

176. Influence of Directing Groups on Nuclear Reactivity in Oriented Aromatic Substitutions. Part IV. Nitration of the Halogenobenzenes.

By MARJORIE L. BIRD and CHRISTOPHER K. INGOLD.

The investigation of the effect of single substituents in benzene on the rate of nitration at each nuclear position, commenced with the examples toluene (Part II) and ethyl benzoate (Part III), is here continued with the four halogenobenzenes, two of which are investigated accurately and two with less precision. The main part of the work consists in determining the rate of nitration of these substances in terms of the rate of nitration of benzene. Experiments have also been carried out on the orientation of nitration. The rates of total nitration by acetyl nitrate in acetic anhydride at 18° are ($C_6H_6 = 1$): C_6H_5F , 0.15; C_6H_5Cl , 0.033; C_6H_5Br , 0.030; C_6H_5I , 0.18. Thus the halogenobenzenes are *op*-orienting by differential deactivation, unlike toluene, which is also *op*-orienting but by differential activation; and also unlike ethyl benzoate, which is *m*-orienting by the opposite kind of differential deactivation. The circumstance that the rates of nuclear nitration pass through a minimum in the halogen series contrasts with the monotonic variation of rates, *i.e.*, the absence of an intermediate minimum or maximum, which in general is observed when nuclear halogens affect reactions in aromatic side chains. The difference is attributed to the greater relative importance of polarisability effects, particularly the electromeric effect, in nuclear than in side-chain substitution; and it is deduced that these effects collectively are electron-releasing in the order $I > Br > Cl > F$.

In the examples of chloro- and bromo-benzenes the effect of conditions has been investigated, three solvents and three temperatures being employed. The solvent effect on the relative reaction rates is small and irregular, but the temperature effect is rather large and regular. It is such as to show that the orienting substituents change the rates of reaction at the several nuclear positions mainly by changing the energies, rather than the entropies, of activation.

THIS paper continues the investigation of the effects of single substituents in benzene on the rate of nitration in the various nuclear positions. The general theory was given in Part I (J., 1927, 2918), where substituents were shown to fall into four classes. Parts II and III (J., 1931, 1959, and preceding paper) having dealt with toluene and ethyl benzoate in exemplification of classes 1 and 2, we are now concerned with the halogenobenzenes which illustrate class 3. As before, our object is to determine the factors by which the original substituent alters the probability of substitution at each nuclear position; and the principal measurement involved is that of the rate of nitration of the substituted benzene in terms of the rate of nitration of benzene. Some preliminary experiments on the halogenobenzenes were recorded in Part I, but the analytical methods were at that time insufficiently studied to give quantitative value to the results.* We have now examined chloro- and bromobenzene rather accurately, fluorobenzene less exactly, and iodobenzene in outline.

In the work on toluene, it was attempted to investigate the influence of change in the nitration medium and the temperature on the factors expressing the effect of the substituent on the rate of substitution; but the variations were small, and the demonstration of them was only partly successful. In the case of ethyl benzoate the analytical procedure was so lengthy that attention was concentrated on establishing values for a single set of conditions. Having available in the examples of chloro- and bromo-benzene a fairly accurate analytical method, we returned to the problem of the influence of conditions; and we are able now to show that the effect of temperature approximately follows a simply interpretable law.

(1) *Relative Rates of Nitration of Chlorobenzene, Bromobenzene, and Benzene by Means of Acetyl Nitrate in Acetic Anhydride, Acetonitrile, or Nitromethane at 0°, 25°, and 35°.*

We have again employed the competition method, which, as pointed out in previous parts, is the correct method for the solution of this problem. It will be recalled that the

* The qualitative result of Part I for iodobenzene, *viz.*, that it is nitrated faster than benzene, was reproduced by us on a single occasion (Expt. 81), but we cannot confirm it at will, and think that it must be in error through some disturbance not yet elucidated (cf. p. 926).

ratio, R , in which the halogenobenzene and benzene are found to have undergone nitration, tends to the ratio, k_y/k_x , of their specific rates of nitration in the limit of small amounts of reaction; and otherwise, R can be corrected accurately to give k_y/k_x .

Analysis.—The problem is the analysis of a mixture of benzene, halogenobenzene, nitrobenzene, and halogenonitrobenzenes, and, in particular, the estimation of the last two constituents, present to the extent of perhaps 5% and 0.2% respectively, each with an accuracy of 1 or 2 units %. The halogenonitrobenzenes consisted practically exclusively of the *o*- and *p*-isomerides, and hence the method was to estimate the total nitro-compounds by reduction with titanous chloride, and then to estimate the halogenonitrobenzenes by alcoholysis with sodium methoxide.

For the measurement of total nitro-compounds, Sempey's stannous chloride method (*J. Amer. Chem. Soc.*, 1930, 52, 88) was tried and found to give inaccurate results. The titanous chloride method (preceding paper) was checked with nitrobenzene, *o*- and *p*-chloro-, and *o*- and *p*-bromo-nitrobenzene and gave values 0.1—0.3% (rarely 0.5%) low—a result which was considered satisfactory.

For the estimation of halogenonitro-compounds the sodium methoxide method, used in similar work by Ingold and Vass (*J.*, 1928, 423), was found to give good results provided the methyl alcohol was carefully dehydrated with magnesium. Our practice was to heat as much of the mixture to be analysed as would contain about 0.001 g.-mol. of halogenonitro-compound with sodium methoxide solution, prepared from 5 g. of sodium and 100 c.c. of methyl alcohol, for 24 hours at 100° under reflux, then to distil off the methyl alcohol with additions of water, and finally to acidify the solution with nitric acid and estimate halide ion. In 10 tests on mixtures comparable in composition to the competitive nitration products the errors in the estimation of halogenonitro-compounds were all negative and averaged 0.5%. The halide ion was at first estimated by Volhard's method, but this was later replaced by the electrometric method of Müller and Cavanagh, with increase in convenience and accuracy.

Nitration.—Materials were purified as follows. Kahlbaum's pure nitric acid was distilled from concentrated sulphuric acid in an all-glass still; it was sometimes freshly vacuum-distilled to remove nitrous acid. Acetic anhydride, acetonitrile, and nitromethane were dried and fractionated. Thiophen-free benzene was fractionally frozen, with subsequent drying and distillation, until the f. p. was constant and correct. Chloro- and bromo-benzene were also fractionally frozen, dried, and fractionally distilled several times.

The nitration of chloro- and bromo-benzene in mixtures of nitric acid and acetic anhydride, diluted with excess of acetic anhydride, acetonitrile, or nitromethane, was first examined with respect to the products. These consisted of unchanged material and mononitro-derivatives, but no dinitro-compounds, since the last fraction obtained on distillation had the correct nitroxyl content for mononitro-compounds. An attempt further to nitrate an artificial mixture of *o*- and *p*-bromonitrobenzene with acetyl nitrate in acetic anhydride led only to a very small increase in nitroxyl content. "Dummy" nitrations were carried out in order to control the possibility of error in the estimation of aromatic nitro-compounds due to the formation of tetranitromethane or any other product of nitration of the solvent. It was shown that under the conditions of the competitive nitration such errors could not amount to more than 0.5%, and would normally be considerably less, and therefore in any case would be within the analytical error.

The general method of nitration was as follows. A mixture of nitric acid (0.0375 g.-mol.) and acetic anhydride (0.0375 g.-mol.) diluted with the solvent (excess of acetic anhydride, acetonitrile, or nitromethane, usually 6 c.c.), was made at 0°. This was added with mechanical stirring to a solution of benzene (0.0500 g.-mol.) and halogenobenzene (0.0500 g.-mol.) in the solvent (usually 20 c.c.) at the required temperature (0°, 25°, or 35°), and the mixture was kept at this temperature for the required time (0.5—8.0 hours), and then poured on ice (400 g.). The next day, when the decomposition of the acetic anhydride was complete, the product was made alkaline with sodium carbonate and extracted with ether (cf. previous paper). The ether, acetonitrile (if any), and much of the benzene were removed by distillation through Dufton columns. If nitromethane had been used as solvent, potassium hydroxide was added before the ether extraction, and the extract was washed with this reagent (N)—a procedure which was shown in control experiments completely to remove the nitromethane without perceptibly hydrolysing *o*- or *p*-chloro- or -bromo-nitrobenzene. The mixture of products, consisting now of nitrobenzene and halogenobenzene together with small quantities of benzene and halogenonitrobenzenes, was made up to 10 c.c. with absolute methyl alcohol, and measured portions of this solution were taken for the estimations of total nitroxyl and of labile halogen.

Results.—The results for chlorobenzene are in Table I(a). The conditions of the several groups of experiments are indicated in the side-headings and in col. 2. The quantities of the materials used are at the head of the table and in col. 3. The amounts of nitro-products formed are given in cols. 4 and 5, whilst the ratios of these quantities are in col. 6, and the ratios of the specific rates of nitration in cols. 7 and 8, together with the formal probable errors in the mean values. The nitric acid used in all these experiments was Kahlbaum's, not redistilled. Previous experiments on bromobenzene had shown that the removal of nitrous acid by distillation does not affect the ratio of the rates of nitration [cf. Table I(b)].

The results for bromobenzene are given in Table I(b). The nitric acid was freshly vacuum-distilled with sulphuric acid before use in Expts. 1—8 and 21—22, but it appears from a comparison of these two groups of experiments with Nos. 8—12 and Nos. 18—20 and 23 respectively that the removal of nitrous acid in this manner makes no marked difference to the relative rates of nitrations.

TABLE I.

Competitive Nitration of (a) Chlorobenzene or (b) Bromobenzene and Benzene by Means of Acetyl Nitrate in Solvents.

Initial Materials: Benzene, 0.0500 g.-mol. Chlorobenzene or bromobenzene, 0.0500 g.-mol. Nitric acid, 0.0375 g.-mol. Acetic anhydride, 0.0375 g.-mol. (initially mixed with the nitric acid). "Solvent" = acetic anhydride additional to the above, or acetonitrile, or nitromethane (quantities tabulated).

Expt. No.	Time (hrs.).	Solvent (g.-mol.).	Products (g.-mol.).		R.	$\frac{k_{\text{PhX}}}{k_{\text{PhH}}}$	Mean.
			PhNO ₂ .	C ₆ H ₄ X·NO ₂ .			
(a) Chlorobenzene.							
Solvent: Acetic anhydride. Temp.: 0°.							
53	1.0	0.275	0.02270	0.000765	0.0337	0.0255	} 0.0273 ± 0.0006
54	"	"	0.01942	0.000720	0.0370	0.0294	
55	"	0.0207	0.02309	0.000860	0.0372	0.0279	
56	"	"	0.02113	0.000718	0.0340	0.0264	
Solvent: Acetic anhydride. Temp.: 25°.							
57	2.0	0.275	0.01185	0.000454	0.0384	0.0338	} 0.0353 ± 0.0007
58	1.0	"	0.01763	0.000830	0.0471	0.0384	
59	"	"	0.01733	0.000732	0.0423	0.0346	
60	"	"	0.02338	0.001066	0.0456	0.0343	
Solvent: Acetic anhydride. Temp.: 35°.							
61	1.0	0.275	0.01747	0.000826	0.0474	0.0387	} 0.0399 ± 0.0008
62	"	"	0.01411	0.000678	0.0480	0.0411	
Solvent: Acetonitrile. Temp.: 0°.							
63	1.0	0.500	0.01545	0.000475	0.0307	0.0258	} 0.0257 ± 0.0001
64	"	"	0.01618	0.000498	0.0308	0.0257	
65	"	"	0.01603	0.000490	0.0306	0.0255	
Solvent: Acetonitrile. Temp.: 25°.							
66	1.0	0.500	0.02198	0.000876	0.0398	0.0306	} 0.0300 ± 0.0003
67	"	"	0.02262	0.000904	0.0399	0.0302	
68	"	"	0.02827	0.001210	0.0426	0.0293	
Solvent: Acetonitrile. Temp.: 35°.							
69	1.0	0.500	0.02523	0.01030	0.0408	0.0328	0.0328
Solvent: Nitromethane. Temp.: 0°.							
70	0.5	0.488	0.02166	0.000784	0.0362	0.0278	} 0.0277 ± 0.0005
71	0.8	"	0.02692	0.000998	0.0370	0.0262	
72	1.0	"	0.02247	0.000862	0.0383	0.0290	
Solvent: Nitromethane. Temp.: 25°.							
73	0.5	0.488	0.02872	0.001380	0.0480	0.0326	} 0.0312 ± 0.0006
74	1.0	"	0.02976	0.001400	0.0472	0.0314	
75	1.5	"	0.03077	0.001390	0.0453	0.0297	

Expt. No.	Time (hrs.)	Solvent (g.-mol.)	Products (g.-mol.)		R.	$\frac{k_{PhX}}{k_{PhH}}$	Mean.
			PhNO ₂	C ₆ H ₄ X·NO ₂			
(b) <i>Bromobenzene.</i>							
Solvent: Acetic anhydride. Temp.: 0°.							
1*	12-0	0.275	0.00612	0.000172	0.0281	0.0264	} 0.0261 ± 0.0013
2*	5.5	"	0.00480	0.000126	0.0262	0.0250	
3*	5.5	"	0.00427	0.000103	0.0242	0.0258	
4*	8.0	"	0.00497	0.000149	0.0300	0.0285	
6*	5.0	0.207	0.00381	0.000115	0.0303	0.0292	
7*	5.5	"	0.00420	0.000127	0.0303	0.0289	
8*	8.5	"	0.00498	0.000127	0.0255	0.0242	
9	1.0	0.275	0.0207	0.000659	0.0318	0.0248	
10	"	"	0.0207	0.000667	0.0322	0.0250	
11	"	"	0.0157	0.000479	0.0304	0.0255	
12	"	"	0.0234	0.000722	0.0309	0.0234	
Solvent: Acetic anhydride. Temp.: 25°.							
13	1.0	0.275	0.01745	0.000673	0.0386	0.0317	} 0.0320 ± 0.0003
14	"	"	0.01755	0.000700	0.0399	0.0326	
15	"	"	0.0176	0.000687	0.0391	0.0318	
16	"	"	0.0155	0.000588	0.0380	0.0318	
Solvent: Acetic anhydride. Temp.: 35°.							
18	1.0	0.275	0.0115	0.000441	0.0387	0.0340	} 0.0339 ± 0.0002
19	"	"	0.00621	0.000220	0.0354	0.0334	
20	"	"	0.0129	0.000503	0.0391	0.0340	
21*	"	"	0.00868	0.000316	0.0365	0.0333	
22*	"	"	0.0108	0.000412	0.0383	0.0341	
23	"	"	0.0163	0.000676	0.0413	0.0343	
Solvent: Acetonitrile. Temp.: 0°.							
24	0.5	0.500	0.00523	0.000141	0.0270	0.0255	} 0.0247 ± 0.0003
25	1.0	"	0.01355	0.000394	0.0290	0.0255	
26	2.0	"	0.0131	0.000385	0.0294	0.0254	
27	"	"	0.0157	0.000462	0.0293	0.0245	
28	4.0	"	0.0147	0.000386	0.0262	0.0223	
29	"	"	0.0163	0.000485	0.0296	0.0247	
30	5.0	"	0.01815	0.000555	0.0305	0.0247	
Solvent: Acetonitrile. Temp.: 25°.							
31	1.0	0.500	0.01935	0.000671	0.0347	0.0276	} 0.0291 ± 0.0005
32	"	"	0.01955	0.000685	0.0351	0.0278	
33	"	"	0.0192	0.000704	0.0366	0.0293	
34	2.0	"	0.02165	0.000882	0.0407	0.0313	
35	"	"	0.0217	0.000835	0.0385	0.0296	
Solvent: Acetonitrile. Temperature: 35°.							
36	0.5	0.500	0.0210	0.000852	0.0406	0.0316	} 0.0322 ± 0.0004
37	"	"	0.02045	0.000824	0.0401	0.0316	
38	1.0	"	0.0250	0.00114	0.0457	0.0333	
Solvent: Nitromethane. Temp.: 0°.							
39	0.5	0.488	0.0255	0.000811	0.0318	0.0229	} 0.0230 ± 0.0001
40	1.5	"	0.0274	0.000915	0.0334	0.0232	
Solvent: Nitromethane. Temp.: 35°.							
41	0.5	0.488	0.0293	0.00129	0.0440	0.0297	} 0.0295 ± 0.0001
42	1.0	"	0.0304	0.00135	0.0444	0.0294	

* Freshly distilled nitric acid of very low nitrous acid content employed.

The formal probable errors in the means of the rate ratios obtained in the different sets of experiments are only a few units %, and it therefore appears that the results are accurate enough for the study of effects due to conditions, since these effects are usually a good deal greater. We collect the mean ratios into the synoptic Table II. It will be seen that chlorobenzene is nitrated 25—39 times, and bromobenzene 29—43 times, more slowly than benzene; so that under corresponding conditions bromobenzene is nitrated a little more slowly than chlorobenzene, the mean difference being about 10%. The effect of solvents on the rate ratios is small and not very regular: the three solvents investigated do not stand in the

same order for chloro- and bromo-benzene. The effect of temperature on the ratios, however, is well marked: the ratios always rise (approach unity) when the temperature is raised, and the ratio in which they change is more than proportional to the increase in the absolute temperature.

TABLE II.

Synopsis of the Ratios for Chloro- and Bromo-benzene.

Temp.	$k_{\text{PhCl}}/k_{\text{PhH}}$			$k_{\text{PhBr}}/k_{\text{PhH}}$		
	Ac_2O .	$\text{CH}_3\cdot\text{CN}$.	$\text{CH}_3\cdot\text{NO}_2$.	Ac_2O .	$\text{CH}_3\cdot\text{CN}$.	$\text{CH}_3\cdot\text{NO}_2$.
0°	0.0273	0.0257	0.0277	0.0261	0.0247	0.0230
25	0.0353	0.0300	0.0312	0.0320	0.0291	—
35	0.0399	0.0328	—	0.0339	0.0322	0.0295

(2) *Orientation in the Nitration of Chlorobenzene and Bromobenzene by Acetyl Nitrate in Various Solvents.*

We have not carried out a very full investigation of orientation in the nitration of chloro- and bromo-benzene under the conditions used in the competitive nitrations for the following reasons. A detailed investigation of orientation in the nitration of toluene and of ethyl benzoate in homogeneous media was recorded in Parts II and III. The results may be compared with those obtained by Holleman for nitration by means of nitric acid without a solvent. The comparison shows that the orientation percentages are only slightly sensitive to changes in the nitrating agent and the medium; so it would have made no significant difference if we had calculated the factors expressing the effect of the original substituents on the probability of substitution in the several nuclear positions by means of our rate ratios and Holleman's orientational data interpolated to the proper temperatures, instead of specially determining the orientational proportions under conditions strictly corresponding to those of the rate experiments. Furthermore Holleman's results show, and ours for toluene as far as they go confirm, that when the temperature is changed the proportions of isomerides exhibit a shift which is in the direction, and of about the magnitude, of the shift calculated by the theory of Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 118; cf. Bradfield and Jones, *J.*, 1928, 1006, 3073); so that, for the purpose of reducing orientational data to the correct temperature for combination with the rate ratios we might without any real loss of accuracy have used the theory, thus avoiding numerous experiments.

We felt that it was not entirely safe to assume that these possible simplifications, which are easy to see in retrospect, can be applied in new examples, and we have therefore carried out a skeleton study of orientation in the homogeneous nitration of chloro- and bromobenzene. This work makes it quite clear that, in these cases also, the effects arising from a change in the nitrating medium are small, and those due to changes of temperature can be predicted sufficiently accurately from either Scheffer's theory or Holleman's results.

Analysis.—Thermal analysis was adopted, clearing points rather than freezing points being employed, however, as is now usual for binary mixtures. Artificial mixtures of *o*- and *p*-chloronitrobenzene and of *o*- and *p*-bromonitrobenzene containing no other compound could be analysed with an accuracy of 0.2%.

The separation of mixtures of *o*- and *p*-chloro- or -bromo-nitrobenzene from accompanying halogeno- and 2 : 4-dinitrohalogeno-benzene was effected by distillation under reduced pressure, controlled, on the one hand, by estimations of nitroxyl with the aid of titanous chloride, and on the other, by m. p.'s. Analysis following such a separation involved errors up to 1%.

Nitration.—A mixture of nitric acid (0.3 g.-mol.) and acetic anhydride (0.3 g.-mol.), prepared at 0°, was added with stirring to a solution of the halogenobenzene (0.2 g.-mol.) in the solvent (90 c.c.) at the necessary temperature. The "solvent" was either more acetic anhydride, or acetonitrile or nitromethane, and the temperature was 0° or 25°. The product was worked up, as for the competitive nitrations (except that here no benzene had to be removed), and the mononitro-compounds were isolated and analysed as described above.

Results.—These are given in the last two sections of Table III under the side-heading "This paper." Each recorded figure is the mean of duplicate experiments, which were concordant to within (usually well within) 1%. The observations on chlorobenzene were

made by Dr. W. M. Morgans, to whom we are indebted for his collaboration. The remainder of the table is occupied by Holleman's results and those of this series for toluene and ethyl benzoate, and Holleman's values for chloro- and bromo-benzene, in illustration of the foregoing remarks on the influence of changes of the nitrating medium on the orientation of the reaction.

TABLE III.

Effect of Changes of Nitration Medium and Temperatures on the Orientation of Substitution, and New Results for Orientation in the Homogeneous Nitration of Chlorobenzene and Bromobenzene.

Ref.	Nitration medium.	Temp.	Proportions of isomerides (%).		
			<i>o</i> -.	<i>m</i> -.	<i>p</i> -.
<i>Toluene.</i>					
Holleman	HNO ₃ (heterogeneous)	+ 30°	55.6	2.7	41.7
"	" "	0	56.0	3.1	40.9
"	" "	+ 60	57.5	4.0	38.5
Part II	AcNO ₃ in Ac ₂ O	0	58.1	3.7	38.2
"	" "	+ 30	58.4	4.4	37.2
"	HNO ₃ in MeNO ₂	+ 30	58.5	4.4	37.1
<i>Ethyl benzoate.</i>					
Holleman	HNO ₃ (heterogeneous)	- 40	25.5	73.2	1.3
"	" "	0	28.3	68.4	3.3
"	" "	+ 30	27.7	66.4	5.9
Part III	AcNO ₃ in Ac ₂ O	+ 18	24.1	72.0	4.0
<i>Chlorobenzene.</i>					
Holleman	HNO ₃ (heterogeneous)	- 30	26.9	0.0	73.1
"	" "	0	30.1	0.0	69.9
This paper	AcNO ₃ in MeCN	0	28.8	0.0	71.2
"	" "	+ 25	30.2	0.0	69.8
"	" " MeNO ₂	0	29.0	0.0	71.0
"	" " "	+ 25	30.2	0.0	69.8
<i>Bromobenzene.</i>					
Holleman	HNO ₃ (heterogeneous)	- 30	34.4	0.0	65.6
"	" "	0	37.6	0.3	62.1
This paper	AcNO ₃ in Ac ₂ O	0	38.5	0.0	61.5
"	" " "	+ 25	42.0	0.0	58.0

For the purpose of calculating the factors by which the chlorine and bromine atoms in chloro- and bromo-benzene change the rate of nitration in the different nuclear positions of these molecules, we shall, in view of the above discussion and the data in Table III, adopt certain values for the orientation proportions obtaining in homogeneous nitration. These adopted values are in Table IV. They are obtained from the new observations recorded in Table III by, first, disregarding the small and uncertain effects of changes of solvent, and secondly, smoothing the temperature effect, partly with the aid of Holleman's more numerous data for the temperature dependence of orientation, and partly by means of Scheffer's relation.

TABLE IV.

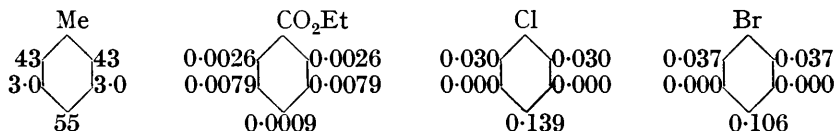
Percentages of Isomerides formed in the Nitration of Chloro- and Bromo-benzene by Acetyl Nitrate.

Temp.	Chlorobenzene.		Bromobenzene.	
	<i>o</i> -.	<i>p</i> -.	<i>o</i> -.	<i>p</i> -.
0°	28.2	71.8	39.0	61.0
25	31.0	69.0	41.4	58.6
35	32.1	67.9	42.4	57.6

(3) *Partial Rate Factors for the Nitration of Chlorobenzene and Bromobenzene by Acetyl Nitrate.*

A partial rate factor is the factor by which the orienting substituent changes the specific rate of substitution in an individual nuclear position. The partial rate factors for the

nitration of chloro- and bromo-benzene can be calculated from the velocity and orientational data of Sections 1 and 2. The rate ratios have simply to be multiplied by orientational fractions (percentages divided by 100) and certain statistical factors, *viz.*, 3 for ortho- and 6 for para-positions. The factors thus calculated for the ortho- and para-nitration of chloro- and bromo-benzene in the three solvents and at the three temperatures used are given in Table V. For comparison with former results we can interpolate the data for acetic anhydride as solvent to 18°, the temperature at which the nitration of ethyl benzoate was examined in this solvent. We thus obtain the comparisons shown in the following formulæ :



The figures illustrate what is already known qualitatively (Part I, *loc. cit.*), *viz.*, that, although substituents of class 3 are *op*-orienting like those of class 1, yet the former work by differential deactivation and not as in class 1 by differential activation; the opposite kind of differential deactivation leads to the *m*-orientation of class 2.

TABLE V.

Partial Rate Factors for the Nitration of Chloro- and Bromo-benzene by Acetyl Nitrate.

Temp.	Chlorobenzene.			Bromobenzene.		
	Ac ₂ O.	CH ₃ ·CN.	CH ₃ ·NO ₂ .	Ac ₂ O.	CH ₃ ·CN.	CH ₃ ·NO ₂ .
<i>Ortho-position.</i>						
0°	0.0231	0.0217	0.0235	0.0305	0.0289	0.0269
25	0.0329	0.0280	0.0291	0.0397	0.0361	—
35	0.0385	0.0317	—	0.0431	0.0409	0.0375
<i>Para-position.</i>						
0	0.118	0.110	0.120	0.0955	0.0904	0.0842
25	0.146	0.124	0.129	0.112	0.102	—
35	0.162	0.135	—	0.117	0.111	0.102

The Temperature Effect.—Concerning the effects of conditions, the partial rate factors are seen to vary with the solvent, though neither largely nor very regularly. They vary both largely and regularly with the temperature, however, increasing as the temperature is raised. The change between 0° and 35° is in a number of cases of the order of 50%, and it is generally greater for the smaller partial rate factors than for the larger ones. Qualitatively, this is the type of variation which would be obtained if the orienting substituent affected the rates of reaction at the several nuclear positions by changing the energies, rather than the entropies, of activation. We can form an estimate of the extent to which this happens, because, if *only* the energy were changed, then, *F* being a partial rate factor, $-T \log F$ should be independent of temperature. Corresponding to the values of *F* in Table V, values of $-T \log F$ are set out in Table VI. They are constant enough to enable us to

TABLE VI.

Values of $-T \log F$ for the Nitration of Chloro- and Bromo-benzene by Acetyl Nitrate.

Temp.	Chlorobenzene.			Bromobenzene.		
	Ac ₂ O.	CH ₃ ·CN.	CH ₃ ·NO ₂ .	Ac ₂ O.	CH ₃ ·CN.	CH ₃ ·NO ₂ .
<i>Ortho-position.</i>						
0°	447	454	445	414	421	430
25	443	462	456	418	430	—
35	436	462	—	421	428	439
<i>Para-position.</i>						
0	254	261	252	279	286	294
25	250	270	265	282	295	—
35	244	269	—	287	295	305

conclude that at least the main effect of the original substituent is on the energy of activation. For instance, between 0° and 35° the absolute temperature is varied over a range of 13%; but the average variation of $-T \log F$ between the same two temperatures is only 2.5%. This latter variation exceeds the experimental error in the determination of F , but there can be no doubt that F varies with T in such a way that most of the change in T is compensated by an opposite change in $-\log F$; the fact that this compensation is nearly complete means that nearly the whole effect of the substituent is concerned with the energy of activation of substitution in the several nuclear positions.

(4) *Relative Rates of Nitration of Fluorobenzene and Benzene by Means of Acetyl Nitrate in Acetic Anhydride and Acetonitrile at 0°, 25°, and 35°.*

Our work on fluoro- and iodo-benzene is less accurate than the foregoing; indeed, that on iodobenzene is hardly more than qualitative. It should be emphasised that for neither of these two halides do we claim to establish standard values with regard to their rates of nitration, and our only reason for including reports of the experiments is that they appear to establish a remarkable relationship between the rates of reaction of the four phenyl halides.

In the case of fluorobenzene our method (for purely practical reasons) was to carry out competitive nitrations of fluorobenzene and bromobenzene. Having thus determined the ratio of the rates of nitration of these substances, we could relate the rate of nitration of fluorobenzene to that of benzene with the aid of the known relation between the rates of nitration of bromobenzene and benzene.

Analysis.—In these competitive nitrations the analytical method was in principle known, since the fluorobenzene simply took the place of the benzene in the previously studied competitive nitrations of bromobenzene and benzene. Total nitroxyl was determined by reduction with titanous chloride. Bromonitrobenzenes were determined by alcoholysis of the total halogenonitrobenzenes, and subsequent estimation of the bromide ion. The difference of the two values represents the fluoronitrobenzenes. These processes were checked with satisfactory results by using artificial mixtures.

Nitrations.—Fluorobenzene was prepared by Balz and Schiemann's method (*Ber.*, 1927, 60, 1186) as modified by Le Fèvre and Turner (*J.*, 1930, 1160), and was carefully fractionated.

"Dummy" nitrations, carried out to test the effect of solvent nitration on the estimated proportion of fluoronitrobenzene, showed that this error, although much larger than for the competitions between benzene and bromobenzene, did not amount to more than a few units %.

The general method of nitration was as follows. A mixture of nitric acid (0.0187 g.-mol.) and acetic anhydride (0.0187 g.-mol.) was made at 0° and diluted with the solvent (excess of acetic anhydride or acetonitrile, usually 3 c.c.). This was added with mechanical stirring to a solution of fluorobenzene (0.025 g.-mol.) and bromobenzene (0.025 g.-mol.) in the same solvent (usually 10 c.c.) at the required temperature (0°, 25°, or 35°), and the mixture was kept at this temperature for the necessary time (0.5—1.0 hour), and then poured on ice. After the hydrolysis of the acetic anhydride, the aromatic products were extracted with ether and the extract was well washed with water, urea solution, water, nitron acetate solution, and water successively. This procedure was adopted, instead of extraction from an alkaline solution, because the fluoronitrobenzenes are rather easily hydrolysed.

The urea and nitron washings were tested for nitroxyl by means of titanous chloride: the amount found was usually less than 1% of the aromatically bound nitroxyl. In some experiments the ethereal extract was also washed with sodium hydrogen carbonate solution, which was subsequently found to contain very little nitroxyl. By working through all these processes with solutions of *o*- and *p*-fluoronitrobenzenes in nitric-acetic anhydride, it was ascertained that not more than 2% of the fluoronitro-compounds is lost by hydrolysis. The extract was finally dried and distilled through Dufton columns, in order to remove ether and some of the fluorobenzene, and the residue was analysed for nitroxyl and alcoholysable bromine as described. In one experiment the bromobenzene was replaced by chlorobenzene.

Results.—These are in Table VII, the arrangement of which corresponds to that of Table I, except that the figures in the last column are calculated from those in the column before

with the aid of the ratios of Table II. In all experiments the nitric acid used was Kahlbaum's, and it was not redistilled.

TABLE VII.

Competitive Nitration of Fluorobenzene and Bromobenzene (or Chlorobenzene) by Means of Acetyl Nitrate in Solvents.

Initial Materials: Fluorobenzene, 0.0250 g.-mol. Bromobenzene (or chlorobenzene), 0.0250 g.-mol. Nitric acid, 0.0187 g.-mol. Acetic anhydride, 0.0187 g.-mol. (initially mixed with the nitric acid). "Solvent" = acetic anhydride additional to the above, or acetonitrile (quantities tabulated).

Expt. No.	Time (hrs.)	Solvent (g.-mol.)	Products (g.-mols.).		R.	$\frac{k_{\text{PhF}}}{k_{\text{PhBr}}}$	$\frac{k_{\text{PhF}}}{k_{\text{PhH}}}$
			$\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$	$\text{C}_6\text{H}_4\text{F}\cdot\text{NO}_2$			
Solvent: Acetic anhydride. Temp.: 0°.							
85	1.0	0.139	0.000692	0.00362	5.23	5.57	0.145
86	"	"	0.000540	0.00292	5.39	5.68	0.148
87	0.5	"	0.000391	0.00221	5.65	5.87	0.153
88*	1.0	"	0.000968†	0.00503	5.20	5.69	0.155
Solvent: Acetic anhydride. Temp.: 25°.							
90	1.0	0.139	0.000625	0.00310	4.96	5.23	0.167
91	"	"	0.000974	0.00459	4.71	5.10	0.163
Solvent: Acetic anhydride. Temp.: 35°.							
92	1.0	0.139	0.000652	0.00276	4.23	4.43	0.150
93	"	"	0.000931	0.00393	4.22	4.51	0.153
94	0.5	"	0.000361	0.00154	4.26	4.37	0.148
95	1.0	"	0.000636	0.00300	4.72	5.15	0.174
96	"	"	0.000208	0.00101	4.85	4.93	0.167
Solvent: Acetonitrile. Temp.: 0°.							
99	1.0	0.250	0.000735	0.00377	5.13	5.48	0.135
100	"	"	0.000745	0.00379	5.09	5.44	0.134
Solvent: Acetonitrile. Temp.: 25°.							
101	1.0	0.250	0.001497	0.00650	4.34	4.88	0.142
102	"	"	0.001710	0.00661	3.87	4.32	0.126
Solvent: Acetonitrile. Temp.: 35°.							
103	1.0	0.250	0.001919	0.00838	4.36	5.11	0.164
104	"	"	0.002040	0.00859	4.21	4.94	0.158

* Chlorobenzene used in place of bromobenzene.

† $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$.

A synopsis of the mean ratios, $k_{\text{PhF}}/k_{\text{PhH}}$, is given in Table VIII. It will be observed that the variation with temperature is not regular. In view of the regularity of the temperature effect in the more accurately investigated rate-ratios for chloro- and bromobenzene, we take this to mean that the results for fluorobenzene are only semi-quantitative, any of the values recorded being subject to a possible error of the order of 10%.

TABLE VIII.

Synopsis of the Rate Ratios for Fluorobenzene.

Solvent.	$k_{\text{PhF}}/k_{\text{PhH}}$		
	0°.	25°.	35°.
Acetic anhydride	0.149	0.165	0.158
Acetonitrile	0.134	0.134	0.161

(5) *Relative Rates of Nitration of Iodobenzene and Benzene by Means of Acetyl Nitrate.*

Our few experiments on the competitive nitration of iodobenzene and benzene were carried out by the methods described in Section 1, but, as the analytical method, which worked so satisfactorily in those experiments, gave very poor results in the present example, our data have little quantitative value. Nevertheless, they seem to establish the qualitative relations referred to in Section 6.

Analysis.—No difficulty was experienced in the estimation by the use of titanous chloride of nitroxyl in mixtures of *o*- and *p*-iodonitrobenzenes, alone or mixed with benzene, nitrobenzene,

and iodobenzene. The estimation of iodonitrobenzenes by methyl-alcoholysis was, however, unsatisfactory: it tended to give slightly low results with the iodonitrobenzenes themselves, and very high results (up to 15% high) when these substances were treated in admixture with excess of iodobenzene and nitrobenzene, notwithstanding that iodobenzene did not appear to be more than slightly alcoholysed when treated alone with the same reagent. In spite of this we used the method, as there was no intention at the time of seeking more than the order of magnitude of the rate ratio.

Nitration.—Nitrations were carried out, and the products worked up, just as for the competitive nitrations of chlorobenzene and benzene (Section 1).

Results.—These are in Table IX. The values of $k_{\text{PhI}}/k_{\text{PhH}}$ are within the range 0.1—0.3, and in spite of the generally poor consistency, may be taken to indicate an order of magnitude of 0.2, no distinctions being possible with respect to temperature and solvent.

TABLE IX.

Competitive Nitration of Iodobenzene and Benzene by Means of Acetyl Nitrate in Solvents.

Initial Materials: Benzene, 0.0500 g.-mol. Iodobenzene, 0.0500 g.-mol. Nitric acid, 0.0375 g.-mol. Acetic anhydride, 0.0375 g.-mol. (initially mixed with the nitric acid). "Solvent" = acetic anhydride additional to the above, or acetonitrile (quantities tabulated).

Expt. No.	Time (hrs.).	Solvent (g.-mol.).	Products (g.-mols.).		R.	$\frac{k_{\text{PhI}}}{k_{\text{PhH}}}$
			PhNO ₂ .	C ₆ H ₄ I·NO ₂ .		
Solvent: Acetic anhydride. Temp.: 0°.						
76*	1.0	0.275	0.00089	0.000154	0.173	0.172
77*	8.0	"	0.00177	0.000248	0.140	0.138
78	1.0	"	0.00532	0.000620	0.116	0.111
79	"	"	0.00110	0.000302	0.273	0.271
Solvent: Acetic anhydride. Temp.: 25°.						
80	1.0	0.275	0.00644	0.000120	0.187	0.177
Solvent: Acetic anhydride. Temp.: 35°.						
82	1.0	0.275	0.00309	0.000708	0.229	0.223
Solvent: Acetonitrile. Temp.: 25°.						
83	1.0	0.500	0.0121	0.00346	0.284	0.258

* Freshly distilled nitric acid of low nitrous acid content used.

(6) *Relative Rates of Nitration of the Four Halogenobenzenes.*

From the results of Sections (1), (4), and (5), we can compare the rates of nitration of the halogenobenzenes under constant conditions, *e.g.*, for nitration by means of acetyl nitrate in acetic anhydride as solvent at 18°:

Nitration rate (PhH = 1)	PhF	PhCl.	PhBr.	PhI.
	0.15	0.033	0.030	~0.18

The rate passes through a minimum, and although both the extremes of the series need further investigation, it seems unlikely that future experiments will change the qualitative result.* We may therefore consider its significance.

In the theory of organic reactions it is recognised that in the most general case a group can exert four distinct polar effects; these comprise two polarisations, termed (1) the inductive, and (2) the mesomeric, effect, and two polarisabilities, *viz.*, (3) the inducto-meric, and (4) the electromeric, effect. The two polarisabilities (3) and (4) may be disregarded in considerations of chemical equilibria, which depend only on unenergised ground states. Effects (2) and (4), which depend on conjugation, can be excluded unless the appropriate unsaturation is present.

The order of the halogens with respect to these polar effects has already been con-

* The qualitative relations, PhH ≫ PhF ~ PhI ≫ PhCl > PhBr, are confirmed in the next paper, which describes an investigation by a different method.

siderably discussed, and much that was obscure has been cleared up by the work of Bennett and of Branch particularly. As the rather voluminous literature of the subject can easily be traced through the more recent papers by these authors (since 1933), we do not here review it, but merely summarise the accepted conclusions. These are as follows. (1) From the influence on chemical equilibria of halogens in saturated aliphatic combination, it follows that the inductive effect of halogens is electron-attracting ($-I$), as it should be theoretically, and is in the order $F > Cl > Br > I$. (2) From the influence on chemical equilibria of *op*-halogens in direct combination with the benzene ring, it follows that the mesomeric effect of halogens is electron-repelling ($+M$), as it must be theoretically, and is in the order $F > Cl > Br > I$. (3) The last-named group of equilibria show that the *differential* mesomeric effect amongst the halogens so far outweighs the differential inductive effect that processes which require an increased electron-density at the reaction site are suppressed least by fluorine and most by iodine, an inversion of the relationship which would obtain if the differential inductive effect controlled the order. These three conclusions account for the whole of the observations of the effects of halogens on equilibria.

The interpretation of the influence of halogens on reaction velocity is complicated by the additional presence of polarisability effects. The data hitherto considered in this connexion relate practically exclusively to the influence of halogens directly bound to the benzene ring on reactions in an aromatic side chain. For such examples we must expect both polarisabilities, the inductomeric and the electromeric effects, to contribute to the observed result. Actually, the observed result is remarkably uniform: as before, reactions which require electrons to be supplied are suppressed, least by fluorine and most by iodine; and correspondingly, those that want electrons withdrawn are assisted, least by fluorine and most by iodine. It follows that, whatever the polarisability effects may be doing quantitatively in these examples, they are not qualitatively upsetting the relationships which would in their absence have been established by the polarisations. It will be suggested below that this is because the polarisability effects are too weak.

Our experiments bring data of another type into the field under review: they relate to the effect of aromatically bound halogens on a *nuclear* reaction—one which strongly demands electrons. Here we find the old uniformity upset: the sequence determined by a dominating differential mesomeric effect has partly reverted to that which would be produced by the inductive effect if the mesomeric effect disappeared. Now we cannot, of course, suppose that the mesomeric effect does, even partly, disappear: like the inductive effect, it is a permanent property of the molecule. The observed disturbance must therefore be attributed to the incursion of polarisability effects, which, for nuclear substitution, in contrast to side-chain reactions, are strong enough to become qualitatively evident. The observed result would be explained if the extra effect due to the polarisabilities were an electron-release, as theoretically it must be, and were in the order $I > Br > Cl > F$.

It is not an unexpected conclusion that polarisability effects are more prominent in aromatic nuclear than in side-chain reactions; for in nuclear reactions, the reagent, whose field excites polarisability effects, comes in closer proximity to the influencing group. Furthermore, in ortho- and para-substitution, with which alone we are concerned in the nitration of halogenobenzenes, the reagent attacks positions particularly favourable to the excitation of a strong electromeric effect. Apart from any special cases, the electromeric effect is recognised to be generally prominent in aromatic nuclear substitution, which forms one of the best known illustrations of its distinctive operation. It was, for instance, shown in Part I that the two polar effects whose co-existence is essential in the interpretation of the connexion between orientation and reaction rate are inductive polarisation and electromeric polarisability with their fundamentally distinctive time relations.

Therefore we interpret our results as making it probable that the modification attributed to increased polarisability is due mainly to increased electromeric polarisability; and that the sequence given above for the total polarisability effect is the sequence for the electromeric effect ($+E$): $I > Br > Cl > F$. Bennett has assumed the opposite sequence on the grounds that the electromeric and mesomeric effects "have a common origin" (J., 1935, 1830), but we cannot see that common origins necessitate common behaviour; for example, mesomeric energy and polarisation have a common origin but are far from parallel in be-

haviour. Nevertheless it must be admitted that the conclusions to which our experiments inevitably lead relate only to the total polarisability effect, and that in specialising these conclusions to the electromeric effect we also are supplementing deduction by personal judgement.

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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