

452. The  $S_N$  Mechanism in Aromatic Compounds. Part XXI.\*

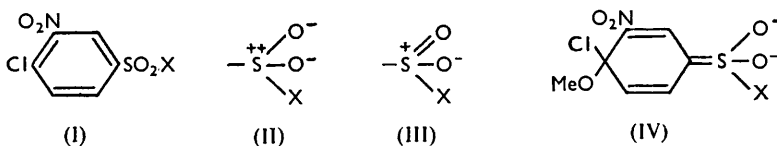
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The activating power of a series of  $p$ -SO<sub>2</sub>·X groups in an aromatic nucleophilic displacement has been investigated, and found to be in the theoretical order: X = H < SO<sub>2</sub>·NH<sup>-</sup>, SO<sub>3</sub><sup>-</sup> < SO<sub>2</sub>·NC<sub>5</sub>H<sub>10</sub>, SO<sub>2</sub>·NMe<sub>2</sub>, SO<sub>2</sub>·NMePh < SO<sub>2</sub>·Me < SO<sub>2</sub>·Ph. Comparisons are made with -I and -I-T groups, and particularly with corresponding COX groups. Orders found are: (a) N<sub>2</sub><sup>+</sup> > NO<sub>2</sub> > SO<sub>2</sub>·Me > NMe<sub>3</sub><sup>+</sup> > COMe > H; (b) SO<sub>2</sub>·X > COX > H.

The results are discussed in detail and shown also to support (III) as the single structure most nearly representing SO<sub>2</sub>·X groups.

SUBSTITUENT effects of COX groups have been considered earlier in this series,<sup>1-4</sup> and those of  $p$ -COX groups<sup>1,3</sup> found to be in the expected theoretical order.<sup>5,6</sup>

This paper considers the substituent effects of  $p$ -SO<sub>2</sub>·X groups in the mononitro-series (I): a preliminary note<sup>7</sup> has appeared. These effects are compared with those of -I and -I-T groups, and particularly with those of corresponding COX groups.



In discussing SO<sub>2</sub>·X groups it is necessary to consider the two common ways (II and III) by which their structure is represented, according to whether an octet (II) or a decet (III) is assumed for the outer electronic shell of the sulphur atom.

Structure (III) resembles that usually written for the nitro-group, though in such a structure the sulphur atom must be using a  $d$ -orbital, and, while the overlap with the  $\pi$ -electrons of the ring is expected to be less than for ordinary  $p$ - $\pi$ -bonds, any deviation of the SO<sub>2</sub>·X group from coplanarity with the ring would have less effect on the extent of conjugation. In any event such a structure would allow SO<sub>2</sub>·X groups to exercise a powerful -I-T effect (though much weaker when X is negative, as discussed below) in aromatic  $S_N$  reactions, such as proceed through an intermediate complex (IV).<sup>6, 8a, 9</sup>

With restriction of the outer electronic shell of sulphur to an octet, as in (II), an SO<sub>2</sub>·X group can exercise only a -I effect, and this is expected to be smaller than that of a cation such as NMe<sub>3</sub><sup>+</sup>. This is because, apart from the reduced effect due to the larger size of sulphur than of nitrogen<sup>8b</sup> and the direct effect of two negatively charged oxygen atoms, the electron duplets joining the two O<sup>-</sup> to S<sup>++</sup> would be very strongly displaced towards the sulphur, thus reducing the effective positive charge to a comparatively small value. The relative acidities of methylsulphonylacetic acid and of trimethylbetaine<sup>10</sup> confirm this view.

It would be inconsistent to assume an intermediate complex (IV), involving a -T effect for the SO<sub>2</sub>·X group, while representing the latter by (II), since this would imply acceptance

\* Part XX, *Austral. J. Chem.*, 1956, **9**, in the press.

<sup>1</sup> Miller, *J. Amer. Chem. Soc.*, 1954, **76**, 448.

<sup>2</sup> Miller and Williams, *ibid.*, p. 5482.

<sup>3</sup> Miller, *ibid.*, 1955, **77**, 180.

<sup>4</sup> Heppolette, Miller, and Williams, *ibid.*, 1956, **78**, in the press.

<sup>5</sup> Ingold, *Chem. Rev.*, 1934, **15**, 225.

<sup>6</sup> Miller, *Rev. Pure Appl. Chem.*, 1951, **1**, 171.

<sup>7</sup> Heppolette and Miller, *Chem. and Ind.*, 1954, 1457.

<sup>8</sup> Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell & Sons, Ltd., London, 1953, (a) p. 281, (b) p. 69, (c) p. 252, (d) p. 266.

<sup>9</sup> Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273; Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 340; Bolto and Miller, *Austral. J. Chem.*, 1956, **9**, 74.

<sup>10</sup> Branch and Calvin, "The Theory of Organic Chemistry," Prentice Hall Inc., New York, 1941, Chapter VI.

of a decet for sulphur joined to a quinonoid structure, and rejecting it for conjugation with a benzenoid structure and for the internal conjugation of an  $\text{SO}_2\cdot\text{X}$  group. The concept that sulphur may utilise  $d$ -orbitals in bond formation is not new.<sup>11</sup>

The theoretical order of activating power for  $p$ - $\text{SO}_2\cdot\text{X}$  groups in aromatic  $\text{S}_\text{N}$  reactions,  $\text{H} < \text{SO}_2\cdot\text{X}^- < \text{SO}_2\cdot\text{NR}_2 < \text{SO}_2\cdot\text{R} < \text{SO}_2\cdot\text{Ar}$ , is confirmed by the results presented in this paper and our preliminary (unpublished) results for the dinitro-series (cf. ref. 3). It corresponds to that found for  $p$ - $\text{COX}$  groups.<sup>1,3</sup> Since even  $\text{SO}_2\cdot\text{X}^-$  groups have a formal positive charge on sulphur, a  $-I-T$  effect (though very weak) is expected for these as well as for the neutral  $\text{SO}_2\cdot\text{X}$  groups, whereas  $\text{COX}^-$  groups (only  $\text{CO}_2^-$  being important) may not really be classifiable<sup>1,3,6</sup> as  $-I-T$  with the neutral  $\text{COX}$  groups, but rather as  $-T$  alone, or even as  $+I-T$ ,<sup>8c</sup> though in the latter case the  $-T$  effect must be the greater.<sup>1,3</sup>

The order of activating power was determined experimentally by measuring and comparing the rates of replacement of chlorine in the following compounds: (i) *o*-chloronitrobenzene,<sup>1</sup> (ii) 4-chloro-3-nitrobenzenesulphonamide (sodium salt formed in alkaline solution), (iii) potassium 4-chloro-3-nitrobenzenesulphonate, (iv) 4-chloro-3-nitrobenzenesulphonpiperidine, (v) 4-chloro-*NN*-dimethyl-3-nitrobenzenesulphonamide, (vi) 4-chloro-*N*-methyl-3-nitro-*N*-phenylbenzenesulphonamide, (vii) 4-chloro-3-nitrophenyl methyl sulphone, and (viii) 4-chloro-3-nitrophenyl phenyl sulphone. Table 1 gives the experimental and some calculated rate constants for the reaction of these compounds with  $\text{OMe}^-$  in absolute methanol, except where stated, together with the Arrhenius parameters ( $E$  and  $\log_{10} B$ ), and some derived quantities. Where measurements were not made with  $\text{OMe}^-$  in methanol, the rates were estimated as discussed below.

The reaction with compound (iii) was with  $\text{OH}^-$  in water. An ionic strength ( $\mu$ ) correction was applied, but the measurements made for this purpose will be included in a later paper dealing with the general problem of ionic-strength effects in aromatic  $\text{S}_\text{N}$  reactions. The rates for  $\text{OMe}^-$  in methanol were estimated from the ratio of rates for  $\text{OMe}^-$  in methanol and  $\text{OH}^-$  in water found for a similar carboxylate<sup>12</sup> after correction to zero ionic strength.<sup>13</sup> The reaction with compound (viii) was with  $\text{OMe}^-$  in 1:1 (v/v) benzene-methanol, and rates for  $\text{OMe}^-$  in methanol were estimated by using the same solvent comparison made for compound (vii).<sup>14</sup>

The ionic-strength correction was found to be unnecessary for compound (ii), and this is discussed below. The corrections and estimates are of such magnitude that the same conclusions would be drawn from uncorrected results.

Before considering the various  $\text{SO}_2\cdot\text{X}$  groups in detail it is valuable to compare the whole series, represented by  $\text{SO}_2\cdot\text{Me}$ , with representative  $-I$  and  $-I-T$  groups. For the former a cation  $\text{NMe}_3^+$ <sup>15,16</sup> is chosen, and this has been shown to be more activating than a powerful neutral  $-I$  group such as  $\text{CF}_3$ <sup>17</sup> even though the latter is assisted by a  $-E$  hyperconjugative effect. For the latter, formally neutral, dipolar, and cationic groups are chosen, *viz.*,  $\text{COMe}$ ,<sup>1</sup>  $\text{NO}_2$ ,<sup>1,18</sup> and  $\text{N}_2^+$ .<sup>15</sup>

The required comparison is for all these as 4-substituents in the 1-chloro-2-nitrobenzene series, and neither cation was thus measured, but reliable estimates may be made as follows. The  $\text{NMe}_3^+$  group was compared with H and  $\text{NO}_2$  in the 1-bromo-2-nitrobenzene series, and it has been shown<sup>16</sup> that both the chloro- and the bromo-series give very similar results. However, an adjustment to the S.R.F. and activation energy ( $E$ ) was made by equating the nitro-group as standard in each series. The  $\text{N}_2^+$  group was compared with H and  $\text{NO}_2$  in the 4-substituted fluorobenzene series, and this series, though more sensitive, gives results of the same general character. The larger adjustment required was made by

<sup>11</sup> See, *e.g.*, Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367; "Nature of the Chemical Bond," Cornell Univ. Press, New York, 1945, pp. 93, 251; Craig, MacColl, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

<sup>12</sup> Briner and Miller, *J.*, 1954, 4682.

<sup>13</sup> Bolto and Miller, unpublished work.

<sup>14</sup> Heppolette, Lantzke, and Miller, *Austral. J. Chem.*, 1956, **9**, in the press.

<sup>15</sup> Bolto, Liveris, and Miller, *J.*, 1956, 750.

<sup>16</sup> Bolto, Miller, and Williams, *J.*, 1955, 2926.

<sup>17</sup> Heppolette, Miller, and Williams, *J.*, 1955, 2929.

<sup>18</sup> Beckwith, Miller, and (in part) Leahy, *J.*, 1952, 3552.

use of the Hammett equation constants for the two series.<sup>19</sup> The changes in frequency factor ( $\log_{10} B$ ) needed to make adjustments between the series were too small to be used satisfactorily, and since the experimental values clearly showed the high value expected for anion-cation reactions no adjustment was made. The comparison of  $\text{SO}_2\cdot\text{Me}$  with the other named groups is shown as Table 2.

TABLE 1. *4-Substituted 1-chloro-2-nitrobenzenes.*

Substituent :	H	$\text{SO}_2\text{-NH}^-$	$\text{SO}_3^-$ <sup>a</sup>	$\text{SO}_2\text{NC}_5\text{H}_{10}$ <sup>d</sup>
Rate constant ( $10^6k_2$ ) (1. mole <sup>-1</sup> sec. <sup>-1</sup> )		18.8 (60.1)	1.33 (60.2) [0] <sup>b</sup>	75.1 (19.9)
(a) at temp. shown in parentheses	Ref. 1	19.2 <sub>5</sub> (60.1)	1.93 (60.2) [0.169]	150 (25.9)
		140 (82.6)	1.93 (60.2) [0.169]	213 (29.5)
		143 (82.6)	15.8 (82.0) [0.169]	355 (35.0)
		569 (100.4)	15.8 (82.0) [0.169]	382 (35.4)
		579 (100.4)	54.9 (100.4) [0]	987 (45.0)
		580 (100.4)	82.5 (100.4) [0.169]	
			84.8 (100.4) [0.169]	
(b) calc. at 0°	0.0,297	0.0143	0.0,611	0.0,375 * [0]
50°	0.252	6.56	0.462	1.37 * [0]
100°	35.0	583	52.5	91.9 * [0]
E (cal.)	23,6 <sub>50</sub>	21,500	23,1 <sub>50</sub>	18,800
			23,000 [0]	
			20,4 <sub>50</sub> * [0]	
			10.5 [0.169]	10.9
			10.2 [0]	
			8.8 <sub>5</sub> * [0]	
			12.6 * [0]	24,300
			5.44 * [0]	6090
			2.63 * [0]	2220
			3.37 [0]	—
			1.61 * [0]	—
Substituent rate factor (S.R.F.) <sup>c</sup>	{ 0° 1	48.0	12.6 * [0]	24,300
	{ 50° 1	26.0	5.44 * [0]	6090
	{ 100° 1	16.6 <sub>5</sub>	2.63 * [0]	2220
S.R.F. of the corresponding COX compound at 50°	—	—	3.37 [0]	—
S.R.F. ratio, $\text{SO}_2\cdot\text{X}/\text{COX}$ , at 50°	—	—	1.61 * [0]	—
Substituent :	$\text{SO}_2\cdot\text{NMe}_2$	$\text{SO}_2\cdot\text{NMePh}$	$\text{SO}_2\cdot\text{Me}$	$\text{SO}_2\cdot\text{Ph}$ <sup>e</sup>
Rate constant ( $10^6k_2$ ) (1. mole <sup>-1</sup> sec. <sup>-1</sup> )	27.9 (10.2)	60.1 (15.0)	195 (20.05)	137 (11.4)
(a) at temp. shown in parentheses	28.1 (10.2)	196 (25.9)	314 (24.9)	138 (11.4)
	65.9 (17.3)	198 (25.9)	529 (29.9)	230 (20.0)
	165 (25.6)	512 (35.4)		392 (25.1)
	165 (25.6)	521 (35.4)	910 (35.4)	396 (25.1)
	257 (30.0)	1300 (45.0)	914 (35.4)	692 (30.1)
	258 (30.0)		2200 (44.9)	
	451 (34.9)			1240 (35.6)
				1240 (35.6)
(b) calc. at 0°	7.86	9.77	15.7	20.5
50°	1900	2050	3220	4970
100°	106,000	100,000	158,000	277,000
E (cal.)	19,2 <sub>50</sub>	18,600	18,6 <sub>50</sub>	18,880 *
log <sub>10</sub> B	11.3	10.9	11.1 <sub>5</sub>	11.7
	26,100	32,900	52,900	56,200 *
Substituent rate factor (S.R.F.) <sup>c</sup>	{ 0° 26,100	32,900	52,900	56,200 *
	{ 50° 7570	8140	12,800	18,400 *
	{ 100° 3040	2860	4510	8110 *
S.R.F. of the corresponding COX compound at 50°	40.0 <sup>f</sup> {86.2}	—	1990	2660
S.R.F. ratio, $\text{SO}_2\cdot\text{X}/\text{COX}$ , at 50°	87.8	—	6.43	6.92 *

\* Estimated for  $\text{OMe}^-$  in MeOH (see text).

<sup>a</sup> With  $\text{OH}^-$  in water. <sup>b</sup> Values in square brackets are ionic strengths ( $\mu$ ). <sup>c</sup> Miller, *J.*, 1952, 3550. <sup>d</sup>  $\text{C}_6\text{H}_{11}$  = cyclohexyl. <sup>e</sup> With  $\text{OMe}^-$  in 1 : 1 (v/v) benzene-methanol. <sup>f</sup> In a dinitro-series.<sup>4</sup> The estimated value in this series (see text) is shown in braces.<sup>4</sup>

Inspection of Table 2 shows the relatively low activating power of a  $-I$  group, even when positively charged, compared with  $-I-T$  groups as shown by the order :  $\text{N}_2^+ > \text{NO}_2 > \text{SO}_2\cdot\text{Me} > \text{NMe}_3^+ > \text{COMe} (>\text{CF}_3)^{17} > \text{H}$ . The  $-I$  cation causes comparatively small lowering of  $E$  whereas  $-I-T$  groups, irrespective of electrical state, cause a marked lowering of  $E$ . However, while both cations have high frequency factors ( $\log_{10} B$ ) this

<sup>19</sup> Miller, *Austral. J. Chem.*, 1956, 9, 61.

parameter distinguishes the various  $-I-T$  groups, the changes being a large rise for the cation, a small rise for the formal dipole, and zero change for the formally neutral group. The  $\text{SO}_2\cdot\text{Me}$  group is clearly to be placed with the  $\text{NO}_2$  group, as regards S.R.F.'s and Arrhenius parameters, and structure (III) for  $\text{SO}_2\cdot\text{X}$  groups is thus supported against structure (II).

It is also relevant to compare the effects of the same groups on neighbouring O-H, N-H, and C-H bonds as indicated by acidity. For this purpose sufficient information is available from results quoted by Branch and Calvin,<sup>10</sup> Pearson and Dillon,<sup>20</sup> and

TABLE 2. 4-Substituted 1-chloro-2-nitrobenzenes.

Substituent :	H	$\text{N}_2^+$	$\text{NO}_2$	$\text{SO}_2\cdot\text{Me}$	COMe	$\text{NMe}_3^+$
S.R.F. at $\left\{ \begin{array}{l} 0^\circ \\ 50^\circ \end{array} \right.$	1	$3.83 \times 10^8$ *	$6.73 \times 10^5$	$5.29 \times 10^4$	$8.08 \times 10^3$	$2.59 \times 10^4$ *
	1	—	$1.14 \times 10^5$	$1.28 \times 10^4$	$1.99 \times 10^3$	$1.30 \times 10^4$ *
$\Delta E$ (cal.)	0	-7100 *	-6200	-5000	-4900	-2650 *
$\Delta \log_{10} B$	0	+3.6 <sup>a</sup>	+0.8 <sub>8</sub>	+0.7 <sub>8</sub>	0	+1.8 <sup>b</sup>

\* Estimated values (see text).

<sup>a</sup> Original value for 4-substituted fluorobenzene. <sup>b</sup> Original value for 4-substituted 1-bromo-2-nitrobenzene.

Hammett<sup>21</sup> (if in addition the greater acidity of sulphonamides than ordinary amides is derived from general knowledge of their reactions such as differential solubility in water and aqueous sodium hydroxide), and from the work of Jureček<sup>22</sup> on estimation of active hydrogen. Orders thus obtained are: (a) acids,  $\text{X}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and  $\text{X}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ :  $\text{NMe}_3^+ > \text{SO}_2\cdot\text{Me} > \text{COMe}$ ;  $\text{NO}_2 > \text{COMe}$ ; (b) acids,  $\text{XOH}$ :  $\text{SO}_2\cdot\text{Me} > \text{NO}_2 > \text{COMe}$ ; (c) acids  $\text{X}\cdot\text{NH}_2$ :  $\text{NO}_2 > \text{SO}_2\cdot\text{Me} > \text{COMe}$ ; (d) acids  $\text{X}\cdot\text{CH}_3$ :  $\text{NO}_2 > \text{COMe} > \text{SO}_2\cdot\text{Me}$ . The different orders are due presumably to the different relative importance of the  $-T$  effect, increasing from approximately zero in (a), in the order (a) < (b) < (c) < (d). The equivalence of order (c) with that in the aromatic  $\text{S}_\text{N}$  reactions is noteworthy as indicating there the importance of both  $I$  and  $T$  effects. As a final corollary these results suggest the  $-I$  order,  $\text{NMe}_3^+ > \text{SO}_2\cdot\text{Me} > \text{NO}_2 > \text{COMe}$ , and the  $-T$  order  $\text{NO}_2, \text{COMe} > \text{SO}_2\cdot\text{Me}$ ; and in conjunction with the earlier discussion that the true structure of  $\text{SO}_2\cdot\text{X}$  groups might well be between the structures (II) and (III) rather than (III) alone, though nearer the latter.

The order within the  $p\text{-SO}_2\cdot\text{X}$  series and relative to H may now be considered. The theoretical order of activating power,  $\text{H} < \text{SO}_2\cdot\text{X}^- < \text{SO}_2\cdot\text{NR}_2 < \text{SO}_2\cdot\text{R} < \text{SO}_2\cdot\text{Ar}$ , has already been given.<sup>1,3,5,6</sup> The series position relative to H is simply the result of the combined  $-I-T$  effects, while the order within the series is due to internal conjugation decreasing from left to right<sup>5,6</sup> and also the  $I$  effects of X. In particular, the large  $+T$  effects of  $\text{O}^-$  and  $\text{NH}^-$  must be reinforced by their  $+I$  effects, and in the sulphones the relative values of Me and Ph are regarded as due to a  $+I$  effect of Me and  $-I$  effect of Ph.

The  $\text{SO}_2\cdot\text{X}$  series chosen includes experimental comparisons of a finer nature than were considered for  $p\text{-COX}$  groups,<sup>1,3,5</sup> though the effect of a NPh group was measured in an  $o\text{-COX}$  series.<sup>2</sup> The order  $\text{SO}_2\cdot\text{NC}_5\text{H}_{10} < \text{SO}_2\cdot\text{NMe}_2 < \text{SO}_2\cdot\text{NMePh}$  is that expected from the relative  $I$  effects of the  $N$ -substituents, but the order  $\text{SO}_2\cdot\text{NH}^- > \text{SO}_3^-$  is opposite to that expected from the  $+T$  effects of  $\text{NH}^-$  and  $\text{O}^-$ , even though the position of both relative to the electrically neutral groups confirms the general discussion very satisfactorily. A possible explanation of the anomaly is the presence of a small amount of un-ionised amide, even though a considerable (three-fold) excess of  $\text{OMe}^-$  was used. If the S.R.F. of un-ionised  $\text{SO}_2\cdot\text{NH}_2$  is taken as about equal to that of  $\text{SO}_2\cdot\text{NMe}_2$ , then about 0.25% of free amide in equilibrium with the conjugate base would be sufficient to raise the S.R.F. above that of  $\text{SO}_3^-$  to the value found. An alternative explanation takes into account other anomalies of the  $\text{SO}_2\cdot\text{NH}^-$  group, *viz.*, the fact that no correction for ionic-strength effect was found necessary, and that the frequency factor was normal, instead of being low as

<sup>20</sup> Pearson and Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

<sup>21</sup> Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co. Inc., New York, 1940, p. 261.

<sup>22</sup> Jureček, *Chem. Listy*, 1946, **40**, 239.

would be expected for anion-anion reactions (cf. *p*-CO<sub>2</sub><sup>-1-3</sup>), and could be reliably estimated for SO<sub>3</sub><sup>-</sup>. It is suggested that all the anomalies of the SO<sub>2</sub>·NH<sup>-</sup> group result from the slight alteration in character due to hydrogen bonding N<sup>-</sup> ··· H-OMe. Such hydrogen bonding would not be expected with oxygen atoms of a sulphonate.

The Arrhenius parameters for the *p*-SO<sub>2</sub>·X series are also as expected. The *-I-T* effect causes the usual marked lowering of *E*; the dipolar groups cause a moderate rise in log<sub>10</sub> *B*; SO<sub>3</sub><sup>-</sup>, but not SO<sub>2</sub>·NH<sup>-</sup> causes a lowering of log<sub>10</sub> *B* as discussed above.

While SO<sub>2</sub>·Me and COMe have been compared as part of an extended sequence of substituent groups, it is of interest to compare a series of SO<sub>2</sub>·X and corresponding COX groups. There are four comparisons available, and for all the ratio of S.R.F.'s SO<sub>2</sub>·X/COX is greater than unity. More specifically, however, whereas for three comparisons the ratio does not exceed 7, it is about 88 for the fourth (X = NMe<sub>2</sub>). The general excess over unity expresses a greater overall *-I-T* effect in the SO<sub>2</sub>·X than in the COX series. The earlier discussion leads to the view that the difference lies in the *-I* effect, and that the *-T* effect might well be *less* in the SO<sub>2</sub>·X series. In addition to the factors already mentioned, the comparatively low *-T* effect could be due to the competition of internal and external conjugation as in the nitro-group.<sup>8d</sup>

The high value of the ratio for X = NMe<sub>2</sub> is regarded as due to special factors in CO·NMe<sub>2</sub> *only*, which are steric in origin. The size and geometry of the CO·NMe<sub>2</sub> group even when flanked in *ortho*-positions by only hydrogen (cf. ref. 4) causes it to be twisted out of the plane of the ring,<sup>23</sup> thus reducing its S.R.F. compared with that of CO·NH<sub>2</sub>.<sup>4</sup> If this effect were not present, however, the bulk of the NMe<sub>2</sub> group would still be expected to twist it relatively to the CO, thus reducing internal conjugation. This purely internal effect would result in a "true" S.R.F. greater than that of a CO·NH<sub>2</sub> group. If this "true" S.R.F. is arbitrarily estimated as five times larger than that of the CO·NH<sub>2</sub> group (to give a value approximately that of the CO<sub>2</sub>Me group, justified also by the ease with which NMe<sub>2</sub>, but not NH<sub>2</sub>, is displaced in *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO·NR<sub>2</sub><sup>4</sup>), then the SO<sub>2</sub>·X/COX ratio would be about 7 as found for X = Me and Ph. It should be noted that the S.R.F. for CO·NMe<sub>2</sub> was not obtained directly since side-reactions occur when 4-chloro-*NN*-dimethyl-3-nitrobenzamide is treated with OMe<sup>-</sup> in methanol.<sup>4</sup> Fortunately the corresponding 4-chloro-*NN*-dimethyl-3 : 5-dinitrobenzamide behaves normally,<sup>4</sup> and since the values of the Hammett constants for both the series are known with a high degree of precision<sup>19</sup> a reliable estimate of the S.R.F. of CO·NMe<sub>2</sub> in the mononitro-series is easily made if no side-reactions occur. In any case the ratio of X = NMe<sub>2</sub> is so large that the conclusions do not depend on the accuracy of the estimate. Models of SO<sub>2</sub>·NMe<sub>2</sub> and other SO<sub>2</sub>·X groups indicate that steric factors should be unimportant, particularly when the *d<sub>r</sub>* nature of the SO double bond is taken into account.

The SO<sub>2</sub>·X/COX ratio for X = O<sup>-</sup> is little more than unity, as compared with about 7 for X = Me and Ph, and a "true" value of the same order which can be reasonably estimated for X = NMe<sub>2</sub>. Since the ratio greater than unity has been ascribed to the *-I* effect, and since this is much smaller in the anionic groups the reduced value is to be expected.

#### EXPERIMENTAL

Runs were carried out with equimolar concentrations of reagents or about 40% excess of base (300% excess for the sulphonamide). In some cases the concentration of aromatic compound was 0.025M, and in others 0.05M. Rate constants (*k*<sub>2</sub>) were obtained by graphical plots after estimation of Cl<sup>-</sup> potentiometrically in aliquot parts "quenched" in excess of chloride-free dilute nitric acid or by potentiometric back-titration of acid after "quenching" in a known amount of dilute hydrochloric acid. Constants were measured at not less than three temperatures for each compound over a range 25–40°, and the Arrhenius parameters (*E* and log<sub>10</sub> *B*) were obtained by least-squares analysis of not less than six separately determined values of log<sub>10</sub> *k*<sub>2</sub> and reciprocal temperature. The estimated error in *E* is ±400 cal., and in log<sub>10</sub> *B* ±0.3. The "probable error" by least squares was always less than this, *e.g.*, for 4-chloro-3-nitrophenyl methyl sulphone *E* = 18,660 ± 100; log<sub>10</sub> *B* = 11.13 ± 0.06.

<sup>23</sup> Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714.

A typical run, for 4-chloro-*N*-methyl-3-nitro-*N*-benzenesulphonamide at 25.9°, is shown.

Log term .....	0.1917	2057	2183	2397	2613	2945	3286	3642	3973
Time (min.) .....	0	20	40	70	100	150	200	250	300

$k_2$  (graph) :  $1.964 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>;  $k_2$  (least squares) :  $1.967 \pm 0.004 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

*Materials.*—Potassium 4-chloro-3-nitrobenzenesulphonate. A modification of Gunstone and Tucker's procedure<sup>24</sup> was used in which chlorobenzene was sulphonated with 10% oleum at 40°, then nitrated by added potassium nitrate at 35° for 24 hr. The product was washed, refluxed with benzene, washed, recrystallised from water, washed with methanol, and dried at 100°.

4-Chloro-3-nitrobenzenesulphonyl chloride. The potassium sulphonate was treated with phosphorus pentachloride and oxychloride. After recrystallisation from light petroleum the product had m. p. 62° (lit.,<sup>25</sup> 40—41°, 61°, 61—62°, 101—102°).

4-Chloro-3-nitrobenzenesulphonamide. This was obtained in 65% yield by reaction of the sulphonyl chloride with ammonia in acetone at room temperature and formed pale yellow needles, m. p. 175.5° (lit.,<sup>26</sup> 175—176°), from methanol.

4-Chloro-3-nitrobenzenesulphonpiperidide. The sulphonyl chloride (5 g.) was allowed to react with piperidine (3.3 g.) in acetone (20 ml.) for 1 hr. at room temperature. The piperidide (70%), precipitated by water, recrystallised from methanol as pale yellow needles, m. p. 132° (Found : C, 43.8; H, 4.4. C<sub>11</sub>H<sub>13</sub>O<sub>4</sub>N<sub>2</sub>SCl requires C, 43.4; H, 4.3%).

4-Chloro-*NN*-dimethyl-3-nitrobenzenesulphonamide. The sulphonyl chloride (5 g.) and dimethylamine (4.5 g.) in acetone (10 ml.) (1 hr. at room temp.) gave the amide, pale yellow needles (from methanol), m. p. 103.5° (Found : C, 36.8; H, 3.6; Cl, 13.8. C<sub>8</sub>H<sub>9</sub>O<sub>4</sub>N<sub>2</sub>SCl requires C, 36.3; H, 3.4; Cl, 13.4%).

4-Chloro-*N*-methyl-3-nitro-*N*-phenylbenzenesulphonamide. The sulphonyl chloride (5 g.) in acetone (20 ml.) with *N*-methylaniline (2.1 g.) (2 hr. at room temp.) gave the amide, pale yellow needles (from methanol), m. p. 103° (Found : C, 47.7; H, 3.4; O, 19.4. C<sub>13</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SCl requires C, 47.8; H, 3.4; O, 19.6%).

4-Chloro-3-nitrophenyl methyl sulphone. See ref. 14.

4-Chloro-3-nitrophenyl phenyl sulphone. Prepared in 15% yield by a Friedel-Crafts reaction<sup>27</sup> and crystallised from benzene-methanol, this had m. p. 127°.

*Products.*—The expected methoxy(hydroxy for the sulphonate)-products were isolated in all cases, as follows : 4-Hydroxy-3-nitrobenzenesulphonic acid trihydrate,<sup>28</sup> m. p. 49°. 4-Methoxy-3-nitrobenzenesulphonamide,<sup>29</sup> m. p. 147°.

4-Methoxy-3-nitrobenzenesulphonpiperidide, after recrystallisation from methanol, had m. p. 122.5° (Found : C, 48.5; H, 5.8; O, 26.6; S, 10.85. C<sub>12</sub>H<sub>16</sub>O<sub>5</sub>N<sub>2</sub>S requires C, 48.0; H, 5.4; O, 26.6; S, 10.7%).

4-Methoxy-*NN*-dimethyl-3-nitrobenzenesulphonamide, recrystallised from methanol, had m. p. 110.5° (Found : C, 41.8; H, 4.8; O, 30.7. C<sub>9</sub>H<sub>12</sub>O<sub>5</sub>N<sub>2</sub>S requires C, 41.5; H, 4.65; O, 30.7%).

4-Methoxy-*N*-methyl-3-nitro-*N*-phenylbenzenesulphonamide (from methanol) was very pale yellow and had m. p. 121° (Found : C, 52.1; H, 4.8; O, 24.8; S, 10.2. C<sub>14</sub>H<sub>14</sub>O<sub>5</sub>N<sub>2</sub>S requires C, 52.2; H, 4.4; O, 24.8; S, 9.95%).

4-Methoxy-3-nitrophenyl methyl sulphone<sup>30</sup> had m. p. 145.5° (Found : C, 41.55; H, 3.9; O, 34.6. Calc. for C<sub>8</sub>H<sub>9</sub>NO<sub>5</sub>S : C, 41.8; H, 4.1; O, 34.6%).

4-Methoxy-3-nitrophenyl phenyl sulphone (from methanol) had m. p. 92° (Found : C, 53.2; H, 3.8; S, 10.9. C<sub>13</sub>H<sub>11</sub>NO<sub>5</sub>S requires C, 53.3; H, 3.9; S, 11.0%).

M. p.s are corrected. Analyses are by Dr. W. Zimmerman, Microanalytical Laboratory, C.S.I.R.O., Melbourne.

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<sup>24</sup> Gunstone and Tucker, *J. Appl. Chem.*, 1952, **2**, 205.

<sup>25</sup> Respectively, Fischer, *Ber.*, 1891, **24**, 3190; Seymour, Salbin, and Jones, U.S.P. 2,511,547; McNalley and Dickey, B.P. 585,940; U.S.P. 2,391,180.

<sup>26</sup> Kulka, *J. Amer. Chem. Soc.*, 1950, **72**, 1215.

<sup>27</sup> Loudon, *J.*, 1936, 221.

<sup>28</sup> Kekulé, *J.*, 1867, 638; King, *J.*, 1921, **119**, 2108.

<sup>29</sup> Gnehm and Knecht, *J. prakt. Chem.*, 1906, **74**, 96.

<sup>30</sup> Bunnnett, Draper, jun., Ryason, Noble, jun., Tonkyn, and Zahler, *J. Amer. Chem. Soc.*, 1953, **75**, 642.