu}$ were approximated according to Pariser and Parr[16] as the difference between the ionization potential and the electron affinity of valence states. Repulsion integrals $\gamma_{\mu\nu}$ between μ-th and ν-th atom orbital were calculated from Mataga–Nishimoto formula[20] (*1*):

$$\gamma_{\mu\nu} = \frac{14 \cdot 399}{R_{\mu\nu} + a_{\mu\nu}} \text{ eV},\tag{1}$$

where $R_{\mu\nu}$ (Å) is the distance between atoms μ and ν, and the constant $a_{\mu\nu}$ is given by the expression (*2*).

$$a_{\mu\nu} = \frac{28 \cdot 794}{\gamma_{\mu\mu} + \gamma_{\nu\nu}}.\tag{2}$$

Resonance integrals $\beta_{\mu\nu}^{core}$ were calculated according to Wolfsberg and Helmholz[21], using the relation (*3*),

$$\beta_{\mu\nu}^{core} = kS_{\mu\nu}(I_\mu + I_\nu),\tag{3}$$

where I_μ is the ionization potential of valence state. In calculations we used the value of constant $k = 0.39$. The values of overlap integrals $S_{\mu\nu}$ were taken from the tables[22]. The values of the empirical parameters used are listed in Table II.

RESULTS AND DISCUSSION

Table III presents the values of rate constants k_1 and k_2 of the reaction of substituted anilines with p-tolyl glycidyl ether obtained by graphical method of Issacs and

Parker[13] (M_1), Frost–Schwemer method[9,10] (M_2), and by our modifications of the two methods worked out by Svirbely and Blauer[11,12] (M_3, M_4). The agreement between the values of the rate constants obtained by individual methods is more than good. On expressing the relationship between the values of the rate constants

TABLE II

Empirical Parameters for SCF MO Calculations

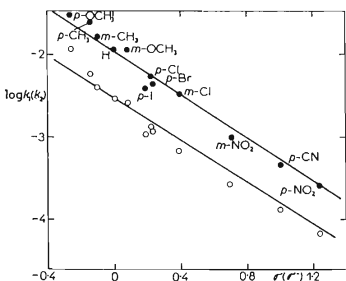| Group	I_μ, eV	$\gamma_{\mu\mu}$, eV	$\beta_{\mu c}$, eV	Z_μ	$R_{c\mu}$, Å
C	11·16	11·13	−2·318	1	1·39
CH_3[23]	10·41	10·98	−1·912	1	
OCH_3[23]	33·8	23·0	−2·10	2	1·40
F[24,25]	30·24	13·87	−2·486	2	1·40
Cl[23,25]	25·07	9·57	−0·927	2	1·77
Br	30·0	10·03	−1·642	2	1·92
I[25]	25·0	9·06	−1·141	2	2·10
NH_2[26]	22·6	14·45	−2·09	2	1·38
≡N	14·12	12·34	−2·852	1	1·2
$N(O_2)$[23]	25·0	16·6	−1·55	2	1·48
O (v NO_2)[23]	17·3	13·9	−2·328	2	1·2

FIG. 1

Plot of Logarithms of Rate Constants k_1 and k_2 vs Hammett σ Constants
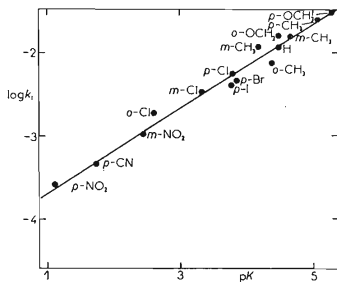● log k_1, ○ log k_2.

FIG. 2

Effect of pK_B of Substituted Anilines on Rate Constants k_1

TABLE III
Results of Kinetic Measurements

Substituent	pK_A / ε_{440}	$cTGE^a$ mol/l	$k_1 \cdot 10^3$, l mol⁻¹ min⁻¹				$k_2 \cdot 10^3$, l mol⁻¹ min⁻¹			
			M_1	M_2	M_3	M_4	M_1	M_2	M_3	M_4
o-OCH₃	4.49[27]	0.4	—	15.9	15.85	16.06	—	4.70	4.68	4.58
	—	0.4	—	15.7	15.3	15.7	—	5.04	5.27	5.06
m-OCH₃	4.20[27]	0.4	11.5	11.8	11.5	11.2	2.76	2.50	2.20	—
	5842	0.4	—	11.7	11.4	—	—	2.76	2.76	—
		0.2	—	13.8	13.0	—	—	3.63	3.72	—
p-OCH₃	5.29[27]	0.4	—	30.9	30.1	30.3	—	11.6	11.9	11.5
	5192[b]	0.4	—	30.6	30.3	30.2	—	11.4	11.2	11.5
		0.2	36.2	36.4	35.7	—	12.3	12.0	13.0	—
		0.1	37.9	—	37.7	—	13.5	—	12.4	—
m-CH₃	4.68[28]	0.4	16.9	16.1	15.9	16.1	3.89	4.10	4.00	4.15
	5167	0.4	—	16.5	16.0	—	—	4.20	4.08	—
		0.2	18.7	18.7	19.5	—	—	4.69	4.71	—
o-CH₃	4.38[28]	0.4	6.79	6.86	6.96	6.95	1.90	1.89	1.87	1.90
	—	0.4	—	6.98	6.89	—	—	1.86	1.91	—
p-CH₃	5.07[28]	0.4	—	23.4	24.7	24.9	—	6.04	5.94	5.98
	5877	0.4	—	22.6	23.9	—	—	6.72	5.75	—
		0.2	24.4	27.0	26.8	26.1	6.21	6.37	5.97	6.26
o-Cl	2.62[28]	0.4	—	1.84	2.02	1.93	—	0.446	0.317	0.373
		0.4	—	1.83	2.00	1.90	—	0.447	0.332	0.391
m-Cl	3.33[28]	0.4	2.93	3.32	3.39	—	0.710	0.766	0.646	—
	6062	0.4	3.14	3.26	3.27	3.18	0.750	0.726	0.721	0.769
p-Cl	3.81[28]	0.4	5.70	5.35	5.38	5.42	1.40	1.32	1.30	1.30
	7192	0.4	—	5.26	5.34	—	—	1.28	1.35	—
		0.2	—	6.06	6.27	—	—	1.65	1.47	—

		a								
p-Br	3·91[29]	0·4	—	4·65	4·27	4·42	—	0·992	1·09	0·983
	8 200	0·4	—	4·55	4·60	—	1·92	1·20	1·20	—
p-I	3·79[30]	0·2	5·02	5·61	5·65	3·97	—	1·43	1·46	1·04
	9 140[b]	0·4	—	4·08	3·86	—	0·987	1·03	1·12	—
H	4·58[27]	0·2	4·37	4·51	4·38	—	2·10	1·07	1·09	—
	5 542	0·4	12·3	—	11·9	11·9	—	—	1·60	2·91
p-CN	1·779[31]	0·2	—	12·0	11·2	11·2	0·140	2·63	3·02	2·73
	6 340[c]	0·4	0·503	11·6	13·0	—	—	2·67	2·87	—
m-NO[c]	2·45[28]	0·4	—	13·3	0·439	0·437	—	3·54	3·84	0·112
	—	0·4	—	—	0·460	—	—	—	0·110	—
p-NO₂	1·11[32]	0·4	—	0·910	0·895	1·01	—	0·208	0·135	—
	—	0·4	—	1·01	1·09	0·250	—	0·276	0·300	0·300
					0·236	0·260			0·240	0·0646
					0·271				0·147	0·0610
									0·070	

[a] Concentration of p-tolyl glycidyl ether in the reaction mixture; [b] measured at $\lambda_{max} = 450$ nm; [c] measured at $\lambda_{max} = 445$ nm.

we used linear dependence, method M_2 being chosen as standard. On using linear regression we obtained the relations described by equations (4).

$$
\begin{aligned}
M_1 &= 0.0668 + 0.9715\, M_2\,, & N &= 20\,, & R &= 0.9979\,, \\
M_3 &= -0.0034 + 0.9969\, M_2\,, & N &= 58\,, & R &= 0.9989\,, \\
M_4 &= 0.0157 + 0.9856\, M_2\,, & N &= 18\,, & R &= 0.9996\,, \\
M_4 &= 0.0165 + 0.9957\, M_3\,, & N &= 20\,, & R &= 0.9998\,.
\end{aligned} \tag{4}
$$

N denotes the degrees of freedom and R is the coefficient of linear regression. From equations (4) it is evident that individual methods yield practically equivalent results, without systematic deviations. Obtained dependences are significant already on testing on 0.1% level of significance.

As already mentioned, the rate constant of the reaction of amines with epoxy group depends on the concentration of hydroxyl ions in the reaction mixture. In Table III is this dependence clearly demonstrated, since pseudo-second order rate constants k_1 and k_2 mildly decrease with increasing concentration of reaction components. For this reason, the correlations were made with the rate constants measured under identical conditions, the concentration of the amines being 0.2 gmol/l, and that of p-tolyl glycidyl ether 0.4 gmol/l. The final value is the average of the two values calculated by method M_3.
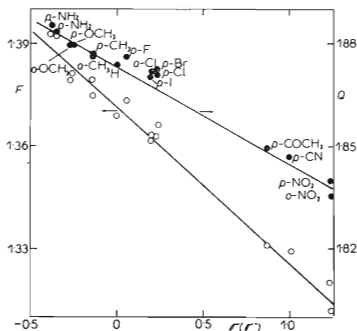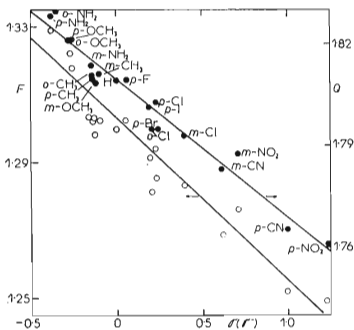

Fig. 3

Dependence of the Electron Densities and Free Valence Indices of the Amino Group of Substituted Anilines on Hammett σ Constants (HMO Method)

● Correlation with electron densities, ○ correlation with free valence indices.

Fig. 1 shows the plot of $\log k_1$ or $\log k_2$ *versus* Hammett σ constants[33,34]. For *p*-nitroaniline and *p*-cyanoaniline we used σ_p^- constants. The dependences are linear

FIG. 4

Dependence of the Electron Densities and Free Valence Indices of the Amino Group of Substituted Anilines on Hammett σ Constants (SCF MO Method)
● Correlation with electrondensities, ○ correlation with free valence indices.
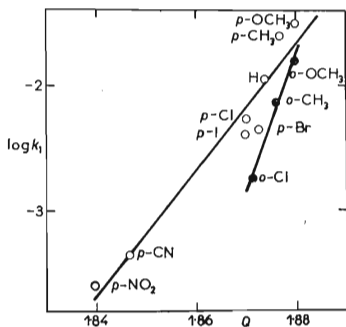

FIG. 5

Plot of Logarithms of Rate Constants k_1 *vs* Electron Densities at the Amino Group of Substituted Anilines Calculated by HMO Method

and have the form $\log k_1 = -1.32\sigma - 2.00$, $R = 0.9712$; $\log k_2 = -1.27\sigma - 2.57$, $R = 0.9642$. Standard deviations are $s_1 = \pm0.139$ and $s_2 = \pm0.154$.

The values of parameters $\varrho - 1.32$ and -1.27 agree with those found by Sakai[35] for the reaction of substituted N-methylanilines with phenyl glycidyl ether in n-butanol $(-1.0$ to $-1.2)$. Laird and Parker[36] reported for the reaction of substituted benzylamines with epoxyethylbenzene still lower value (-0.27). This is not surprising, since here the methylene bridge reduced transmission of substituent effects to the amino group. The low values of reaction constants ϱ observed for the reaction of amines with epoxy group indicates that the cleavage of the epoxy group plays a predominant role in the rate determining step of the reaction.

Fig. 2 shows dependence of $\log k_1$'s on the pK_A values of the amines, which are listed in Table III for standard conditions. A good linear correlation of the form $\log k_1 = 0.507\ pK_A - 4.21$, $R = 0.9900$, was found, with standard deviation

TABLE IV

The HMO and SCF MO Indices of Electronic Structure of the Nitrogen of the Amino Group of Substituted Anilines

Substituent	Q	F	S_n (β^{-1})	Q^{SCF}	F^{SCF}
H	1.8738	1.3688	0.0983	1.8088	1.2996
p-NH$_2$	1.8852	1.3924	0.0826	1.8279	1.3284
p-CH$_3$	1.8765	1.3744	0.0947	1.8092	1.3016
p-OCH$_3$	1.8795	1.3810	0.0911	1.8208	1.3175
p-COCH$_3$	1.8492	1.3310	1.1613	—	—
p-CN	1.8468	1.3292	0.2109	1.7652	1.2515
p-NO$_2$	1.8398	1.3199	0.3452	1.7606	1.2466
p-Cl	1.8706	1.3628	0.1037	1.8022	1.2936
p-Br	1.8720	1.3655	0.1012	1.7944	1.2855
p-I	1.8698	1.3613	0.1049	1.8011	1.2915
p-F	1.8759	1.3730	0.0951	1.8089	1.3019
m-NH$_2$	1.8741	1.3686	0.0967	1.8131	1.3030
m-CH$_3$	1.8739	1.3686	0.0976	1.8109	1.3021
m-OCH$_3$	1.8739	1.3685	0.0974	1.8083	1.2979
m-CN	1.8744	1.3699	0.0983	1.7829	1.2683
m-NO$_2$	1.8701	1.3641	0.0854	1.7875	1.2757
m-Cl	1.8738	1.3687	0.0973	1.7927	1.2829
o-NH$_2$	1.8831	1.3921	0.0899	1.8294	1.3356
o-CH$_3$	1.8760	1.3793	0.0964	1.8100	1.3025
o-OCH$_3$	1.8794	1.3826	0.0929	1.8206	1.3219
o-NO$_2$	1.8349	1.3116	0.3464	—	—
o-Cl	1.8712	1.3630	0.1011	1.7944	1.2808

$s = \pm 0.086$. The correlations of logarithms of rate constants of the reaction under study with Hammett σ constants and basicities are statistically significant already on 0.1% level of significance.

On correlating theoretical reactivity indices with logarithms of the rate constants of the reaction of substituted anilines with p-tolyl glycidyl ether (or with Hammett σ constants) we used electron densities Q at the amino nitrogen, indices of free valence F for the same atom, defined similarly as for carbon atom $F = \sqrt{3} - \sum p_{Ni}$ (p_{Ni} is the bond order of the bond between the amino nitrogen and carbon atom), and nucleophilic superdelocalizabilities S_n. The use of electron density Q as a theoretical index of chemical reactivity is both based on electrostatic arguments and it was theoretically substantiated[14,37]. In Table IV are presented the calculated values of reactivity indices for the amino groups of the substituted anilines studied. The values were calculated on the basis of HMO and SCF MO's. In Fig. 3 is graphically represented the dependence of electron densities at the indices of free valence for the amino group, calculated in HMO approximation, on σ substituent constants. An analogous dependence, calculated in SCF MO approximation, is shown in Fig. 4. As evident from Table IV, in HMO approximation the values of all the reactivity

TABLE V
Results of Analyses of Linear Dependences $y = ax + b$

y	x	a	b	N	R	s
Q	σ	-0.028	1.874	16	-0.9908	0.002
F	σ	-0.048	1.372	16	-0.9929	0.003
S_n	σ	-0.141	$-\ 0.106$	16	-0.8970	0.037
$\log k_1$	Q	50.239	$-\ 96.117$	8	0.9625	0.170
$\log k_1$	F	33.822	$-\ 48.315$	8	0.9832	0.128
$\log k_1$	S_n	7.536	$-\ 1.252$	8	0.8937	0.338
$\log k_2$	Q	46.531	$-\ 89.757$	8	0.9439	0.217
$\log k_1{}^a$	Q	111.492	-211.345	3	1	0.014
$\log k_1{}^a$	F	46.645	$-\ 66.298$	3	1	0.017
$\log k_1{}^a$	S_n	110.939	8.499	3	1	0.019
$\log k_2{}^a$	Q	133.029	-252.292	3	1	0.029
Q^{SCF}	σ	-0.041	1.809	20	-0.9838	0.003
F^{SCF}	σ	-0.050	1.303	20	-0.9664	0.006
$\log k_1$	Q^{SCF}	35.448	$-\ 66.045$	12	0.9711	0.145
$\log k_1$	F^{SCF}	31.080	$-\ 42.362$	12	0.9724	0.146
$\log k_1{}^a$	Q^{SCF}	34.721	$-\ 65.021$	3	1	0.010
$\log k_1{}^a$	F^{SCF}	21.868	$-\ 30.714$	3	1	0.040

Correlation for *ortho*-substituted anilines.

indices for *meta*-substituted anilines remain practically constant and do not correlate with σ constants. Figs 5 and 6 show the dependences of log k_1's of the reaction of substituted anilines with *p*-tolyl glycidyl ether on the electron density at the amino nitrogen. With the use of HMO approximation (Fig. 5) a very good linear dependence was found to exist between Q and log k_1's for *para*-substituted anilines. *ortho*-Substituted anilines correlate as well, but experimental points lie on separate line with the greater slope. We failed to find any correlation with *meta*-substituted anilines, since calculated indices of electron density remain constant for all the substances of this series. This is likely due to the fact that HMO method does not express inductive effect of substituents on the reaction centre. This effect is better expressed by SCF MO method (Fig. 6). However, even here separate dependence was found for *ortho*-substituted anilines. Scattering of the points is similar in both cases. The rate constants of the reaction of the amines with epoxy group increase with increasing electron density at the amino nitrogen, in harmony with nucleophilic character of the reaction. Parameters of linear dependences of the theoretical reactivity indices and the logarithms of the rate constants and the Hammett σ constants are given in Table V. The dependences, except log k_1 *vs* S_n plot, are significant already on 0·1% levels of significance. The accuracy of the correlation of experimental data with theoretical quantities calculated by both metods lies within the region commonly encountered in quantum chemistry. As follows from the correlations obtained, the reactivity of substituted anilines in their reaction with *p*-tolyl glycidyl ether can be satisfactorily described and interpreted with the use of the quantum chemical quantities calculated by HMO and SCF MO methods. Better results were obtained on correlating experimental data with the quantities calculated by SCF MO method, since here the correlation included also *meta*-substituted anilines.
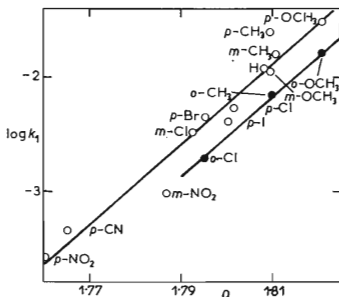

Fig. 6

Plot of Logarithms of Rate Constants k_1 *vs* Electron Densities at the Amino Group of Substituted Anilines Calculated by SCFMO Method

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