The equilibria can be essentially "frozen" throughout the reaction by using large excesses of sulfide and polysulfide, and by adding alkali or otherwise strongly buffering the reaction mixtures. The apparent third-order kinetics found in such cases (runs 14–17) may be only apparent, and may be due to the fact that the equilibria were not "frozen" identically in these experiments.

Reaction of 2-Octyl Nitrate with Ammonium Hydrosulfide.—In 70% ethanol at 26.7°, 2-octyl nitrate reacted with ammonium hydrosulfide to produce four gram-atoms of polysulfide sulfur per mole of nitrate. The rate of polysulfide formation early in the run was much slower than in a run using *n*-butyl nitrate under identical conditions. The same autocatalytic effect was observed.

Possible Mechanisms.—The results of these experiments eliminate from consideration a number of possible reaction mechanisms. Isolation of butyl alcohol in nearly quantitative yield and the absence of nitrate ion and mercaptan indicate that the reaction does not involve displacement by the hydrosulfide reagent at the carbon atom bearing the nitrate group. Also removed from consideration are elimination processes to give olefin or aldehyde. The Nadai mechanism referred to earlier is untenable because both intermediate reactions are slower than the denitration reaction. The reaction does not proceed through the intermediate formation of butyl nitrite, since different products are obtained from the reaction of this substance with hydrosulfides.

The most reasonable mechanism appears to be one in which the rate-determining step involves attack of a sulfide or polysulfide ion, upon the nitrate group. At least two reaction paths suggest themselves, fulfilling the conditions that the rate-determining step should involve butyl nitrate and a sulfide or polysulfide ion, and that rapid subsequent steps should lead to the formation of butanol, nitrite ion and polysulfide. They are

(a) $RONO_2 + S_x^{=} \longrightarrow RO^- + NO_2S_x^- \ (x \geqq 1)$

$$NO_2S_x^- + HS^- \text{ (or } S^{=}) \longrightarrow NO_2^- + HS_{x+1}^- \text{ (or } S_{x+1}^{=})$$

$$HS_{x+1} + HS^- \rightleftarrows HS_x^- + HS_2^-, \text{ etc.}$$

$$RO^- + HS_x^- \rightleftarrows ROH + S_x^{=}$$

$$HO^- + HS_x^- \rightleftarrows H_2O + S_x^{=}$$

(b) $RONO_2 + S_x^{=} \longrightarrow ROS_x^- + NO_2^-$

$$ROS_x^- + HS^- \longrightarrow RO^- + HS_{x+1}^-$$

$$HS_{x+1}^- + HS^- \rightleftarrows HS_x^- + HS_2^-, \text{ etc.}$$

$$RO^- + HS_x^- \rightleftarrows ROH + S_x^{=}$$

$$HO^- + HS_x^- \rightleftarrows H_2O + S_x^{=}$$

The first mechanism suggested involves attack by sulfide or polysulfide ion upon the nitrogen atom, with either concerted or subsequent displacement of alkoxide ion, forming "polythionitrate" ion. This substance, to which no literature reference has been found, would be expected to be unstable, giving up its sulfur atoms to the reducing agent, hydrosulfide ion. The remaining steps involve acid–base transfers (presumably rapid), and the equilibria among the various polysulfide species.

The second alternative involves attack by polysulfide on the oxygen atom, displacing nitrite ion. The data presently available do not distinguish between the two mechanisms.

These mechanisms are consistent with the second-order kinetics observed if the first reaction in each case is slow and rate determining. The variation in the values for the second-order rate constant is believed due to the differences in reactivity among the various polysulfide ions and to changes in the equilibria among these species. It is not possible at this time to define a termolecular mechanism nor one involving an equilibrium reaction preceding the rate determining step which would be consistent with the apparent third-order kinetics observed in certain cases.

China Lake, Calif.

[Contribution from the Department of Chemistry, University of Western Australia]

The S_N Mechanism in Aromatic Compounds. V. Halogen Substituents[1]

By Robert L. Heppolette[2] and Joseph Miller

Received March 26, 1953

The activating power of halogens in a group of aromatic S_N reactions has been measured and found to be in the order $I > Br > Cl > F \simeq H$. The results are discussed in terms of inductive (I) and tautomeric (T) effects.[3] Crudely quantitative values of the individual effects for the different halogens are obtained.

The substituent effects of halogen atoms in aromatic S_N reactions have been discussed recently[4] and it was concluded that activation by any one halogen would be similar in all positions and this has been confirmed for Cl.[5–7] It was also assumed that the permanent mesomeric (M) effects would not be large enough to reverse the order due to the total inductive (I) effects, but the results given below show this assumption to be incorrect.

In contrast with aromatic S_E reactions the halogens are classified as $-I+M$ instead of $-I+T$. The $-I$ effects include the inductomeric (I_d) as well as the permanent (I_s) effect.

The order of the I_s effect, due to electronegativity, is well known to be in the order $F > Cl > Br > I$ and has already been discussed[8] in connection with the nucleophilic replacement of halogens.

---

[1] From a thesis submitted by R. L. Heppolette as part of the requirements for the degree of Bachelor of Science with Honours.

[2] A Scholarship awarded to R. L. Heppolette by the Universities Commission (Australia) is gratefully acknowledged.

[3] The terminology for electronic effects is that used by Ingold, *et al.*, and discussed fully by Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1949.

[4] J. Miller, *Revs. Pure and Applied Chem.* (*Aust.*), **1**, 171 (1951).

[5] J. Miller, *J. Chem. Soc.*, 3550 (1952).

[6] M. Liveris, P. G. Lutz and J. Miller, *Chem. and Ind.*, 1222 (1952).

[7] J. Miller and V. A. Williams, *J. Chem. Soc.*, 1475 (1953).

[8] A. L. Beckwith, J. Miller and (in part) G. D. Leahy, *ibid.*, 2552 (1952).

TABLE I

4-Substituent of 1-chloro-2-nitro compound	10^5k, liters moles^{-1} sec.$^{-1}$ Exptl. at temp. shown in parentheses				Calcd. from Arrhenius parameters 0°	50°	100°	S.R.F. at 0°	50°	100°	Activation energy (E), cal.	Frequency factor ($\log_{10}B$)
H[5]	3.62		6.82	37.4	0.0_3297	0.2515	34.95	1	1	1	23640	10.39
	(75.3)		(81.6)	(100.8)							±120	±0.07
F	0.720		7.36	37.1	0.0_3213	0.225	36.8	0.717	0.895	1.05	24420	10.87
	(60.2)		(82.0)	(100.1)							±210	±0.12
Cl[5]	23.8	30.4	86.0	418								
	(68.4)	(71.7)	(81.8)	(100.8)	0.0_2558	3.51	392	18.8	14.0	11.2	22600	10.83
											±200	±0.12
Br	13.05		112	665	0.0_2363	3.87	636	12.2	15.4	18.2	24550	12.18
	(60.8)		(81.8)	(100.5)							±110	±0.07
I	14.6		116	683	0.0_24675	4.385	656.5	15.7	17.4	18.8	24000	11.87
	(60.8)		(81.8)	(100.5)							±160	±0.11

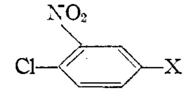
TABLE II

H	6.42	23.1	46.4	0.0_5466	0.01595	6.16	1	1	1	28540	12.51
	(100.4)	(113.2)	(120.8)							±250	±0.14
Cl	1.29	13.63	93.4	0.0_31745	0.3525	92.5	37.4	22.1	15.0	26690	12.60
	(60.2)	(82.0)	(100.1)							±520	±0.30

The order of I_d effects will follow from the order of constraint put upon the Ar–Hal bond electrons[9] and is in the order I > Br > Cl > F. Molar refractions may indicate the relative values of the effect.[3]

The M effects are generally accepted to be in the reverse order to that expected from the forces constraining the outer shell p-electrons,[10,11] and this is ascribed to the difficulty for larger atoms in forming partial double bonds.[12] The order usually given is therefore F > Cl > Br > I. According to the relative importance of these effects any order can be found for the resultant $-I+M$ effects.

In the reactions described here, this resultant is determined by measuring the substituent rate factors (S.R.F.'s[5]) of the halogens, *i.e.*, their activating power compared to hydrogen, for the attack by OMe^- in dry methanol on compounds, where X = halogen or hydrogen.



The kinetic results so obtained for replacement of Cl by OMe^- are given as Table I.

The fluoro compound replaces its F atom at a rate similar to that for its Cl atom. This is not unexpected, since in aromatic compounds a fluorine atom is much more easily replaced than other halogens when equally activated.[8] A method was devised to obtain the separate rate constants for replacement of F and Cl and this is outlined in the Experimental section.

By comparing the rate of replacement of F in this compound with that in *m*-fluoronitrobenzene,[13] another value for the S.R.F. of a *p*-Cl atom is obtained. The relevant results are given in Table II: the headings being as in Table I except that the first column reads 4-substituent in 1-fluoro-3-nitro compound.

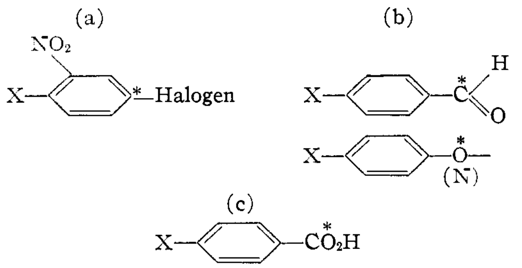
Table I shows that in the temperature range in which replacement occurs at a reasonable rate, the order of activating power is clearly I > Br > Cl > F ≃ H.

Table II shows that where the standard activation is by the much less powerful *m*-NO_2 instead of *o*-NO_2 group, the activating power of a substituent is somewhat larger.

Discussion of Results

It is instructive as a preliminary to the discussion to tabulate (Table III) the results obtained here with some other quantitative measurements which indicate the over-all $-I+M$ effects of the halogens. The table also includes values for their $-I_s$ effect, and results for a $-I-T$ group (NO_2) and a $+I+M$ group (CH_3). The latter are to show the sensitivity of each group of measurements to electronic effects.

The substituent effects shown in Table III fall into three levels (a) nucleophilic replacements; (b) cyanohydrin formation; strengths of phenols and amines; (c) strengths of aromatic acids. The order is (a) > (b) > (c) and corresponds to progressive removal, relative to the ring, of the point at which the substituent effect is measured. This is shown below by an asterisk.



In further contrast with the nucleophilic replacements, the cyanohydrin reaction is part of a reversible reaction and a catalyst is used.

The over-all substituent effects are not a simple function of either E or $\log B$ alone but of both, as shown in Table IV.

---

[9] C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

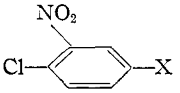
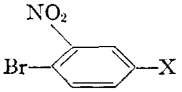
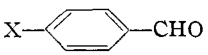
[10] J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 644 (1936).

[11] J. W. Baker and H. B. Hopkins, *ibid.*, 1089 (1949).

[12] K. S. Pitzer, THIS JOURNAL, **70**, 1936 (1948).

[13] Previously unpublished results of M. Liveris, P. G. Lutz and J. Miller.

TABLE III

Quantity measured		Electronic effect for halogens	NO_2	I	Br	Cl	F	H	CH_3
Ratio of K acid[a] XCH_2CO_2H		$-I_S$	....	41	76	85	119	1	0.74
Ratio of K acid[a] p-$XC_6H_4CO_2H$		$-I_S+M$	6.00	...	1.71	1.68	1.15	1	0.68
Ratio of K acid[a] p-XC_6H_4OH		$-I_S+M$	642	6.84	4.84	4.13	0.81	1	0.58
Ratio K^{-1} base[a] p-$XC_6H_4NH_2$		$-I_S+M$	570	8.35	5.75	4.37	1.05	1	0.31
S.R.F.'s replacement of Cl by OMe in	100°		31300[b]	18.8	18.2	11.2	1.05	1	0.33[b]
	50°	−I+M	114300	17.4	15.4	14.0	0.895	1	...
	0°		673400	15.7	12.2	18.8	0.717	1	...
S.R.F.'s at 25° replacement of Br by piperidine in[c] 		−I+M	"Large"	5.41	7.83	5.59	0.26	1	0.15
Ratio of rate constants at 20° cyanhydrin formation from[d] 		−I+M	22.4	5.69	5.54	4.21	2.18	1	0.

[a] H. B. Watson, "Modern Theories of Organic Chemistry," Oxford University Press; I. M. Heilbron, "Dictionary of Organic Compounds," Eyre and Spottiswoode; W. A. Waters, "Physical Aspects of Organic Chemistry," Routledge and Kegan Paul Ltd.; D. R. Boyd, *J. Chem. Soc.*, **107**, 1540 (1915). [b] Previously unpublished result of D. T. Downing and J. Miller. [c] Calculated from results, in a pseudo unimolecular reaction, of E. Berliner and L. C. Monack, THIS JOURNAL, **74**, 1575 (1952). [d] Calculated from the results of J. W. Baker and H. B. Hopkins, ref. 11.

TABLE IV

Substituent =	H	F	Cl	Br	
ΔE, cal.	0	+780	−1040	+910	+360
$\Delta \log B$	0	+ 0.44	+ 0.44	+ 1.79	+ 1.48

For F and Cl the activation energy and frequency factors are of similar importance, but for Br and I the latter are the more important. This is ascribed to the relative importance of the I_d effect for the latter pair. The I_d effect appears to be an important factor in increasing the probability of formation of the transition state, while on the other hand as shown particularly by the iodo compound it appears to have rather less influence on the activation energy.

The E values may be used to obtain a crudely quantitative estimate of the +M effect. One may set up the equation

$$M_{\text{Hal}} + I_{s(\text{Hal})} + I_{d(\text{Hal})} = \Delta E$$

where $M_{(\text{Hal})}$ = the raising of E due to the +M effect; and the $I_{(\text{Hal})}$ terms = the lowering of E due to the two I effects, respectively. Insufficient information is available to obtain all these individual values, but minimum values for the +M effect are obtained with the following assumptions. (i) The I_s effect is regarded as proportional to the differences between the electronegativity indices[14] of H and the atom in question. Relevant values are: I, 0.4; Br, 0.7; Cl, 0.9; N^+, 1.2; F, 1.9.

(ii) The activating power of a $-NMe_3^+$ group is regarded as due solely to the $-I_s$ effect. In a series very similar to that considered here the ΔE due to a $-NMe_3^+$ group is −2040 cal.[15] Each increase of 0.1 in electronegativity index is taken as causing a $\Delta E = -2040/12 = -170$ cal.

(iii) The I_d effect is proportional to the difference in molar refractions of C–Hal and C–H.[3,11] The values are: I, 12.9; Br, 7.86; Cl, 4.96; F ∼ 0.

From the general equation and the values in Table IV we obtain

(i) $-680 + M_I + I_{d(I)} = 360$ therefore $M_I = 1040 - 12.9x$

(ii) $-1190 + M_{Br} + I_{d(Br)} = 910$ therefore $M_{Br} = 2100 - 7.86x$

(iii) $-1530 + M_{Cl} + I_{d(Cl)} = -1040$ therefore $M_{Cl} = 490 - 4.96x$

(iv) $-3230 + M_F = 780$ therefore $M_F = 4010$

where x = the lowering of E due to each unit difference in molar refractivities. The value of x cannot be very large and the influence of the I_d effect is to bring closer the ratios of the above numerical results, *viz.:* I, 1.00; Br, 2.02; Cl, 0.47; F, 3.85; for $x = 0$.

While I, Br and F are in the expected order, Cl is below all the others, and this suggests that the smaller electronic binding forces in Br and I more than make up for the increased difficulty in forming the partial double bond. It appears that double bond formation is facile only for fluorine.

The factors affecting the frequency factor are even less well known, and even a roughly quantitative treatment is not attempted.

Conclusions

In aromatic S_N reactions: (i) the resultant −I+M effects of halogens in the p-position in the benzene ring are in the order I > Br > Cl > F ≃ H. (ii) The order of +M effects alone is F > Br > I > Cl. (iii) The I_d effect is relatively more important for Br and I. (iv) The halogens are rather weakly activating compared to hydrogen and substituent rate factors range from about 20 for I to 1 for F.

Experimental

Thermostats were controlled to 0.02° or better. The methanol used was dried by distillation once from concen-

---

[14] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942.

[15] Previously unpublished result of B. A. Bolto and J. Miller.

trated sulfuric acid and twice from aluminum amalgam and according to the method of Weaver[16] contained not more than 0.001% water.

Runs which were carried out in sealed tubes were followed usually by estimation of base, using a standard back-titration procedure. End-points were obtained by using mixed brom cresol green–methyl red as indicator.

For 4-chloro-3-nitrofluorobenzene, volumes were withdrawn in duplicate. One of each pair was used to estimate base as above and in the other the concentration of chloride ion was measured potentiometrically. The end-points in the latter case were obtained using a Müller capillary electrode system with silver wire. Equal initial concentrations of base and aromatic compound were used with the fluoro compound but not the others.

Rate constants were obtained from titration values by graphical plots. Values for each temperature are from duplicate runs. In the case of 4-chloro-3-nitro-fluorobenzene the reaction taking place is

$$\mathrm{FArCl} + \mathrm{OMe}^- \longrightarrow \mathrm{FArOMe} + \mathrm{ClArOMe} + \mathrm{F}^- + \mathrm{Cl}^-$$

The rate constant (K) calculated from the rate of disappearance of base is the sum of the rates of displacement of Cl (k_{Cl}) and F (k_{F}), whence the individual values are readily derived.

TYPICAL RUN

Log term	Time, sec.	Log term	Time, sec.	Log term	Time, sec.
0.2061	0	0.2465	600	0.3214	1920
.2093	120	.2522	840	.3485	2280
.2136	240	.2699	1080	.3706	2640
.2205	360	.2832	1320	.3923	3000
.2277	480	.3048	1620		

This leads to a value of $k_2 = (6.789 \pm 0.067) \times 10^{-3}$ liters moles^{-1} sec.$^{-1}$.

Preparation of Materials. 4-Chloro-3-nitroaniline.—From *p*-chloroaniline by the method of Morgan and Porter[17] except that the reaction was carried out at −15° and the product purified by charcoaling the solution in concd. HCl, precipitating with alkali, then crystallizing from water; yield 53%, m.p. 102° (lit. 102°).

4-Chloro-3-nitrobenzenediazonium Fluoroborate.—By a standard procedure[18]; yield 81%, m.p. 164° dec. This compound has not been previously reported.

4-Chloro-3-nitrofluorobenzene.—By a standard procedure,[18] followed by vacuum distillation; yield 10%, m.p. 38° (lit. 38°).

2,5-Dichloronitrobenzene.—The commercial product was recrystallized to constant melting point from ethanol, m.p. 54° (lit. 54°).

4-Bromo-2-nitroaniline.—From *o*-nitroaniline by the method of Bradfield, Orton and Roberts[19]; yield 60%, m.p. 109–110° (lit. 111°).

4-Chloro-3-nitrobromobenzene.—From 4-bromo-2-nitroaniline by the Sandmeyer reaction. The product was vacuum distilled and recrystallized from petroleum ether; yield 49%, m.p. 72° (lit. 72°).

4-Chloro-3-nitroiodobenzene.—This was prepared by an adaptation of a method of Derbyshire and Waters[20] used for preparing *m*-iodobenzoic acid; 16 g. of *o*-chloronitrobenzene, 16 g. of silver sulfate, 240 ml. of concd. H_2SO_4 and 30 ml. of water were mixed in a 3-necked flask fitted with stirrer. The mixture was heated on a boiling water-bath and 26 g. of finely powdered iodine added over 2–3 hours. Heating and stirring were continued for 15 hours, during which time silver iodide precipitated. After cooling, the reaction mixture was poured onto ice and unreacted iodine destroyed with sodium sulfite. The mixture was extracted with ether, the extract dried and then the ether evaporated off. The product was crystallized from ethanol; yield 54%, m.p. 74.5° (lit. 74.5°). This one step procedure seems superior to other methods in the literature.

Acknowledgment.—Assistance from the Research Grant to Australian Universities is gratefully acknowledged.

---

[16] E. R. Weaver, THIS JOURNAL, **26**, 2463 (1914).

[17] G. T. Morgan and J. W. Porter, *J. Chem. Soc.*, **107**, 652 (1915).

[18] "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., pp. 119–202.

[19] A. E. Bradfield, K. J. P. Orton and I. C. Roberts, *J. Chem. Soc.*, 784 (1928).

[20] D. H. Derbyshire and W. A. Waters, *ibid.*, 3694 (1950).

NEDLANDS, WESTERN AUSTRALIA

[CONTRIBUTION FROM THE EXPERIMENT STATION, HERCULES POWDER COMPANY]

Mechanisms of Reduction of Cumene Hydroperoxide. I. Reduction by Electron Transfer with Ferrocyanide Ion

BY HAROLD BOARDMAN

RECEIVED FEBRUARY 23, 1953

Cumene hydroperoxide is reduced by a one-electron transfer to the α,α-dimethylbenzyloxy radical. This radical decomposes to acetophenone and methyl radical. The kinetics of the reaction of ferrocyanide ion with cumene hydroperoxide indicate that the mechanism consists of the coördination of a proton with the hydroperoxy group followed by a one-electron transfer. The effect of oxygen on the reaction is discussed.

Cumene hydroperoxide may be reduced by a one-electron transfer, two successive one-electron transfers, or nucleophilic displacements.[1] The one-electron transfer process is the subject of this paper. A one-electron transfer results in the formation of the α,α-dimethylbenzyloxy radical[2,3]: $C_6H_5C(CH_3)_2O\cdot$ Kharasch[4] has obtained direct evidence for formation of this radical by its addition to an olefin.

The reduction of hydroperoxides by electron-transfer reagents is often accompanied by induced reduction caused by free radical attack on the hydroperoxide.[5] Induced reduction may be avoided by using very dilute solutions of the hydroperoxide. The ferrocyanide–cumene hydroperoxide system was found to be very suitable for studying the kinetics of reduction because of the ease with which the concentration changes of all the constituents could be followed in dilute solution.

The kinetics of the reduction of cumene hydroperoxide by ferrocyanide ion was determined by following spectrophotometrically at 430 mμ the

---

[1] See the 2d paper of this series, THIS JOURNAL, **75**, 4272 (1953).

[2] J. W. L. Fordham and H. L. Williams, *ibid.*, **72**, 4465 (1950).

[3] M. S. Kharasch, A. Fono and N. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

[4] M. S. Kharasch, W. Nudenberg and F. S. Arimoto, *Science*, **113**, 392 (1951).

[5] Unpublished material to be incorporated in a future paper of this series.