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Studies on Sulfinic Acids

IV.* Oxidation of Aromatic Sodium Sulfinates with Hydrogen Peroxide

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The oxidation of a series of aromatic sodium sulfinates with hydrogen peroxide in aqueous solution has been kinetically investigated. The reaction rates were measured by polarographic methods, and a special method was developed for measurements with polarographically active substituents. The rate constants obtained for the *para*- and *meta*-substituted members agree with the Hammett equation. Results with the *ortho*-substituted members are discussed and compared with results from corresponding members in alkylation reactions.

Alkali metal salts of sulfinic acids are easily oxidized by hydrogen peroxide to the corresponding sulfonic acid salts. In an earlier investigation by Gonzalez dealing with the hydrogen peroxide oxidation of thiols [1] the kinetics of the hydrogen peroxide oxidation of some aromatic sulfinic acids (substituents: H, p-CH_3, p-Cl, p-Br) was also investigated from the reaction mechanism point of view, because it had been found that sulfinic acids constitute intermediates in the auto-oxidation of thiols. It was concluded that the reaction was first order with respect to sulfinic acid but dependent on the hydrogen peroxide concentration. The stoichiometry of the reaction was proved to correspond to the oxidation to sulfonic acid without any side reactions. A further investigation appended to Ref. 1 showed that the apparent dependence on hydrogen peroxide concentration was due to an analytical error ** and a correction was applied. The final result was then that the reaction was of straight forward second order kinetics. The employment of the polarographic technique used in the present work made it possible to eliminate analytical difficulties.

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* Part III: *Acta Chem. Scand.* **17** (1963) 393.

** Iodine used in iodometric determination of hydrogen peroxide reacted with the sulfinates.

In part III of this investigation series the reaction of aromatic sodium sulfinates with alkyl halides to sulfones was investigated kinetically and the good correlation with the Hammett equation was taken as an indication that no resonance or conjugation effects involving the *d*-orbitals of the sulfur atom occur in the sulfinates. In this investigation some more substituents have been included, and the results correlate very well with the Hammett equation thus furnishing further evidence that sulfinate sulfur does not show any resonance or conjugation effects.

KINETICS

The measurements were made in aqueous neutral phosphate buffer solutions with sodium nitrate as swamping electrolyte at 40.0° and 50.0°. Hydrogen peroxide shows a good polarographic wave in this medium with a diffusion current proportional to concentration, Figs. 1 and 2. Sulfinic and sulfonic acids show no polarographic activity within the potential range that can be covered in aqueous medium. The reaction is therefore well suited for pseudo-first order kinetics with the sulfinate in excess, except for sulfinates substituted with the nitro group, which is polarographically reduced.

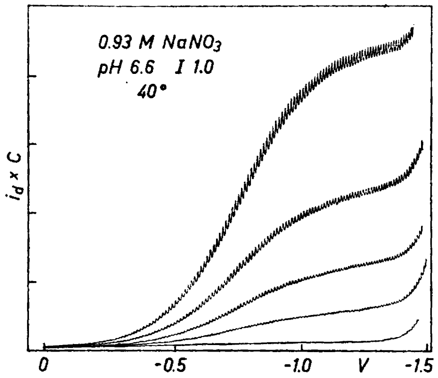


Fig. 1. Polarograms of hydrogen peroxide. Applied voltage *vs.* SCE.

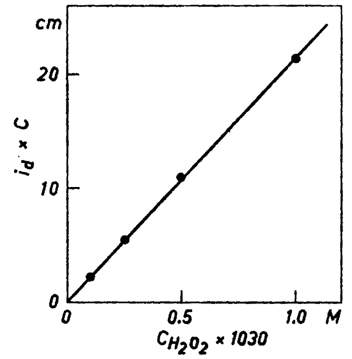


Fig. 2. Proportionality between polarographic diffusion current and concentration of hydrogen peroxide. Applied voltage −1.35 V *vs.* SCE.

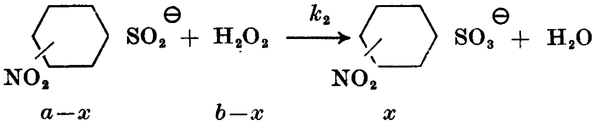
As the nitro group has a strong —M effect, it was regarded as particularly important to include the nitro substituted compounds in this study. The nitro group is reduced at a lower negative potential than hydrogen peroxide and therefore the pseudo-first order kinetics could not be used in this case. A special method for second order kinetics was therefore developed for this case, and as it is of general applicability for kinetic measurements with polarographically active reactants, this method is described in some detail.

Pseudo-first order kinetics. Preliminary measurements with excess sulfinate gave good pseudo-first order kinetics and variation of the sulfinate and hydrogen peroxide concentrations showed that the over all reaction was of the second order. The kinetics of the polarographic pseudo-first order case is exactly the same as described in the previous paper of this series, obeying the following equation:

$$\ln(i_{\mathrm{d}} - i_{\mathrm{d}\infty}) = -k_1 \times a\,t + C \tag{I}$$

k_1 = rate constant
a = sulfinate concentration
i_{d} = diffusion current at a given time, t
$i_{\mathrm{d}\infty}$ = final residual diffusion current

Second order kinetics. The second order case is governed by the following relations:



(II)

$$\frac{dx}{dt} = k_2\,(a-x)\,(b-x)$$

$$k_2 = \frac{1}{(a-b)t} \ln \frac{b}{a} \frac{(a-x)}{(b-x)} \tag{III}$$

k_2 = rate constant
a = initial sulfinate concentration
b = initial hydrogen peroxide concentration
x = sulfonate concentration at a given time, t

The concentrations a and b were measured analytically. Wave height measurements were all made at a fixed potential, E_{m}, and the following relations between measured wave heights and the data required for calculation of k_2 were used, Fig. 3 a:

$$\begin{aligned} b &= C \times i_{\mathrm{b}} \\ x &= C \times i_{\mathrm{x}} \\ i_{\mathrm{b}} &= i_0' - i_0 \\ i_{\mathrm{b}} - i_{\mathrm{x}} &= i_{\mathrm{t}} - i_{\mathrm{m}} \end{aligned}$$

C = proportionality constant between hydrogen peroxide concentration and wave height.
i_{b} = diffusion current due to initial hydrogen peroxide concentration expressed in wave height units.
i_{x} = decrease of diffusion current due to consumption of hydrogen peroxide at a given time, t, expressed in wave height units.
i_0 = initial wave height before addition of hydrogen peroxide.
i_0' = initial wave height immediately after addition of hydrogen peroxide at time t_0.
i_{t} = wave height at a given time, t.
i_∞ = final wave height at time t_∞.
i_{m} = sum of contribution to i_{t} from nitro groups of sulfinate and sulfonate.

Substitution in eqn. (III) gives:

$$\mathrm{k}_2 = \frac{1}{(a-b)t} \ln \frac{b(a-C\cdot i_{\mathrm{x}})}{a\cdot C\,(i_{\mathrm{b}}-i_{\mathrm{x}})}$$

$$k_2 = \frac{1}{(a-b)t} \ln \left[\left(1-\frac{b}{a}\right)\frac{i_0'-i_0}{i_{\mathrm{t}}-i_{\mathrm{m}}} + \frac{b}{a}\right] \qquad \text{(IV)}$$

The diffusion current constants of the nitrobenzenesulfinate and the nitrobenzenesulfonate ions were found to be practically equal. Depending on which of the reactants that is in excess, two polarographic wave patterns can be distinguished. If $a > b$, the wave due to hydrogen peroxide will disappear completely, leaving a final single wave, composed of the diffusion currents of formed sulfonate and remaining sulfinate with i_∞ close to i_0, Fig. 3 a. If $b > a$ the wave due to hydrogen peroxide will decrease with an amount corresponding to the initial concentration of sulfinate, leaving a final wave composed of the diffusion currents due to formed sulfonate and remaining hydrogen peroxide, Fig. 3 b. The first case was chosen for two reasons. Firstly, the total disappearance of the hydrogen peroxide wave allows a good control of the approximate equality of i_0 and i_∞. Secondly, the relatively rapid disappearance of hydrogen peroxide eliminates problems with instability of final wave height due to spontaneous decomposition of excess hydrogen peroxide.

For molecules of similar shape and chemical structure and in equal concentrations, the diffusion coefficients, D, can be approximately related to molecular weights, M, by relation V.[2] From the Ilkovic equation relation VI can be derived. From V and VI relation VII between diffusion currents and molecular weights at equal concentrations is obtained. With M_1 and M_2

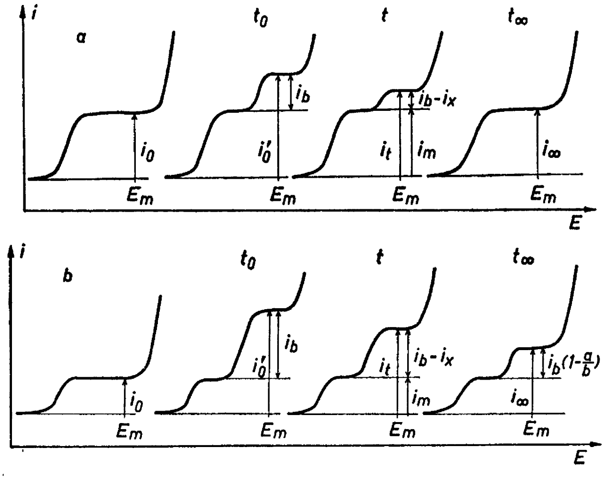


Fig. 3 a, b. Relations between polarographic wave height data for the reaction between sodium nitrobenzenesulfinates and hydrogen peroxide. Second order kinetics.

representing the molecular weights of nitrobenzenesulfinate and nitrobenzenesulfonate, respectively, eqn. VIII is obtained for the relation between i_0 and i_∞. $M_1 = 186$ and $M_2 = 202$ gives relation IX.

$$\sqrt{\frac{M_1}{M_2}} = \frac{D_2}{D_1} \tag{V}$$

$$\frac{i_{d_1}}{i_{d_2}} = \sqrt{\frac{D_1}{D_2}} \tag{VI}$$

$$\frac{i_{d_1}}{i_{d_2}} = \sqrt[4]{\frac{M_2}{M_1}} \tag{VII}$$

$$i_\infty = i_0 \left[1 + \frac{b}{a} \left(\sqrt[4]{\frac{M_1}{M_2}} - 1 \right) \right] \tag{VIII}$$

$$i_\infty = i_0 \left(1 - 0.02 \frac{b}{a} \right) \tag{IX}$$

$$i_\infty = \left(1 - \frac{b}{a} \right) i_0 + \frac{b}{a} i_{d_2} \tag{X}$$

When b is equal to half of a, i_∞ will not be expected to differ from i_0 by more than 1 %. Relation V is of course only strictly valid under certain well defined conditions, but there seems to be no reason to expect that the diffusion coefficients of nitrobenzenesulfinate and nitrobenzenesulfonate ions should differ by more than V allows. Ions or molecules of similar size and structure are usually assumed to have equal diffusion coefficients.[3] This is confirmed by comparing i_0 and i_∞ for the experimental runs, Table 1. The final wave height being composed of remaining sulfinate and the produced sulfonate, and i_{d_1} being equal to i_0, the diffusion current for the sulfonate ion at equal concentration, i_{d_2}, is obtained from eqn. X. The ratio between calculated i_{d_2} and observed i_{d_1} does not indicate any significant difference between the

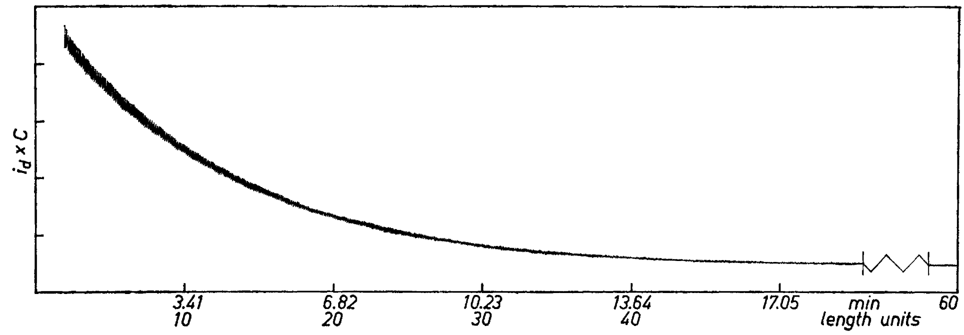


Fig. 4. Polarogram of pseudo-first order reaction between sodium *p*-acetamidobenzenesulfinate and hydrogen peroxide. 50.0°.

Table 1. Limiting diffusion currents of nitro substituted benzenesulfinates and benzenesulfonates in phosphate buffer, pH = 6.4. Temp. 20°C. Applied voltage −1.4 V *vs.* SCE.

Substituent	Conc. × 10^4 M	I	S µA/25 cm	i_∞ cm	Sulfinate $i_{d_1} = i_0$ cm	Sulfonate i_{d_2} calc. cm	i_∞ / i_0	i_{d_2} / i_{d_1}
p-NO_2	9.45	0.083	1.5 × 20	14.97	15.15	14.55	0.988	0.961
p-NO_2	4.64	0.073	1.5 × 10	15.80	15.80	15.80	1.000	1.000
m-NO_2	4.88	0.073	1.5 × 10	15.81	15.50	16.11	1.020	1.038
m-NO_2	4.85	0.083	1.5 × 10	16.11	16.49	15.74	0.978	0.975
o-NO_2	4.47	0.083	1.5 × 10	15.10	14.80	15.38	1.020	1.039
						Mean	1.001	1.003
						Calculated from V		0.98

diffusion coefficients of these ions. Comparison of diffusion currents of *p*-nitrobenzenesulfinate and *p*-nitrobenzenesulfonate prepared and isolated from *p*-nitrobenzenesulfinate leads to a similar result. The results in Table 1 show that a possible difference in diffusion currents between the two ions cannot be of a greater order of magnitude than the ordinary experimental errors.

PSEUDO-FIRST ORDER METHOD

With this method measurements were performed with the following substituents: *p*-NH_2, *o*-CH_3O, *m*-CH_3O, *p*-CH_3O, *o*-CH_3, *m*-CH_3, *p*-CH_3, *p*-CH_3CONH, *o*-Cl, *m*-Cl, *p*-Cl, *p*-CN. The procedure and conditions of measurements were analogous to those of the polarographic method in the previous paper of this series.[4]

Very good linearity was obtained in all cases, and typical examples are shown in Figs. 4 and 5 and Table 2.

SECOND ORDER METHOD

With this method measurements were performed with *o*-NO_2, *m*-NO_2 and *p*-NO_2 substituents. Concentrations of the reactants were chosen to give

Table 2. Reaction of sodium benzenesulfinate and *p*-acetamidobenzenesulfinate with hydrogen peroxide. First order kinetics.

Sodium benzenesulfinate			Sodium-*p*-acetamidobenzenesulfinate		
Temp. 40.0°. a = 0.0958 M. Applied voltage −1.35 V. 3.68 cm = 1 min			Temp. 50.0°. a = 0.0793 M. Applied voltage −1.35 V. 30 length units = 78.63 cm, 3.83 cm = 1 min		
t cm	$i_d - i_{d\infty}$ cm	$\log(i_d - i_{d\infty})$	t length units	$i_d - i_{d\infty}$ cm	$\log(i_d - i_{d\infty})$
15	15.00	1.176	0	19.90	1.299
20	12.60	1.100	2	16.66	1.222
25	10.75	1.031	4	14.08	1.149
30	9.00	0.954	6	11.98	1.079
35	7.55	0.878	8	10.20	1.009
40	6.40	0.806	10	8.53	0.931
45	5.45	0.736	12	7.25	0.860
50	4.60	0.663	14	6.10	0.785
55	3.90	0.591	16	5.15	0.712
60	3.25	0.512	18	4.28	0.631
65	2.75	0.439	20	3.60	0.544
			22	2.95	0.470
			24	2.47	0.393
			26	2.05	0.312
			28	1.67	0.223
			30	1.35	0.130

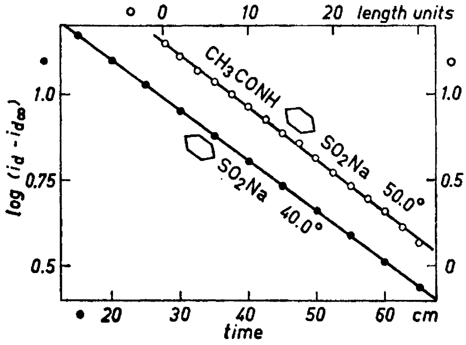


Fig. 5. Reaction of sodiumbenzenesulfinate and *p*-acetamidobenzenesulfinate with hydrogen peroxide. First order kinetics.

a reaction rate small enough to allow an accurate determination of i_0'. Fig. 6 shows the polarographic wave of *m*-nitrobenzenesulfinate from a typical kinetic run and Fig. 7 shows the NO_2 wave after completion of oxidation.

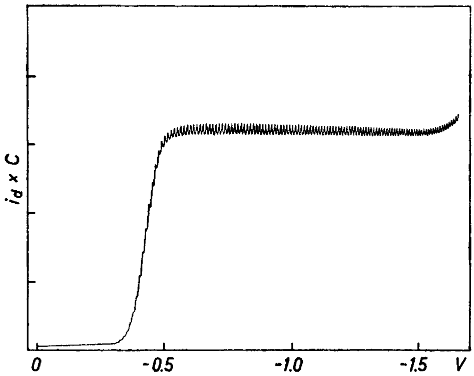


Fig. 6. Polarogram of sodium *m*-nitrobenzenesulfinate. Applied voltage *vs.* SCE.

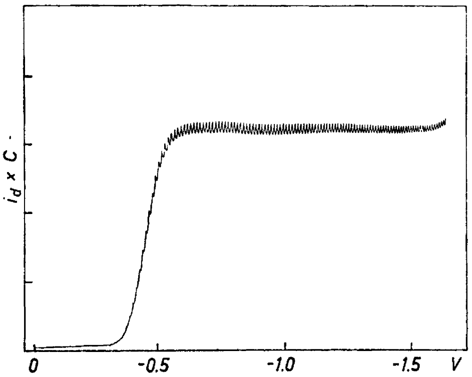


Fig. 7. Polarogram of oxidized sodium *m*-nitrobenzenesulfinate. Applied voltage *vs.* SCE.

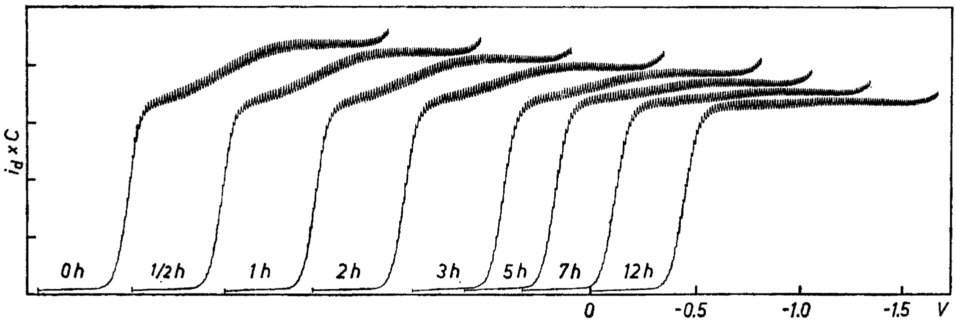


Fig. 8. Polarograms of second order reaction between sodium *m*-nitrobenzenesulfinate and hydrogen peroxide. Applied voltage *vs.* SCE.

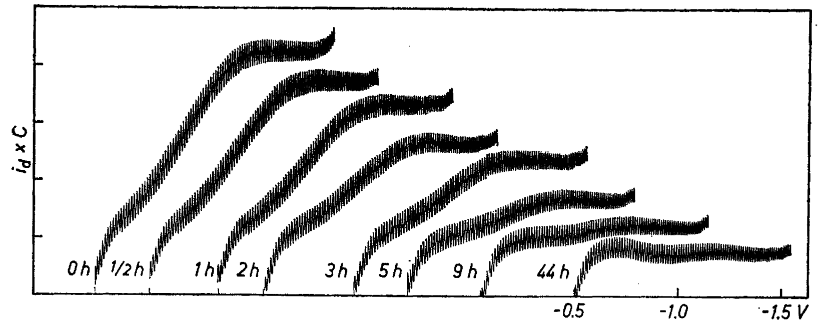


Fig. 9. Polarograms of second order reaction between sodium *m*-nitrobenzenesulfinate and hydrogen peroxide. Hydrogen peroxide wave. Applied voltage *vs.* SCE.

Fig. 8 shows the change of appearance of the waves during the same run. Measurements were also made with a higher sensitivity (S) but recording only the hydrogen peroxide wave, Fig. 9. As only differences between wave heights are involved in the calculation of k_2, corrections for residual currents cancel out and uncorrected wave heights have been used and recorded throughout.

Method of calculation. The quantities used for calculation of k_2 are shown in Tables 3—7. It was not possible to obtain i_m directly from the polarographic

Table 3. Reaction of sodium *p*-nitrobenzenesulfinate with hydrogen peroxide. Second order kinetics. 40.0°.

$a = 0.0189$ M　　$I = 1.00$　　$E_m = -1.37$ V
$b = 0.0057$ M　　pH = 6.4　　$S = 1.5 \times 20$
$i_\infty = i_8 - 0.02\ (i_0' - i_0) = 14.97$ cm

Time h	i_t cm	i_m cm	$\log \left[\left(1-\frac{b}{a}\right)\frac{i_0'-i_0}{i_t-i_m}+\frac{b}{a}\right]$
0	18.25	15.15	0.0000
1	16.90	15.07	0.1735
2	16.12	15.04	0.3627
3	15.66	15.00	0.5443
8	15.03	14.98	Slope 0.182
			k_2 0.530

Table 4. Reaction of sodium *p*-nitrobenzenesulfinate with hydrogen peroxide. Second order kinetics. 40.0°.

$a = 0.00928$ M $I = 0.80$
$b = 0.00464$ M pH $= 6.4$

$E_m = -1.39$ V $S = 1.5 \times 10$
$i_\infty = (i_{12} + i_{24})/2 - 0.04\ (i_0' - i_0) = 15.80$ cm

Time h	i_t cm	i_m cm	$\log\left[\left(1-\frac{b}{a}\right)\frac{i_0'-i_0}{i_t-i_m}+\frac{b}{a}\right]$
0	20.90	15.80	0.0000
1	20.14	15.80	0.0366
2	19.20	15.80	0.0973
3	18.96	15.80	(0.1163)
5	17.54	15.80	0.2936
7	17.05	15.80	0.4048
12	15.80	15.80	Slope 0.0582
24	16.23	15.80	k_2 0.481

$E_m = -1.40$ V $S = 5$
$i_\infty = i_{24} - 0.02\ (i_0' - i_0) = 7.09$ cm

Time h	i_t cm	i_m cm	$\log\left[\left(1-\frac{b}{a}\right)\frac{i_0'-i_0}{i_t-i_m}+\frac{b}{a}\right]$
0	23.44	6.86	0.0000
1	20.15	6.92	0.0519
2	17.17	6.96	0.1179
3	15.07	6.98	0.1844
5	12.44	7.02	0.3043
7	11.00	7.04	0.4136
12	7.68	7.07	Slope 0.0600
24	7.42	7.08	k_2 0.496

waves. If there is a difference between i_0 and i_∞, i_m should be intermediate between these two quantities (Fig. ∀ ·(ɐ Ɛ correct i_m value is thus dependent on a correct i_∞ value. The latter quantity was obtained by correcting the observed final wave height, $i_{\infty,\text{obs}}$, from the time of observation to infinite time according to eqn. XI, where η is the degree of reaction at the time of observation of the final wave height, $i_{\infty,\text{obs}}$. For calculation of η at $t_{\infty,\text{obs}}$ a first approximation for k_2 was obtained by putting $i_m = i_0$ in eqn. IV. If the difference between i_0 and i_∞ is regarded as being caused by some factor dependent on the reaction, i_m should be a function of η. If the difference is due to a difference in the diffusion currents of sulfonate and sulfinate, the function XII should be valid.

$$i_\infty = i_{\infty,\text{obs}} - (1-\eta)\,(i_0' - i_0) \tag{XI}$$

$$i_m = i_0 + \eta(i_\infty - i_0) \tag{XII}$$

$$\eta = \frac{i_x}{i_b} = \frac{i_0' - i_t + i_m - i_0}{i_0' - i_0} \approx \frac{i_0' - i_t}{i_0' - i_0} \tag{XIII}$$

Table 5. Reaction of sodium *m*-nitrobenzenesulfinate with hydrogen peroxide. Second order kinetics. 40.0°.

$a = 0.00970$ M $b = 0.00494$ M			$I = 0.99$ pH $= 6.42$
$E_m = -1.34$ V $i_\infty = i_{44} = 16.11$ cm			$S = 1.5 \times 10$
Time h	i_t cm	i_m cm	$\log \left[\left(1 - \frac{b}{a}\right) \frac{i_0' - i_0}{i_t - i_m} + \frac{b}{a} \right]$
0	21.66	16.49	0.0000
1	20.46	16.40	0.0550
2	19.63	16.33	0.1009
3	18.91	16.29	0.1700
5	17.78	16.23	0.3529
9	16.86	16.16	0.6170
24	16.24	16.12	Slope 0.0704
44	16.11	16.11	k_2 0.569
$E_m = -1.34$ V $i_\infty = i_{44} - 0.01 = 3.53$ cm			$S = 5$
0	21.11	4.47	0.0000
0.5	18.56	4.34	0.0346
1	16.46	4.24	0.0708
2	13.15	4.08	0.1492
3	11.62	3.97	0.1959
5	8.22	3.82	0.3738
9	5.87	3.67	0.6044
24	3.78	3.55	Slope 0.0681
44	3.54	3.53	k_2 0.550

This function was used for the calculations, and η was obtained from XIII, where $i_m - i_0$ is negligible in comparison with $i_0' - i_t$. This procedure will also compensate for the effect of drifts, which causes the greatest effects at advanced stages of reaction, where small quantities obtained as differences are involved in the calculations. Good linearity for the kinetic plots were obtained, and the slopes were calculated by the method of least squares. Other ways of calculating i_m, *e.g.* $i_m = (i_0 + i_\infty)/2$ or $i_m = i_0 + t/t_{\infty,\mathrm{obs}} \times (i_\infty - i_0)$ gave essentially the same results but were less suited for applying the method of least squares. With these, deviations in the kinetic plots at advanced degrees of reaction were obtained. As all points are used with equal weight in the method of least squares, deviations at high degrees of reaction are unduly emphasized with the spacing of t used for the measurements. Finally, it should be taken into account that ordinary indeterminate experimental errors can amount to the same order of magnitude as the observed differences between i_0 and i_∞. Whether the difference is real or due to acci-

Table 6. Reaction of sodium *m*-nitrobenzenesulfinate with hydrogen peroxide. Second order kinetics. 40.0°.

$a = 0.00975$ M $I = 0.80$
$b = 0.00496$ M pH $= 6.42$

$E_m = -1.25$ V $S = 1.50 \times 10$
$i_\infty = i_{36} - 0.002\ (i_0' - i_0) = 15.81$ cm

Time h	i_t cm	i_m cm	$\log\left[\left(1-\frac{b}{a}\right)\frac{i_0'-i_0}{i_t-i_m}+\frac{b}{a}\right]$
0	21.25	15.50	0.0000
0.5	20.58	15.54	0.0290
1	20.09	15.57	0.0542
2	19.36	15.36	0.1021
3	18.88	15.66	0.1418
5	17.92	15.71	0.2516
7	17.12	15.75	0.4098
12	16.34	15.78	0.7442
24	15.98	15.80	Slope 0.0627
36	15.82	15.81	k_2 0.502

Table 7. Reaction of sodium *o*-nitrobenzenesulfinate with hydrogen peroxide. Second order kinetics. 40.0°.

$a = 0.00893$ $I = 0.99$
$b = 0.00390$ pH $= 6.40$

$E_m = -1.36$ V $S = 1.5 \times 10$
$i_\infty = i_{144} - 0.027\ (i_0' - i_0) = 15.10$ cm

Time h	i_t cm	i_m cm	$\log\left[\left(1-\frac{b}{a}\right)\frac{i_0'-i_0}{i_t-i_m}+\frac{b}{a}\right]$
0	20.29	14.80	0.0000
3	19.77	14.83	0.0261
6	19.45	14.86	0.0453
19	17.88	14.94	0.1726
29	17.19	14.99	0.2651
43	16.43	15.03	0.4224
			0.5963
69	15.94	15.06	Slope 0.00893
144	15.25	15.11	k_2 0.0681

$E_m = -1.42$ V $S = 5$
$i_\infty = i_{144} - 0.027\ (i_0' - i_0) = 3.10$ cm

Time h	i_t cm	i_m cm	$\log\left[\left(1-\frac{b}{a}\right)\frac{i_0'-i_0}{i_t-i_m}+\frac{b}{a}\right]$
0	19.94	2.84	0.0000
3	17.88	2.87	0.0326
5	17.07	2.91	0.0481
19	11.48	2.96	0.1951
29	9.59	3.01	0.2788
43	8.05	3.04	0.3727
69	5.89	3.07	(0.5855)
144	3.55	3.11	Slope 0.00893
			k_2 0.0681

dental errors does not matter. It is the magnitude that is of importance. When it is small, as here, the use of i_m only implies a refinement in the calculations.

RESULTS

The results of the kinetic measurements are given in Tables 8 and 9. The results of Gonzalez[1] show that there are no primary salt effects or any general acid or base catalysis. Neither are there any effects of pH in the range 2—9. The third run with the *para*-chloro substituted member in Table 8

Table 8. Oxidation of aromatic sodium sulfinates with hydrogen peroxide in phosphate buffer, pH 6.4. Temp. 40.0°.

Substituent	a M	I	E_m V	k M^{-1} min^{-1}	Mean (corrected)	log k
	0.0964	1.00	−1.35	1.279		
	0.0974	1.00	−1.35	1.284		
	0.0984	1.00	−1.35	1.262		
H					1.220	0.086
	0.0947	0.50	−1.45	1.152		
	0.0967	0.50	−1.35	1.135		
	0.0957	0.50	−1.25	1.157		
o-CH_3	0.0910	1.00	−1.30	0.808	0.783	0.894−1
	0.0889	0.99	−1.35	0.748		
m-CH_3	0.0960	0.99	−1.35	1.386	1.396	0.145
p-CH_3	0.0950	1.00	−1.35	1.558	1.568	0.195
	0.0937	1.00	−1.35	1.555		
o-CH_3O	0.0959	1.00	−1.35	0.634	0.702	0.846−1
	0.0858	1.00	−1.35	0.709		
m-CH_3O	0.1000	0.99	−1.35	1.148	1.156	0.063
p-CH_3O	0.0987	0.99	−1.35	1.615	1.626	0.211
p-CN	0.1026	1.00	−1.35	0.604	0.608	0.784−1
o-Cl	0.0830	1.00	−1.35	0.202	0.203	0.308−1
m-Cl	0.0956	0.99	−1.35	0.761	0.766	0.884−1
p-Cl	0.0913	1.00	−1.35	0.883		
	0.0893	1.00	−1.35	0.904	0.910	0.959−1
	0.0515	1.00	−1.35	0.924		
	1.00	1.00	−1.35	0.1265	0.1265	0.102−1*
p-NHAc	0.0859	0.99	−1.35	1.294	1.303	0.115
p-NH_2	0.0482	1.00	−1.35	2.56	2.60	0.415
	0.0477	1.00	−1.35	2.63		
o-NO_2	0.00893	0.99	−1.36	0.0681	0.0686	0.836−2
	0.00893	0.99	−1.42	0.0681		
m-NO_2	0.00975	0.80	−1.25	0.502		
	0.00970	0.99	−1.34	0.569	0.544	0.736−1
	0.00970	0.99	−1.34	0.550		
p-NO_2	0.00928	0.80	−1.39	0.481		
	0.00928	0.80	−1.40	0.496	0.508	0.706−1
	0.0189	1.00	−1.37	0.530		

* Temp. 21.5°.

was made with a half-oxidized solution. The result shows that there is no significant effect from the sulfonate produced. The changes made in the ionic strength does not have any effect that significantly exceeds experimental errors. The present results are thus consistent with previous findings. However, as this investigation was not primarily concerned with the reaction mechanism, medium effects were not further investigated.

Table 9. Oxidation of aromatic sodium sulfinates with hydrogen peroxide in phosphate buffer. pH 6.4. Temp. 50.0°.

Substituent	a M	I	E_m V	k M^{-1} min^{-1}	Mean (corrected)	log k
o-CH_3	0.0900	0.99	−1.30	1.559	1.618	0.209
m-CH_3	0.0933	0.99	−1.35	3.44	3.48	0.542
o-CH_3O	0.0979	1.00	−1.35	1.391	1.528	0.184
	0.0858	1.00	−1.35	1.629		
m-CH_3O	0.0901	0.99	−1.30	2.67	2.70	0.431
p-CH_3O	0.0428	1.00	−1.35	3.90	3.95	0.597
p-CN	0.1018	1.00	−1.35	1.165	1.259	0.100
	0.0916	1.00	−1.25	1.323		
m-Cl	0.0950	1.00	−1.35	1.941	1.964	0.293
p-NHAc	0.0825	0.99	−1.35	3.14	3.18	0.502
p-NH_2	0.0212	1.00	−1.30	6.79	6.87	0.837
	0.0477	1.00	−1.25	0.971	0.978	0.990−1*

* Temp. 30.0°.

Table 10 contains corrected results from Gonzalez (unknown to the author when the present work was done). They were obtained at a lower ionic strength, but as an increase of the ionic strength to 0.7 using sodium sulfate in another example of his did not have any effect on the reaction rate, these results can be used to supplement the more extensive results of the present investigation.

Table 10. Oxidation of aromatic sodium sulfinates with 0.0696 N hydrogen peroxide in phosphate buffer. pH 6.8. Temp. 30.0°. Ref. 1.

Substituent	a M	I	k M^{-1} min^{-1}	log k
H	0.0552	0.21	0.55	0.740−1
p-CH_3	0.0552	0.21	0.65	0.812−1
p-Cl	0.0552	0.21	0.42	0.625−1

Approximate activation data are given in Table 11. As mostly only two temperatures and single kinetic runs were used for their determination, the entropies of activation are very approximate. However, they show a definite trend towards greater negative values, as the reaction rate decreases.

Table 11. Approximate activation data. Temp. 40.0°.

Substituent	T_1	T_2	$\frac{d \log k}{dT}$	$\Delta H^{\ddagger}$ kcal · mole^{-1}	$\Delta S^{\ddagger}$ E.U.
H	40.0°	30.0°	0.0346	14	−20
o-CH_3	50.0°	40.0°	0.0420	14	−22
m-CH_3	50.0°	40.0°	0.0397	18	−10
p-CH_3	40.0°	30.0°	0.0383	16	−15
o-CH_3O	50.0°	40.0°	0.0338	15	−20
m-CH_3O	50.0°	40.0°	0.0368	16	−14
p-CH_3O	50.0°	40.0°	0.0386	17	−11
p-CN	50.0°	40.0°	0.0316	14	−23
m-Cl	50.0°	40.0°	0.0409	18	− 9
p-Cl	40.0°	30.0°	0.0334	14	−22
p-NHAc	50.0°	40.0°	0.0387	17	−11
p-NH_2	50.0°	40.0°	0.0422	19	− 5
	40.0°	30.0°	0.0425	19	− 4

Log *k* for the *meta*- and *para*-substituted members have been plotted against the substituent constants of Hammett, Fig. 10. The σ constants used are those given by Ritchie and Sager.[5] The reaction constants and statistical correlation data have been calculated according to Jaffé in the same manner as in the previous paper of this series,[4] and are given in Table 12.

Table 12. Reaction constants and statistical data for the oxidation of aromatic sodium sulfinates with hydrogen peroxide.

Temp. °C	ϱ	log k_0	*s*	*r*	$\Delta H_0^{\ddagger}$	$\Delta S_0^{\ddagger}$
30.0	−0.405 ± 0.06	0.731−1	0.012	0.998	15 ± 3	−15 ± 9
40.0	−0.491 ± 0.05	0.094	0.069	0.956	17 ± 3	
50.0	−0.543 ± 0.05	0.482	0.022	0.996		

The ϱ's are negative with the slope increasing with temperature. According to Jaffé's criteria, the correlation with the Hammett equation is very good. Log k_0 has been used for calculation of theoretical heats and entropies of activation, $\Delta H_0^{\ddagger}$ and $\Delta S_0^{\ddagger}$.

Log *k* for the *ortho*-substituted members have been plotted against log *k* for the alkylation reactions of the corresponding *ortho*-substituted sulfinates

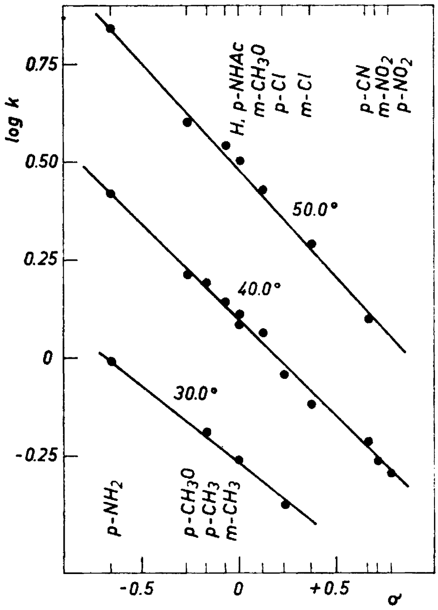


Fig. 10. The Hammett relationship for the oxidation of *m*- and *p*-substituted aromatic sodium sulfinates with hydrogen peroxide.

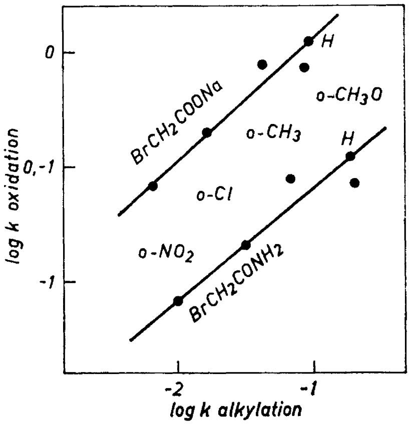


Fig. 11. Correlation of hydrogen peroxide oxidation with alkylations of *ortho*-substituted benzenesulfinates.

investigated in the previous paper of this series,[4] Fig. 11. A fairly good correlation seems to exist. A similar plot of *meta*- and *para*-substituted members has a smaller slope, intersecting the *ortho* line very close to the point for the unsubstituted sulfinate.

DISCUSSION

Kinetic data are available in the literature on the peroxide oxidation of various compounds.[6-9] In most cases the reaction of electron pair donors with peroxides shows the characteristics of a polar type (non-radical) mechanism.[8] It can be treated as a nucleophilic S_N2 displacement of hydroxyl ion from the peroxide. Gonzalez concludes that in the case of sulfinic acids, it is the sulfinate anion and the neutral hydrogen peroxide molecule that are involved in the rate determining step.[1]

In the cases reported in literature the entropy of activation has almost invariably a large negative value, suggesting that the activated complex has a definite orientation. This is also the case in the oxidation of several different types of sulfur compounds with hydrogen peroxide in aqueous solution.[6,8] The present reaction with its second order kinetics, negative ϱ's and negative entropy of activation shows similar characteristics. However, the entropy of activation appears to be less negative than is generally the case with, e.g., neutral sulfides.

The good fit to the Hammett equation indicates that no resonance or through conjugation effects of the sulfinate group are of any importance. No significant deviations can be attributed to the strongly electron donating +M *p*-amino substituent nor to the strongly electron attracting —M *p*-nitro and *p*-cyano substituents.

The approximately linear correlation observed between the *ortho*-substituted members in oxidation and alkylation may be taken to indicate that the *ortho*-effects are of the same nature in the two reaction series. The good correlation for the *ortho*-chloro substituted members gives further weight to the observation made in the previous investigation, that these members deviate from eqn. XIV.[4]

$$\log(k_{ortho}/k_{para}) = \delta E_s \qquad \text{(XIV)}$$

Plots of the logarithm of the $k_{ortho}-k_{para}$ ratios against E_s of the alkylation reactions from the previous paper and from the present reaction are shown in Fig. 12. The slopes indicate that the susceptibility to the steric effect is of the same order of magnitude for the alkylation and oxidation reactions. The unsubstituted member also seems to correlate with eqn. XIV.

If ϱ^* is assumed to be nearly equal to ϱ and E_s is assumed not to be considerably affected by the factors that cause deviations from eqn. XIV, the deviation of the *ortho*-chlorosubstituent is in the direction of a greater polar effect. This indicates that the polar effect of the chloro substituent may be different in the *ortho*-position and *para*-position. A similar result has been reported by Chapman *et al.* who found that the assumption $\sigma^* = \sigma_{para}$ does not hold for the esterification of *ortho*-halogen substituted benzoic acids with diazodiphenyl methane.[10] In this reaction the polar effects of chlorine in the

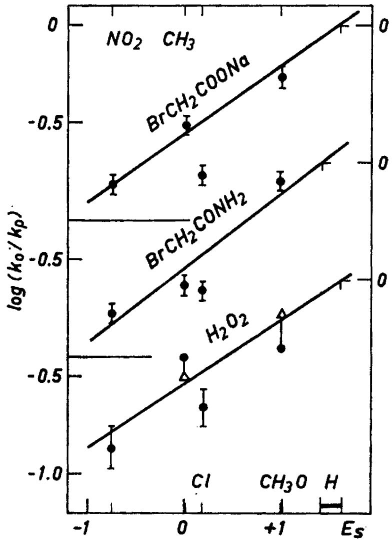


Fig. 12. Plots of hydrogen peroxide oxidation and alkylations of *ortho*-substituted benzenesulfinates against Taft's steric substituent constants, E_S. △ Points from correlation line Fig. 11.

ortho-position is three times greater than in the *para*-position. There are also other examples in literature of such an effect.[11] Chapman *et al.* have also estimated σ^* values from alkaline and acidic hydrolysis of benzoic acid esters by the Taft-Ingold analysis.[12] In this case they found correspondence between σ^* and σ_{para}. They suggest that the discrepancy between this and their first finding is due to different effects of solvation in acidic and basic hydrolysis which invalidates one of the assumptions on which the Taft-Ingold analysis is based, namely that steric effects are equivalent in acidic and basic hydrolysis. Great caution must therefore be exercised in drawing conclusions from *ortho*-effect data. The experimental data from sulfinate reactions are at present too scanty for a more detailed interpretation of the correlations indicated in this discussion.

EXPERIMENTAL

The preparation of benzene sodium sulfinates with substituents *p*-CH_3, *m*-CH_3, *o*-CH_3, *p*-CH_3O, *m*-CH_3O, *o*-CH_3O, *p*-Cl, *m*-Cl, *o*-Cl, *p*-NO_2, *m*-NO_2 and *o*-NO_2 have been described in an earlier paper.[13]

p-*Acetamidobenzenesulfinate* was prepared from *p*-acetamidobenzenesulfonyl chloride according to Smiles and Bere.[14] (E 198.6, $E_{calc.}$ 199.2 for the acid $C_8H_9NO_3S$).

p-*Aminobenzenesulfinic acid* was prepared from *p*-acetamidobenzenesulfinate by hydrolysis with sodium hydroxide. 10 g of *p*-acetamidobenzenesulfinate and 4 g of sodium hydroxide in 50 ml of water was refluxed for 3 h. The acid was precipitated with 5 N sulfuric acid and was well washed with water. (Found: C 46.0; H 4.6; N 8.7; S 20.3. Calc. for $C_6H_7NO_2S$: C 45.9; H 4.5; N 8.9; S 20.4). E_{NaOH} 160; E_{calc} 157).

p-*Cyanobenzenesulfinate* was prepared by reduction of *p*-cyanobenzenesulfonyl chloride. 13.9 g (0.066 mole) *p*-cyanobenzenesulfonyl chloride in 100 ml benzene was stirred with 10 g (0.069 mole) sodium sulfite in 200 ml water at pH 8.0 for 20 min. Ferric sulfinate was precipitated from the water phase at pH 2—3. The precipitate was treated with an equivalent amount of 5 N sodium hydroxide and the resulting solution was evaporated. Yield 11.4 g (87 %). Recrystallization from water. (Found: C 44.6; H 2.0; N 7.3; S 16.7. Calc. for $C_7H_4NNaO_2S$: C 44.5; H 2.1; N 7.4; S 16.9. E_{KMnO_4} 190.2; $E_{calc.}$ 189.1).

p-*Cyanobenzenesulfonyl chloride* was prepared by treating *p*-sulfonamidobenzoic acid with phosphorus pentachloride according to Remsen *et al.*[15]

Sulfinate concentrations were determined by titration with potassium permanganate or sodium nitrite as described in the previous paper of this series.[4] In the case of the *p*-amino substituent, nitrite diazotizes, and potassium permanganate has to be used. Because of the sensitivity of the substituent to oxidation, the titration must be done as follows: Rapid potentiometric titration of phosphate buffered solution (pH ~ 7) with potassium permanganate until the potential jump is observed, that is obtained when potassium permanganate begins to appear in the solution, followed by addition of potassium iodide, acidification and back titration with sodium thiosulfate. Under these conditions potassium permanganate does not attack the sulfanilic acid formed. The same procedure was also applied to the *o*-methoxy substituted sulfinate and in addition to the nitrite titration to the *p*-methoxy substituted sulfinate.

The *p*-aminobenzene sulfonate was shown to consume no hydrogen peroxide during the conditions used for the kinetic runs, wherefore it was regarded as justified to regard the amino group in the *p*-amino substituted sulfinate as indifferent to hydrogen peroxide.

All titrations were made at room temperature, and k_{mean} was corrected for volume temperature dependence. The correction factors were 1.007 for 40° and 1.012 for 50°.

Pseudo-first order kinetics. 0.02 mole of sodium sulfinate, 2 ml of phosphate buffer of pH 6.62, consisting of 1/30 M KH_2PO_4 and 1/30 M Na_2HPO_4, and 1.50 g of sodium nitrate was made up to 20 ml with distilled water at 20°. A 1 ml sample was withdrawn with a microsyringe for determination of sulfinate concentration before and after the kinetic run. For the kinetic run, the solution was placed in a polarographic thermostated cell described by Tilhage and Nygård [16] and deaerated with nitrogen. The reaction was started by adding 0.02 ml of 1 M hydrogen peroxide by means of a microsyringe and stirring by means of the nitrogen stream. The measurements were made under nitrogen atmosphere with applied voltage -1.3 V *vs.* SCE. In the case of the *p*-amino substituent at 40° and 50° and the *p*-methoxy substituent at 50°, smaller concentrations with appropriate adjustments of other data were used because of the high reaction rate with these substituents. The infinity value was regarded as being attained when no change of residual diffusion current could be observed within an appropriate interval of time, and when controlled it correlated well with the zero time diffusion current before addition of hydrogen peroxide. Temperature accuracy was ± 0.02°.

Second order kinetics. The kinetic runs with nitro substituents were made as follows: 0.001 mole of sulfinate, 10 ml of phosphate buffer of pH 6.62, consisting of 1/30 M KH_2PO_4 and 1/30 M Na_2HPO_4 and 6.62 g of sodium nitrate were made up to 100 ml with distilled water at 20°.

For determination of initial sulfinate concentration, a, duplicate samples of 5 ml were pipetted out and titrated with potassium permanganate. Then 80 ml of the solution was thermostated in a reaction flask. For measurement of i_0, 1 ml of solution was pipetted out, 4 ml of phosphate buffer of pH 6.6, consisting of 1/6 M KH_2PO_4 and 1/6 M Na_2HPO_4, and 1 ml of 0.1 % gelatine solution were added, and the volume was made up to 20 ml with distilled water. This solution was placed in the polarographic cell, which was thermostated from the same thermostat as the reaction solution, and a polarogram was taken. After this the reaction was started by rapid addition of 0.04 ml 10 M hydrogen peroxide by means of a microsyringe to the remaining 78 ml of solution. The reaction flask was immediately whirled, and another 1 ml sample was immediately pipetted out for measurement of i_0' in the same way as i_0. During the course of reaction samples were withdrawn and immediately treated in the same manner. It was found to be inadvisable to use solutions that had been kept for a protracted time before measurements. Hence i_∞ was obtained as described under method of calculation. In most cases the final wave height was measured when the degree of reaction had reached at least 98 %.

Hydrogen peroxide was stable under the conditions used for reactions and measurements.

The polarographic measurements were made with registering LKB type 3266 and Radiometer type PO 4c polarographs.

Estimation of accuracy

The experimental conditions with the polarographic pseudomonomolecular method were similar in this and the previous investigation. The previous calculation of accuracy for the polarographic method would therefore be expected to apply to the present results. When successive runs were made on the same solution the reproducibility of the rate constants was always within the ± 3 % limit. However, runs made with different solutions on different occasions sometimes showed a reproducibility which was less good. It is difficult to find any definite reason for this, but it may probably be due to the sensitivity of hydrogen peroxide reactions to catalysts. Small traces of impurities introduced with the reagents may act as catalysis for the reaction investigated, causing additional errors.

In the case of the bimolecular method with the more complicated manipulations and calculations involving differences between wave heights a somewhat smaller accuracy than with the pseudomonomolecular method would be expected. Taking these considerations into account, the rate constants are estimated to be accurate within a ± 10 % limit. The error limits given in Table 12 are based on this estimation.

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