

## NONLINEAR HAMMETT RELATIONSHIPS IN THE REACTION OF PEROXOMONOSULFATE ANION ( $\text{HOOSO}_3^-$ ) WITH *meta*- AND *para*-SUBSTITUTED ANILINES IN ALKALINE MEDIUM

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The  $\text{HOOSO}_3^-$  oxidation of eleven *meta*- and *para*-substituted anilines to the corresponding nitrosobenzenes at  $\text{pH} \approx 11$  was characterized by the rate equation  $v = kK[\text{OX}][\text{An}]/(1 + K[\text{An}])$ . Formation constant of the reactive intermediate and its rate of decomposition were evaluated separately for ascertaining the structure-reactivity relationships. Under the experimental conditions the dianion,  $^- \text{O}-\text{O}-\text{SO}_3^-$  is probably the effective electrophile. Kinetic data can be rationalized by a bimolecular process which involves the attack of nucleophilic nitrogen atom on the peroxidic oxygen. The highlight of the study is the opposite curvatures observed in the nonlinear Hammett plots of first-order rate constant  $k$  and the "equilibrium" constant  $K$ , being concave downward and upward, respectively.

**Keywords:** Nonlinear Hammett plot; Aniline; Peroxomonosulfate; Oxidations; Amines; Nitroso compounds; Substituent effects; Solvent effects.

The oxidation of amines to its oxygenated derivatives is an important industrial reaction. During the course of the reaction, synthetically useful intermediates are obtained. Despite the extensive investigation of the oxidation of anilines<sup>1-9</sup>, studies of the kinetics and mechanistic aspects in alkaline medium are strictly limited.

We have previously<sup>10</sup> examined the kinetic studies on Ru(III)-inhibited oxidation of some anilines with  $\text{HOOSO}_3^-$ . A nonlinear structure-reactivity correlation was observed in the conversion of anilines to nitroso products. The oxidation system was described by a upward-concave Hammett plot, with a rate minimum. In the oxidation of *ortho*-derivatives the steric hindrance is slightly overcompensated by an effective anchimeric assistance. Recently, Maruthamuthu *et al.*<sup>11</sup> have examined the kinetics of reactions involving *para*-substituted anilines in aqueous acetic acid medium with peroxomonosulfate. The results indicate that both electron-releasing and withdrawing groups depress the reactivity. The effect of *para*-substituents

on the rate was not well expressed by the Hammett equation. This interesting phenomenon of nonlinear concave downward and upward plots appears to be common in reactions involving the amino group. In this study, we have tried to obtain further information for this oxidation process in order to build up a more detailed mechanistic picture in alkaline medium. Also, the formation constant of the intermediate and the rate constant of its decomposition are evaluated separately for ascertaining the structure-reactivity relationships.

## EXPERIMENTAL

Pseudo-first-order conditions were maintained by keeping a large excess of anilines over peroxomonosulfate. Anilines (reagent grade) were purified by recrystallization/distillation before use and their purity was checked by their m.p./b.p. (>98% pure). The oxidant, Oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ), was purchased from Aldrich and used as such. Control experiments ruled out the decomposition of the oxidant under the experimental conditions. The kinetic studies were carried out in aqueous methanol (50% v/v) medium. All the solutions were kept in a thermostat at constant temperature which was controlled using a Gallenkamp thermostat to an accuracy of  $\pm 0.1$  °C and the measurements were made between 293 and 313 K. The required volume of these solutions (20 ml) for each run were mixed and 2 ml of aliquots of the reaction mixture were pipetted out at convenient time intervals and quenched in 10 ml of 2% potassium iodide solution and the liberated iodine was titrated against standard thiosulfate to a starch end point. The pseudo-first-order rate constants were evaluated from the slopes of the linear plots of log titre *versus* time. The method of least squares was adopted. The rate constants determined were the average of two or more determinations. The progress of the reaction was monitored for at least two half-lives by iodometric estimation of unchanged oxidant at regular time intervals. Stoichiometric studies reveal that two moles of the oxidant are consumed for one mol of the reductant. The reaction between aniline and oxone under kinetic conditions gave an insoluble residue when kept for 3 h. The recrystallized residue in alcohol was found to be nitrosobenzene. It was established thro' the melting point determination (m.p. 60 °C) which corresponds to the literature data. Similar nitrosoproducts were obtained for *meta*- and *para*-substituted anilines. The products were confirmed by TLC.

## RESULTS AND DISCUSSION

Linear plots of logarithm of the consumption of the oxidant *versus* time under all conditions indicated that these reactions are first-order with respect to the concentration of oxidant ( $r > 0.993$ ;  $s < 0.0233$ ). A plot of  $k_{\text{obs}}^{-1}$  *versus*  $[\text{An}]^{-1}$  shows an intercept on the y-axis indicating Michaelis-Menten dependence on the concentration of aniline (Fig. 1) ( $r = 0.995$ ;  $s = 63.0$ ) (Table I). Same fractional order dependence on concentration of substrate is observed for all the *meta*- and *para*-substituted anilines (Table II). The concentration of  $\text{OH}^-$  has no significant effect on the reactivity. The variation of pH be-

tween 11.3–12.4 does not affect the reactivity. The kinetic results are summarized in Table I.

TABLE I  
Effect of substrate, oxidant and NaOH on the reaction rate at 303 K in 1 : 1 aqueous methanol (v/v)

[aniline] · 10 <sup>2</sup> mol dm <sup>-3</sup>	[HSO <sub>5</sub> <sup>-</sup> ] · 10 <sup>3</sup> mol dm <sup>-3</sup>	[NaOH] · 10 <sup>3</sup> mol dm <sup>-3</sup>	k <sub>obs</sub> · 10 <sup>4</sup> s <sup>-1</sup>
1.00	1.19	11.53	3.73
1.25	1.19	11.53	4.51
1.50	1.19	11.53	5.09
2.00	1.19	11.53	6.97
2.50	1.19	11.53	7.55
2.00	0.89	11.53	6.76
2.00	1.19	11.53	6.97
2.00	1.49	11.53	6.60
2.00	1.79	11.53	6.51
1.00	1.19	5.76	3.70
1.00	1.19	7.68	3.62
1.00	1.19	11.53	3.73
1.00	1.19	19.21	3.81

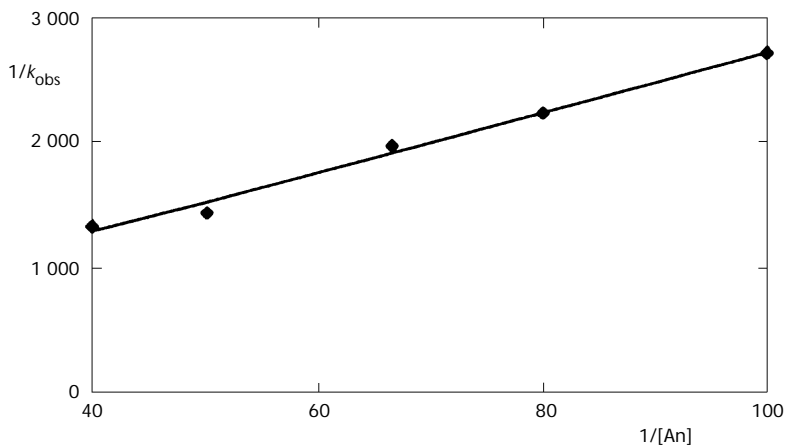


FIG. 1  
Michaelis-Menten plot for the oxidation of aniline at 303 K

TABLE II  
Pseudo-first-order rate constant values for the oxone oxidation of X-substituted anilines in 1 : 1 aqueous methanol (v/v);  $[\text{HSO}_5^-] = 1.19 \cdot 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{NaOH}] = 11.53 \cdot 10^{-3} \text{ mol dm}^{-3}$

No.	X	$[\text{S}] \cdot 10^2$ <sup>a</sup> , mol dm <sup>-3</sup>	$k_{\text{obs}} \cdot 10^4$ , s <sup>-1</sup>
1	H	1.00	3.73
		1.50	5.09
		2.50	7.55
2	3-OCH <sub>3</sub>	1.20	3.98
		2.00	4.71
		3.01	5.31
3	3-CH <sub>3</sub>	1.22	2.99
		1.63	3.67
		2.54	5.12
4	3-Cl	1.27	1.77
		1.69	2.36
		2.11	2.59
5	3-NO <sub>2</sub>	1.20	1.38
		1.61	1.58
		2.51	2.22
6	4-OCH <sub>3</sub>	1.20	4.19
		1.60	5.10
		2.01	5.69
7	4-CH <sub>3</sub>	1.20	4.28
		2.00	5.44
		3.01	7.31
8	4-COOH	1.20	16.40
		1.60	20.53
		2.50	26.76
9	4-Cl	1.21	3.79
		1.61	4.78
		2.51	6.82
10	4-Br	1.62	4.88
		2.53	6.58
		3.03	7.78
11	4-NO <sub>2</sub>	1.20	0.67
		1.61	0.74
		3.01	0.99

<sup>a</sup> [S] stands for the concentration of the respective substrate.

Addition of  $\text{NaHSO}_4$  at a fixed pH did not significantly affect the first-order rate constants. To verify the formation of radicals as intermediates, a free radical scavenger, acrylonitrile (5% aqueous solution) was added to the reaction mixture immediately following the addition of aniline. No turbidity was developed. Invariance of rate with acrylonitrile as shown in Table III rules out a free radical process. Relative permittivity changes have a marked effect in the reactivity. Rate constants increase significantly with increasing water content of the solvent. A plot of  $\log k_{\text{obs}}$  versus  $D^{-1}$  is fairly linear with a negative slope ( $r = 0.995$ ;  $s = 0.021$ ). The negative slope indicates the involvement of negative ions in the rate-limiting step. It appears that the transition state is more polar than the reactant in the initial state.  $\text{D}_2\text{O}$  slightly increases the reactivity of anilines (Table IV). The ratio,  $k_{\text{D}_2\text{O}} / k_{\text{H}_2\text{O}}$  does not seem to indicate any significant solvent isotope effect. The lack of solvent isotope effect excludes a rate-controlling participation

TABLE III

Dependence of sodium hydrogensulfate, acrylonitrile (AN) and solvent composition on the reaction rate at 303 K; [aniline] =  $2.00 \cdot 10^{-2} \text{ mol dm}^{-3}$ , [NaOH] =  $11.53 \cdot 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{HSO}_3^-]$  =  $1.19 \cdot 10^{-3} \text{ mol dm}^{-3}$

$[\text{NaHSO}_4] \cdot 10^4$ $\text{mol dm}^{-3}$	$[\text{AN}] \cdot 10^4$ $\text{mol dm}^{-3}$	$D^a$	$k_{\text{obs}} \cdot 10^4$ $\text{s}^{-1}$
-	-	55.65	6.97
3.17			7.09
6.34			6.84
12.67			7.03
19.01			7.13
	4.72		6.90
	9.44		7.06
	18.90		6.99
		64.80	11.20
		60.20	8.35
		55.65	6.97
		51.06	5.15
		46.47	3.97

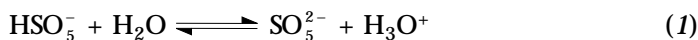
<sup>a</sup> Relative permittivity values are calculated from values of pure solvents.

of water as a nucleophile<sup>12</sup>. The solvent isotope effect on the reaction rate is related to solvation effects in the two solvents<sup>13</sup>.

The Hammett equation provides a general description of substituent effects on rates and equilibria of aromatic molecules. Effect of substituents on the reactivity has been examined by employing eleven *meta*- and *para*-substituted anilines. Generally the rates of *meta*- and *para*-substituted anilines are lower than for the parent (except *p*-COOH). No simple Hammett relationship is expected for the substituent effects. It appears that the nature of the rate-limiting step changes with the nature of the substituents (Table V).

### Mechanism

Although many peroxyanions are effective nucleophiles,  $\text{HOOSO}_3^-$  is a very weak nucleophile<sup>14,15</sup>. Under the experimental conditions maintained ( $\text{pH} > 11$ ) the dianion is the reactive species. Maruthamuthu *et al.*<sup>16</sup> examining the oxidation of dimethyl sulfoxide with peroxomonosulfate found the oxidant existing as  $^-O-O-SO_3^-$  at  $\text{pH} > 9$ .  $\text{HOOSO}_3^-$  exists<sup>17</sup> principally as  $\text{SO}_5^{2-}$  around  $\text{pH} 10$ .



In the  $\text{pH}$  range 12–14, peroxomonophosphoric acid exists<sup>18</sup> as  $\text{HPO}_5^{2-}$  and  $\text{PO}_5^{3-}$ . In the case of sulfides, the nucleophilic attack on peroxy oxygen is made by sulfur; the reverse trend was found to be true in the case of sulfoxides<sup>19</sup>. A complex involving hydrogen bonding of the  $\text{NH}_2$  group to the  $\text{SO}_5^{2-}$  can be envisaged. Electron-pair movements accompanying the

TABLE IV

Effect of  $\text{D}_2\text{O}$  on the reaction rate at 303 K in 1 : 1 aqueous methanol (v/v);  $[\text{aniline}] = 2.00 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{NaOH}] = 11.53 \cdot 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{HSO}_5^-] = 1.19 \cdot 10^{-3} \text{ mol dm}^{-3}$

MeOH : H <sub>2</sub> O : D <sub>2</sub> O, %	$k_{\text{obs}} \cdot 10^4, \text{s}^{-1}$
50 : 50 : 0	6.97
50 : 45 : 5	7.11
50 : 40 : 10	7.23
50 : 25 : 25	7.54

withdrawal of  $\text{SO}_4^{2-}$  ion could then result in the formation of  $\text{PhNHOH}$  in a slow step. In the present study, kinetic data can be rationalized by a bimolecular process which involves the attack of the nucleophilic nitrogen atom on the peroxidic oxygen.

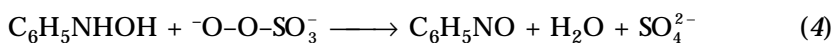
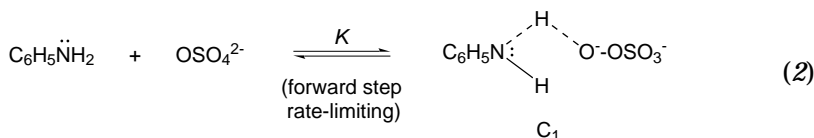


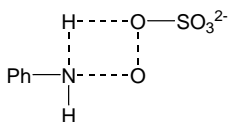
TABLE V

Rate constants for the oxidation of anilines with  $\text{HSO}_5^-$  at various temperatures in 1 : 1 aqueous methanol (v/v);  $[\text{aniline}] = 2.00 \cdot 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{HSO}_5^-] = 1.19 \cdot 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{NaOH}] = 11.53 \cdot 10^{-3} \text{ mol dm}^{-3}$

No.	Substrate	$k_{\text{obs}} \cdot 10^4, \text{ s}^{-1}$		
		293 K	303 K	313 K
1	H	3.73	6.97	13.24
2	3-OCH <sub>3</sub>	2.15	4.71	9.53
3	3-CH <sub>3</sub>	1.94	3.92	8.49
4	3-Cl	1.29	2.54	4.63
5	3-NO <sub>2</sub>	0.75	1.61	3.19
6	4-OCH <sub>3</sub>	2.62	5.69	11.07
7	4-CH <sub>3</sub>	2.85	5.44	10.83
8	4-COOH	10.16	18.78	34.83
9	4-Cl	3.10	5.25	11.47
10	4-Br	2.82	4.44	11.66
11	4-NO <sub>2</sub>	0.36	0.77	1.63

A nonlinear concave downwards type Hammett plot with a positive and negative  $\rho$  value can be explained by invoking a mechanism involving a shift in the rate-limiting step within the same overall reaction pathway. The  $\rho$  values indicated the development of cationic character on nitrogen. Step (2) is favoured by electron-releasing groups since there is a possibility of development of positive charge at the nitrogen atom. Step (3) is favoured by electron-releasing groups since there is the possibility of dispersal of positive charge at the reaction site.

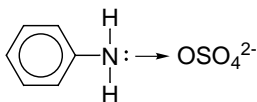
The formation of  $S_N2$  intermediate by nucleophilic attack of aniline lone-pair on the electrophilic peroxy oxygen of oxone is also not ruled out.



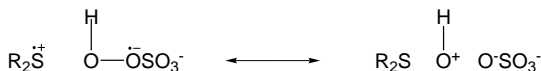
This intermediate closely resembles the cyclic transition state proposed in the oxidation of *para*-substituted anilines by peroxomonosulfate in aqueous acetic acid medium<sup>11</sup>.

In the oxidation of anilines by hydrogen peroxide as catalyzed by methylrhenium trioxide<sup>20</sup>, the reaction constant value of  $-1.19$ , has been explained by assuming a rate-controlling attack of nitrogen lone-pair electrons of anilines on peroxidic oxygen.

Similar type of intermediate can also be envisaged in the present study.



Edwards<sup>21</sup> has pointed out that oxidations with peroxy acids may involve  $HO^+$  as an electrophilic intermediate, and the transition state for sulfide oxidation can be represented as resonance hybrids.



Similar type of resonance hybrid is not ruled out in the present investigations. The kinetic data is insufficient to distinguish between all these possibilities.



The phenomenon of a Hammett plot concave downwards is explained by assuming shifts in the rate-limiting step within the same overall reaction pathway. Step (2) is slow and rate-limiting for electron-withdrawing groups and step (3) slow for electron-releasing groups. The reaction can be characterized by the rate equation

$$v = \frac{kK[\text{OX}][\text{An}]}{1 + K[\text{An}]}, \quad (5)$$

where [OX] represents the concentration of the oxidant.

$$k_{\text{obs}} = \frac{kK[\text{An}]}{1 + K[\text{An}]} \quad (6)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK[\text{An}]} + \frac{1}{k} \quad (7)$$

From the double reciprocal plot of  $1/k_{\text{obs}}$  versus  $1/[\text{An}]$  ( $r = 0.995$ ;  $s = 63.0$ ), rate constant ( $k$ ) and equilibrium constant ( $K$ ) can be determined. The substrate effect studies were carried out for all the listed anilines at 303 K and the corresponding  $k$  and  $K$  values ( $r > 0.977$ ;  $s < 270.9$ ) are calculated for all the substrates. The determined  $k$  and  $K$  parameters for all the substituted anilines at 303 K are listed in Table VIII.

*p*-COOH is known to react with peroxomonosulfate; in any case, it will be ionized at the pH of the present investigations. Hence, the  $\sigma$  value should be closer to zero. The  $\sigma^-$  values are generally used when either a "lone pair to substituent" conjugation is present in the starting state or *vice versa*. If  $\sigma^-$  value is used for *p*-NO<sub>2</sub> (1.24) and the -COOH/-CO<sub>2</sub><sup>-</sup> value is omitted or set close to zero, then the Hammett plot becomes "more linear" with a slight  $\rho$ .

A linear plot of  $k_{\text{obs}}$  versus [aniline] shows a good correlation ( $r \approx 0.99$ ) while the inverse plot does give a slightly better  $r = 0.995$  value. Hence, the evidence for saturation in [aniline] (and hence the pre-equilibrium) is not found. A pre-equilibrium is still possible, but with  $1 \gg K[\text{An}]$ , it would give  $k_{\text{obs}} = kK$ . Thus the loss of lone pair in the equilibrium ( $K$ ) step would be offset by its re-gain in the  $k$  step resulting in a very small overall  $\rho$  value.

### Effect of Substituents on $k$

The rates of all the substituted anilines studied are lower than for the parent aniline. In spite of the obvious imperfections, a nonlinear concave-downwards Hammett plot is demonstrated (Fig. 2). The Brown–Okamoto relation does not improve the situation. The nonlinear plot obtained is a composite of two straight lines, one with positive and the other with negative  $\rho$  value. A negative  $\rho$  value indicates that the nucleophilic nitrogen atom is more positively charged in the transition state than in the reactant, while a positive  $\rho$  value indicates dispersal of positive charge. The reaction constant values are listed in Table VI.

The rate coefficients are analyzed using multiparameter extensions of the Hammett equation (Table VII). Goodness of fit is judged by high  $R$ , low SE, small  $f$  and  $\psi$  values. Four scales of  $\sigma_R$  values are used in the analysis;  $\sigma_R^0$ ,  $\sigma_R^{(BA)}$ ,  $\sigma_R^-$  and  $\sigma_R^+$ . These analyses including the Swain–Lupton treatment failed to explain the reactivity. Nor are the  $k$  values well expressed by the Yukawa–Tsuno equation<sup>22</sup>, which can give an idea regarding the extent of involvement of cross conjugation in the transition state. The picture remains the same with  $\sigma^0$  form of the Yukawa–Tsuno equation.

Considerable deviation is observed in the Hammett plot (Fig. 2) for the reactivity of 4-carboxyaniline, *i.e.* the rate coefficients of 4-carboxyaniline are not falling on the predicted curve. Quite likely, it behaves as a substituted carboxylic acid in its reactivity. In the oxidation of 4-aminophenol

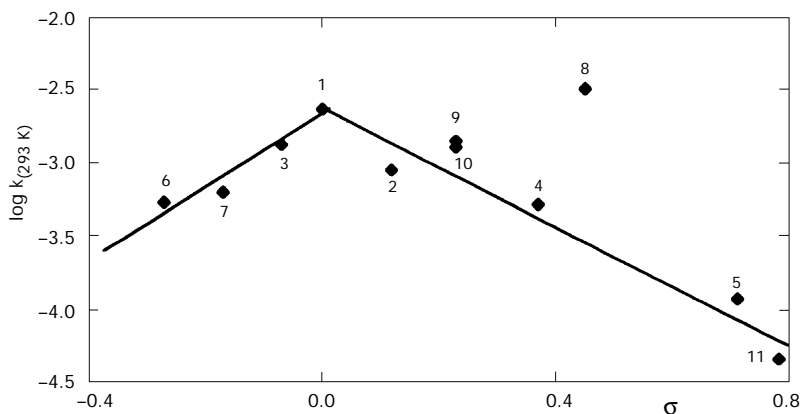


FIG. 2

The Hammett relationship (for numbering see Table II)

TABLE VI  
The reaction constant values for  $\rho\sigma$  and  $\rho\sigma^+$  correlations (for  $k$  values)

Temperature, K	Correlation	$\rho$	$r$	$\rho$	$r$
293	$\rho\sigma$	2.40	0.963	-1.90 (-2.20)	0.810 (0.980)
	$\rho\sigma^+$	0.72	0.860	-1.78 (-2.09)	0.810 (0.990)
303	$\rho\sigma$	1.18	0.846	-1.47 (-1.80)	0.740 (0.970)
	$\rho\sigma^+$	0.31	0.680	-1.37 (-1.78)	0.740 (0.980)

The values in the parentheses are  $\rho_-$  values determined excluding *m*-OCH<sub>3</sub> and *p*-COOH groups.

TABLE VII  
Multiple regression analyses of oxidation rate coefficients ( $k$ ) in oxidation of some *p*-substituted anilines with HSO<sub>5</sub><sup>-</sup> in alkaline medium (MeOH : H<sub>2</sub>O = 50 : 50 (v/v))

No.	Substituent constants	Temperature K	100R	SE	$\psi^a$	$f$	$n$
1	$\sigma_I, \sigma_R^0$	293	48.9	0.656	1.154	1.259	7
		303	50.4	0.555	1.412	1.212	7
		313	49.4	0.509	1.151	1.244	7
2	$\sigma_I, \sigma_R^{(BA)}$	293	48.4	0.658	1.158	1.278	7
		303	49.7	0.558	1.148	1.235	7
		313	48.9	0.511	1.154	1.262	7
3	$\sigma_I, \sigma_R^-$	293	67.5	0.555	0.976	0.773	7
		303	72.7	0.441	0.908	0.668	7
		313	75.4	0.385	0.869	1.001	7
4	$\sigma_I, \sigma_R^+$	293	50.0	0.651	1.146	1.224	7
		303	49.3	0.559	1.152	1.251	7
		313	46.5	0.518	1.171	1.345	7

$$^a \psi = \left[ \frac{n(\text{RSS})}{(n-2)(\text{TSS})} \right]^{1/2}, \text{ where RSS is Residual Sum of Squares and TSS is Total Sum of Squares.}$$

with horseradish peroxidase<sup>23</sup> (HRP), the fit of the data for 4-aminophenol in the Hammett plot for anilines was taken as evidence for the reaction taking place at the amino group instead of at the hydroxy group.

The activation parameters have been determined from the Eyring's plot of  $\ln k/T$  versus  $1/T$  ( $r > 0.97$ ;  $s < 0.281$ ) (Table VIII). Near constancy of  $\Delta G^\ddagger$

TABLE VIII

Rate constants and activation parameters for the oxidation of anilines with  $\text{HSO}_5^-$ ;  $[\text{NaOH}] = 11.53 \cdot 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{HSO}_5^-] = 1.19 \cdot 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{aniline}] = 2.00 \cdot 10^{-2} \text{ mol dm}^{-3}$ ;  $\text{MeOH} : \text{H}_2\text{O} = 50 : 50$  (v/v)

No.	Substituent	$k \cdot 10^3, \text{s}^{-1}$			$\Delta H^\ddagger$ $\text{kJ mol}^{-1}$	$-\Delta S^\ddagger$ $\text{JK}^{-1} \text{mol}^{-1}$	$\Delta G^\ddagger(303 \text{ K})$ $\text{kJ mol}^{-1}$	$r$	$s$
		293 K	303 K	313 K					
1	H	2.31	2.90 (14.66)	3.61	14.5	245.9	89.0	0.999	0.006
2	3-OCH <sub>3</sub>	0.89	1.08 (35.84)	1.31	12.2	261.7	91.5	0.999	0.003
3	3-CH <sub>3</sub>	1.33	1.79 (15.94)	2.82	16.4	243.7	90.3	0.995	0.030
4	3-Cl	0.52	0.87 (20.66)	2.75	61.1	100.2	91.5	0.971	0.281
5	3-NO <sub>2</sub>	0.12	0.28 (81.22)	0.68	65.2	97.9	94.9	0.999	0.038
6	4-OCH <sub>3</sub>	0.54	1.39 (66.16)	3.22	65.7	83.3	90.9	0.999	0.015
7	4-CH <sub>3</sub>	0.63	1.24 (42.43)	2.30	46.9	146.0	91.2	0.999	0.002
8	4-COOH	3.12	5.27 (42.02)	9.81	41.1	152.7	87.4	0.997	0.057
9	4-Cl	1.40	1.95 (19.88)	2.78	23.6	218.9	90.0	0.999	0.018
10	4-Br	1.27	2.16 (18.02)	3.50	36.3	176.6	89.8	0.999	0.006
11	4-NO <sub>2</sub>	0.05	0.12 (118.1)	0.26	65.3	105.3	97.2	0.999	0.036

The values given in the parentheses are  $K$  values ( $\text{dm}^3 \text{mol}^{-1}$ ) calculated from double reciprocal plots at 303 K

values implies that a common mechanism is operating in all the anilines studied. Entropies of activation in this series do not remain constant. Entropies of activation are largely negative as expected for a bimolecular reaction<sup>24</sup>. The variation in  $\Delta S^\ddagger$  is linearly related to changes in  $\Delta H^\ddagger$ . However, Exner<sup>25a</sup> criticized the validity of such a linear correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  as these quantities are dependent on each other. The high degree of organization which this mechanism implies, explains the high negative entropy values observed. The linear plot of  $\log k(T_2)$  versus  $\log k(T_1)$  with satisfactory correlation coefficient (Fig. 3) ( $r = 0.97$ ;  $s = 0.097$ ) further supports a similar mechanism in all the listed anilines. The isokinetic temperature  $\beta$  was calculated using the relation<sup>25</sup>

$$\beta = \frac{T_1 T_2 (1 - f)}{(T_1 - T_2 f)}.$$

The value of  $\beta$  (362.6 K) is much above the experimental temperature (303 K). Since  $\beta - T$  is positive ( $\approx 60$  K), the reaction shows isokinetic behaviour.

ESR measurements are carried out at room temperature on a E-4 Varian, EPR spectrometer (microwave frequency and receiver gain of 9.37 GHz and  $3.2 \cdot 10^3$ ). Neither signals nor kinetic evidence in favour of radical process have been recorded. Radical processes are characterized by very low  $\rho$  values<sup>26,27</sup>.

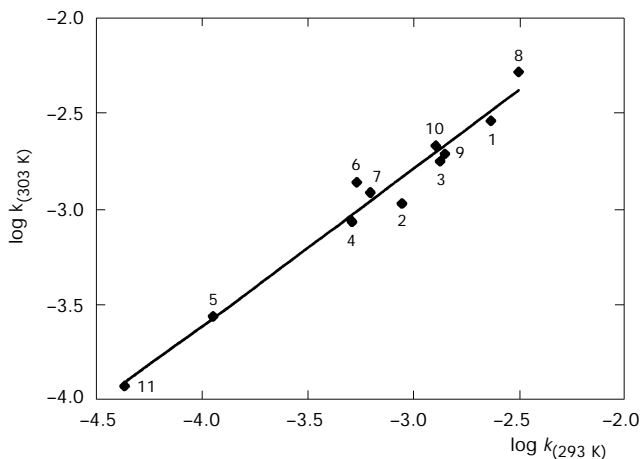


FIG. 3  
The Exner plot (for numbering see Table II)

### Effect of Substituents on $K$

The effect of substituents on  $K$  is depicted in the Hammett plot (Fig. 4). The  $K$  values for all the substituents, both electron-releasing and -withdrawing, are higher than for the parent. It appears that there is a wide scatter in the Hammett  $\rho\sigma$  relationship. Considering the uncertainties in the determination of  $K$  and in spite of the scatter, the Hammett relationship can be roughly treated as a case of "nonlinear concave-upward Hammett plot".

In the reaction system, contrasting behaviours are observed in the effect of substituents on  $k$  and  $K$ . The  $k$  values are described by a nonlinear concave-downwards Hammett plot, while the  $K$  values by a concave-upward plot. We have examined the behaviour of the second-order constant obtained as the product of the two terms,  $k$  and  $K$  and found that for H and the *para*-substituents, the data are well fitted, without curvature, by the multiple regression equation:

$$\log k_2 = -1.382 - 0.498 \sigma_1 - 1.024 \sigma_R^0 \quad (8)$$

$$(\pm 0.021) \quad (\pm 0.498) \quad (\pm 0.062)$$

with  $R^2 = 0.993$ ,  $F = 222.266$  and probability 99.89%. Clearly, the "curvatures" cancel. This correlation excludes the outlying data for *p*-COOH. By contrast, the *meta*-set does not behave similarly well. The kinetics looks much more complex than expected.

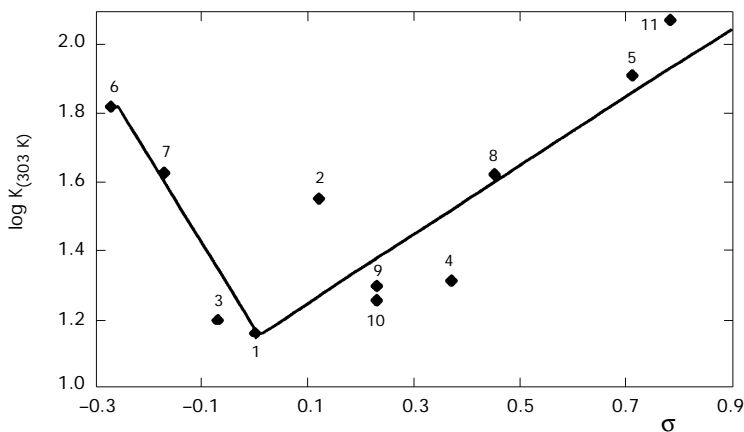


FIG. 4  
Plot of  $\log K_{(303\text{ K})}$  versus  $\sigma$  (for numbering see Table II)

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