## **128.** *Complex Formation between Polynitro-Compounds and Aromatic Hydrocarbons. Part I. Finite Reaction Rates.*

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THE existence in the solid state of well-defined complexes of aromatic polynitro-compounds with aromatic hydrocarbons in simple stoicheiometric proportions has long been recognised. That interaction of some kind may occur between the components in the liquid state is indicated by the colour change that frequently follows their admixture in solution. Further evidence for interaction comes from cryoscopic experiments by the addition to solvents of the components separately and together, the depression in the latter case being less than the sum of the depressions in the former (Behrend, *Z. physikal. Chem.*, 1894, **15**, 183; Brown, J., 1925, **127**, 345). Again, the partition of picric acid between water and an immiscible second solvent is influenced by aromatic hydrocarbons and their derivatives in the latter in such a way that interaction between the picric acid and the hydrocarbon in the non-aqueous layer must be inferred (Bamberger and Dimroth, *Annalen*, 1924, **438**, 67; Moore, Shepherd, and Goodall, J., 1931, 1447). It is not possible, however, to conclude with certainty from these and analogous results (cf. Baker and Bennett, *Ann. Reports*, **1931**, **28**, 137, for bibliography) that the interaction which undoubtedly occurs in the liquid phase is of the nature of true chemical combination, involving the rearrangement of co-ordinate linkages. The nitro-group is highly polar, and aromatic hydrocarbons are polarisable. It may, therefore, well be that equilibrium constants derived from the alterations in the solubility or miscibility of a polar solute caused by the addition of a polarisable second component have no more real significance than the apparent dissociation constants of strong electrolytes calculated from the depressions they cause in the freezing point of water.

As was pointed out by Bamberger and Dimroth (*loc. cit.*), there is one reliable criterion that can be applied to distinguish between polar interaction, resulting possibly in the formation of " dipole aggregates," and true chemical interaction. In the first case, reaction will be analogous to ionic interaction and be practically instantaneous. Chemical interaction, on the other hand, involves activation of the reacting molecules, and in suitable circumstances may be expected to take place at measurable rates. If, therefore, cases can be found of polynitro-compounds reacting slowly with hydrocarbons, the conclusion can be drawn with certainty that ordinary valency forces are involved in the formation of the complexes. We have found one such case in the system methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate–indene, for we find that a *complex* can be both formed and decomposed at finite rates. We were led to seek for suitable polynitro-compounds among the derivatives of diphenyl by the observations of Lesslie and Turner (J., 1930, 1758) and others that such compounds form unusually stable solid complexes with benzene and similar hydrocarbons. Indene was chosen as the second component because it can be estimated rapidly and accurately by means of bromine.

## EXPERIMENTAL.

The rates of formation and of dissociation of the specified complex have been studied in carbon tetrachloride solution at 38°, this temperature being necessary in order to obtain sufficiently concentrated solutions of the sparingly soluble ester.

*Preparation of Materials.*—Methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate was prepared by Ullmann and Engi's method (*Annalen*, 1909, **366**, 79), m. p. 176·1° (corr.). The indene used was distilled three times before each experiment (b. p. 182°); a sample prepared in this way and distilled directly into a tared standard flask containing carbon tetrachloride can be preserved for weeks at concentrations up to *M*/10 without its titre against a standard solution of bromine in carbon tetrachloride changing appreciably. The bromine was purified by Cohen's method (*J. Amer. Chem. Soc.*, 1930, **52**, 2827).

The *compound* of indene with the nitro-ester was prepared by crystallising 1 mol. of ester in the presence of 4 mols. of indene from methyl alcohol; m. p. 159° (corr.) (Found : C, 48·9; H, 2·9. $2C_{16}H_{10}O_{12}N_4,C_9H_8$ requires C, 48·6; H, 2·8%. 0·0173 G. reduced 13·1 c.c. of 0·0617*N*-$TiCl_3$. Calc. : 13·1 c.c.) : it is decomposed into its constituents on recrystallisation from methyl alcohol in the absence of excess indene.

*Estimation of Indene.**—We find that indene in dilute solution (*M*/10 or less) can be estimated accurately by adding an excess of bromine in carbon tetrachloride, the unreacted bromine being immediately removed by shaking with an aqueous solution of potassium iodide. The liberated iodine is titrated with standard thiosulphate. Under these conditions exactly 2 atoms of bromine react with 1 mol. of indene.

The carbon tetrachloride used as solvent was free from sulphur and free chlorine, and was distilled from phosphoric oxide before use.

*Decomposition of the Compound in Solution.*—Weighed quantities of the compound were dissolved as rapidly as possible in carbon tetrachloride at the temperature of the thermostat and made up to 50 c.c., either with pure solvent or with a solution of indene in carbon tetrachloride. Aliquot parts were removed at successive intervals of time, and the free indene estimated as described above. The following results were obtained at 38° for the rates of decomposition of the compound alone (Expts. I and II) and in the presence of free indene (Expts. III and IV). 5-C.c. portions of the solution of compound were treated with 5 c.c. of

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* The conditions under which indene can be preserved and estimated have been worked out and will be described in a later communication.

0·054*N*-bromine in carbon tetrachloride in Expt. I, and with 10 c.c. of 0·0445*N*-bromine in carbon tetrachloride in Expts. II, III, and IV. In all cases the unreacted bromine was estimated in terms of *N*/100-thiosulphate. In the tabulated results, $C_0$ is the initial concentration of the compound, and all concentrations are expressed as g.-mols. per 1000 litres.

*Experiment I.* $C_0$ = 9·614.

| *t* (mins.) | 5 | 10 | 20 | 29·5 | 40 | 78 | 121 | 1095 |
|---|---|---|---|---|---|---|---|---|
| C.c. *N*/100-$Na_2S_2O_3$ | 24·4 | 23·0 | 22·3 | 21·4 | 20·3 | 20·0 | 20·0 | 20·0 |
| Indene | 2·6 | 4·0 | 4·7 | 5·6 | 6·7 | 7·0 | 7·0 | 7·0 |

*Experiment II.* $C_0$ = 9·444.

| *t* (mins.) | 4 | 10 | 16 | 19 | 39 | 64 | 107 | 1008 |
|---|---|---|---|---|---|---|---|---|
| C.c. *N*/100-$Na_2S_2O_3$ | 43·0 | 41·5 | 40·1 | 39·65 | 38·1 | 37·6 | 37·5 | 37·6 |
| Indene | 1·5 | 3·0 | 4·4 | 4·85 | 6·4 | 6·9 | 7·0 | 6·9 |

*Experiment III.* $C_0$ = 22·550; $C_0$ indene = 11·50.

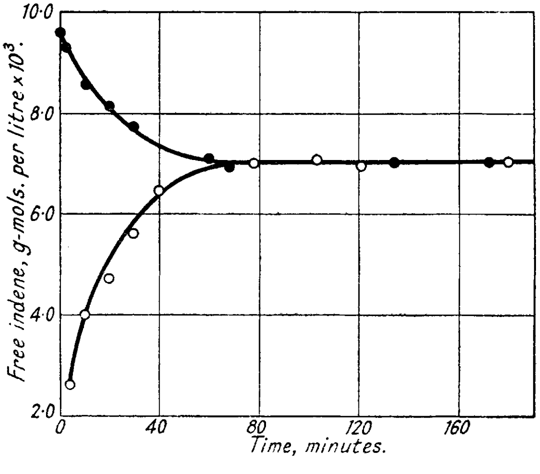
| *t* (mins.) | 2 | 5 | 8 | 13 | 18·5 | 26 | 36 | 98·5 |
|---|---|---|---|---|---|---|---|---|
| C.c. *N*/100-$Na_2S_2O_3$ | 30·1 | 28·5 | 27·0 | 26·3 | 25·9 | 25·5 | 25·5 | 25·5 |
| Indene | 14·4 | 16·0 | 17·5 | 18·2 | 18·6 | 19·0 | 19·0 | 19·0 |

*Experiment IV.* $C_0$ = 18·115; $C_0$ indene = 26·50.

| *t* (mins.) | 2 | 3·5 | 6·75 | 12 | 23·3 | 32·3 | 48·5 | 103 |
|---|---|---|---|---|---|---|---|---|
| C.c. *N*/100-$Na_2S_2O_3$ | 16·6 | 15·0 | 14·15 | 13·5 | 12·8 | 12·5 | 12·4 | 12·4 |
| Indene | 27·9 | 29·5 | 30·4 | 31·0 | 31·7 | 32·0 | 32·1 | 32·1 |

It is apparent from these results that the indene compound dissociates slowly to reach an equilibrium corresponding to about 70% decomposition.

*Formation of the Compound in Solution.*—In order to show that the same position of equilibrium is reached when the components unite as when the compound dissociates, the nitro-ester and indene in quantities equivalent to the weight of compound in Expt. I were made up to the same molar concentration as in that experiment. Free indene was determined in 10-c.c. portions at successive intervals of time by the addition of 5 c.c. of 0·186*N*-bromine in carbon tetrachloride, excess bromine being found in terms of *N*/100-thiosulphate. Results are given below (Expt. V), and the data for decomposition and combination (Expts. I and V) are plotted in the figure.



*Experiment V.* $C_0$ ester = 19·20; $C_0$ indene = 9·60.

| *t* (mins.) | 2 | 10·25 | 20·5 | 28·8 | 51 | 70 | 134 | 173 |
|---|---|---|---|---|---|---|---|---|
| C.c. *N*/100-$Na_2S_2O_3$ | 74·4 | 75·9 | 76·6 | 77·6 | 78·8 | 79·2 | 79·0 | 79·0 |
| Indene | 9·8 | 8·55 | 8·2 | 7·7 | 7·1 | 6·9 | 7·0 | 7·0 |

Slow formation of the complex in presence of excess of indene is shown in Expt. VI.

*Experiment VI.* $C_0$ ester = 66·60; $C_0$ indene = 56·19. 5 C.c. portions with 5 c.c. of 0·1244*N*-bromine.

| *t* (mins.) | 6 | 8 | 13 | 20 | 27·5 | 38·8 | 46·3 | 94·3 |
|---|---|---|---|---|---|---|---|---|
| C.c. *N*/100-$Na_2S_2O_3$ | 21·3 | 25·6 | 28·1 | 30·4 | 31·0 | 31·2 | 31·2 | 31·2 |
| Indene | 40·9 | 36·6 | 34·1 | 31·8 | 31·2 | 31·0 | 31·0 | 31·0 |

## Discussion.

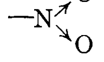
The experimental results described above show that when the crystalline complex containing 2 mols. of methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate to 1 mol. of indene is dissolved in carbon tetrachloride at 38°, free indene is slowly produced, but that it slowly disappears when the two compounds are mixed in this solvent. Further, it has been established that the same position of equilibrium is reached from either direction. From these facts we can conclude that combination in the strict chemical sense takes place in this particular case. Also, from the fact that the complex in solution does not react with bromine under conditions in which indene readily reacts, we can infer that the ethylenic linkage in the combined indene is no longer able to function as a centre of unsaturation towards bromine, and is therefore a point of attachment of a molecule of nitro-ester.

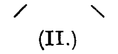
It is improbable on general grounds that the tetranitrodiphenic ester reacts in solution by a termolecular process to produce ternary molecules $N_2I$, corresponding to the molecular composition of the solid complex. (N and I represent molecules of ester and indene respectively.) The most likely course of the interaction is a primary addition of nitro-ester to the reactive ethylenic linkage of the indene molecule (which must be the process upon which the method used to analyse the reacting systems depends), succeeded by the addition of a second molecule of nitro-compound. We should then have in solution the following equilibria: (i) $N + I \rightleftharpoons NI$; (ii) $NI + N \rightleftharpoons N_2I$. Seeing that the only molecular species in solution that can be estimated directly is the free indene, it is not possible to compute separately the concentrations of the two compounds NI and $N_2I$, and so to test the quantitative implications of the above equilibrium equations. However, the second molecule of nitro-compound is presumably attached to the more saturated benzenoid part of the indene molecule and is consequently less firmly held than the first. The actual concentration of $N_2I$ molecules may therefore be small, their preferential separation from solution being due to their greater insolubility. If this view is accepted, conditions in solution will be controlled mainly by (i), and, from a knowledge of the initial concentrations and the amount of free indene present at equilibrium, approximate data can be obtained for evaluation of the equilibrium constant $K = [NI]/[N][I]$. Data and values for $K$ are given in the following table, and it will be seen that a satisfactory constancy is obtained.

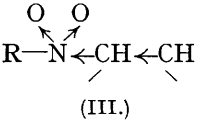
| | Expt. I. | Expt. II. | Expt. III. | Expt. IV. | Expt. V. | Expt. VI. |
|---|---|---|---|---|---|---|
| $[NI] \times 10^3$ ............ | 2·6 | 2·4 | 15·0 | 12·6 | 2·6 | 25·2 |
| $[N] \times 10^3$............... | 16·6 | 16·4 | 30·1 | 23·6 | 16·6 | 41·4 |
| $[I] \times 10^3$ ............... | 7·0 | 7·0 | 19·0 | 32·1 | 7·0 | 31·0 |
| $K$ ......................... | 22 | 21 | 26 | 17 | 22 | 20 |

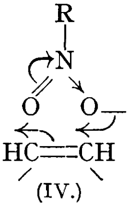
If the actual rates measured in Expts. I—VI are those of the decomposition and formation of the binary NI molecules, it should be possible to calculate the value of the equilibrium constant $K$ from the initial rates of decomposition and combination. We thus find, from the first two amounts of free indene produced in Expts. I—IV, a mean unimolecular velocity constant $k_1 = 0{\cdot}053$. From Expts. V and VI a mean bimolecular constant $k_2 = 1{\cdot}0$ (0·8, 1·2) is obtained from the first points on the indene concentration–time curves. The ratio $k_1/k_2$ gives for the equilibrium constant $K$ the value 18·9, which is in satisfactory agreement with the mean observed value 21.

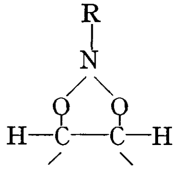
A possible mode of attachment of the nitro-group to aromatic hydrocarbons has been discussed by Bennett and Willis (J., 1929, 256; see also Baker and Bennett, *Ann. Reports*, 1931, 137), who suppose that the group functions in the kationoid form (I) and reacts with an ethylenic linkage in its polarised form (II) to give the structure (III). An alternative


(I.)


(II.)


(III.)


(IV.)


(V.)

process for the attachment of the nitro-group would be (IV), leading to (V). In this process the postulated recession of an electron pair from the doubly linked oxygen to the nitrogen is in the direction opposite to that in which polarisation of the $-N=O$ linkage is usually supposed to occur, and might not be expected to take place unless forced to do so by electron-attracting groups such as $-NO_2$, $-CO_2Me$, $-SO_2Cl$, etc., attached to the aromatic nucleus R. Bennett (*loc. cit.*) has pointed out that the presence of such groups is necessary before complexes of the type under discussion can be formed. The general instability of the complexes may tentatively be correlated with the fact that the above ring structure has hitherto not been associated with any known organic compound.

A decision between the two structures given above would seem to be possible on chemical grounds, since Bennett's formula indicates the presence in the molecule of a centre of kationoid reactivity. Preliminary experiments have failed, however, to give decisive evidence of such reactivity, and the question of structure must remain open until more definite experimental data are available.

## SUMMARY.

A solid compound of methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate (2 mols.) with indene (1 mol.) has been obtained, and found not to react with bromine in carbon tetrachloride solution. It has therefore been possible to follow the rate of formation and decomposition of the compound in solution. A state of equilibrium is reached, for which equilibrium constants have been evaluated on the supposition that, in solution, combined indene is mainly in the form of a binary compound with the nitro-ester.

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