270. *The Rate of Chlorination of Anilides and Phenols as affected by Association.*

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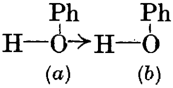
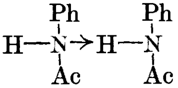
THE ease of *op*-substitution of anilides and phenols is, according to Allan, Oxford, Robinson, and Smith (J., 1926, 403) and Ingold and Ingold (*ibid.*, p. 1310), to be ascribed to the tendency of the nitrogen or oxygen atom respectively to act as an electron source. The fact that the halogenation of the negative phenoxide ion by hypochlorous and hypoiodous acids is many thousand times more rapid than that of the un-ionised phenol (Soper and Smith, J., 1926, 1582; 1927, 2757) is in harmony with this principle. Further, it was shown by Orton and Bradfield (*ibid.*, p. 986) that, in a series of acylanilides in which the acyl group was varied, the more positive the nitrogen atom became as a result of the electron affinity of the acyl group (shown by the ionisation constant of the acid, AcOH), the less rapidly did chlorination occur.

The principle being accepted that the rate of substitution of anilides and phenols is closely dependent on the negativity of the oxygen and nitrogen atoms, a study of the rate of chlorination of associated phenols and anilides should be of interest, as affording evidence for their mode of association from the simple substances. According to Sidgwick (" The Electronic Theory of Valency," 1927, p. 134), association arises through a hydrogen atom acting as acceptor and a nitrogen or oxygen atom as donor, which would result in the atom *a* becoming more positive and *b* more negative by

(I.)



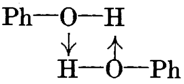
$\mathrm{H{-}\underset{(a)}{\overset{Ph}{O}}{\rightarrow}H{-}\underset{(b)}{\overset{Ph}{O}}}$



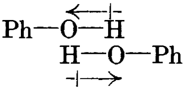
$\mathrm{H{-}\underset{Ac}{\overset{Ph}{N}}{\rightarrow}H{-}\underset{Ac}{\overset{Ph}{N}}}$

(II.)

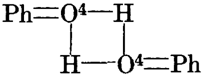
the electron displacement in its direction (I). The molecule as a whole would therefore be more reactive than an unassociated molecule, since one of its oxygen atoms has become more negative. A similar remark applies also to the anilide (II). If, however, the associated molecules tend to become co-ordinated to form ring systems, both oxygen (or nitrogen) atoms tend to become more



(III.)



(IV.)



(V.)

positive and the associated phenol (or anilide) should undergo substitution, *e.g.*, chlorination, more slowly than the unassociated substance (III).

A similar conclusion seems unavoidable even if the association is merely an attraction of dipoles (Smith and Engel, *J. Amer. Chem. Soc.*, 1929, **51**, 2669) and not actual co-ordination (IV).

The mode of association proposed by Sugden ("The Parachor, etc.," London, 1930, 168) to account for the parachor anomaly of associated liquids is a conversion of two or three molecules of the substance into a ring system by single-electron links, represented in the bimolecular formula (V) by short dashes. Here, the oxygen retains its four unbound electrons and shares two with hydrogen as in the unassociated molecule. The negativity of the oxygen atom is therefore similar to that of these atoms in the unassociated molecules, and the reactivity of associated and unassociated molecules might also be expected to be similar.

A comparison of the relative rates of chlorination of associated and unassociated molecules of anilides and phenols may be made in a simple manner by examining the speeds of chlorination, different initial concentrations of these substances being used in an associating solvent. In the more concentrated solutions the degree of association is greater, and a study of the relation of reaction speed to concentration of anilide or phenol will allow of a decision as to the relative reactivities of the associated and unassociated molecules.

Carbon tetrachloride, pentachloroethane, and chlorobenzene were selected as suitable associating solvents, the range of which was restricted by the necessary condition of stability to chlorine. Blank experiments were first carried out using methylacetanilide in pentachloroethane. This anilide shows no association in benzene, chloroform, or ether (Meldrum and Turner, J., 1910, **97**, 1605) and doubling its initial concentration whilst keeping the initial concentration of chlorine the same should therefore double the initial speed, and halve the time of one-third disappearance of chlorine. The bimolecular velocity coefficients obtained increased with time, showing a drift of some 10—15% from 30—50% change. That this is probably due to the medium effect of the polar hydrogen chloride produced in the reaction, was confirmed by its addition initially to the reaction mixture, an enhancement of the speed being then observed. In the following table, only the initial molar concentrations and time of one-third reaction are therefore recorded.

Chlorination of methylacetanilide in pentachloroethane at 20°.

Initial [Cl_2].	Initial [anilide].	$t_{1/3}$, hrs.
0·0107	0·0340	136
0·0105	0·0674	62

Similar normal behaviour was observed for an ether, *viz.*, diphenyl ether, in chlorobenzene. Five-fold increase of its initial concentration decreased the time of half-decomposition from 255 to 47 mins. :

Chlorination of diphenyl ether in chlorobenzene at 20°.

Initial [Cl_2].	Initial [ether].	$t_{1/2}$, mins.
0·0120	0·0485	255
0·0120	0·2425	47

Since, when association is absent, the course of chlorination appears to be normal in these solvents, anomalous relations between the time of half-disappearance of chlorine and the initial concentration of anilide and phenol may be attributed to the different reactivities of the associated and unassociated molecules. The results at 20·0° for acetanilide, which is known to associate in benzene (Beckmann, *Z. physikal. Chem.*, 1890, **6**, 437 ; Landsberger, *Z. anorg. Chem.*, 1898, **17**, 422), and for *p*-chlorophenol, which associates in naphthalene (Auwers, *Z. physikal. Chem.*, 1895, **18**, 595; Auwers and Orton, *ibid.*, 1896, **21**, 337), are given in the following table.

In each case doubling the concentration of the anilide or phenol causes a decrease in the time of half-decomposition, *i.e.*, a 3- to 7-fold increase in the speed of reaction. The associated molecules must therefore be more reactive than the unassociated, and one of the nitrogen or oxygen atoms, respectively, more negative in the associated than in the unassociated state. This is in harmony with the singly co-ordinated mode of association proposed by

Acetanilide in pentachloroethane.

Initial [Cl_2].	Initial [anilide].	$t_{1/2}$, mins.
0·00350	0·01662	1·4
0·00455	0·00831	10·0

Acetanilide in chlorobenzene.

Initial [Cl_2].	Initial [anilide].	$t_{1/4}$, mins.
0·0037	0·00374	4·10
0·0037	0·00749	1·50
0·0037	0·0112	0·53

p-*Chlorophenol in carbon tetrachloride.*

Initial [Cl_2].	Initial [phenol].	$t_{1/2}$, mins.
0·00768	0·0333	21
0·00760	0·0166	79

Sidgwick, and definitely negatives the idea of double co-ordination (III). An alternative mechanism of association which would be in agreement with the observed results for acetanilide may be advanced, in which the donating atom is the oxygen atom of the acetyl group. Here single as double co-ordination would increase the negativity of the nitrogen. No such alternative mode of association exists for phenols.

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