MOLECULAR COMPLEXES OF PICRIC ACID WITH AROMATIC HYDROCARBONS AND THEIR DERIVATIVES

Part I.—Association Constants of 1:1 Substituted Naphthalene-Picric Acid Complexes

I.H. RESHAMWALA

337, Bahadurabad, Road No. 14, Karachi-5

(Received June 26, 1965)

Interaction between aromatic nitro and polynitro compounds such as symmetrical trinitro—benzene, picric acid, picryl chloride etc., and aromatic hydrocarbons and their derivatives has been a subject of study by various physical methods. In the present investigation association constants of 1:1 complexes of Naphthalene, 1—and 2—methyl naphthalenes, 1—and 2—me thoxy naphthalenes, 2—naphthol, 1—chloro and 1—and 2—bromo naphthalenes with picric acid have been determined in chloroform medium by partition method. These values have been utilised to compare the donor capacities of the compounds studied and the effect of the substituent groups on the stability of complexes. Also an attempt is made to throw light on the nature of interaction between the two components of the complex by studying the temperature dependence of their complexation.

Introduction

It has long been recognised that many aromatic hydrocarbons and some of their substitution products such as amines, phenols and ethers are capable of combining additively, in apparent violation of the classical rules of valency, with other organic compounds such as quinones, polynitro aromatic derivatives, maleic anhydrides and also with inorganic compounds such as sulphur dioxide, silver perchlorate and hydrogen halides. A large majority of these aromatic molecular complexes cannot be isolated in pure state as they dissociate very readily into their components in solution and therefore their existence has been recognised only through the investigation by physical methods of solutions or mixtures of their compounds. As the dissociation occurs in accordance with the law of mass action it was soon recognised that the evaluation of the equilibrium constants for the formation of these complexes in solution would provide a quantitative study of the extent of interaction between the components.

The comparative study of these complexes in solution has been made by various workers employing different methods such as Solubility Measurements, Cryoscopic Studies, Distribution Studies, Vapour Pressure Measurements, Melting-point Composition Diagram, Viscosity Measurements and the like. In recent years Spectrophotometric, Colorometric and Conductivity measurements have also been used. The determination of association constants of 1:1 picric acid complexes with certain hydrocarbons and their derivatives in chloroform solution by method of partition has recently been carried out in a series of investigations by Moore Shepherd and Goodal,[1] Anderson and Hammick,[2] Gardner and Stump[3] etc. The method adopted by the author is the one used by Moore and coworkers and further refined and improved by the others already mentioned.

Experimental

Theory.—The method is based on the study of the distribution of picric acid between chloroform and water as influenced by the presence of varying amounts of aromatic substances in the chloroform phase. In the presence of the latter two effects serve, in opposition to each other, to alter the normal partition of picric acid between the two phases. The first effect corresponding to the formation of the complex in the chloroform layer causes an increase in the total concentration of picric acid in chloroform layer while the second effect due to salting out of picric acid from the chloroform phase by the uncomplexed aromatic material tends to lower its concentration in that phase. By determining the alteration in the concentrations of picric acid in two layers, the concentration of the complex formed in the chloroform phase can be calculated and hence the association constant of the interaction can be evaluated.

Consider the distribution of picric acid between water and chloroform, in the latter of which the concentration is P. Let an addition of an aromatic substance in concentration Z, soluble in chloroform, depress the concentration of picric acid to y by the amount (P—y). At the same time its concentration in chloroform is increased owing to interaction with the added substance to y_1, by the amount (y_1—P). Assuming that the two opposite effects are arithmetically additive, the experimentally observed picric acid concentration Y is given by:

$$Y=P+(y_1-P)-(P-y).$$
$$Y=y+y_1-P \qquad (1)$$

Now the solubility depression constant can be defined as the lowering of solubility due to 'salting out' per unit concentration of picric acid and added substance

$$\text{i.e. } k = \frac{P - y}{y \cdot Z}$$

$$\therefore y = \frac{P}{1 + kZ} \doteqdot P\,(1-kZ+k^2Z^2)$$

Substitution of this value of y in equation (1) we get $y_1-P=Y-y=Y-P+PkZ-Pk^2Z^2$ (2)

The stability constant for the reaction

Picric acid + Hydrocarbon $\rightleftarrows$ Additive complex

can be written as

$$K=\frac{y_1 - P}{P_a[Z-(y_1-P)]}$$

$$\therefore K = \frac{Y-P+PkZ-Pk^2Z^2}{P\,[Z-(Y-P+PkZ-Pk^2Z^2)]}$$ substituting for y_1-P from equation (2).

Neglecting the terms involving higher powers of k we get

$$K = \frac{Y - P + PkZ}{P\,[Z-(Y-P+PkZ)]} \qquad (3)$$

In the procedure described above it has been assumed as was shown by Moore and coworkers (Loc. cit.) that the complexes are 1:1 type and any association of chloroform with either picric acid or hydrocarbon is negligible.

Materials Used.—Picric acid was recrystallised from alcohol and dried in an oven at 100°C. for six to eight hours. It has M.P. 122°C.

Pure chloroform was washed four to five times with cold distilled water to remove about 1 percent of alcohol it contained as stabiliser. It was then dried over calcium chloride overnight and stored in ambered colour bottles keeping them completely filled. Everytime before use it was tested for the absence of acidity.

The hydrocarbons and their derivatives were obtained in pure state and further purified by recrystallisation or distillation and the purity ascertained by determining their M.P. or B.P. 1- and 2- methoxy naphthalene which could not be procured were prepared by the standard method of methylation and the 1- derivative was purified by vacuum distillation and the 2-derivative by recrystallisation from benzene.

Sodium—thio—sulphate, Potassium iodide and Potassium iodate used in the estimation of picric acid were of A.R. Grade.

The water used as solvent in the distribution studies was distilled water redistilled over Potassium hydroxide and Potassium Permanganate.

Procedure

The procedure adopted in the present studies was essentially that used by Gardner and Stump (loc. cit.) which is modification of one used by Anderson and Hammick (loc. cit.). Picric acid in the amount 0.8 to 1.0 g. was weighed and transferred to equilibrium vessels (N.M. 4 oz. bottles) 50 ml. of the equilibrium water was then delivered into each vessel from a calibrated pipette followed by similar addition of 50 ml. of chloroform solution of aromatic substance under investigation. The latter solution was prepared on weight—volume basis and its concentration was chosen depending upon its solubility and that of its complex in chloroform. The stoppered vessels were then initially shaken at room temperature for 10 to 15 minutes and then placed in water thermostat which was maintained at the working temperature (18°C. or 27°C. with an accuracy of ±0.1°) for at least 3 hours, shaking them every half an hour for about 5 minutes, leaving in thermostat finally for one hour for complete separation of two layers. Two lots of 10 ml. of the aqueous phase was withdrawn from each vessel and analysed after dilution with 20 ml. of distilled water by adding an excess of 0.1 N Potassium iodate and 10 percent potassium iodide solution and titrated the librated iodine against 0.01 N Sodium—thio-sulphate. The mean of at least two readings in close agreement was used for the calculation of total picric acid in aqueous layer and the difference between the quantity and the amount of picric acid weighed out initially gave the amount of picric acid in chloroform phase Y.

From distribution studies of picric acid between water and chloroform in the absence of hydrocarbon at the temperature of investigation the equilibrium concentrations of picric acid in chloroform and in water were determined. The logarithm of these concentrations were plotted and from the co-ordinates of the points on or very near the straight line plot, the equation for the partition curve was derived using the method of least

squares. The equilibrium concentration of picric acid X in water and Y in chloroform at 18°C. and 27°C. are plotted in Figs. 1 and 2 respectively and the equation derived are:

$Y = 1.723\,X + 1.283$ at 18°C.

and $Y = 1.620\,X + 1.118$ at 27°C.

For the substituents in naphthalene position 1 the stabilities at both the temperatures decrease in the order:

$$OCH_3 > CH_3 > H > Br > Cl$$

whereas for the substituents in the 2- position the order of decreasing stability is

$$OH > CH_3 > OCH_3 > H > Br$$

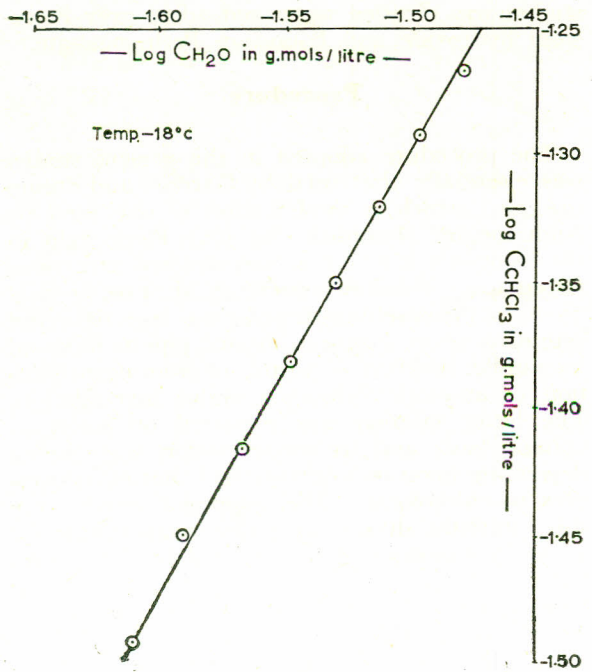

Fig. 1.

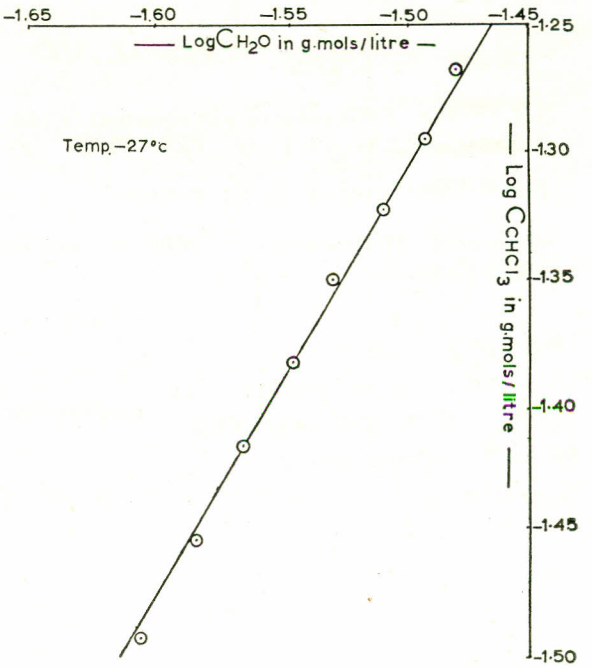

Fig. 2.

The values of free picric acid P in the chloroform phase corresponding to its concentration in the aqueous phase X were calculated from these equations. The values of stability constant K used are those worked out by Gardner and Stump (loc. cit.) but for 2-naphthol it was calculated using equation $k = 0.0038\,V$, the value of molecular volume V obtained from density data of this compound from literature. Thus knowing Y, P, Z and k the stability constants were calculated using equation (3).

Results and Discussion

The results of the experiment are summarised in Table 1. The values of constants are expressed in lit. $mole^{-1}$.

None of these orders follow strictly either the p- or m- order of Hammett's σ functions as expected from the behaviour of complexes of picryl chloride and picric acid with substituted benzenes which are probably of the same type. Except, however for the reversal of the order in the case of the halogen substituents also found by Gardner and Stump (loc. cit.) the two orders observed appear to follow quantitatively Hammett's σ P- order. For the methyl and methoxy derivatives the contribution due to mesomeric effect seems to be, considerable so that in the latter case Hammett's m—order is violated. For the first series, however, there is better agreement with Hammett's P—order. Evidently contribution due to mesomeric effect appears to be stronger in naphthalene position 1—than in position 2.

TABLE 1.

Donor hydrocarbon	K lit. mole^{-1}	K at 18°C. lit mole^{-1}	K at 27°C. lit mole^{-1}
Naphthalene	0.47	2.99	2.73
1—methyl naphthalene	0.53	3.61	3.12
2—methyl naphthalene	0.54	4.32	3.77
2—naphthol	0.45	6.52	3.81
1—methoxy naphthalene	0.56	6.31	4.84
2—methoxy naphthalene	0.56	3.63	3.27
1—chloro naphthalene	0.52	2.07	1.84
1—bromo naphthalene	0.53	2.41	1.99
2—bromo naphthalene	0.53	2.02	1.51

In the case of the first series the relative positions of the CH_3 group and the halogen substituents are in keeping with their known electron donating and electron withdrawing natures respectively. At a first sight it might appear that the inductive effect controls the order of stability constants in series but the position of hydroxy and methoxy groups clearly indicate that even in this series the contribution due to mesomeric effect appears to far outweigh that by the inductive effect so that the K values for these substituents are higher than those for the methyl and unsubstituted naphthalene complex respectively. In case of the halogen substituents, however, the inductive effect appears to dominate over either mesomeric or polarisation effect, the contribution due to these latter effects being either small or in mutual opposition so that Pauling's electronegativity order ultimately prevails.

Among the complexes of this type steric factors usually play an important role. Though this effect is not in evidence in halogen substituted naphthalenes studied by the author, it acquires its due importance in the complexes of methyl derivatives, the greater facility of hyperconjugation of methyl group in position 1—as compared with position 2—with the naphthalene nucleus failing to bring about a higher increase in π-electron density. The observations are generally in agreement with those of Gardner and Stump (loc. cit.).

TABLE 2.

Donor Hydrocarbon	T°A	K lit. mole^{-1}	$-\Delta F$ K-cal.mole^{-1}	$-\Delta H$ K-cal.mole^{-1}	$-\Delta S$ K-cal. mole^{-1}/°C.
Naphthalene	291	2.99	0.63	1.62	0.00334
	300	2.73	0.60		0.00334
1—methyl	291	3.61	0.74	2.82	0.00715
naphthalene	300	3.12	0.68		0.00715
2—methyl	291	4.32	0.84	2.63	0.00957
naphthalene	300	3.77	0.79		0.00947
2—naphthol	291	6.52	1.08	10.35	0.00318
	300	3.81	0.80		0.00318
1—methoxy	291	6.31	1.06	5.13	0.01395
naphthalene	300	4.84	0.94		0.01395
2—methoxy	291	3.63	0.74	2.00	0.00432
naphthalene	300	3.27	0.71		0.00432
1—chloro	291	2.07	0.42	2.23	0.00622
naphthalene	300	1.84	0.36		0.00621
1—bromo	291	2.41	0.56	3.73	0.00109
naphthalene	300	1.99	0.41		0.00110
2—bromo	291	2.02	0.40	5.53	0.00142
naphthalene	300	1.51	0.25		0.00143

From the values of stability constants of picric acid complexes in chloroform solution at 18°C. and 27°C., the values of heat of formation ΔH of the complexes, in this temperature range, have been calculated along with the values of free energy of formation ΔF at the two temperatures. From these, the values of entropies ΔS at the corresponding temperatures have been determined. The values of these thermodynamic functions for the complexes are given in Table 2.

The enthalpy values are of the order of -2 to -5.5 and are comparable to those observed by Bier[4] for 1:1 complexes of substituted benzenes and naphthalenes with S—trinitro benzene in chloroform solution and also Briegleb[5] for 1:1 complexes of benzene and naphthalene with the same acceptor in carbon—tetra—chloride solution. The observed values of ΔH rule out the possibility of covalent binding for these complexes. The higher enthalpy values for 2—naphthol complex indicated a rather stronger bond between the components. In this case the possibility of an intramolecular hydrogen bond between O—atom of the donor substituent and an O—atom of the nitro groups of the acceptor along with other electrostatic binding forces such as dipole—dipole, dipole—induced dipole etc. between the components should be considered. There may also be a contribution from possible orbital overlapping of the π —electron system of the donor with the vacant orbital of the nitro groups.

The low entropy values indicate the absence of any strong covalent binding as the process of removal of solvation sheet inherent in such an interaction in solution would require a much higher order of entropy magnitude. The entropy values for the picric acid complexes of 1—and 2—methyl naphthalenes are a little higher and for 1—and 2—methoxy complex substantially higher. As the enthalpy values for the complexes of these hydrocarbons, however, are 2 to 3 K—calories only the presence of a convalent binding in their complexes appear to be doubtful.

In conclusion it may be stated that forces between components of the complexes studied appear in most cases to be composite and electrostatic in nature, dipole—dipole, dipole—induced dipole and probably dispersion interactions all making their contributions to the complex stabilities. It is less likely that an ionic bond involving the complete transfer of an electron is involved. The formation and stability of molecular complexes of aromatic hydrocarbons and their derivatives with poly—nitro aromatic compounds must be ascribed to the susceptibility of nitro group to undergo favourable polarisation on the approach of an electron—rich reagent. The seat of coordination of the donor molecule in such complexes need not necessarily be the nitrogen atom of a specific nitro group; the electron attracting force in the acceptor molecule may well be exerted through the aromatic nucleus to which the nitro group is attached.

Acknowledgement.—The author expresses his deep sense of gratitude to Prof. R.N. Merchant, Lecturer in Chemistry, Elphinston College, Bombay, for his guidance in research work.

References

1. T.S. Moore, F. Shepherd and E. Goodall, J. Am. Chem. Soc., 1447 (1931).
2. H.D. Anderson and D.L. Hammick, J. Chem. Soc., 1089 (1950).
3. P.D. Gardner and W.E. Stump, J. Am. Chem. Soc., **79,** 2759 (1957)
4. A. Bier, Recueil des Travax, **75,** 866 (1956).
5. G. Briegleb, Z. Physik. Chem., **B 31,** 58 (1936); **B 32,** 305 (1936).