[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA, UNIVERSITY OF CALIFORNIA AT BERKELEY AND THE UNIVERSITY OF SOUTH CAROLINA]

The SN Mechanism in Aromatic Compounds. Part XIX

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RECEIVED MARCH 8, 1955

A quantitative comparison of *meta* with *para* substituent effects in aromatic SN reactions has been made, though the *meta* substituent effects are complicated by steric and conjugative interactions between the *meta* and other substituents. Divergences from the Hammett relationship caused by these interactions are discussed, and when quantitative estimates of necessary amendments are applied to the normal σ_{meta} values, the Hammett relationship is obeyed. Major differences between *meta* and *para* substituent effects are shown to be due to the conjugative (T) effect.

It is a well known characteristic of aromatic substituents that their conjugative (T) effects[3a] are much smaller at *meta* than *ortho* and *para* positions, whereas their inductive (I) effects are larger at *ortho* than at *meta* and *para* positions. There is still doubt whether the order of I effects is $o > m > p$,[4] implying relay mainly through the σ-bonds, or $o > p > m$,[5,6] implying relay also through the π-bonds. It is hoped that later papers of this series will give definite indications on this point.

While there has been a good deal of recent quantitative work on aromatic SN reactions,[7–13] *meta* substituent effects have received little attention. Such effects as applied to aromatic nucleophilic substitution were included in a general survey by one of us[14] and a number of qualitative predictions, both in an absolute and a relative sense were made, but until recently no quantitative relationships were available. Bevan and Bye[15] have compared the effects of *m*- and *p*-nitro groups, and we have published a preliminary note[16] relating to a number of *meta* and *para* substituents.

The present discussion uses results of Miller and co-workers alone, including some from earlier papers of this series (unquoted); however, only newly determined rate constants are given in the Experimental section.

Tables I, II and III list calculated rate constants (k_2) at 50°, activation energy (E) and frequency factor (log B), and other quantities derived from experimental rate constants, for the replacement of an activated halogen atom in 17 compounds by OMe^- in absolute MeOH (except where stated).

TABLE I

SUBSTITUTED FLUOROBENZENES[a]

Substituent	10^5k_2 at 50°, l. mole^{-1} sec.$^{-1}$	S.R.F.[17] at 50°	C.I.[b] at 50°	E, cal.	log B
m- and *p*-H	0.0_6216	1		34900	12.0
m-NO_2	0.0156	7.22×10^4	1.84×10^4	286_{50}	12.5_5
p-NO_2	264	1.33×10^9		21200	11.7

[a] *Cf.* reference 15b. [b] See Discussion.

TABLE II

4-SUBSTITUTED 1-CHLORO-2,6-DINITROBENZENES

Substituent	10^5k_2 at 50°, l. mole^{-1} sec.$^{-1}$	S.R.F. at 50°	E, cal.	log B
H[a,b]	739	1	17550	9.75
Cl[a,b]	5860	7.91	17300	10.45
SO_3^-[c,d]	2020	..	16900	9.75
	(6000)	(8.11)	(14350)	(8.45)
CH_3[b]	122.5	0.166	19400	10.25
OCH_3[b]	14.8	.0200	22100	11.15
NH_2	0.869	.00118	20400	8.75

[a] *Cf.* reference 18 at one temperature only. [b] *Cf.* reference 19 at two temperatures only. [c] R. L. Heppolette and J. Miller, not previously recorded. Corrected to zero ionic strength. [d] With OH^- in water. Values in parentheses estimated for OMe^- in MeOH using the results of Briner and Miller[20] after correction to zero ionic strength.[21]

TABLE III

5-SUBSTITUTED 1-CHLORO-2,4-DINITROBENZENES

Substituent	10^5k_2 at 50°, l. mole^{-1} sec.$^{-1}$	S.R.F. at 50°	C.I.[a] at 50°	E, cal.	log B
H[b]	28800	1	1	174_{50}	11.2_5
Cl[c]	233000	4.05[d]	1.95	15400	10.7
SO_3^-[e,f]	282	.....	......	16500	8.6
	(838)	(0.0291)	(279)	(139_{50})	(7.3)
CH_3	7300	0.254	0.654	18300	11.2_5
OCH_3[b]	109_{50}	.380	.0526	18300	11.4
NH_2	384	.0133	.0887	203_{50}	11.3_5
$N(CH_3)_2$	550	.0191	......	17600	9.6_5
O^-[e,g]	0.0901	.....	......	21600	8.7
	(0.268)	$.0_5931$	......	(190_{50})	(7.4)

[a] By correlating the S.R.F. values of Tables II and III. [b] *Cf.* reference 22. [c] *Cf.* reference 18. [d] Taking half the calculated value since there are two identical replaceable Cl atoms. [e] As footnote *d* of Table II. [f] Corrected to zero ionic strength. [g] Using the same correction to zero ionic strength as for the SO_3^- compound.

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[3] Terminology for electronic effects is that used by C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953: (a) p. 64, (b) p. 252, (c) p. 259.

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Discussion

Previous discussion of substituent effects in this series of papers has been in terms of direct comparison with H in terms of a Substituent Rate Factor or S.R.F.[17] Jaffé[23] has discussed the application of the Hammett equation[24,25] to aromatic nuclear substitutions and has found that some such substitutions fit the Hammett equation.[7,26] There has also been demonstrated[27] the applicability of the Hammett equation to electron attracting *para* substituents but some divergence shown for electron-releasing substituents; similar divergences in aromatic substitutions are recorded by de la Mare[28] and Pearson, Baxter and Martin.[29]

In 5-substituted 1-chloro-2,4-dinitrobenzenes there are conjugative interactions between the 5- and 2- and 4-substituents and steric interactions between the 5- and 4-substituents. These will affect the fit of the *meta* (5-) substituents to the Hammett equation and also the *p*/*m* ratio of the S.R.F.'s, which is now defined as the Conjugative Index or C.I. because it will be useful in discussion in this and later papers. A C.I. considerably greater than unity will normally reflect an important conjugative electron attraction (−T) by the *para* as compared with the *meta* substituent; similarly a value considerably smaller than unity indicates a corresponding electron release (+M). Values close to unity will indicate either small effects or the resultant of counteracting influences and will therefore not be so useful.

The data of Table I can be used for a Hammett plot by plotting $\log_{10}$ S.R.F. against the σ-value for the m-NO_2 group and the σ^*-value[24,25,30] of the p-NO_2 group. This gives a good plot with a ρ value of 7.55 at 50°, among the highest recorded in the literature and corresponding with the large C.I. (18400 at 50°). It also demonstrates, as already pointed out,[31,32] that the S.R.F. of an activating group substituted initially into a halobenzene is greater than for further substitution of such groups.

It appears that for nuclear substitutions without complications due to interactions between multiple substituents, the normal σ-values for *meta* substituents should give a reasonable Hammett plot. It has been shown[27] that in a mononitro series, and the dinitro series of Table II, good Hammett plots are obtained for electron-attracting substituents using σ^*-values where applicable. At 50° the values for the former series are $\rho = 3.897$; correlation coefficient $(r) = 0.999$; standard deviation $(s) = 0.076$; for the latter series the values are $\rho = 3.353$, $r = 0.999$, $s = 0.075$. However, electron-releasing substituents, except Me, deviated considerably.

The Hammett plot of the 5-substituted 1-chloro-2,4-dinitrobenzenes (using the data of Table III) is shown as Fig. 1 and is clearly unsatisfactory: (i) the points do not fit a straight line; (ii) a line through H and OMe has a reverse slope compared with other possible lines; (iii) a line through H and Cl (which as a *meta* substituent is normally well behaved in Hammett plots) gives a ρ-value $= 2.17$, less than for either the mono- or dinitro series quoted above, while a line which approximately fits the maximum number of points (*i.e.*, the electron-releasing groups) gives the much larger ρ-value of about 5.8. These may be compared with an expected value based on the other dinitro series, and its relation to the unsubstituted and mononitro series, of about 3.5 at 50°.

These four deficiencies in the plot and the amendments which are made below, imply the reliability of the point for H (*i.e.*, the rates for reaction of 1-chloro-2,4-dinitrobenzene). It is therefore relevant to note that this compound reacts quantitatively with OMe^- in MeOH to give pure 2,4-dinitroanisole direct from reaction mixtures; excellent second-order kinetics are obtained with rate constants repetitive to 1–1.5%, even including measurements by three different workers in this group at well separated times; the rate constants so obtained give an excellent straight line plot of $\log k_2$ against reciprocal temperature over a range of 25°.

Figure 1 supports the expectation that conjugative effects, particularly between OMe, NH_2, NMe_2 and O^- and the two NO_2 groups *ortho* and *para* to them, cause the usual σ_{meta}-values to be insufficiently negative. This finding is in agreement with those of other workers[23,27–29] concerning electron-releasing *para* substituents, which may be exemplified by Jaffé's listing and discussion of σ_{para}-values for NMe_2 ranging from -0.206 to -1.049.

The second reason for a poor Hammett plot, the cause of a perturbation in the same sense, is a steric effect which is a secondary one as far as the replacement of Cl is concerned, *viz.*, the steric interaction of the 5- or *meta* substituent with 4-NO_2 group *ortho* to it but *para* to the replaceable Cl. The magnitude of the primary interaction between the 5- and 4-substituents is thought to be larger than that discussed by Miller and Williams[33,34] in connection with the effect of substituents *ortho* to a replaceable atom. Formation of the transition state in their work probably involves a weakening of steric influences. However, since the effect on the replaceable atom here is a secondary one, it does not necessarily affect the rate of replacement to the same extent.

The usual σ_{meta}-values, implying mainly inductive effects for *meta* substituents would lead to the activating order: $Cl > OMe > H > CH_3 > NH_2$ and $NMe_2 > O^-$. The cross conjugation is expected to be in the order: $O^- > NH_2$ and $NMe_2 > OMe > Cl > CH_3 > H$. The electrical charge on O^- makes it difficult to compare its steric effect too closely with the electrically neutral groups, but

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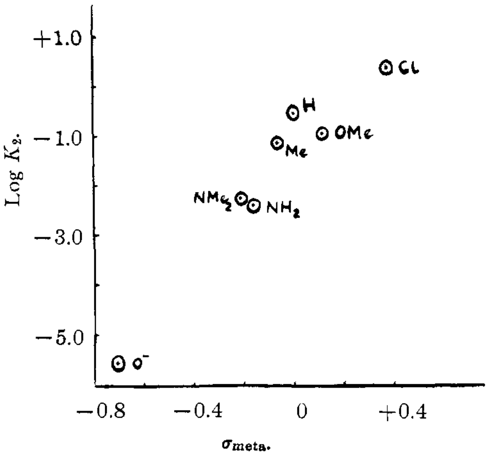


Fig. 1.—Hammett plot: reaction of 5-substituted 1-chloro-2,4-dinitrobenzenes with OMe^- in MeOH at 50°.

the expected order of the steric effect is: O^- and $NMe_2 > CH_3 > NH_2 > OMe > Cl > H$.

The steric and conjugative influences may be taken together as perturbations of the σ_{meta}-values, both modifying in the direction of more negative values and thus leading to a smaller ρ-value. The two effects may be combined to give the order of perturbation: $O^- > NMe_2 > NH_2 > OMe > CH_3 > Cl > H$.

Apart from the conclusion that the S.R.F. values given here must be minimal, it follows also that the "true" value of ρ for this series (*i.e.*, if the conjugative and steric interactions between the substituents were absent) must be between the slope given by H and Cl (2.17) and the large value (about 5.8) and rather nearer the former.

An arbitrary estimate of specific amendments to the normal σ_{meta}-values is made by taking the intervals in the combined perturbation order as −0.05 (commencing from H equal to zero) and giving extra weight to the conjugative effect on general grounds, and because there are *two* nitro groups affected by the additional amendments: Cl, −0.05; OMe, −0.1; NH_2 and NMe_2, −0.15; and O^-, −0.35. The log k_2 values of the 5-substituted 1-chloro-2,4-dinitrobenzenes when plotted against the amended σ_{meta}-values (Table IV) give a good Hammett plot, shown as Fig. 2, and thus support the use of the amendments. Further the "true" value of ρ thus obtained is 3.676, with $r = 0.999$ and $s = 0.072$ in good agreement with that expected (see above).

TABLE IV

5-SUBSTITUTED 1-CHLORO-2,4-DINITROBENZENES

Substituent	Calculated rate constant at 50°, $\log_{10} k_2$	σ_{meta}	Amendment to σ_{meta}	Amended value of σ_{meta}
H	−0.541	0	0	0
Cl	+0.367	+0.373	−0.100	+0.273
CH_3	−1.137	− .069	− .100	− .169
OMe	−0.961	+ .115	− .250	− .135
NH_2	−2.416	− .161	− .350	− .511
NMe_2	−2.260	− .211	− .400	− .611
O^-	−5.572	− .708	− .650	−1.358

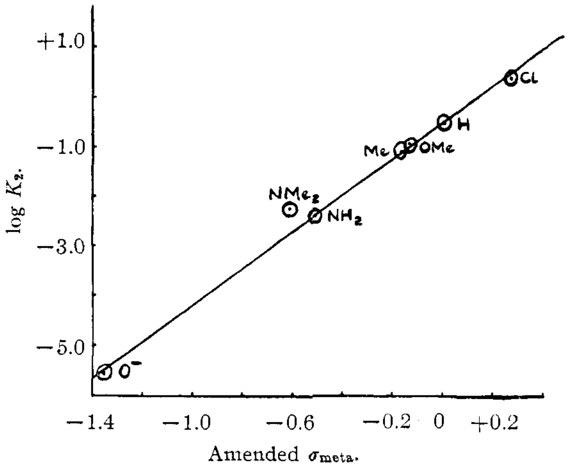
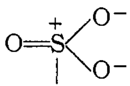
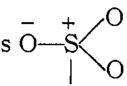


Fig. 2.—Amended Hammett plot: reaction of 5-substituted 1-chloro-2,4-dinitrobenzenes with OMe^- in MeOH at 50°.

It is very unlikely that the SO_3^- group, represented as  $\mathrm{O{=}\overset{+}{S}(O^-)_2}$ or even as  $\mathrm{\overset{-}{O}{-}\overset{+}{S}(O^-)_2}$, has any important −I effect, but a definite −T effect has been indicated for SO_2X (including SO_2X^-) groups by Heppolette and Miller,[35,36] and also by other workers,[37−40] and shown here by SO_3^- as a *para* activating group. This result leads to a C.I. greater than unity. At the *meta* position the −I effect will be absent or very small, and the small −T effect will scarcely affect either the NO_2 groups or the Cl atom. However, the steric effect will be large, mainly a repulsion between the negative oxygen atoms of both SO_3^- and NO_2 groups. In this position, therefore, the SO_3^- group should be deactivating, as is found, and thus also lead to a C.I. greater than unity. The reinforcement of the earlier effect leads to the large C.I. actually found.

The rates of Cl replacement in the *m*-NMe_2 compound are very similar to those of the *m*-NH_2 compound, while the Arrhenius parameters are rather different. This is probably associated with additional but nearly cancelling effects (on rates and thus S.R.F.'s) in the case of the NMe_2 compound, *viz.*, the larger steric interaction of NMe_2 and NO_2 while reducing activation by the NO_2 group, also reduces deactivation by the NMe_2 consequent to the conjugative interactions already discussed.

The powerful deactivation by *m*-O^- indicates a correspondingly large +I effect and cross conjugation.

Arrhenius parameters generally reflect the trends discussed, with −T effects lowering, and +M effects raising the activation energy, the effects being larger for single substitution into fluorobenzene as expected. A detailed analysis of the parameters is not attempted.

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Experimental

Runs were usually carried out with excess of OMe$^-$ (about 0.08 *M* OMe$^-$ and 0.05 *M* ArHal) and the rate constants obtained graphically. Reaction in aliquot portions was stopped with standard dilute acid, and base estimated by back-titration, potentiometrically or using indicators. Occasional runs were checked by potentiometric estimation of Cl$^-$. Values of k_2 were determined at not less than three temperatures, mostly over a range of 20–40°, and at least six separately determined values of k_2 were used in determination of the Arrhenius parameters by a least squares analysis of corresponding values of log k_2 and reciprocal temperature. The "probable errors" thus obtained were less than the estimated errors ±350–400 cal. in *M* and ±0.3 in log *B*. For three compounds, however, larger errors are estimated.

For these three compounds it was necessary to use equimolar initial concentrations of reagents—about 0.05 *M* for two and 0.025 *M* for the third. The first compound, 1,3-dichloro-4,6-dinitrobenzene, is one in which the initial product reacts further with OMe$^-$, though more slowly than the starting material. Accuracy is further reduced by fast rates and a short temperature range of measurements, and the estimated errors are about ±1 kcal. in *E* and ±0.9 in log *B*. The second compound, 4-chloro-3,5-dinitroanisole, gave good values of k_2 for not less than the first 30% of reaction,[26b]) but then OMe$^-$ consumption began to exceed Cl$^-$ formation. Only the first parts of runs were used to determine k_2, and the estimated errors are about ±600 cal. in *E* and ±0.6 in log *B*. The third compound, 4-chloro-3,5-dinitroaniline, exhibited a similar but larger discrepancy between OMe$^-$ consumption and Cl$^-$ liberation. The runs fortunately were slow, even at the elevated temperatures used, and satisfactory values of k_2 could be obtained by estimation of Cl$^-$ and taking initial slopes. The error in the Arrhenius parameters is difficult to estimate but would be not less than ±1 kcal. in *E* and ±1.0 in log *B*.

The expected methoxy compounds were readily isolated from the first two of these compounds, but the mixture of products from the aniline was not analyzed. It is probable that the well known reduction of dinitro compounds by alkoxide ion on heating was the side reaction involved in the anisole and aniline reactions, particularly the latter.

All the starting materials were known compounds, except for **sodium 5-chloro-2,4-dinitrobenzenesulfonate**, and this was prepared from the corresponding dichloro compound by a nucleophilic replacement of Cl analogous to that used in runs and preparation of other compounds.

Preparation of Materials.—Most compounds were prepared by standard procedures, and for these only physical constants are shown: ***m*-fluoronitrobenzene**, b.p. 198–200° (lit.[41,42] 197.5° (760 mm.), 200° (756 mm.)); **1,3-dichloro-4,6-dinitrobenzene**, m.p. 103° (lit.[43–45] 101°, 103°).

Sodium 5-Chloro-2,4-dinitrobenzenesulfonate Monohydrate.—1,3-Dichloro-4,6-dinitrobenzene (10 g.) was dissolved in ethanol, and an aqueous solution of 5.5 g. of sodium sulfite added. After 2 hr. reflux the mixture was evaporated to dryness on the water-bath, extracted with acetone and the product, obtained in 70% yield, crystallized by concentration of the extract. *Anal.* Calcd. for $C_6H_4ClN_2O_8NaS$: C, 22.3; H, 1.2$_5$; Cl, 11.0; N, 8.7; O, 39.7; S, 9.9. Found: C, 22.8; H, 1.7$_5$; Cl, 11.1; N, 8.3; O, 39.2; S, 10.1. After drying the hydrate at 100° for one week, the **anhydrous salt** was obtained. *Anal.* Calcd. for $C_6H_2ClN_2O_7NaS$: C, 23.7; H, 0.6$_5$; Cl, 11.6; S, 10.5. Found: C, 24.2; H, 1.2$_5$; Cl, 11.4; S, 10.7

5-Chloro-2,4-dinitrotoluene, m.p. 91° (lit.[46] 91°); **5-chloro-2,4-dinitroanisole**, m.p. 105° (lit.[47] 105°); ***p*-(N-methanesulfonyl)-anisidine**, m.p. 116° (lit.[48,49] 115°, 116°); **4-(N-methanesulfonyl)-amino-3,5-dinitroanisole**, m.p. 183° (lit.[50] 183°); **4-chloro-3,5-dinitroanisole**, hexagonal prisms, m.p. 124–125° (lit.[19,51] 124–125°, 123°); **5-chloro-2,4-dinitroaniline**, m.p. 178° (lit.[52] 178°); **5-chloro-2,4-dinitro-N,N-dimethylaniline**, m.p. 129° (lit.[53] 129°); **5-chloro-2,4-dinitrophenol**, m.p. 92° (lit.[54,55] 92°, 92–93°).

Experimental Rate Constants.—Only the newly determined rate constants are given in this section, Table V. Values for compounds (iii) and (ix) at zero ionic strength are shown in square brackets.

TABLE V

EXPERIMENTAL RATE CONSTANTS

Compound[a]	Rate constants (10^5k_2, l. mole^{-1}sec.$^{-1}$) at temperatures shown in parentheses
i	6.42 23.1 46.4 49.5 110.$_5$ 111.$_5$ (100.4) (113.2) (120.8) (130.2)
ii	2200 2200 2870 2890 5000 8800 (−4.8) (0) (4.9) (8.85)
iii	40.7 41.0 102 103.$_5$ 246 250 (25.0) (35.35) (45.3) [32.4] [80.9] [193]
iv	400 404 667 1150 4380 4510 (20.0) (25.0) (35.0) (44.3)
v	574 597 706 1010 2680 6380 6520 (20.0) (21.8) (25.0) (35.0) (44.3)
vi	8.92 8.96 33.4 38.1 67.0 299 395 396 (45.35) (57.2) (60.2) (62.0) (81.9) (83.4)
vii	86.5 87.6 89.1 184 184 1010 1010 (35.6) (43.05) (60.2)
viii	88.8 90.1 141.$_5$ 379 127$_5$ 1280 (30.0) (35.0) (45.65) (60.2)
ix	11.7 30.0 51.1 52.6 107.$_5$ 109.$_5$ (100.4) (113.2) (120.8) (131.4) [8.43] [20.7] [35.9] [75.1]

[a] i, *m*-fluoronitrobenzene; ii, 1,3-dichloro-4,6-dinitrobenzene; iii, sodium 5-chloro-2,4-dinitrobenzene sulfonate; iv, 5-chloro-2,4-dinitrotoluene; v, 5-chloro-2,4-dinitroanisole; vi, 4-chloro-3,5-dinitroanisole; vii, 5-chloro-2,4-dinitroaniline; viii, 5-chloro-2,4-dinitro-N,N-dimethylaniline; ix, sodium 5-chloro-2,4-dinitrophenate.

Rates for potassium 4-chloro-3,5-dinitrobenzene sulfonate will be reported by Heppolette and Miller. Our earlier kinetic results[17] for 1-chloro-2,6-dinitrobenzene (xi) were measured over a range of only 10°. They have now been measured over a range of 35° and will be reported by Miller, Parker and Roper, but calculated results given in this paper are from their work.

Details of runs at varying ionic strengths will be included in a later paper dealing with ionic strengths in aromatic S_N reactions.

Products.—All but three of the compounds not previously reported in this series were allowed to react with OMe$^-$ in MeOH and the known OMe compounds were obtained from the reaction mixtures. Compounds iii, ix and x (see footnotes to Table V) were treated with OH$^-$ in water. The expected OH compounds were obtained from these reaction mixtures, the products from ix and x being known. From compound iii after completion of reaction the mixture was poured into excess HCl and evaporated down until crystals formed. These were washed, dried and analyzed as **sodium 5-hydroxy-2,4-dinitrobenzenesulfonate monohydrate**. *Anal.* Calcd. for $C_6H_5N_2O_9NaS$: C, 23.7; H, 1.6$_5$; N, 9.2; S, 10.5. Found: C, 24.2; H, 2.1; N, 8.9; S, 10.9.

Apart from the difficulty of analyzing the sodium sulfonates, the analysis for H in compounds with so little H is estimated to be of the order of 0.4% too high. Analyses are by Dr. K. W. Zimmerman of Melbourne, Australia. M.p.'s are corrected.

Acknowledgment is gratefully made by J. M. to the Department of State for an award under the Fulbright and Smith–Mundt Acts, and to the Universities of California and South Carolina for their hospitality and facilities provided.

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