[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN AUSTRALIA]

The SN Mechanism in Aromatic Compounds. XXII. The Activating Power of *para* CHO and CN Groups

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The reactions of 4-iodo-3-nitrobenzonitrile and -benzaldehyde with SCN^- in MeOH in which iodine is replaced by the thiocyano group appear to take place without concurrent reversible interaction of the reagent with the CHO and CN groups such as occurs with OMe^- and to a lesser extent with N_3^-. It has therefore been possible to determine satisfactory values for the activating power of *para*-CHO and CN groups in aromatic SN reactions in terms of both substituent rate factors and σ^*-values, and to make comparisons with other -I–T groups. The relative nucleophilicity of OMe^-, N_3^- and SCN^- is considered.

In previous papers of Miller and co-workers which have dealt specifically with CN and COX groups as activating substituents in aromatic SN reactions,[2-7] *ortho*- and *para*-CHO and *para*-CN, but *not ortho*-CN, were shown to behave anomalously in reactions with OMe^- in MeOH. This was explained, and later confirmed, as consequent on a fast concurrent reversible interaction of OMe^- with CHO and CN to form hemiacetal and imido ester, respectively.

It was thought possible that if less nucleophilic reagents were used the position of the reagent substituent equilibrium might change in favor of the CHO and CN compounds *and/or* that the reactivity of the CHO and CN groups in the formation of the equilibrium product might fall more rapidly than that of the activated nuclear (C–Hal) carbon atom. If such change or changes occurred and were large enough, it would then be possible to determine reliable values for the activating power of the CHO and CN groups without the interference due to the side reaction.

The first reagents tested for this purpose were azide and thiocyanate ions, and it was then necessary for practical reasons to use iodo instead of chloro compounds. The hoped-for result was obtained with SCN^- while the N_3^- showed intermediate behavior. It is not certain that either or both of the explanations given account for the satisfactory result. It has however been found possible to determine the true activating power of *para*-CHO and CN in the form of σ^*-values and substituent rate factors (S.R.F.),[8] (see Table II). The latter are in good agreement with previous estimates.[6]

The new results presented in this paper are reactions of the five following 4-substituted 1-iodo-2-nitrobenzenes: (i) 4-H, (ii) 4-$COCH_3$, (iii) 4-CHO, (iv) 4-CN, (v) 4-NO_2. Compounds i, iii, iv, v were treated with azide ion in absolute MeOH, and compounds ii, iii, iv, v were treated with thiocyanate ion in absolute MeOH. Table I presents the rate constants at 0, 50 and 100° and other derived quantities, together also with relevant data for reaction of i and v and the chloro compounds corresponding to i to v, with OMe^- in absolute MeOH.[9,10]

Discussion

The 4-substituted-1-chloro-2-nitrobenzenes in their reactions with nucleophilic reagents form a series which is very sensitive to substituent effects[11] as expected for nuclear substitution, and in which electron attracting substituents fit the Hammett equation.[11-13]

A closely similar behavior for the series with other halogens as replaced groups is to be expected, and is indicated by the similarity in the activating power of the *para*-NO_2 group in four series.[9,10] In the reaction of the 1-chloro series with OMe^- the 4-$COCH_3$ and 4-NO_2 groups behave as typical -I–T groups[14a,15] and act almost entirely by a marked lowering of the activation energy (E). For the $COCH_3$ group, E is lowered by 4.9 kcal., while for the NO_2 group E is lowered by 6.2 kcal. The formally neutral $COCH_3$ group causes no change in log B, while the formally dipolar NO_2 group increases it by 0.85. Formally dipolar SO_2X groups have been shown[16] by Heppolette and Miller to behave almost identically with the NO_2 group.

The anomalous behavior of *para*-CHO and CN (and also *ortho*-CHO[6]) shows conspicuously in the very high apparent values of E and log B and the unexpectedly low apparent values of S.R.F. and σ^*. In the reaction of the 1-iodo series with SCN^- the values for 4-substituent = H were not measured, but the values of the Arrhenius parameters for all the four substituents for reaction with SCN^- were normal, and with the CHO and CN groups having an activating power between $COCH_3$ and NO_2 as expected on theoretical grounds. Further, the well behaved nature of the series and its correspondence with OMe^- reactions is indicated by almost identical differences between the Arrhenius parameters for the $COCH_3$ and NO_2 compounds in both, *viz.*, in the OMe^- reactions $\Delta E = 1.4$ kcal., and $\Delta \log B = 0.85$; in the SCN^- reactions $\Delta E = 1.25$, and $\Delta \log B = 0.75$.

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TABLE I

REACTIONS OF 4-SUBSTITUTED-1-HALO-2-NITROBENZENES IN MeOH

1-Halogen	4-Substituent	Reagent	Calcd. rate constant, l. mole $^{-1}$ sec. $^{-1}$ at 0°	50°	100°	S.R.F. of the 4-substituent at 0°	50°	100°	E, kcal.	$\log_{10} B$	ρ at 50°	σ^*-value
Cl	H	OMe^-	2.97×10^{-9}	2.52×10^{-6}	3.50×10^{-4}	1	1	1	23.6_5	10.4		0
Cl	$COCH_3$	OMe^-	2.40×10^{-5}	5.00×10^{-3}	2.49×10^{-1}	8.08×10^3	1.99×10^3	7.12×10^2	18.7_5	10.4		0.874[c]
Cl	CHO[a]	OMe^-	4.76×10^{-6}	5.64×10^{-3}	1.09×10^0	1.60×10^3	2.24×10^3	3.11×10^3	25.2	14.8	3.897	0.860[a,d]
Cl	CN[a]	OMe^-	4.73×10^{-6}	7.06×10^{-3}	1.48×10^0	1.59×10^3	2.80×10^3	4.24×10^3	25.6_5	15.2		0.885[a,d]
Cl	NO_2	OMe^-	2.00×10^{-3}	2.88×10^{-1}	1.09×10^1	6.73×10^5	1.14×10^5	3.13×10^4	17.4_5	11.2_5		1.270[c]
I	H	OMe^-	4.29×10^{-10}	8.29×10^{-7}	2.11×10^{-4}	1	1	1	26.5	11.9		0
I	NO_2	OMe^-	3.08×10^{-4}	6.88×10^{-2}	3.61×10^0	7.18×10^5	8.30×10^4	1.71×10^4	18.9_5	11.7	3.874	1.270[c]
I	H	N_3^-	3.67×10^{-10}	4.22×10^{-7}	7.35×10^{-5}	1	1	1	24.7	10.3		0
I	CHO[b]	N_3^-	1.26×10^{-7}	1.27×10^{-4}	2.01×10^{-2}	3.43×10^2	3.00×10^2	2.74×10^2	24.2_5	12.5		0.827[b,d]
I	CN[b]	N_3^-	5.60×10^{-7}	2.60×10^{-4}	2.34×10^{-2}	1.53×10^3	6.16×10^2	3.18×10^2	21.5	11.0	3.118	0.895[b,d]
I	NO_2	N_3^-	1.74×10^{-5}	3.85×10^{-3}	2.00×10^{-1}	4.74×10^4	9.12×10^3	2.72×10^3	18.9_5	10.4		1.270[c]
I	$COCH_3$	SCN^-	2.71×10^{-9}	1.17×10^{-6}	1.65×10^{-4}	....	....	....	21.3	8.5	5.046	0.874[c]
I	CHO	SCN^-	4.86×10^{-9}	2.50×10^{-6}	2.40×10^{-4}	....	....	....	21.8_5	9.2		0.939[d]
I	CN	SCN^-	1.20×10^{-8}	4.91×10^{-6}	4.10×10^{-4}	....	....	....	21.2	9.0		0.997[d]
I	NO_2	SCN^-	3.84×10^{-7}	$1.16_5 \times 10^{-4}$	7.63×10^{-3}	....	....	....	20.0_5	9.2_5		1.270[c]

[a] Reversible side reactions affect rates and therefore derived quantities. [b] Values of E and $\log_{10} B$ suggest that corresponding side reactions occur in these reactions with similar effects. [c] Values quoted by Jaffe.[17] [d] Values derived from data of this table.

The literature values of σ^* for *para* $COCH_3$ and NO_2 have been shown[11] to be satisfactory for aromatic SN reactions, and these substituents may be used with confidence therefore to determine (a) ρ for the SCN^- reactions = 5.046; (b) values of σ^* for *para*-CHO and CN = 0.939 and 0.997, respectively; and by a further use of the Hammett equation (c) values of the S.R.F. of *para*-CHO and CN for methanolysis at 0° of the 4-substituted 1-chloro-2-nitrobenzenes = 20,200 and 38,100, respectively.[3]

The value of σ^* for *para*-CN is almost identical with the literature value,[18] but that for *para*-CHO is a little low. This divergence could be due to a minor interaction of SCN^- with CHO but *not* CN, and/or could be a consequence of the choice of the literature value for *para*-CHO from a wide range of possible values.

The nucleophilicity of N_3^- is shown to be intermediate between that of SCN^- and OMe^- and it is therefore not surprising that with N_3^- the anomaly in behavior of CHO and CN is of lesser magnitude than with OMe^-. The intermediate behavior is itself evidence for the satisfactory nature of the SCN^- reactions.

The S.R.F. for the *para*-CN group may be compared with the value for the *ortho*-CN group[6] to give the *p*/*o* ratio (Steric Index[19]) equal to only 1.34. The value close to unity shows the essential absence of steric effects.[3,7]

The activating power of *para*-CHO and CN groups is now seen to be in the expected position at the head of the COX series, but it is still markedly less (about $^1/_{20}$th–$^1/_{30}$th) than that of the *para*-NO_2 group.[3,8] This is because both I and T effects are important in aromatic SN reactions, and the –I effect of the NO_2 group is considerably larger. A fuller discussion of this point has been given[16] in a paper dealing with the activating power of *para*-SO_2X groups.

The relative nucleophilicity of OMe^-, N_3^- and SCN^- needs some consideration. Miller and co-workers[20] have recently discussed in outline factors affecting nucleophilicity, and leading to orders: $R_2N^- > OR^-$; $SR^- > OR^-$. These two orders are already well known, though in aromatic SN reactions the latter comparison has been made by Bunnett and Davis,[21] and Bevan and Hirst,[22] with somewhat contradictory results. Experimentally the order $N_2R^- > SR^-$ is also well known. More generally the problem of nucleophilicity has been discussed in a quantitative manner by Swain and Scott[23] and Edwards.[24]

There is an important similarity of N_3^- and SCN^- and difference of both from OMe^-. In both N_3^- and SCN^- the nucleophilicity of the anionic forms N^- and S^- is considerably reduced by (i) conjugation of the nucleophilic unshared electrons with a neighboring multiple bond and (ii) a neighboring positive atom (*formally* positive for the azide only). Although the experimental order is well understood on the basis of the above arguments it could not have been predicted from them. It is illustrated by Table II which also includes OPh^-.[20]

TABLE II

NUCLEOPHILICITY RATIOS

Reagent Temp., °C.	OMe^-	N_3^-	OPh^-	SCN^-
0	1.00	0.0565	0.0249	0.00125
50	1.00	.0560	.0365	.00169

The major differences between the three reagents lie in the diminishing values of the entropy term (log B). The value of log B for the OMe^- is expected to be rather high because in MeOH proton transfers between reagent and solvent (its conjugate acid) are expected to facilitate attack. The higher value of log B for N_3^- than SCN^- though both are similar in shape and size may well be due to the fact that both ends of the N_3^- may initiate a nucleophilic attack. However, differ-

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TABLE III

4-SUBSTITUTED 1-IODO-2-NITROBENZENES

4-Substituent	Reagent	Rate constant (10^5k_2), l. mole^{-1} sec.$^{-1}$ at temp. shown in parentheses						
H	N_3^-	93.2	98.2	335	570	693		1050
		(131.6)		(150.0)	(155.5)	(157.5)		(166.1)
CHO	N_2^-	16.7	17.0	62.1	62.8	390	396	400
		(52.4)		(64.0)		(82.4)		
CN	N_3^-	15.3	25.9	118	119	757		774
		(44.95)	(49.85)	(66.0)		(86.1)		(86.2)
NO_2	N_3^-	19.0	90.6	92.0	226	226	856	889
		(20.05)	(35.25)		(44.25)		(59.3)	
$COCH_3$	SCN^-	21.5	22.2	89.6	91.6	137		140
		(110.6)		(131.3)	(131.4)	(137.8)		
CHO	SCN^-	23.3	25.0	558	564	236		240
		(100.4)	(100.5)	(110.7)		(131.4)		(131.6)
CN	SCN^-	9.48	10.2	38.6	39.0	357		392
		(82.0)		(100.3)		(131.2)		(131.6)
NO_2	SCN^-	13.1	13.3	83.5	84.9	330		332
		(60.2)		(81.9)		(100.0)		

ences in the importance of desolvation of the reagent in forming the transition state could account for all or part of the difference.

Experimental

Kinetic runs were carried out with equimolar concentrations of reagent and aromatic compound. This was usually 0.05 *M*, but in occasional runs concentrations of 0.025 *M* were used. Reaction in aliquot portions was stopped by dilution with cold doubly distilled water (solid barium nitrate being added also to the aliquots from SCN^- runs), and iodide ion estimated potentiometrically. Values of rate constants (k_2) were determined at not less than three temperatures (T) over a range of about 30–50°, and not less than six separately determined values of k_2 were used in determining the Arrhenius parameters (E and $\log_{10} B$) by a least squares analysis of corresponding values of $\log_{10} k_2$ and $1/T$. The standard deviations thus obtained were less than the estimated errors ±0.35 to 0.4 kcal. in E, and ±0.3 in log B. Thus for 1-iodo-2,4-dinitrobenzene with N_3^- the values were $E = 20.03 \pm 0.10$; $\log B = 10.40 \pm 0.08$. For *o*-iodonitrobenzene larger errors are estimated, *ca.* 1 kcal. in E and *ca.* 1.0 in log B.

Experimental Rate Constants.—The newly determined experimental rate constants are given as Table III.

Preparation of Materials.—*o*-Iodonitrobenzene was prepared as in ref. 10; *p*-aminobenzaldehyde, as ref. 25.

***p*-Iodobenzaldehyde** was prepared in 30% yield from *p*-aminobenzaldehyde by a standard diazotization procedure. The product recrystallized from ligroin had m.p. 79–80° (lit.[26] 77–78°).

4-Iodo-3-nitrobenzaldehyde was prepared in 86% yield by nitration of *p*-iodobenzaldehyde analogously to van der Lee's methods for the chloro compound.[27] The product recrystallized from chloroform–light petroleum had m.p. 141° (lit.[28] 141°).

***p*-Iodoaniline**, as ref. 29.

***p*-Iodobenzonitrile** was prepared as in ref. 30.

4-Iodo-3-nitrobenzonitrile was prepared by nitration of *p*-iodobenzonitrile analogous to the method of Mattaar for the chloro and bromo compounds.[31] The nitrile recrystallized several times from ethanol–light petroleum was obtained in 55% yield and had m.p. 133.5°.

Anal. Calcd. for $C_7H_3N_2O_2I$: C, 30.68; H, 1.10; N, 10.22; I, 46.3. Found: C, 30.75; H, 1.32; N, 10.18; I, 45.9.

1-Iodo-2,4-dinitrobenzene was prepared as in ref. 6.

***p*-Iodoacetophenone** was prepared in 60% yield from *p*-aminoacetophenone by a standard diazotization procedure. The product recrystallized from ligroin had m.p. 82–84° (lit.[32] 85°).

4-Iodo-3-nitroacetophenone was prepared in 44% yield by nitration of *p*-iodoacetophenone with absolute HNO_3 at −5° and then by standing for 1 hour at room temperature. The product recrystallized from ethanol had m.p. 113–114° (lit.[33] 112–115°).

Sodium Azide.—The commercial product was purified as in ref. 34.

Potassium Thiocyanate.—The A.R. product was made up into a stock solution in absolute MeOH and standardized against standard $AgNO_3$ solution.

Products.—It is known that *o*-nitro aryl azides decompose on heating to give *o*-dinitroso compounds. *o*-Nitro- and 2,4-dinitrophenyl azides were prepared and shown to decompose in this manner, and the same dinitroso compounds were also obtained from the reaction mixtures using N_3^- on *o*-iodonitrobenzene and 1-iodo-2,4-dinitrobenzene; in later stages of runs there was considerable gas pressure in tubes due presumably to the N_2 also produced when the azides decompose. The other products from N_3^- runs were not isolated.

It is known[35,36] that aryl thiocyanates are alcoholyzed, and that this reaction is particularly facile when electron attracting substituents are present.[35] The products usually obtained as a consequence of further reactions of the aryl thiocyanate are some unchanged aryl thiocyanate together with the diaryl sulfide and disulfide. No attempt was made therefore to isolate the products from the thiocyanate runs except that an analysis of one crude reaction product (the $COCH_3$ compound) corresponded to such a mixture.

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