

**47. The Formation and Structure of Some Organic Molecular Compounds.**

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The formation of the deeply coloured molecular compounds from quinones and nitro-compounds, on the one hand, and certain unsaturated hydrocarbons and their derivatives, on the other, is ascribed to a complex molecule, essentially ionic in character, which is formed from the two components by an electron transfer from the unsaturated hydrocarbon or its derivative (donor A) to the quinone or polynitro-compound (acceptor B) according to the net reaction  $A + B \rightleftharpoons [A]^+[B]^-$ .

A brief quantum-mechanical discussion of this process is put forward, and the following points are then discussed in support of the theory: (a) The structure and the rate of formation of the molecular compounds. (b) The heats of formation. (c) The equilibrium in solution (and the influence of hydrostatic pressure upon it). (d) The colour of the molecular compounds. (e) The crystal structure and intermolecular distances. (f) The dipole moment in solution. (g) The electrical conductivity in solution. (h) Their relationship to the semiquinones and other free radicals and radical ions.

MOLECULAR compounds have long been known and have found many applications in organic chemistry, particularly in recent years. In spite of this their structure has remained somewhat obscure.

The field of even the purely organic molecular compounds is a very large one (Pfeiffer, "Organische Molekülverbindungen," Stuttgart, 1927), and we shall confine ourselves to those typical classes where the colour of the molecular compound is deeper than that of either of the two components. The first group includes compounds of benzoquinones, or substances derived from them, with aromatic hydrocarbons, amines, or phenols, the quinhydrones being the best known representatives in this group. The second large group includes molecular compounds of nitro-compounds with unsaturated hydrocarbons and their derivatives: picrates are a well-known example.

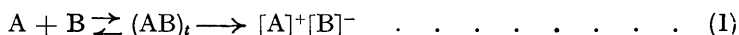
Two main ideas have been put forward to explain the structure of these molecular compounds: (i) the formation to some extent of covalent links between the two components (cf. Moore, Shepherd, and Goodall, J., 1931, 1447); (ii) the saturation of residual valencies. The latter theory, originally proposed by Pfeiffer (*op. cit.*), has recently been developed by Briegleb ("Zwischenmolekulare Kräfte und Molekülstruktur," Stuttgart, 1937), according to whom the colour and compound formation are due to electrostatic interactions between the two molecules ("polarisation aggregates"). Both these theories are difficult to reconcile with the facts. More recently, Hammick (cf. Hammick and Yule, J., 1940, 1539 and earlier papers; Hammick and Sixsmith J., 1935, 580) and Gibson and Loeffler (*J. Amer. Chem. Soc.*, 1940, 62, 1324) have suggested a polarisation mechanism similar to an oxidation-reduction reaction for the formation of molecular compounds between aromatic amines and nitro-compounds. It will now be shown that a modification and extension of this idea to the whole group of molecular compounds explains their formation and structure in every detail.

(a) *The Structure and the Rate of Formation of the Molecular Compounds.*—(1) *The ionic bond.* The components must be held together more firmly than by dipole interaction or dispersion forces. The molecular complexes very often persist in solution, and also the colour cannot be due to the saturation of residual valencies. In every case there is a simple stoichiometrical ratio (usually 1 : 1, sometimes 1 : 2) and this alone is strong evidence against ordinary polarisation interactions.

The first analysis of the problem was made by Werner (*Ber.*, 1909, 42, 4324). Although he did not give any detailed theory, he recognised the significance of the nitro- and carbonyl groups in the one component (irrespective of whether this is aromatic or aliphatic) and the fundamental importance of the unsaturated nature of the second component (hydrocarbons or their amino- or hydroxy-derivatives).

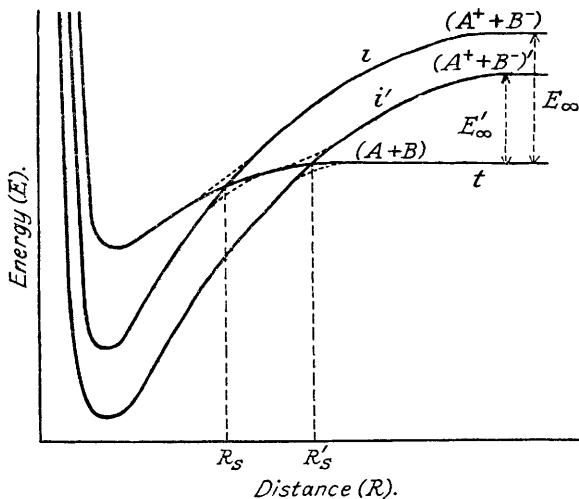
According to the author [*Nature*, 1941, 147, 512; *Trans. Faraday Soc.*, 1941, 37, 780 (Discussion)], the formation of the deeply coloured molecular compounds is due to a complex molecule, essentially ionic in character, which is formed from the two components by an electron transfer from the unsaturated hydrocarbon or its derivative (donor) to the quinone or polynitro-compound (acceptor). In general terms the donor-acceptor idea has already been put forward by other authors (*e.g.*, Bennett and Willis, J., 1929, 253; Kremann, "Ahrens Vorträge," 1924, 27, 58), although they never proposed any detailed theory on these lines.

The acceptor molecule (B) must be one having a positive electron affinity, so it must possess one or more electronegative groups. The increase in the number of these groups favours the formation of the molecular compound through an increased electron affinity. The donor molecule (A) should have a low ionisation potential, *i.e.*, it should be capable of forming a (univalent) positive ion. The molecular compound formation is represented by the reaction



The first step is the formation of a transition complex,  $(AB)_t$  (probably through dipole and dispersion interactions), and this is followed by the actual electron transfer.

The potential curves for the ionic state ( $i$  or  $i'$ ) and the (van der Waals) transition state ( $t$ ) are schematically represented in the figure (cf. London, *Z. Physik*, 1928, **46**, 472; 1932, **74**, 143). Dispersion and dipole potentials fall off very rapidly with increasing separation  $R$  (approximately as  $C/R^6$ ), and beyond a certain distance this potential is practically constant. The ionic potential ( $i$  and  $i'$ ) decreases more slowly [as  $(I_A - E_B) - e^2/R$ ] for univalent ions, where  $I_A$  is the ionisation potential of the donor molecule, and  $E_B$  the electron affinity of the acceptor molecule.



Schematic representation of the potential curves for the van der Waals complex ( $t$ ) and two different ionic states ( $i$  and  $i'$ ) corresponding to different values of  $E_\infty$  and  $E'_\infty$ .

a low heat of activation. This is in agreement with facts. The formation of the molecular compounds is often completely reversible without any considerable time lag. Rapid production of colour has been observed in some cases even at  $-96^\circ$  (Hammick, *loc. cit.*). The rate of formation of the molecular (ionic) compound is given by the following expression, which is derived on the basis of the theory of the transition complex (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; Eyring and Wynne-Jones, *J. Chem. Physics*, 1935, **3**, 107):

$$d(AB)/dt = (kT/h)K^*[A][B] \sim 2.1 \times 10^{10}TK^*[A][B] \quad \dots \quad (2)$$

where  $K^*$  denotes the equilibrium constant between the initial and the transition state (equation 1) and  $k$ ,  $T$ , and  $h$  have their usual significance. The slow formation of certain molecular compounds, observed by Hammick (*loc. cit.*), can also be derived from equation (2) if we have reason to assume very small values for  $K^*$ .

(2) *The electron affinity of the acceptor molecule.* In the polynitro-compounds the nitro-group is responsible for the electron affinity of the molecule; consequently, this property is enhanced in, *e.g.*, tetranitromethane or *s*-trinitrobenzene. This is due to resonance between the different nitro-groups: the electron is distributed over all the groups, resulting in a decrease of its zero-point energy and an increase in the electron affinity of the molecule. A more detailed picture is the following (cf. Pauling, "The Nature of the Chemical Bond," Ithaca, N.Y., 1939; Ingold, *Chem. Reviews*, 1934, **15**, 225).

Through the inductive effect, electrons will be removed from the *o*- and *p*-positions with reference to one nitro-group, but this group can also accept an electron pair from the ring, and then we have resonance with *o*- and *p*-positions. The result of the inductive and resonance effect is that, *e.g.*, in *s*-trinitrobenzene the excess electron can resonate between all the three nitro-groups (which are in *m*-positions to each other) and the unoccupied places as well.

The formation of the picrate molecular compounds is not due to the acid character of the hydroxyl group (which manifests itself in solutions in water or other solvents of a high dielectric constant). This is shown by the fact that picric acid can form two types of compound with aromatic amines: (i) ordinary salts, formed only with strong bases, picric acid acting as an acid; (ii) true molecular compounds, formed by weak bases. These two types of compound are respectively lightly and deeply coloured. Bases of medium strength sometimes form both types, a phenomenon mainly investigated by Hertel and Schneider (*Z. physikal. Chem.*, 1930, **151**, 413; 1931, *B*, **13**, 387), who called it "complex isomerism."

The influence of other substituents on the electron affinity of the acceptor molecule can be explained in a similar way; nitro-, chloro-, and bromo-substituents increase the electron affinity, whereas the

If crossing occurs at a distance ( $R_s$ ) where both potentials have an appreciable value, the mutual perturbation must be taken into account, and certain linear combinations of the ionic and of the wave function derived from the van der Waals potential must be used for the description of the bond. At any rate, we will have ionic binding in the equilibrium state if the ionic state corresponds to a lower state of energy. The amount of ionic binding can be judged if one calculates the distance where the crossing occurs. If this distance is considerably greater than the intermolecular distance within the complex, the respective ionic clouds do not overlap and we have essentially an ionic bond. This distance depends largely on the value of  $E_\infty (= I_A - E_B)$ , small values favouring the ionic bond.

From this theory it follows that, in general, the formation will be a fairly rapid reaction, having rather

amino-group (which through the resonance effect acts as electron repelling) and the methyl group show the opposite effect.

(3) *The ionisation potential of the donor molecule.* The only organic molecules with a low ionisation potential are those containing conjugated double bonds. The non-localised  $\pi$ -electrons present in these systems show a behaviour somewhat similar to that of metallic electrons. An increase in the number of conjugated double bonds reduces the ionisation potential (Price, private communication). This holds, not only for conjugated systems built up from carbon atoms, but also for those where the  $\pi$ -electrons come from nitrogen, oxygen, or sulphur atoms. In the donor molecule, "electron-repelling" groups as substituents, such as  $\text{CH}_3$ ,  $\text{OH}$ ,  $\text{NH}_2$ ,  $\text{NMe}_2$  (resonance effect through their lone pair of electrons), decrease the ionisation potential, whereas  $\text{Cl}$  and  $\text{Br}$  have the reverse effect.

(b) *Heats of Formation.*—From the theory given above, the heats of formation can be calculated in a manner similar to those of other ionic compounds. Normally, we are dealing with the molecular compound in the solid state or in solution. As the solvent effects are often very complex, we shall first consider the heat of formation in the gaseous state ( $\Delta Q$ ), given by the equation

$$\Delta Q = -I_A + E_B + U_C + U_P + U_D - U_R \dots \dots \dots (3)$$

The most important contribution (after the ions have been formed) is due to the Coulombic attraction ( $U_C$ ) between them. In the case of large polarisable ions or molecules, the energy due to polarisation forces ( $U_P$ ) and dispersion forces ( $U_D$ ) will assume greater importance. Finally, there is the term ( $-U_R$ ) representing the repulsion potential. In the gaseous state, stable compounds should be connected with large positive values of  $\Delta Q$ . The calculation of the various energy terms in equation (3) is difficult. At any rate, it would be almost impossible to compare it with the experimental values available, because all these are determined from the temperature coefficient of the light absorption in solutions of the molecular compounds (cf. Baker and Bennett, *Ann. Reports*, 1931, **28**, 137). The total heats of interaction measured in this way ( $\Delta H$ ) must naturally include the heats of solution of the initial products ( $Q_A, Q_B \dots$ ) and those of the final product ( $Q_{AB}$ ) in the particular solvent, as well as  $\Delta Q$  itself.  $\Delta H$  is given by

$$\Delta H = -Q_A - Q_B + Q_{AB} + \Delta Q \dots \dots \dots (4)$$

in which the individual heats of solution involved can again be positive or negative.

Although the problem is simple in principle, the actual evaluation of equation (4) is difficult. This is why the values for the interaction energy calculated by Briegleb and Kambeitz (*Z. physikal. Chem.*, 1936, *B*, **32**, 305) are without great significance, for the solvent effects are not taken into account.

With inert solvents we often have  $\Delta H > 0$ , because there the first three terms in equation (4) roughly cancel each other and one measures essentially only  $\Delta Q$ . In solvents containing dipole molecules (alcohol, acetone, etc.), where there are strong interactions,  $\Delta H$  may be very small or even negative (Hammick, *loc. cit.*), as can be deduced from equation (4).

(c) *The Equilibrium in Solution.*—A quantitative measure of the stability of a molecular compound in solution is given by the equilibrium



The concentration of the molecular compound in solution ( $\text{AB}_{\text{sol.}}$ ) can be measured, for instance, by the light absorption. It is well known that an equilibrium constant for a reaction in solution ( $K_{\text{sol.}}$ ) can be split up into a part which is independent of the solvent ( $K_{\text{gas}}$ ) multiplied by the ratio of the solubilities ( $S_c$ ) of the molecular species ( $S_A, S_B, S_{AB}$ ) occurring in the reaction, as follows :

$$K_{\text{sol.}} = \left( \frac{[\text{AB}]}{[\text{A}][\text{B}]} \right)_{\text{solution}} = \left( \frac{[\text{AB}]}{[\text{A}][\text{B}]} \right)_{\text{gas}} \left( \frac{S_{AB}}{S_A S_B} \right) = K_g \cdot S_c \dots \dots \dots (6)$$

This is derived by assuming Henry's law, *e.g.*,

$$[\text{A}]_{\text{sol.}} = S_A [\text{A}]_{\text{gas}} \dots \dots \dots - \dots \dots (7)$$

The solubility of the dipole molecule ( $\text{A}^+\text{B}^-$ ) should be favoured in solvents of a high dielectric constant, and this should result in a greater stability and deeper colour of the molecular compound in these solutions. However, these solvents will only be of use if the solubility of the initial products (A and B) is not too low, and if there are no specific interactions with the solvent which remove them from the equilibrium (5).

This is, *e.g.*, the case if picrates are brought into contact with water, for then the simple considerations based on the solubility and on the validity of Henry's law (7) can no longer be applied, as has been done by Dimroth and Bamberger (*Annalen*, 1924, **438**, 67). In the aqueous solution, picric acid dissociates in the ordinary way and the undissociated molecules are removed from the equilibrium (5) and transformed into picrate ions, which are not capable of acting as acceptor molecules, and consequently the molecular compound is decomposed. For the same reason alkali will decompose picrate molecular compounds even

more easily. On the other hand, hydrochloric acid decomposes molecular compounds of the amines by transforming the  $R \cdot NH_2$  molecules into the  $R \cdot NH_3^+$  ions.

*The influence of hydrostatic pressure* (II). Gibson and Loeffler (*loc. cit.*) have measured the influence of pressure on the formation of the coloured compound between nitrobenzene and aniline in a solution of 50% of each compound. Although they interpret their results in terms of reaction velocity, they have actually measured the influence of the pressure on the equilibrium corresponding to reaction (5), which is established without time lag, in a solvent mixture of the two components. The well-known thermodynamic relation can be applied to the equilibrium constant of equation (6), giving :

$$d \log K_{\text{sol.}}/d\pi = d \log K_{\text{gas.}}/d\pi + d \log S_c/d\pi = - (\Delta_1 V + \Delta_2 V) = - \Delta V \quad . \quad . \quad (8)$$

$\Delta_1 V$  corresponds to the volume change of the actual association reaction in the gaseous state, and  $\Delta_2 V$  to the solvent effect, *i.e.*, the influence of the pressure on the solubilities of the initial and final substances.

Gibson and Loeffler's results are somewhat contradictory at first sight because, on mixing aniline and nitrobenzene, an *increase* in volume is observed (*J. Amer. Chem. Soc.*, 1939, **61**, 2877) ( $\Delta V$  positive), whereas the colour-producing equilibrium is favoured by higher hydrostatic pressure. However, it is evident from the experiments that in a solution containing 50% of each component only a very small amount of the initial products is transformed into the light-absorbing complex (probably  $[PhNO_2]^- [PhNH_2]^+$ ). From the influence of the pressure on the light absorption, one must conclude that the coloured complex is formed with decrease in volume ( $\Delta V < 0$ ), as is to be expected for an association reaction. This small volume decrease resulting from it must be completely superseded by another effect which occurs in the mixing of the two components (probably a change in the structure of the polar solvents) and is accompanied by an increase in volume but has nothing to do with the formation of the coloured compound.

(d) *The Colour of Molecular Compounds*.—Formation of molecular compounds is accompanied by production of a colour considerably deeper than that of the components. This also follows from the structure of such compounds as suggested above. The ions composing the compound have each an odd number of electrons, like a free radical (with a corresponding unoccupied electronic level). This gives rise to a small excitation energy and hence to light absorption in the visible. Within the ions themselves there is resonance on account of their conjugated systems of bonds, and this is accompanied by a number of polar valency structures which can contribute to the ground state and the excited state. According to Mulliken (*J. Chem. Physics*, 1939, **7**, 570 and earlier papers) this gives rise to a large transition moment and to strong absorption (charge resonance spectra).

The light absorption in a solution of the molecular compound depends on the number of ionic complexes present in the solution (*i.e.*, on the equilibrium corresponding to equation 5) and on the ionic structure of the complex. The region of absorption depends mainly on the extension of the conjugated systems of which the molecular complex is composed. Increase in the number of conjugated bonds shifts the absorption towards longer wave-lengths (cf. Foerster, *Z. Elektrochem.*, 1939, **45**, 548). All the factors which contribute towards a greater stability of the molecular compound (small value of  $E_\infty$ ) tend towards a deepening of the colour and an increased extinction of light. Therefore, all those substituents which decrease  $E_\infty$  deepen the colour and *vice versa*. A more direct confirmation is indicated by the fact that in the acceptor molecule the influence of substituents closely parallels their effect on the reducibility of the nitro- (or carbonyl) group (Gibson and Loeffler, *loc. cit.*, 1940). (The ease of reduction is obviously accompanied by a large value of  $E_B$ .) In the formation of the quinhydrone molecular compounds in a series of different quinones the change in the absorption spectrum brought about by the second component (forming the molecular compound) increases with increasing oxidation-reduction potential of the quinone (Hunter and Northey, *J. Physical Chem.*, 1933, **37**, 875). On the other hand the oxidation-reduction potential (of the quinone molecule and its reduced form) runs parallel to the electron affinity of the quinone. This result can be directly deduced from the above theory.

The nitro-compounds or quinone compounds of aromatic amines or phenols are more deeply coloured (more stable) than those of the hydrocarbons. The nitrogen atom has undoubtedly a greater tendency to form a positive ion than has the carbon atom. However, the binding between the aromatic amine and the acceptor molecule is not directly connected with the amino-group, as was suggested by some authors. It is again the "total" conjugated system which is responsible for the binding effect, although the resonance structures where the positive charge is on the nitrogen atom instead of on one of the carbon atoms will assume greater importance in this case. This is demonstrated by the fact that aniline and nitrobenzene give a deeply coloured compound whereas  $\alpha$ -phenylethylamine (which is a much stronger base) does not produce any colour with nitrobenzene (Gibson and Loeffler, *loc. cit.*, 1940), because the amino-group is not directly connected to the conjugated system (and the benzene ring itself is not sufficient in this case). This view is also confirmed by the extensive work of Pfeiffer (*op. cit.*).

(e) *Crystal Structure and Intermolecular Distances*.—The crystal structure and crystallographic distances can be easily understood on the basis of the ionic character of the molecular compounds. The difference compared with simple ionic crystals (such as the alkali halides) mainly arises from the fact that in this case the ions are not spherical but are more like flat, cylindrical plates (the original molecules and the ions formed from them being essentially coplanar). Also, the ions are much larger and more polarisable, and consequently we do not usually find the simple structures as in ordinary ionic crystals. The interionic distances (3—3.5 Å.) as measured by X-rays are of the same order as in other univalent ionic crystals (*e.g.*, potassium chloride 3.15 Å., rubidium iodide 3.7 Å.). In a molecular compound formed between a polycyclic hydrocarbon and, *e.g.*, picric acid, a rough estimate of the distance follows from the radius of action of the carbon atom ( $r_w$ ) (cf. Schmidt, *Z. physikal. Chem.*, 1939, B, 42, 83). It can be assumed that the radius of the positive ion will be somewhat smaller, and that of the negative ion presumably larger, than that of the carbon atom itself. Therefore to a first approximation the interionic distance will be of the order  $\sim 2r_w \sim 3.2$  Å.

The sodium chloride type of structure has actually been observed in the system acenaphthene-2 : 6-dinitro-*m*-xylene (Hertel and Kleu, *ibid.*, 1930, B, 11, 59), whereas in many other cases we find the layer lattice type (Hertel and Römer, *ibid.*, p. 77), as is to be expected with larger and polarisable ions (Hund, *Z. Physik*, 1925, 34, 833).

(f) *The Dipole Moments of Molecular Compounds*.—According to the theory outlined above, we should expect the molecular compounds to have an electric moment due to the separation of the positive and negative charge. One should be able to measure this in the solution of the molecular compound in an inert solvent (*e.g.*, hexane). This electric moment cannot be measured in the usual way because the solubilities are too low and the molecular compound is dissociated into its components to a considerable extent. However, the existence of this dipole moment can be established in the following way. It is best to consider those molecular compounds where the polynitro-components (in virtue of their structure) must themselves have a zero dipole moment. This is the case with *s*-trinitrobenzene and *p*-dinitrobenzene, both of which have a planar configuration (Hertel and Römer, *Z. physikal. Chem.*, 1939, B, 22, 267). In solvents like benzene or (molten) naphthalene these polynitro-compounds form molecular compounds (Kremann, *Monatsh.*, 1908, 29, 863), the stability of which is favoured on account of one component being present in a high concentration. Therefore we should find a finite dipole moment for these nitro-compounds in these solvents, whereas in other solvents (which do not give rise to compound formation) the measured dipole moment will be zero. [For *s*-trinitrobenzene the non-vanishing dipole moment in benzene has already been interpreted by Bennett and Willis (*loc. cit.*) as due to the formation of a molecular compound (cf. Glasstone, "Recent Advances in Physical Chemistry," 3rd Edn., 1936, pp. 180, 181).] This is actually the case, as can be seen from the following data, in which  $P_2(f_2 = 0)$  is the total molecular polarisation at infinite dilution,  $P_0$  is the orientation polarisation, and  $\mu$  is the dipole moment.

<i>s</i> -Trinitrobenzene.					<i>p</i> -Dinitrobenzene.			
$[R_L]_D = 43.5 \pm 0.4$ c.c. <sup>1</sup> ; $[R_L]_\infty = 41.7 \pm 0.4$ c.c.					$[R_L]_D = 38.5$ c.c. (calc. from group refractions); $[R_L]_\infty = 36.0$ c.c. (estimated).			
Solvent.	Temp.	$P_2(f_2 = 0)$ , c.c.	$P_0$ .	$\mu$ , D.	Temp.	$P_2(f_2 = 0)$ , c.c.	$P_0$ .	$\mu$ , D.
CCl <sub>4</sub>	25°	46.6 <sup>2</sup>	~ 4	0 (0.2)	25°	38.9 <sup>2</sup>	~ 2	0 (0.1)
CHCl <sub>3</sub>	25	41.3 ± 0.5 <sup>3</sup>	~ 0	0	25	34.1 ± 0.5 <sup>3</sup>	0	0
C <sub>6</sub> H <sub>6</sub>	25	55 <sup>2</sup>	13	0.79	25	46 <sup>2</sup>	~ 10	0.69
C <sub>10</sub> H <sub>8</sub>	85	55.5 <sup>4</sup>	13.5	0.88	—	—	—	—
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	25	61.5 <sup>2</sup>	19.5	0.96	25	47 <sup>2</sup>	~ 11	0.73

<sup>1</sup> Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, B, 27, 11.

<sup>2</sup> Lefèvre and Lefèvre, *J.*, 1935, 957.

<sup>3</sup> Jenkins, *J.*, 1936, 862.

<sup>4</sup> Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, B, 25, 251.

The actual values for the dipole moments given above have only a qualitative significance: the real values for the ionic complexes are probably about 10—12 times greater (8—10 D.). For accurate calculation of these from the given data an independent knowledge of the equilibrium constant of the association equilibrium (corresponding to equation 5) in the solvents benzene or molten naphthalene would be necessary.

The equilibrium constant for the association reaction is given by

$$K = C e^{-\Delta H/RT} \dots \dots \dots (9)$$

where  $\Delta H$  is the heat of reaction, and  $C$  an entropy term (to a first approximation independent of the temperature) which gives a measure of the statistical probability of the associated state. For instance, for *s*-trinitrobenzene in benzene, an equilibrium constant of  $10^{-3}$ — $10^{-4}$  (at 25°) would be necessary to account for a dipole moment of about 10 D. for the molecular compound (as compared to the experi-

mentally determined overall value of about 1 D.). This is calculated on the basis that the total polarisation of the compound AB is made up additively from the (electronic) polarisations of its (non-polar) components plus the dipole moment created by the compound formation.

A value for the equilibrium constant smaller than unity is also supported by the experimental fact that the total polarisation of *s*-trinitrobenzene and of *p*-dinitrobenzene (although exceeding the electronic polarisation) is practically independent of the temperature over the range 25—45°. According to Debye's theory, the orientation polarisation is inversely proportional to the absolute temperature. An endothermic equilibrium will counterbalance this effect by means of the increased concentration of the association complexes at the higher temperature. For an equilibrium constant small compared to unity one can easily derive the equation

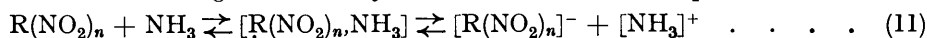
$$K_{T_1}/K_{T_2} = T_1/T_2 \dots \dots \dots (10)$$

From this it is found that if the equilibrium in solution were endothermic with about 1—2 kg.-cals., this would be sufficient to account for the above-mentioned experimental fact.

For  $\Delta H = 1-2$  kg.-cals. the exponential factor in the equilibrium constant (equation 9) is of the order  $10^{-1}$ . This leaves for the entropy term a value of  $10^{-2}-10^{-3}$ . The small value of this can be easily understood from the comparatively small statistical probability of the associated state caused by the complexity (and restricted orientation) of the associating particles (cf. Evans and Polanyi, *loc. cit.*).

(g) *Electrical Properties of the Molecular Compounds in Solution.*—If the ionic molecule is dissolved in a suitable ionising solvent we should obtain a conducting solution with the (coloured) ions migrating in the electric field. The ordinary ionising solvents (*e.g.*, water) cannot be used because the respective solubilities are too low and decomposition of the molecular compound takes place. However, the naphthalene-picric acid compound and the anthracene-trinitrobenzene compound give yellow solutions in liquid sulphur dioxide which show a small but measurable conductivity.\* It is possible to demonstrate more clearly the (negative) acceptor ions and the (positive) donor ions in the following way.

If *s*-trinitrobenzene (Kraus and Bray, *J. Amer. Chem. Soc.*, 1913, **35**, 1315) or dinitrobenzene is dissolved in liquid ammonia it forms an ionic molecular compound (with the ammonia as donor) which dissociates to some extent in the (excess) liquid ammonia. These solutions are deeply coloured owing to the negative  $[\text{R}(\text{NO}_2)_n]^-$  ion, the anion  $[\text{NH}_3]^+$  being colourless. On electrolysis, the coloured nitro-ion migrates to the anode, as shown by Garner *et al.* (Field, Garner, and Smith, *J.*, 1925, **127**, 1227; Garner and Gillbe, *J.*, 1928, 2889), who also found that these solutions behave like a binary electrolyte (*e.g.*, ammonium chloride) in liquid ammonia. According to our theory the interaction must be represented as



The conductivity in liquid ammonia is proportional to the concentration of the ions (Garner *et al.*, *loc. cit.*), as deduced from their light absorption, which also follows from equation (11).

*m*-Dinitrobenzene gives a more stable and more deeply coloured solution than either the *o*- or the *p*-compound. This follows from the discussion in section (d). The rate of ionisation was found to be of the first order with regard to the *m*-dinitrobenzene (*idem, ibid.*), as can be deduced from equation (2).

Just as liquid ammonia can be used to demonstrate the acceptor ions, the solutions of hydrocarbons or amines in liquid sulphur dioxide demonstrate the donor ions. The positively charged anthracene ion is indicated by the experiments of Walden (*Z. physikal. Chem.*, 1903, **43**, 385), who found that even dilute solutions of this hydrocarbon in liquid sulphur dioxide are deeply yellow and show a measurable conductivity (at a concentration of  $10^{-2}$  mol./l. the equivalent conductivity is  $\Lambda \sim 0.1 \Omega^{-1}$  at 0°). This is due to the primarily formed compound  $[\text{C}_{14}\text{H}_{10}]^+[\text{SO}_2]^-$  which is (slightly) dissociated in liquid sulphur dioxide. More basic substances such as diphenylamine, dimethylaniline, and  $\alpha$ -picoline have a much lower ionisation potential and can form molecular compounds with sulphur dioxide more easily (cf. Foote and Fleischer, *J. Amer. Chem. Soc.*, 1934, **56**, 870). These complexes, which are soluble in liquid sulphur dioxide with a deep red or brown colour, show a considerable conductivity in this solvent (Walden, *loc. cit.*) ( $10^{-2}$  mol. of  $\alpha$ -picoline per l. shows an equivalent conductivity of  $\Lambda_\infty = 6.63 \Omega^{-1}$  at 0°).

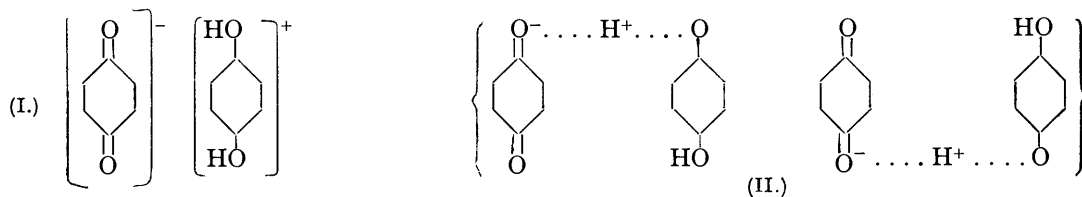
(h) *The Structure of Molecular Compounds and their Relation to the Semiquinones.*—(1) *The hydrogen bond and dismutation.* With quinones and polynitro-compounds we have the following groups of molecular compounds:

Acceptor (anion). Quinones  Nitro-compounds	Donor (cation). { Hydrocarbons { Phenolic compounds { Amino-compounds
------------------------------------------------------	--------------------------------------------------------------------------------

The best-known compound in the first group is quinhydrone. Benzquinones (*e.g.*, tetrachlorobenzquinone) are also capable of forming deeply coloured compounds with aromatic hydrocarbons.

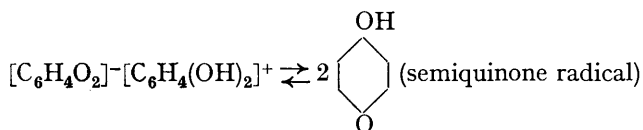
\* Unpublished experiments (at concentrations of about  $10^{-3}$  mol./l. the equivalent conductivity is of the order of  $0.1 \Omega^{-1}$  at 0°).

The relationship to the semiquinones (cf. Michaelis, *Chem. Reviews*, 1935, **16**, 243) becomes apparent if we consider, for instance, the structure of quinhydrone from the point of view of our theory. Introducing the idea of the simple electron transfer, one obtains the structure (I). Generally, the positive and the negative charges are "smeared out" over the whole of the respective conjugated system. However, there is a tendency for the negative charge to stay on the oxygen of the carbonyl group and for the positive charge to concentrate on the hydroxyl groups. Actually we have the ideal conditions for a

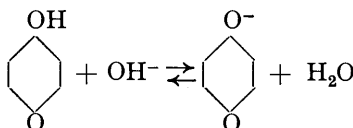


hydrogen bond (Pauling, *op. cit.*): the proton is held between the neutral and the negatively charged oxygen. The structure of quinhydrone in the solid state and in non-ionising solvents is then represented by the resonance structures shown in (II) with hydrogen bonds. In agreement with this, the quinhydrones in the solid state are diamagnetic (Coryell, quoted by Pauling, *op. cit.*). The deep colour of these compounds (in non-ionising solvents) is not due to the formation of semiquinones (cf. Litschitz, *Ber.*, 1915, **48**, 1734; Wagner and Grünwald, *Z. Elektrochem.*, 1940, **46**, 265), but must again be attributed to the polar structure.

If the proton is *completely* transferred we get in this particular case :

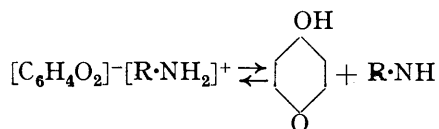


*i.e.*, the formation of 2 molecules of semiquinone according to a dismutation equilibrium. In the solid state and in media of low dielectric constant the equilibrium is usually towards the left-hand side of the equation. In aqueous solutions and particularly in the presence of alkali the semiquinone is transformed into its ion :



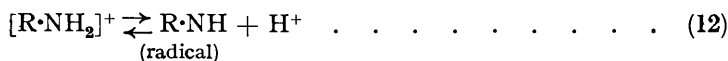
This ion is rather stable because of the resonance of the electron between the oxygen atoms, and it cannot undergo dismutation on account of its negative charge (Coulombic repulsion). It has all the properties of a free radical, and the alkaline solutions of quinhydrone are therefore paramagnetic (Michaelis, Schubert, Reber, Kuck, and Granick, *J. Amer. Chem. Soc.*, 1938, **60**, 1678).

The same ideas can be applied to the molecular compounds with amines :



In this case we get two different semiquinones. The "quinhydrone" formation between phenazine and dihydrophenazine must be treated on exactly the same lines as above (Clemo and McIlwain, *J.*, 1934, 1991).

(2) *Ions and free radicals.* We have seen that the positive ions of the phenolic compounds and amines which appear in the structure of the molecular compounds are really identical with the well-known semiquinones. The connection between them is given through the equilibria :



In the solution it depends entirely on the hydrogen-ion concentration whether they are present as radicals or as ions according to the reactions (12) and (13).

The same idea, when applied to conjugated hydrocarbons which behave similarly to their hydroxy- or amino-derivatives, leads to a new type of " semiquinone " which must be described as a positive hydrocarbon ion. This is in equilibrium with the free radical and hydrogen ions :



An independent confirmation of these new types of ions can be found in the recent experiments (Weiss, *loc. cit.*) on the formation of various positive ions from conjugated systems such as anthracene, coronene, and even graphite.\*

In the case of the quinhydrones the negatively charged quinones are also identical with the semiquinone. The existence of singly negatively charged polynitro-molecules is confirmed independently by the formation of a coloured negative ion in the solutions of polynitro-compounds in liquid ammonia. This is also supported by the formation of a deeply coloured compound from s-trinitrobenzene (and similar nitro-compounds) with metallic sodium or potassium,† the complex probably containing the same negative ion.

There are a few cases of molecular compounds where the molecular ratio is 1 : 2 instead of the usual 1 : 1 (cf. Cook and Robinson, J., 1938, 509). This is to be expected, for instance, in the comparatively rare cases in which we have two more or less separate regions of influence in the same molecule (cf. Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 144), which is then capable of forming a doubly charged positive (or negative) ion. It can also be expressed in another way, *viz.*, that the 1 : 1-molecular compound (which is in any case the primary product) must still be able to act either as an acceptor or as a donor towards one of its components. The doubly charged ions would again have an even number of electrons and should therefore be chemically more stable and less deeply coloured than the univalent ions which correspond to free radicals.

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