CCIII.—*The Laws of Aromatic Substitution.   Part V.
The Directing Effect of Electrolytically Dissociated
Groups.**

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IN previous communications of this series (*J. pr. Chem.*, 1902, **66**,
321; 1905, **71**, 497; 1907, **76**, 165, 185) it was shown, *inter alia*,
that the position in which a second substituent will enter a mono-
substituted benzene ring (whether *op-*, or *m-*) can be unequivocally
predicted from the affinity demand of the first substituent.   In
subsequent papers, a more general theory of reactivity was evolved,
in which, beside the *affinity demand* (the " quantitative factor " $= q$),
the varying *nature of the affinity* of atoms (" polar factor " $= p$) and
their *steric effects* (" steric factor " $= s$) were taken into consideration.
A review of the whole subject has recently been published in
Chemistry and Industry (1925, **44**, 246).

* A brief preliminary communication of the ideas and the scope of the
experiments contained in this paper is to be found in *Chem. and Ind.*, 1926,
45, 43.

Whereas generally account must be taken of all three factors, there are cases, and even classes, of reactions where one or even two of them can be neglected. Thus the steric hindrance exercised by a first substituent in benzene affects substitution in the o-position, but its effect, and still more the difference of its effects, in the m- and p-positions are negligible. On the other hand, the polar effect of most substituents cannot be neglected in *any* position, but even here the *difference* of their influence on the m- and p- carbon atoms could be ignored in all the cases hitherto examined. This has been definitely established by numerous observations; thus, not even an accumulation of "negative" groups such as obtains in bromocyanophenylnitromethane, $C_6H_5 \cdot CBr(CN) \cdot NO_2$, can prevent the essentially exclusive op-substitution predicted from the affinity demand of the substituent (compare *J. pr. Chem.*, 1902, **66**, 321).

In view of this, an observation by Noelting and Kregczy (*Bull. Soc. chim.*, 1916, **19**, 355) seemed at first sight surprising. These authors nitrated diethylbenzylamine in sulphuric acid solution and obtained 35 to 40% of the m-nitro-derivative. Since the affinity demand of the substituent should lead to op-nitration only, this experiment has now been repeated, and through the use of very accurate methods of separation the yield of the m-nitro-compound has been found to be even higher, *viz.*, 44% of the isomerides formed.

This result could not be ascribed to nitration of the *free base*, since the hydrolysis of such a relatively strong base in an excess of strong sulphuric acid would be negligible. Neither could it be due to nitration of the *salt*, which should occur only in the o- and p-positions. Reference to the work of Walden and others having shown that salts possess a high degree of electrolytic dissociation in strong sulphuric acid, even at high concentrations, the question whether m-nitration of the *electrolytic ion* would be in accordance with the theory was next considered. Concerning the relative polar effects of different atoms, it had already been pointed out (J., 1909, **95**, 719) that an electric charge may be regarded as the most polar element. The meaning of this statement may be briefly explained.

Discarding all speculations concerning the origin and nature of chemical affinity, what we really *know* about it appears to be this : 1. Chemical affinity, like gravitational and magnetic forces, is *some* function of an atom. 2. Although atoms contain positive and negative electrical charges, there is no compelling reason for assuming that chemical force, any more than gravitational or magnetic force, is electrostatic. 3. The behaviour of atoms, not only towards electrical charges, but also *towards one another*, proves that chemical affinity varies in different atoms both in *amount* and in *kind*. The difference in kind is most pronounced between the

3 G*

atoms of the elements situated at the opposite ends of a period in the periodic table and *gradually* diminishes with the number of intervening members of the period. The more two atoms differ as to the kind of their affinity, the greater is the difference in their tendencies to combine, either with a third atom located towards either end of a period, or with an electrical charge of a given sign.

We may conclude that the variation in kind exhibited by chemical affinity implies a *gradual transition in polarity*, involving a change of sign at a given point in a period. *This gradual transition, if extended far beyond the terminal members of a period, would lead to polarity in its extreme form—electropolarity.* In other words, *whilst electropolarity exists only in two extreme kinds of opposite sign, chemical polarity, gradually varying in kind, bridges a limited central region in the wide gap between the two electropolar extremes.* Thus, in view of the strong affinity of fluorine for an electron as well as for lithium, the corresponding period might be written :

$$\ominus \quad \ldots \ldots \quad \overset{\overleftarrow{}\overset{-}{}\overset{+}{}\overrightarrow{}}{\text{Li,Be,B,C,N,O,F}} \quad \ldots \ldots \quad \oplus,$$
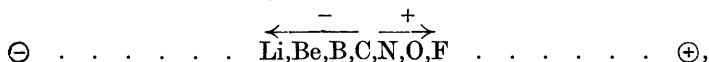
polar attraction between two members of opposite sign, and polar repulsion * between a given member and a more polar one of the same sign, running parallel with their distance apart within the period. This is what is meant by the polar factor p or " polar effect," or, to use the term recently introduced by Lapworth, by "general polarity."

The polar attraction by a negative charge, and the polar repulsion by a positive charge, of a halogen atom, nitro-group, etc., therefore considerably exceed the corresponding effects of an electrically neutral atom or group on these atoms or groups. Accordingly, since the polarity of such a charge is transmitted to different nuclear carbon atoms in different degrees ascertainable from the theory itself (J., 1910, **97**, 85), a positive charge tends to direct an entering nitro-group, etc., to the least affected nuclear carbon atom, whereas a negative charge tends to direct it to the most affected carbon atom. In the benzoic anion and the diethylbenzylammonium kation, for instance, the nuclear atoms are affected in the order $o->p->m-$ (on account of the direct neutralisation of residual affinity between the p-atoms which results in the *direct* transmission of the polar effect from the substituted atom to the p-atom) (see *loc. cit.*), so that the overpowering p of the electrical charge must favour substitution in the order $o->p->m-$ in the benzoic anion and $m->p->o-$ in the diethylbenzylammonium kation. Besides, it must have an acceler-

* " Repulsion " is used in a relative sense only, to denote a reduced potential at corresponding points in the field of mutual attraction of the atoms. The affinity of neon, whilst much smaller in amount than that of fluorine, must be even more polar in kind.

ating effect in the anion and a retarding effect in the kation, as compared with the corresponding neutral compound.*

This is exactly what has been found to occur. Electrolytically dissociated sodium benzoate is chlorinated by hypochlorous acid (Lossen, D.R.-P. 146, 174) with remarkable ease and in the order $o->p->m-$, whereas benzoic acid itself is brominated, by hypobromous acid, slowly and in the meta-position (Stark, *Ber.*, 1910, **43**, 473). Electrolytically dissociated benzyldiethylammonium hydrogen sulphate is nitrated in the meta-position and more slowly than the undissociated salt, since m-substitution in an approximately normal solution amounts to 44% only, although the degree of dissociation of binary salts in strong sulphuric acid at a corresponding concentration is of the order of 80 or 90%.

The theoretical support thus afforded for the assumption that the observed *meta*-nitration is due to the electrolytic ion has been supplemented by direct experimental proof. The assumption requires that increased electrolytic dissociation should lead to increased *meta*-substitution, and *vice versa*. This has been found to be the case. At double the dilution, 52% of the m-nitro-derivative was formed, the increase being in approximate agreement with the value calculated from the increase in dissociation required by Sugden's cubic root law on the basis of *exclusive* m-nitration of the ion and exclusive op-nitration of the undissociated salt (see experimental part); any appreciable op-substitution in the ion and/or m-substitution in the salt would, according to Sugden's law and still more according to other dilution laws, have caused the increase in the amount of m-nitration to be correspondingly below the experimental result. Similarly, the introduction of a common ion by saturation of the nitrating solution with ammonium sulphate resulted in lowering the amount of *meta*-compound formed to 34%. In this case, only an approximate calculation is feasible, but it shows the decrease to be of the right order. If the dissociation of the sulphuric acid solvent itself (to which Dr. Sugden has kindly called the authors' attention) produced a common ion, then the change in m-nitration with varying concentration would be even greater than required by Sugden's law.

Complications such as have now been dealt with, where the uniquely strong p of an electrical charge conflicts with and outweighs q, can occur only where the charge is carried by an atom separated from the nucleus by *one* intervening atom. When the charged

* This effect of the polar factor on the *velocity* of aromatic substitution has repeatedly been emphasised by one of the authors (*e.g.*, *Ber.*, 1906, **39**, 2016; *J. pr. Chem.*, 1907, **76**, 200), and its electronic equivalent recently by Robinson (this vol., p. 410) and co-workers.

atom is directly attached to the nucleus, p and q support each other. When the charged atom and the nucleus are separated by two or more atoms, the polar factor even of an electrical charge may be presumed to become negligible, at least as regards its effect on m- versus p-substitution.

The present results appear to supply a conclusive solution of the problem of m-nitration in solutions of benzylammonium salts and to be in complete agreement with the theory advanced by one of the authors. Apart from this they seem to show, for the first time, a way in which the changes of the " degree of dissociation " can be ascertained without interference from disturbing factors such as variations in viscosity, ionic mobility, and solvation. The results also furnish, perhaps not a final proof, but at least a strong argument against the theory of the complete dissociation of strong electrolytes and of the intramolecular ionisation of undissociated ammonium salts. On these views, the undissociated salt in solution would have to be replaced by its two ions in more or less close proximity. But in this case, the charge on the kation would be substantially nearer to the benzene ring than would the charge on the anion, and though it is perhaps not entirely impossible, it is at least highly improbable that the latter charge could seriously interfere with the transmission to the ring of the pronounced polar effect of the first charge. What appears quite certain, however, is that it could not do so in the case of Robinson's mechanism of transmission. Robinson, who has adopted the electronists' view that an ammonium group is ionised even in the undissociated salt (J., 1922, **121**, 430), attributes *meta*-substitution to a "Lewis" electron shift towards the ammonium group caused by its positive charge (*Chem. and Ind.*, 1925, **44**, 563 ; this vol., p. 410). But such a shift would occur both in the electro-lytically dissociated and in the undissociated state, since in the latter the attraction of the electron by the positive charge would, according to Coulomb's law, be compensated by the repulsion of the more distant anionic charge only to a fractional extent (less than one-quarter). It would be less compensated than a positive charge on carbon in carboxyl, carbonyl, trichloromethyl, or on nitrogen in a nitro-group (since the acid radical is generally recognised to be at a greater distance from ammonium nitrogen than oxygen is from carbon or nitrogen, or than chlorine is from carbon), all these being cases where Robinson (*loc. cit.*) attributes *meta*-substitution to such a positive charge, thus obviously assuming it to be insufficiently compensated. Contrary to the experimental results, Robinson's theory would therefore require *meta*-substitution in the undis-sociated as well as in the dissociated portion, especially since his alternative (conjugation) cannot be applied in this case.

Neglect of the polar and steric factors in classes of reactions where —as has repeatedly been emphasised—they must not be neglected, has recently led several authors to erroneous objections, which will be dealt with in a subsequent communication.

EXPERIMENTAL.

Three series of nitrations of diethylbenzylamine were carried out. The first of these served to establish the best method of separating the isomerides formed. The second series (nitrations 1 to 5 in the table) gave the approximate results obtained by that method, whereas in the final series (nitrations 7 to 10) quantitative values were obtained by the determination of that portion of the *m*-nitro-compound which could not be separated as such.

The nitrations were carried out by Noelting and Kregczy's method (*loc. cit.*), but at −10° to 0° instead of −5° to +5°. Nitric acid (Kahlbaum, " *d* 1·52 ") was used, except in No. 5, where ordinary fuming nitric acid served both as nitrating agent and as solvent. In Nos. 8 and 10, the nitrated mixture was kept at room temperature for 1½ hours, and 4 hours, respectively, instead of the usual 1 hour. To prevent any volatilisation of the nitro-bases formed, the benzene extract containing them was treated with picric acid before evaporation to dryness. The yield of crude nitro-bases was always close to 97·0% of the theoretical, and the picric acid added (2·60, 4·0, 6·71, 7·10, 2·60, 3·417, 6·48, 4·286, and 4·480 g., respectively, in nitrations 1 to 5 and 7 to 10) was either 97% of the theoretical or slightly more. The freezing-point method being untrustworthy in the presence of even small amounts of impurities, and fractional distillation of the free bases having failed, there only remained the following method, involving the use of an analytical balance throughout and weeks of work for each nitration of the final series :

The bulk of the relatively insoluble picrate of the *m*-isomeride was obtained pure by prolonged fractional recrystallisation from alcohol (see Noelting and Kregczy); this was preferably preceded by fractional extraction with small amounts of the solvent. This fractionation was carried especially far in Nos. 1, 8, and 10. In Nos. 2, 3, and 5, the pure picrate of the *p*-nitro-compound was also isolated, by further recrystallisation from glacial acetic acid, to the extent of 1·60, 2·30, and 1·09 g., respectively. The purity of the picrate of the *m*-nitro-compound was established by its correct and constant melting point, by the melting point of a mixture with a sample prepared from *m*-nitrobenzyl chloride and diethylamine, and by its oxidation to *m*-nitrobenzoic acid. The purity of the picrate of the *p*-compound, where isolated, was established by its correct

and constant melting point, and by the melting point of a mixture with synthetic material. The pure picrate, m. p. 122°, of the *o*-nitro-compound could only be obtained synthetically (Noelting and Kregczy give 117°). The *picrate* of diethylbenzylamine itself crystallises in stout, yellow prisms, m. p. 120°. In the final series, the picrate of the *m*-nitro-compound left behind in the *op*-mixture was thus determined : 1 part of the picrate mixture was boiled under reflux with 120 parts of water and 2 parts of potassium permanganate. At intervals of 30 minutes three further additions of 2 parts of permanganate were made, then another after 40 minutes, where-after boiling was continued for 3 hours. After the excess of per-manganate had been destroyed by alcohol, the nitrobenzoic acids were extracted in the usual way, except that any portion held back by manganese dioxide was freed by dissolving the latter in sulphurous acid. The *m*-nitrobenzoic acid was exhaustively separated from its isomerides by fractionation of the barium salts (the relatively insoluble *m*-salt crystallising in its characteristic needles), then of the free acids, then again of the barium salts, and so on as often as was necessary. Traces of benzoic acid, only found in Nos. 8 and 9, were determined by the loss in weight of the acid mixture when heated below 100° to constant weight, the sublimed benzoic acid being subsequently identified. Experiment 6 was carried out to ascertain whether the proportions of the isomeric nitrobenzoic acids obtained by oxidation (whereby about 80% of the theoretical quantity was recovered as crude acids) corresponded exactly with the proportions of the isomeric picrates oxidised. This was found to be the case. Corroboration was obtained by oxidising 2 g. of the picrate of the *o*-nitro-compound under identical conditions, whereby 0·579 g. of pure *o*-nitrobenzoic acid was obtained (76% of the theoretical), whereas 2·50 g. of the *m*-isomeride gave 0·76 g. of acid (79·6%) ; also by boiling 2 g. of *o*-nitrobenzoic acid in 240 c.c. of water with 1·5 g. of potassium hydrogen carbonate and 4 g. of potassium permanganate during 3 hours, whereby 1·789 g. (89·5%) of the unchanged acid was recovered. This proves that, in the particular method employed, undue further oxidation of *o*-, as compared with *m*- and *p*-nitrobenzoic acids, does not occur.

The yields of *m*-compound were calculated in Nos. 1, 7, 8, and 10 on the total separated picrates obtained, less a correction for any excess of picrate (0 to 0·1 g.) used beyond the normal equivalent of 97% of the theoretical quantity, and also for any traces of benzoic acid found and calculated as the picrate of the unnitrated amine. In Nos. 2, 3 and 5, where the picrates of the *op*-mixture had been worked up further for the *p*-compound before its weight was taken, and in No. 9, where this mixture was inadvertently oxidised before

No.	Amine (g.)	Acid (c.c.) H₂SO₄	HNO₃	(NH₄)₂SO₄	Separated picrates (g.)	m-Picrates (g.)	Picrates oxidised (g.)	m-Acid (g.)	o- plus p- Acids (g.)	Benzoic acid (g.)	m-Nitro-compound formed %
1	1·85	11	0·8	0	4·65	1·87	—	—	—	—	>40·92
2	2·75	15	1·2	10	6·86	2·3	—	—	—	—	>33·1
3	4·647	26	2·1	25	11·65	3·978	—	—	—	—	>33·9
4	5·12	25	2·2	25	13·04	Insufficient separation	—	—	—	—	—
5	1·90	0	6	0	4·64	1·74	—	—	—	—	>36·45
6	—	—	—	—	—	—	1·50 p. / 0·75 o- / 0·25 m-	0·08	0·72	—	—
7	2·511	15	1·1	0	6·398	2·446	1·79	0·040 pure { + 0·011 impure	0·440	0	43·95 ± 0·7
8	4·678	25	1·9	25	12·13	3·92	3·28	0·010 impure	0·932	0·026	33·83 ± 0·35
8							2·46	0·008 impure	0·698	0·030	34·30 ± 0·37
9	3·058	39·7	1·3	0	7·95 Unseparated	3·042	?	0·266 pure { 0·01 impure	1·046	0	51·89 ± 0·23
10	3·277	42·2	1·4	0	8·433	3·937	2·24	0·069 pure { 0·007 impure	0·490	0	53·51 ± 0·33

its weight had been *accurately* taken, the yield of m-compound was calculated on the normal yield of separated picrates amounting to 94% of the theoretical. The proportion of m-acid in the separated nitrobenzoic acids gave the percentage of m-picrate in the inseparable portion of the picrates.

The $\pm$ corrections in the last column of the table are due to adding one-half of the small fraction of impure m-nitro-acid to the pure for calculation of the yield. In Nos. 9 and 10 the concentration of the amine in the sulphuric acid was accurately one-half of that obtaining in No. 7. The ammonium sulphate added in Nos. 2, 3, 4, and 8 was in excess of the amount soluble at the nitration temperature. The amount dissolved can be calculated from the following experiment : 15 c.c. of the sulphuric acid and 2·523 g. of the amine gave 17·5 c.c. of solution and 17·3 c.c. at 0°. 6·2 G. of ammonium sulphate gave a clear solution in the above liquid of 20·4 c.c. at 0°; a further 0·2 g. produced a distinct cloudiness (total volume 20·5 c.c.).

The average m-nitration in Nos. 9 and 10 is 52·7%. For an average degree of dissociation of 90% in nitration No. 7, Sugden's cubic root dilution law requires a yield of 50·3% of the m-compound in Nos. 9 and 10, whereas for 80% and 70% dissociation in No. 7, 51% and 51·9% of the m-compound should be obtained in Nos. 9 and 10. Walden's dilution law $(1-\alpha = K/v^{0.45})$ (quoted in Walden, " Leitvermogen der Lösungen," III, 59) requires 52·5, 53·3, and 54·3%, respectively.