

Studies on Sulfinic Acids

III*. Reaction of Aromatic Sodium Sulfinates with Sodium Bromoacetate and Bromoacetamide

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The reaction of a series of aromatic sodium sulfinates with sodium bromoacetate and bromoacetamide in aqueous solution has been kinetically investigated. Results from preliminary experiments of second-order kinetics gave some indication that the presence of the sulfinate catalyzed the spontaneous hydrolysis of the bromoacetate. The effect of the hydrolysis was eliminated by using pseudo-first-order kinetics. A potentiometric and a polarographic method were independently employed for measuring the reaction rates. The rate constants obtained agreed with the Hammett equation.

Alkali metal salts of sulfinic acids react with alkyl halogenides and yield only sulfones but no ester¹. Esters of sulfinic acids have to be prepared by other methods²⁻⁶ and are easily hydrolyzed⁷ or rearranged into sulfones^{8,9}. At an early stage, the reaction of sulfinates with alkyl halogenides and their derivatives was studied in connection with the problem of the constitution of sulfinic acids. The reaction has been widely used also as a synthetic method for the preparation of various sulfones¹⁰. This investigation deals with the reaction from a kinetic point of view. A series of substituted aromatic sodium sulfinates have been prepared and their reaction with sodium bromoacetate and bromoacetamide has been measured in aqueous solution at 60°. These halogenides were chosen so as to permit of measurements being made in aqueous solution at a reasonable rate. The following substituents have been included: *p*-CH₃, *m*-CH₃, *o*-CH₃, *p*-CH₃O, *m*-CH₃O, *o*-CH₃O, *p*-Cl, *m*-Cl, *o*-Cl, *p*-NO₂, *m*-NO₂, *o*-NO₂.

KINETICS

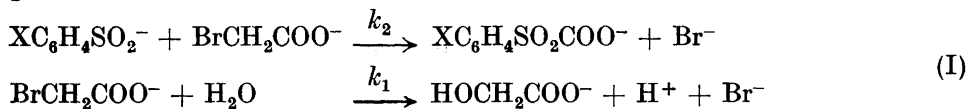
Preliminary experiments were performed with sodium *p*-toluenesulfinate and sodium bromoacetate with reactant concentrations that gave second-

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order kinetics. These experiments showed that the main reaction was too slow, compared with the hydrolysis of the bromoacetate, for the latter to be neglected. The fact that hydrolysis had to be taken into account, led to complications. A relatively large concentration of buffer is also necessary to reduce the acidity caused by the hydrolysis, since acidity endangers the stability of the sulfinate (disproportionation of sulfinic acid).

As sulfinic acids are strong enough¹¹⁻¹⁴ to permit of undissociated acid being regarded as absent in neutral solution, the following reactions take place:



If the rate of formation of sulfone is postulated to be of the second order, the following system of rate equations is obtained:

$$\frac{dx}{dt} = k_2(a-x)(b-y) = -\frac{dz}{dt} = k_2z(b-y) \quad (\text{II})$$

$$\frac{dy}{dt} = k_2(a-x)(b-y) + k_1(b-y) \quad (\text{III})$$

k_1, k_2 = rate constants according to (I)

a = sulfinate initial concentration

b = halogenide » » » »

x = sulfone concentration at a given time, t

y = halide ion » » » »

z = sulfinate » » » » = $a-x$

Since it was not possible to integrate this system in a simple way, a semigraphical method was applied (compare a similar procedure by Hughes *et al.*¹⁵):

κ_2 = a function of time defined by:

$$\kappa_2 t = I_1 = \int_0^x \frac{dx}{(a-x)(b-x)} = \frac{1}{a-b} \ln \frac{b}{a} \cdot \frac{a-x}{b-x}$$

κ_2' = a function of time defined by:

$$\kappa_2' t = I_2 = \int_0^y \frac{dy}{(a-y)(b-y)} = \frac{1}{a-b} \ln \frac{b}{a} \cdot \frac{a-y}{b-y}$$

$$dI_1/dt = (dI_1/dx) (dx/dt) = \kappa_2 + t(d\kappa_2/dt) = k_2(b-y)/(b-x)$$

$$dI_2/dt = (dI_2/dy) (dy/dt) = \kappa_2' + t(d\kappa_2'/dt) = k_2(a-x)/(b-y) + k_1/(a-y)$$

κ_2 and κ_2' are plotted, from analytical data, against time. If $d\kappa_2/dt$ is determined graphically, k_2 can be calculated from each point on the κ_2 plot. If $d\kappa_2'/dt$ is determined graphically, k_2 can be calculated for each point on the κ_2' plot. k_1 can be obtained also by direct integration:

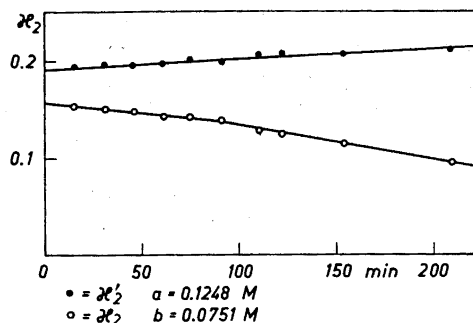


Fig. 1. Reaction of sodium *p*-toluenesulfinate with sodium bromoacetate, 2nd-order kinetics.

Divide eqn. (III) by eqn. (II) and integrate:

$$\frac{dy}{dx} = 1 + \frac{k_1}{k_2} \cdot \frac{1}{a-x}$$

$$k_1 = k_2(y-x)/\ln(a/a-x)$$

If κ'_2 is extrapolated to $t = 0$, $\kappa'_{2t \rightarrow 0} = k_2 + (k_1/a)$

» κ_2 » » » $\kappa_{2t \rightarrow 0} = k_2$

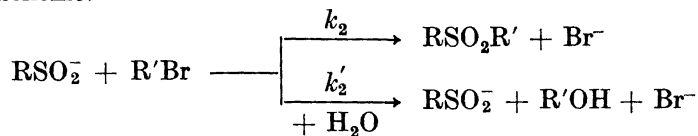
Table 1. Second order kinetics for the reaction of sodium *p*-toluenesulfinate with sodium bromoacetate in bicarbonate buffer.

<i>a</i> M	<i>b</i> M	Buffer M	<i>I</i>	<i>T</i>	<i>k</i> ₂ M ⁻¹ min ⁻¹	<i>k</i> ₁ × 10 ⁴ min ⁻¹
0.0761	0.1248	0.122	0.323	60.0°	0.170	17
0.1248	0.0751	0.171	0.370		0.166	27
0.509	0.0095	—	2.00		0.277	—
0.1248	0.0751	0.165	3.24		0.374	44
0.1000	0.0750	0.150	1.000	40.0°	0.0381	—
0.0750	0.0750	0.150	1.000		0.0379	—
0.0500	0.0750	0.150	1.000		0.0380	—
0.861	0.497	0.261	1.629		0.475	—

Table 2. Hydrolysis of sodium bromoacetate and bromoacetamide at 60.0°, NaNO₃ ad *I*.

Halogenide	M	Buffer	M	pH	<i>I</i>	<i>k</i> ₁ × 10 ⁴ min ⁻¹
BrCH ₂ COONa	0.125	Bicarbonate	0.125	—	0.250	4.19
	0.0076	Phosphate	0.088	6.6	0.78	2.30
	0.0076	Borate	0.165	8.9	0.78	2.50
BrCH ₂ CONH ₂	0.0076	Phosphate	0.088	6.6	0.78	2.04
	0.0076	Borate	0.165	8.9	0.78	2.17

y and z were measured by potentiometric titration with silver nitrate and nitrous acid, respectively. A typical plot of κ_2 and κ'_2 is shown in Fig. 1. Results obtained by this method are given in Table 1. The value of k_1 obtained by this method is much greater than its value when determined separately under the same conditions, Table 2. That is to say, the difference between dy/dt and dx/dt is greater than can be accounted for by the spontaneous hydrolysis of the bromoacetate. This indicates that the presence of sulfinate catalyzes the hydrolysis of the bromoacetate; and the reaction might be represented by the following scheme:



The experimental material fits this scheme much better. The material is too small, however, to afford a definite proof; and the reaction conditions are also not altogether unambiguous, as the bicarbonate buffer used also exerts base catalysis on the hydrolysis of the bromoacetate^{16,17}. The extent to which the greater difference between dy/dt and dx/dt was due to k'_2 and to the increase in k_1 , respectively, could not be definitely determined. For this reason the reaction was made pseudo-first-order by using excess sulfinate, so as to obtain simple kinetics; and the results were only employed to predict how this should best be attained.

Pseudo-first-order kinetics. If the rate of formation of the halide ion is postulated to be represented by eqn. (IV a), the rate of reaction can be kept at the original order of magnitude by increasing a and decreasing b . If a is made so much greater than b , that x , which can never exceed b , becomes negligible compared with a , then eqn. (IV b) is obtained. Further, if the order of magnitude of a is so chosen, that k_1/a becomes negligible compared with $k_1 + k'_2$, the reaction should be of pseudo-first-order with a second-order rate constant independent of a , eqn. (IV c).

$$\frac{dy}{dt} = [(k_2 + k'_2)(a-x) + k_1] (b-y) \quad (\text{IV a})$$

$$\frac{dy}{dt} = \left(k_2 + k'_2 + \frac{k_1}{a} \right) a (b-y) \quad (\text{IV b})$$

$$\frac{dy}{dt} = (k_2 + k'_2) a (b-y) \quad (\text{IV c})$$

According to the data given in Table 1, a had to be 0.5–1 M. As b was made $10^{-2} \times a$, y became too small to be determined by titration, especially at the beginning of the reaction, when y is very much smaller than b . For this reason y was measured potentiometrically with a silver-silverbromide electrode. In order to ensure that electrode response inertia did not introduce any consider-

able error, it was desirable to check the measurements by some other method. This was done by using bromoacetamide as halogenide, which could be readily determined polarographically. Since there was no method available for measuring the rate of formation of sulfone, dx/dt could not be evaluated.

By the method outlined, rate constants were obtained which were independent of sulfinate concentration. It should be pointed out that these constants are the rate constants for the interaction of sulfinate with the halogen compounds expelling halide ion; but they are not necessarily identical with the rate constants for the formation of sulfone, although, undoubtedly, the halogen expulsion mainly results in sulfone formation. On a preparative scale the reaction gives high yields of sulfone.

THE POTENTIOMETRIC METHOD

When the bromide concentration is measured by an Ag/AgBr electrode against a constant reference electrode, the bromide concentration can be obtained in various ways as a function of time, *e.g.* by referring the series of recorded potentials to the potential that the electrode shows in a reference solution of known bromide concentration, or by letting the reaction proceed to completion and using the end value as a reference, or by standard addition methods, or, if the reaction proves to be strictly of the first order during the whole range of measurement, by the so-called Guggenheim method¹⁸. For the present purpose all these methods had more or less serious disadvantages. In order for the potentiometric method to be valid for kinetical measurements the rate of response of the measuring electrode must be not only much greater than the reaction rate measured, but also constant during the time of measurement. Consequently, all measurements ought to be made within the shortest possible time, and the manipulations of the electrodes should be reduced to a minimum. The required conditions were satisfactorily met by applying the following procedure:

Two sulfinate solutions of exactly the same volume are prepared. To one of these a certain amount of halogen compound is added, and the reaction is allowed to proceed to completion. During the time required for this, both solutions are treated in exactly the same way. Out of a number of identical, freshly and simultaneously prepared Ag/AgBr electrodes two are chosen that are found to match well when checked against each other. One electrode is inserted into the reacted solution, the other into the unreacted solution, and the solutions are connected by a salt bridge. Exactly the same amount of halogen compound is now added to the unreacted solution as had been added to the first solution. The electromotive force, E , of the element is measured as a function of time. Eqn. (V) is obtained according to Nernst's law. Integration of eqn. (IV c) where, to simplify $k_2 + k'_2$ is replaced by k , gives eqn. (VI).

$$E = \frac{RT}{F} \ln \frac{b}{y} \quad (\text{V})$$

$$\ln \frac{1}{1-(y/b)} = k \cdot a \cdot t \quad (\text{VI})$$

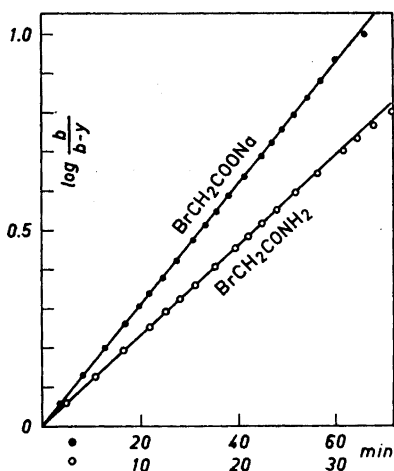


Fig. 2. Reaction of sodium *m*-nitrobenzenesulfinate with sodiumbromoacetate and bromoacetamide, 1st-order kinetics, potentiometric method.

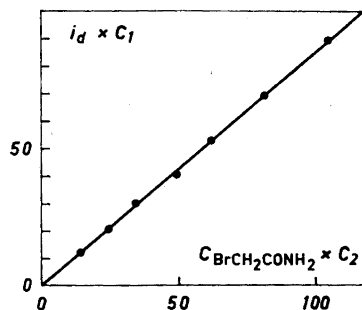


Fig. 3. Proportionality between polarographic diffusion current and concentration of bromoacetamide. Applied voltage 1.65 V vs. internal Hg ref. electrode. Temp. 20°.

y/b is now very easily obtained from (V), without having to determine the absolute value of b . When the reaction is completed, $y = b$ and $E = 0$. If time is measured at preselected potentials, then the left member of eqn. (VI) need only be calculated once, and is tabulated or plotted against E .

As a is known, k is now represented by the slope of a linear function of time. Good linearity was obtained by the method described and typical examples are shown in Fig. 2 and Table 3.

THE POLAROGRAPHIC METHOD

Organic halogen compounds are reduced at the dropping mercury electrode^{19,20}. In the negatively charged bromoacetate ion the reduction potential was too high for the polarographic registration of its disappearance during reaction. Bromoacetamide was used instead, as it was a water-soluble compound of the same order or reactivity, but with a lower reduction potential.

Since the polarographic diffusion current is a linear function of concentration, very simple relationships are obtained for the kinetics. The difference between the current, i_d , recorded at a certain time, and the current, when the reaction has proceeded to completion, $i_{d\infty}$, represents the concentration of bromoacetamide at this time, provided that no other reactants or reaction products are polarographically active at the potential used. The following equations are then obtained:

$$d(i_d - i_{d\infty})/dt = -k \cdot a(i_d - i_{d\infty})$$

$$\ln(i_d - i_{d\infty}) = -k \cdot a \cdot t + C$$

Table 3. Measurements with sodium *m*-nitrobenzenesulfinate. Potentiometric method. 60.0°.

Sodium bromoacetate $\alpha = 0.768$ M			Bromoacetamide $\alpha = 0.782$ M		
E mV	t min	$\log \frac{b}{b-y}$	E mV	t min	$\log \frac{b}{b-y}$
58.5	3.45	0.061	59.5	2.15	0.059
38.5	8.23	0.138	39.5	5.17	0.127
28.5	10.55	0.202	29.5	8.12	0.193
22.5	16.55	0.265	23.5	10.50	0.251
19.5	19.50	0.308	20.5	12.30	0.293
17.5	21.55	0.342	18.5	13.50	0.324
15.5	24.20	0.381	16.5	15.27	0.360
13.5	27.18	0.428	14.5	17.25	0.404
11.5	30.52	0.481	12.5	19.44	0.454
10.5	33.00	0.515	11.5	20.57	0.481
9.5	35.19	0.550	10.5	22.18	0.515
8.5	37.55	0.590	9.5	23.57	0.550
7.5	41.05	0.639	8.5	26.00	0.590
6.5	44.52	0.693	7.5	28.15	0.639
6.0	46.40	0.725	6.5	31.00	0.693
5.5	48.60	0.759	6.0	32.25	0.725
5.0	51.27	0.797	5.5	33.50	0.759
4.5	54.10	0.839	5.0	35.50	0.797
4.0	57.00	0.886	4.5	37.50	0.839
3.5	60.45	0.941	4.0	40.40	0.886
3.0	65.45	1.004	3.5	44.00	0.941

Sulfones are reported to have very high reduction potentials²¹, and the sulfinate group was not reduced within the potential range that could be covered in aqueous solution. The change in diffusion current was demonstrated to be due only to the change in bromoacetamide concentration, and strictly proportional to it. Fig. 3 shows the proportionality between diffusion current and concentration, and Fig. 4 shows the constancy of the diffusion current within a sufficiently wide potential range.

As in potentiometry, a necessary condition for the validity of the polarographic method for kinetic measurements is, of course, that the rate of the electrode reaction or measuring process is rapid compared with that of the

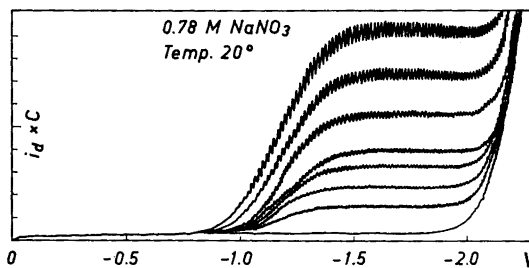


Fig. 4. Polarograms of bromoacetamide. Applied voltage vs. internal Hg ref. electrode.

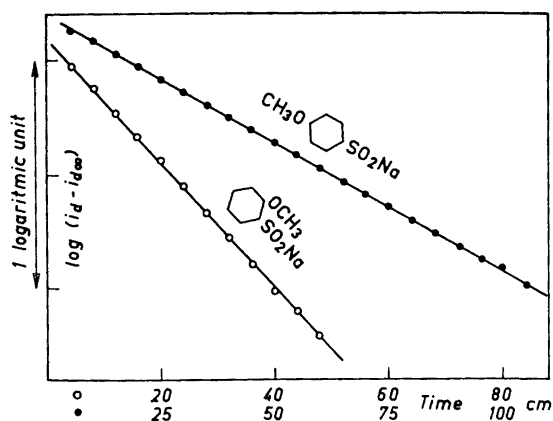


Fig. 5. Reaction of bromoacetamide with sodium *p*-methoxybenzenesulfinate and sodium *o*-methoxybenzenesulfinate, 1st-order kinetics, polarographic method.

Table 4. Measurements with the polarographic method. 60.0°.

Sodium <i>p</i> -methoxybenzenesulfinate			Sodium <i>o</i> -methoxybenzenesulfinate		
Applied voltage -1.60 V, $\alpha = 0.180$ M, 113.3 cm = 30 min			Applied voltage -1.60 V, $\alpha = 0.698$ M, 112.2 cm = 30 min		
<i>t</i> cm	$i_d - i_{d\infty}$ cm	$\log(i_d - i_{d\infty})$	<i>t</i> cm	$i_d - i_{d\infty}$ cm	$\log(i_d - i_{d\infty})$
5	8.50	0.929	2	9.40	0.973
10	7.50	0.875	4	8.30	0.919
15	6.60	0.820	6	7.40	0.869
20	5.80	0.763	8	6.50	0.813
25	5.05	0.703	10	5.80	0.763
30	4.50	0.653	12	5.15	0.712
35	3.90	0.591	14	4.52	0.655
40	3.50	0.544	16	4.05	0.608
45	3.05	0.485	18	3.60	0.556
50	2.70	0.431	20	3.10	0.491
55	2.37	0.375	22	2.80	0.447
60	2.09	0.320	24	2.45	0.389
65	1.80	0.255	26	2.17	0.337
70	1.60	0.204	28	1.93	0.286
75	1.42	0.152	30	1.70	0.230
80	1.25	0.096	32	1.48	0.170
85	1.10	0.041	34	1.32	0.121
90	0.95	0.978-1	36	1.15	0.061
95	0.85	0.929-1	38	1.00	0.000
100	0.78	0.892-1	40	0.88	0.945-1
105	0.65	0.813-1	42	0.80	0.903-1
			44	0.70	0.845-1
			46	0.60	0.785-1

Table 5. Reaction of aromatic sodium sulfinates with sodium bromoacetate, potentiometric method, 60.0°.

Substi- tuent	α M	I	Additional	pH	k M ⁻¹ min ⁻¹	Mean (Cor- rected)	log k
H	0.782	0.79	NaNO ₃ , Phosphate buffer	7	0.142	0.144	0.158-1
	0.372	0.79		6.6	0.141		
<i>o</i> -CH ₃	0.781	0.79		5	0.0557	0.0567	0.754-2
<i>m</i> -CH ₃	0.735	0.77	NaNO ₃	—	0.173	0.172	0.236-1
	0.392	0.79		—	0.165		
<i>p</i> -CH ₃	0.762	0.78	NaNO ₃ CH ₃ C ₆ H ₄ SO ₃ Na CH ₃ C ₆ H ₄ SO ₂ CH ₂ COONa	—	0.182	0.186	0.270-1
	0.372	0.78		—	0.185		
	0.432	0.78		—	(0.196)		
	0.370	0.78		9	(0.211)		
<i>o</i> -CH ₃ O	0.760	0.78		7	0.129	0.131	0.117-1
<i>m</i> -CH ₃ O	0.750	0.75		6	0.126	0.130	0.114-1
	0.748	0.78		7	0.131		
	0.803	0.81		7	0.128		
<i>p</i> -CH ₃ O	0.401	0.78	NaNO ₃ NaNO ₃	7	0.226	0.238	0.377-1
	0.403	0.78		7	0.242		
<i>o</i> -Cl	0.787	0.79		8	0.0180	0.0183	0.263-2
<i>m</i> -Cl	0.762	0.77		9	0.0784	0.0789	0.897-2
	0.779	0.79		8	0.0766		
<i>p</i> -Cl	0.792	0.79	Phosphate buffer » » » »	6	0.108	0.109	0.037-1
	0.789	0.79		6	0.105		
	0.624	0.78		6.9	0.109		
	0.568	0.78		6.8	0.105		
	0.517	0.78		6.9	0.109		
<i>o</i> -NO ₂	0.777	0.79		—	0.00598	0.00609	0.785-3
<i>m</i> -NO ₂	0.711	0.72	NaNO ₃	—	0.0471	0.0478	0.679-2
	0.763	0.77		7	0.0462		
	0.768	0.78		6	0.0466		
	0.728	1.54		7	(0.0678)		
<i>p</i> -NO ₂	0.770	0.78		9	0.0394	0.0401	0.603-2
	0.769	0.78		7	0.0394		

reaction measured. In conventional polarography it is the time factor of the galvanometer that limits the application of the method. The polarograph employed permitted of a half life of reaction which was, with a safe marginal, less than that of the fastest reaction measured.

Table 6. Reaction of aromatic sodium sulfinates with bromoacetamide.

Temp. 60.0°								
Substituent	Method	<i>a</i> M	<i>I</i>	Additional	pH	<i>k</i> M ⁻¹ min ⁻¹	Mean (Corrected)	log <i>k</i>
H	pot.	0.717	0.79	Phosphate buffer	6.7	0.327	0.336	0.526 - 1
	»	0.782	0.79		5	0.339		
	pol.	0.649	0.79	NaNO ₃	7	0.324		
<i>o</i> -CH ₃	pot.	0.782	0.78		5	0.0972	0.0980	0.991 - 2
	pol.	0.692	0.78	NaNO ₃	5	0.0953		
<i>m</i> -CH ₃	pot.	0.797	0.80		—	[0.318]	0.358	0.554 - 1
	»	0.402	0.79	NaNO ₃	—	0.364		
	pol.	0.358	0.79	»	8	0.348		
	»	0.683	0.79	»	8	0.346		
	»	0.683	0.79	»	—	0.344		
	»	0.683	0.79	»	—	0.349		
<i>p</i> -CH ₃	pot.	0.605	0.81	Phosphate buffer	6.6	[0.388]	0.423	0.626 - 1
	pol.	0.679	0.68		7	0.417		
	»	0.557	0.74	Phosphate buffer	6.6	0.416		
	»	0.620	0.82	»	6.6	0.409		
	»	0.453	1.85	NaNO ₃	—	(0.425)		
<i>o</i> -CH ₃ O	pot.	0.759	0.78		8	[0.313]	0.348	0.542 - 1
	pol.	0.731	0.78	NaNO ₃	6	0.346		
	»	0.698	0.78	»	6	0.338		
<i>m</i> -CH ₃ O	pot.	0.395	0.78	NaNO ₃	7	0.252	0.254	0.405 - 1
	pol.	0.778	0.79		7	0.243		
	»	0.775	0.78		7	0.242		
	»	0.419	0.87	NaNO ₃	7	0.255		
	»	0.419	0.87	»	7	0.251		
<i>p</i> -CH ₃ O	pot.	0.378	0.78	NaNO ₃	7	0.528	0.547	0.738 - 1
	»	0.193	0.78	»	7	0.536		
	pol.	0.348	0.78	»	7	0.549		
	»	0.180	0.78	»	7	0.536		
<i>o</i> -Cl	pot.	0.795	0.80		—	0.0392	0.0399	0.601 - 2
<i>m</i> -Cl	pot.	0.789	0.79		9	0.134	0.137	0.137 - 1
	»	0.770	0.78		9	0.134		
<i>p</i> -Cl	pot.	0.750	0.80	Phosphate buffer	6.8	0.183	0.184	0.265 - 1
	»	0.749	0.80	Borate buffer	9.1	0.181		
	pol.	0.872	0.87		5	0.180		
	»	0.781	0.78		5	0.177		
	»	0.710	0.71		5	0.181		
	»	0.651	0.65		5	0.185		
<i>o</i> -NO ₂	pot.	0.774	0.78		—	0.00999	0.0102	0.009 - 2
<i>m</i> -NO ₂	pot.	0.715	0.72		6	0.0656	0.0673	0.828 - 2
	»	0.764	0.77		—	0.0657		
	»	0.782	0.79		6	0.0669		
<i>p</i> -NO ₂	pot.	0.770	0.78		7	0.0598	0.0616	0.790 - 2
	»	0.780	0.79		7	0.0608		

Table 6 continued.

Temp. 50.0°								
<i>p</i> -CH ₃	pol.	0.786	0.79		5	0.142	0.144	0.158-1
<i>m</i> -CH ₃ O	pot.	0.785	0.79		7	0.0991		
	pol.	0.783	0.79		7	0.0985	0.0996	0.998-2
	»	0.783	0.79		7	0.0945		
<i>p</i> -Cl	pot.	0.790	0.79		5	0.0810		
	pol.	0.825	0.83		5	0.0811	0.0820	0.914-2
	»	0.751	0.75		5	0.0793		
Temp. 40.0°								
<i>p</i> -CH ₃	pol.	0.766	0.77		5	0.0526	0.0530	0.724-2

The rate constant k can be obtained as the slope of a linear function of time, without it being necessary to know the absolute concentration of the bromoacetamide. With the polarographic method there is no disadvantage connected with having to wait until the reaction is completed, as the electrode constantly reproduces itself. There was good linearity; and typical examples are shown in Fig. 5 and Table 4.

RESULTS

The results are given in Tables 5 and 6. Within reasonable limits of error, the rate constants are independent of the sulfinate concentration, which shows that the reaction is of the second order. The results of the potentiometric and of the polarographic methods agree when both are applied to the same reaction. With the potentiometric method a velocity effect can be observed in the reactions with the highest velocity, which is most probably due to electrode response inertia. Figures for such cases are placed in square brackets. By decreasing a , the same constants are obtained potentiometrically for those reactions as with the higher velocity polarographically. Minor variations in

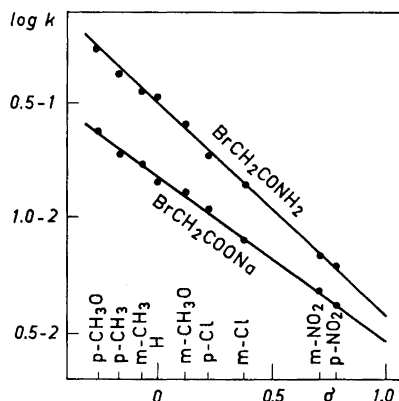


Fig. 6. The Hammett relationship for the reaction of *m*- and *p*-substituted aromatic sodium sulfinites with bromoacetamide and sodium bromoacetate.

Table 7. Reaction constants and statistical data for the reaction of aromatic sodium sulfonates with sodium bromoacetate and bromoacetamide.

Halogenide	ρ	$\log k_0$	s	r
$\text{BrCH}_2\text{CONH}_2$	-0.914	0.491-1	0.015	0.992
$\text{BrCH}_2\text{COONa}$	-0.712	0.179-1	0.009	0.994

pH do not influence the rate constants. Specific salt effects are either slight or absent, at least when sodium sulfinate is replaced by sodium nitrate. This is very expedient, as the large sulfinate concentration, that is required made it impossible to maintain a constant medium by a large excess of inert salt. For this, and other practical reasons the ionic strength could not be kept constant with a high degree of accuracy, but a slight variation as regards ionic strength does not have any significant effect on the rate constants (see Estimation of accuracy).

$\log k$ for the *meta*- and *para*-substituted members has been plotted against the substituent constants, σ , of Hammett²², Fig. 6. The reaction constants, ρ , of the Hammett equation (VII) have been calculated according to Jaffé²³, Table 7, where k_0 is the rate constant for the unsubstituted compound, and s and r standard deviation and correlation coefficient respectively. According to Jaffé's criteria the fit to the Hammett equation is excellent.

The ρ 's are negative, which implies that the reaction is facilitated by a high electron density at the reaction centre. This is consistent with an $\text{S}_{\text{N}}2$ type of reaction being responsible for the expulsion of the halide ion. The bromoacetate has lower reactivity than the bromoacetamide.

According to Taft Jr.²⁴ the Hammett equation has been extended to include also certain *ortho*-substituted compounds by introducing a steric term δE_s , where E_s is a steric substituent coefficient and δ the susceptibility of the reaction to the steric effect, equation (VIII). The conditions for the validity of this equation are that resonance, and effects other than polar and steric, are absent.

$$\log k = \log k_0 + \rho \sigma \quad (\text{VII})$$

$$\log k = \log k_0 + \rho^* \sigma^* + \delta E_s \quad (\text{VIII})$$

$$\log (k_{ortho}/k_{para}) = \delta E_s \quad (\text{IX})$$

If $\rho^* \sigma^*_{ortho}$, representing the polar effect of the *ortho*-substituent, is assumed to be approximately equal to $\rho \sigma_{para}$ for the corresponding *para*-substituent, then eqn. (IX) is obtained. If the logarithm of the *ortho-para* rate constant ratio, Table 8, is plotted against Taft's E_s values, a fairly good linear relationship is obtained, provided the *o*-Cl-substituted sulfinate is excepted.

Table 8. The steric effect in the reaction of *o*-substituted aromatic sodium sulfinates with bromoacetamide and sodium bromoacetate.

Substituent	E_s	$\log (k_{ortho}/k_{para})$	
		BrCH ₂ COONa	BrCH ₂ CONH ₂
CH ₃ O	0.99	-0.278	-0.197
Cl	0.18	-0.774	-0.661
CH ₃	0	-0.516	-0.635
NO ₂	-0.75	-0.818	-0.781

DISCUSSION

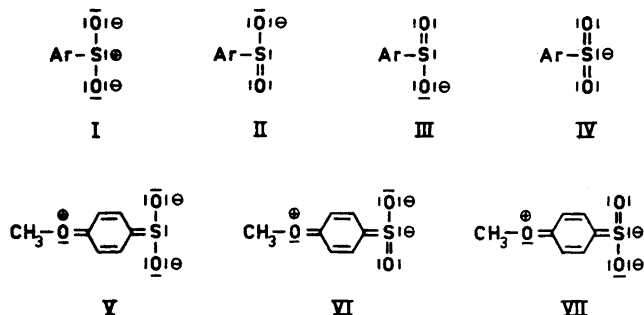
The fit to the Hammett equation is of interest as regards the possibility of the expansion of the outer electron shell of sulfur by involving the *d* orbitals in resonance or conjugation. Strong resonance causes a duality of σ constants for *p*-substituents²³; a well-known example of this is the *p*-nitro group in derivatives of aniline and phenol. Clear duality of σ constants is mostly observed with electron-attracting substituents, whereas electron-releasing substituents, capable of partaking in resonance, are more liable to yield graded series of σ values. Deviations from the usual σ value of the *p*-methoxy group is not uncommon.

Resonance effects on σ constants have been observed in connection with thiophenol acidity²⁵, and with sulfides and sulfoxides in oxidation reactions²⁶. Sulfide sulfur showed a resonance effect with both *p*-nitro and *p*-methoxy substituents, whereas with sulfoxide sulfur this effect occurred only with the *p*-methoxy group. Neither of these effects was observed in connection with sulfinate in this investigation.

Like sulfoxide sulfur, sulfinate sulfur has an unshared pair of electrons. In oxidation of sulfoxide as well as in the reaction of sulfinate in this investigation, the unshared pairs of electrons are used for forming new bonds. Similar to sulfone sulfur, sulfinate sulfur has two oxygens attached to it. The sulfonyl group with its two oxygens is more strongly electron-attracting than the sulfinyl group ($\sigma_{\text{CH}_3\text{SO}_2^-} > \sigma_{\text{CH}_3\text{SO}^-}$ ²³). Hence the sulfinate group may be expected to be electron-attracting, but the negative charge must weaken its electron-attracting power. On the other hand, it lacks an alkyl group. Consequently, it would appear, that the electron-attracting power of the sulfinate group may be similar to that of the sulfinyl group, and the fact, that it did not show any conjugation effect with the *p*-nitro group, indicates that the electron-donor properties of the sulfinate group are similar to those of the sulfinyl group.

The fact that no conjugation effect occurred with the *p*-methoxy group, indicates that the contribution of the conjugated structures (V)–(VII) to the resonance hybrid of the sulfinate ion must be weak. The distribution of charges in these structures appear rather unfavourable. The energy-like structures (II) and (III) may be regarded as making a strong contribution to the

sulfinate structure^{27,28}, and Parker suggests that the formation of sulfones in alkylation reactions is best represented by the structure (IV)²⁸.



EXPERIMENTAL

The preparation of the sulfonates has been described in an earlier paper²⁹.

Sodium bromoacetate was prepared according to Bischoff and Walden³⁰. Redistilled bromoacetic acid (equiv.wt. 139.1; 139.0 calc. Br 57.4; 57.5 calc.) in ether solution was mixed with an aliquot of sodium ethylate solution. The precipitated salt was washed with ether and dried *in vacuo*. (Found: C 14.9; H 1.4; Br 49.4. Calc. for $\text{C}_3\text{H}_5\text{BrNaO}_2$: C 15.2; H 1.2; Br 49.6.)

Bromoacetamide was prepared according to Papendick³¹ by treating monobromoacetic ethylester with 10% ammonia. Recrystallization from chloroform. (Found: C 17.5; H 2.84; Br 58.0; N 10.1. Calc. for $\text{C}_3\text{H}_6\text{BrNO}$: C 17.4; H 2.90; Br 58.0; N 10.15.)

In the preliminary experiments the stability of the sulfinate solution during the time of reaction was ascertained. The ionic strength 0.78 was determined by the solubility of the *p*-toluenesulfinate.

The sulfinate concentration was determined by potentiometric titration with sodium nitrite in a mixture of dilute sulfuric acid and potassium bromide, or by oxidimetric titration with potassium permanganate in neutral solution according to methods previously described³². The nitrous acid titration was unaffected by the presence of nitrate. Not all sulfonates react satisfactorily with nitrous acid, and the permanganate titration cannot be used for sulfonates with substituents sensitive to oxidation. The sulfinate concentrations of the kinetic solutions were usually determined by double titrations and, when possible, by both of these methods; the concentrations shown in the tables are means of these determinations. Accuracy was within the 1% limit.

The reaction volume was 11 ml, and 15 ml rubber stoppered tubes were used as reaction vessels. These tubes were inserted in the thermostat up to the rim. Volumetric measurements, for making up and determining concentrations, were made at 20°. The concentrations in Tables 5 and 6 are the concentrations measured at this temperature; and k_{mean} is corrected for volume temperature dependence. The experimentally determined correction factors were 1.018 at 60°, 1.012 at 50° and 1.007 at 40°, respectively.

Potentiometry. The Ag/AgBr electrodes were principally prepared according to Brown³³ by electrolytic coating of a platinum spiral with silver, followed by electrolytic bromidation. As regards details, many different opinions exist in respect to the best treatment in preparation³⁴. Prolonged washing was avoided. Subsequent to coating the electrodes were washed with concentrated ammonia according to Shedlovsky and McInnes³⁵. As, for practical reasons, the electrodes had to be prepared and stored at room temperature, but were to be used at 60° under difficult conditions, it was not possible to require too strict matching. Experience showed that a difference less than 1 mV generally remained stable within 0.1–0.2 mV during the measurements. Electrodes that differed by more than 1 mV were discarded.

The reactions were started by the injection of a tempered halogenide solution into 10 ml of sulfinate solution by means of a 1 ml tempered syringe which was so arranged and operated that it gave a reproducible volume. A magnetic stirrer, operated only during the first seconds of the reaction, was employed for mixing. The halogenide solutions were prepared by dropping a weighing flask, charged with halogenide, into 25 ml of water tempered in the thermostat, and then quickly mixing. Special care was taken to prepare the solutions for the reference and the measuring sample in exactly the same way.

Eqn. (V) requires identity of electrodes and of solutions. Corrections for any electrode differences were easily made by matching the electrodes before and after measurement. The requirement of identical solutions was more difficult to satisfy. Diffusion potentials and small concentration differences, due to salt bridge leakage, evaporation or experimental errors by making up volumes etc., represent much larger sources of error than any defects in the electrodes. Consequently, great care had to be taken to produce satisfactory salt bridges. The best results were obtained with salt bridges that were carefully plugged with asbestos and filled with sulfinate or sodium nitrate solutions. The supporting tubes of these salt bridges were connected with flexible rubber tubing, which enabled them to be easily refilled and to be kept, between the measurements, in a small tube of the solution that was to be measured.

Non-identity of the solutions causes an error in the measured EMF. This gives rise to a curvature in the plot of eqn. (VI) at the end of the reaction, since an EMF error causes a much greater error in the slope at the end of reaction than at the start (see Estimation of accuracy and Table 10). When, in cases of curvature, the reaction was allowed to proceed to its completion provided it was rapid enough to permit of this, the infinity value of E differed from zero. By using this difference as a correction term, the whole series of recorded E -values can be corrected to identical solutions. When this was done, curvature was eliminated. In fact, the straightness of the plot can be taken as a criterion of identical solutions. When correction was applied, the change from initial slope was always well within the calculated range of error (see Estimation of accuracy). Therefore, curvature, occurring towards the end of a reaction that is too slow to proceed to infinity, may be safely tolerated.

It is also possible to extrapolate the infinity value by the successive fitting of end values to the initial slope. This was done for the *p*-nitro-substituted series, which behaved anomalously. When the reaction was allowed to proceed, insoluble sulfone was precipitated, owing to decarboxylation of the reaction product^{39,40}; and this disturbed the proper functioning of the electrodes. Before the end of the reaction E had an abnormally large negative value, and became increasingly unsteady. This gave rise to exceptionally large negative curvature, which started at an early stage of the reaction; but by successive fitting of end values, a large part of the curve could be well fitted to the initial slope. Because of the polarographic activity of the nitro-groups, the results could unfortunately not be checked by the polarographic method. From the difference between the largest and the smallest possible initial slope, the accuracy was estimated to be within a limit of $\pm 8\%$.

Using the infinity value is, in principle, the same as employing any arbitrary reference electrode. But eqn. (VI) has a great advantage also in this case, as it makes it possible to immediately read off the extent of the reaction without any calculations.

The potentiometric measurements were made with a Radiometer, type PHM 3i, potentiometer. Temperature accuracy was $\pm 0.03^\circ$.

Polarography. For the polarographic measurements, at first, a saturated calomel electrode with a salt bridge was used as a reference system. Besides the usual disadvantages of salt bridges, its resistance had a diminishing effect on the potential range of the constant diffusion current of the bromoacetamide. Therefore, Heyrovsky's reference system, with a mercury pool on the bottom of the reaction vessel, was adopted. It functioned excellently. The polarographic cell had to be thermostated in a separate Dewar vessel in order to avoid vibrations from the thermostat, which were detrimental to the measurements. Circulation from the thermostat was maintained by a siphon device. Consequently the temperature control was slightly less accurate than in the potentiometric method; and temperature accuracy was now $\pm 0.05^\circ$. The measurements were made with the potential set at the constant part of the $i-V$ curve. Variation in this potential gave reproducible results, which proves the constancy of i_d . At first, gelatin was

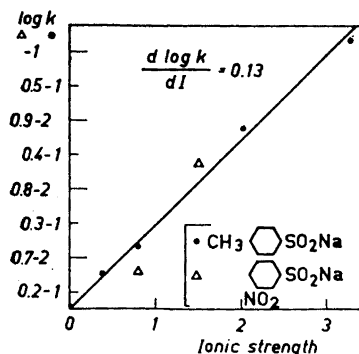


Fig. 7. Influence of ionic strength on the reaction of sodium bromoacetate with sodium *p*-toluenesulfinate and sodium *m*-nitrobenzenesulfinate at 60°.

used as a maximum damper, but was soon discarded as unnecessary. The measurements were made under nitrogen atmosphere.

As the absolute value of *b* is of no importance, the reaction was started by directly adding a small amount of the bromoacetamide, and quickly mixing by means of a nitrogen stream. The current multiplier of the recorder was then set to cover the whole range of the recorder. Variation in the initial bromoacetamide concentration by two powers of ten within the range of $(10^{-2}-10^{-4}) \times a$ had no effect on *k*.

A Radiometer, type PO 3h, polarograph was used.

Estimation of accuracy

Influence of ionic strength. In the case of bromoacetate, the two reactants being charged with charge of the same sign, the rate of reaction increases with increasing ionic strength, Table 1. If, for estimating accuracy, the effect of the ionic strength on $\log k$ is assumed to be linear, Fig. 7, the maximum error due to the experimental uncertainty, ± 0.01 , in the ionic strength is, for *p*-toluenesulfinate $\pm 0.3\%$. Moreover, $d \log k/dI$ is assumed to be of the same order of magnitude for the other members of the sulfinate series.

As regards bromoacetamide, one reactant being uncharged, the rate of reaction should, according to theory, be unaffected by ionic strength in dilute solutions. No significant effect, due to variation of ionic strength, could be detected (see *p*- CH_3 , *p*-Cl, *m*- NO_2 , Table 6) at concentrations of the same order of magnitude as those used for the bromoacetate reaction.

Table 9. Approximate activation data. $I = 0.78$.

Sulfinate	Halogenide	<i>T</i>	$\log k$	$\frac{d \ln k}{dT}$	$\Delta H \neq$ kcal·mole ⁻¹	$\Delta S \neq$ E.U.
<i>p</i> - CH_3	$\text{BrCH}_2\text{COONa}$	60.0°	0.270-1	0.0825	16	-20
		40.0°	0.553-2			
<i>m</i> - CH_3O	$\text{BrCH}_2\text{CONH}_2$	60.0°	0.405-1	0.0938	19	-11
		50.0°	0.998-2			
<i>p</i> -Cl	$\text{BrCH}_2\text{CONH}_2$	60.0°	0.265-1	0.0808	17	-20
		50.0°	0.914-2			
<i>p</i> - CH_3	$\text{BrCH}_2\text{CONH}_2$	60.0°	0.626-1	0.108	22	-6
		50.0°	0.158-1	0.100		
		40.0°	0.724-2			

Table 10. Calculation of error for the potentiometric method, $dE = 0.35$ mV.

E mV	Per cent turnover	$dk/k \times 100$
0.5	98.3	42
1.0	96.5	10
1.5	95	7.7
2.0	93	6.2
2.5	91.5	5.4
3.0	90	4.8
4.0	87	4.0
5.0	84	3.5
6.0	80	3.1
7.0	78	2.9
8.0	75	2.7
10.0	70	2.4
12.0	65	2.2
15.0	59	2.0
19.0	48	1.8
24.0	43	1.6
40.0	25	1.4
60.0	12.5	1.3
80.0	6.3	1.2
110.0	2.2	1.1

Influence of temperature. Approximate activation energies are calculated from the data of Table 9. $(d \ln k/dT)_{\text{mean}} = 0.091$ causes an error in k of $\pm 0.3\%$ for $dT = \pm 0.03^\circ$ (potentiometric method) and $\pm 0.5\%$ for $dT = \pm 0.05^\circ$ (polarographic method).

The potentiometric method. The precision of the EMF measurements is estimated to be ± 0.2 mV. Deviations from identity of solutions are estimated as not exceeding $\pm 0.5\%$. This deviation causes an error of ± 0.15 mV in the measured EMF. For the influence of this error on k , the following expression can be derived:

$$\frac{dk}{k} = dE/0.0662 \left(\frac{b}{y} - 1 \right) \log \frac{b}{b-y}$$

In Table 10 dk/k is represented as a function of reaction turnover for $dE = \pm 0.35$ mV. If this function is plotted, it will be evident that linearity is not perceptibly affected until a turnover exceeding 65% is reached, and the error in initial slope will then be about $\pm 1.5\%$. Most reactions gave good linearity up to or exceeding this turnover. Consequently, if the limit of error of k is estimated to $\pm 3\%$, this allows also for the analytical error and for the errors due to temperature and ionic strength uncertainty.

The polarographic method. $i_d - i_{d\infty}$ is measured as a length on the polarographic recorder, with an accuracy of 0.2 mm. The whole width of the recorder, 100 mm, was used. A simple calculation shows that $d(i_d - i_{d\infty}) = \pm 0.2$ mm cannot cause an error in the slope of the kinetic expression greater than $\pm 1\%$, except for extreme turnovers. The experimental plots never showed any tendency to curvature. Since the errors due to analytical and temperature uncertainty are $\pm 1\%$ and $\pm 0.5\%$, respectively, the known sources of error amount to a total not exceeding $\pm 3\%$. The influence of other sources of error are difficult to estimate, but since k is calculated from differences of measured diffusion currents that are shown to have a linear dependence on concentration, these sources of error are assumed to have only a minor influence on the result.

Thus it has been demonstrated that the polarographic and the potentiometric methods have about the same degree of accuracy. The experimental reproducibility agrees well with the accuracy estimated for both methods.

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