MOLECULAR COMPLEXES OF PICRIC ACID WITH AROMATIC HYDROCARBONS AND THEIR DERIVATIVES

Part II.—Association Constants of 1:1 Complexes of Polynuclear Aromatic Hydrocarbons and Picric Acid

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In part I of this paper[1] the author has described the formation of complexes of picric acid with few mono-substituted naphthalenes and has discussed the stability of complexes and the nature of complexation. The work is further continued selecting a few polynuclear hydrocarbons viz. naphthalene, anthracene, fluorine, phenanthrene, pyrene, stilbene and acenaphthene, and complexes of these with picric acid are studied in chloroform solution at 18°C. and 27°C. The data collected is used to examine the factors governing the stability of complexes and the extent of the magnitude of the binding force between the components.

Introduction

Association constants of 1:1 complexes of polynuclear hydrocarbons with polynitro compounds have been determined by various workers [2-7] in most cases at any one temperature and in a few cases the ehats of fromation have been determined. [7,8] Foster, Hammick and Pierce[8] have recently studied stabilities of fourteen hydrocarbon picrates in chloroform solution at 18°C. by the partition method and related the corresponding values of free energy of formation of these complexes to the frequencies of the charge transfer bands of the complexes of the same hydrocarbons with chloranil. All these authors observed that in the complexes with multi-ring compounds as donors, the donor acceptor ratio is usually 1:1 unless two or more structurally independant co-ordination sites are present in the donor molecule as in stilbenes and diphenyl polyenes which form 1:2 complexes with S-trinitrobenzene. Even when two such sites are available the presence of unfavourable steric factors may prevent the simultaneous occupation of both these sites by an acceptor. It has been found that polynuclear aromatic hydrocarbons frequently function as single donor units in spite of their large size as the donor character of the 1:1 complexes would be considerably less than that of the uncomplexed hydrocarbons both from an electronic and a steric point of view.

Summerising the results of the investigations cited the present author concludes that in general the stabilities of 1:1 complexes of a given acceptor increase as the number of rings in the donor or fused rings in polynuclear donor system is increased. Favourable relationships in the size and the shape of the donor and the acceptor molecules may also contribute towards increase in stability. Other factors such as polarisability, compactness, facility for resonance, etc., which contribute to the stability of complexes have to be considered. The present author has made an attempt to show how the stabilities of compelexes are related to these structural factors.

Experimental

This part has been fully described in Part I of this paper by the author.[1]

Results and Discussion

Table 1 gives the values of solubility depression constants k and stability constants K expressed in lit. mole^{-1}. From K values at 18° and 27°C. the values of free energy of formation ΔF, enthalpy ΔH and entropy ΔS are calculated and expressed in K—calories mole^{-1}. The entropy is per °C. Table 2 records the values of K for complexes of benzene and diphenyl from literature and are compared with that determined for stilbene complex. In Table 3 are collected the values of molar polarisabilities as calculated from refarctive index for the D line of sodium and of total molar polarisation as calculated from dielectric constants, for the hydrocarbons along with the values of the stability constants at 18°C.for their complexes with picric acid.

A glance at Table 1 immediately gives supports to the views of other authors that increase in the number of fused rings enhances the stabilities. Thus we have the increasing stabilities of complexes in the order Naphthalene < Fluorene < Acenaphthene < Anthracene < Phenanthrene < Pyrene. The Table also reads very low enthalpy values indicating weak interaction between the components. Similar results are obtained by Briegleb and Coworkers[11] for complexes of s-trinitrobenzene in carbon tetrachloride solution and by Bier[7] for similar complexes in chloroform. There seems to be no correlation between donor structure and the heat of formation of its picric acid complex.

Table 1.

Donor hydrocarbon	k lit. mole^{-1}	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 ..	0.47	291	2.99	0.63	1.62	0.0034
		300	2.73	0.60		0.0034
Anthracene ..	0.764	291	7.91	1.20	5.28	0.0014
		300	6.02	1.07		0.0014
Phenanthrene ..	0.60	291	8.12	1.21	3.68	0.0085
		300	6.71	1.14		0.0085
Pyrene ..	0.607	291	18.47	3.55	2.21	0.0046
		300	16.47	2.97		0.0025
Fluorene ..	0.58	291	3.15	0.664	0.89	0.0077
		300	3.01	0.667		0.0077
Acenaphthene ..	0.58	291	4.39	0.85	5.68	0.0016
		300	3.27	0.71		0.0016
Stilbene ..	0.66	291	1.88	0.37	1.56	0.0041
		300	1.73	0.33		0.0038

Table 2.

Complex of	K at 18°C.	Source
Benzene	0.43	Reference 10
Diphenyl	0.97	Reference 9
Stilbene	1.88	Author

Table 3.

Hydrocarbon	K of complex at 18°C.	Moler polarisability	Total moler polarisation
Naphthalene	2.99	44.36	45.3
Fluorene	3.15	—	54.7
Anthracene	7.91	48.71	64.1
Phenanthrene	8.12	53.84	60.7
Pyrene	18.47	56.54	67.5

It may be pointed out that all these measurements of heats of formation have been made in solution wherein no allowance has been made for the heats of solution. It is evident from some of the measurements of Briegleb that the effect of the solvent is not to be neglected, for the percentage difference between the heats of formation of some complexes in two different, but similar solvents is considerable. Although it may be assumed that the differences in the heats of solution of the hydrocarbons studied, in chloroform, would be small, particularly as no large structural differences are involved, it would not be safe to derive any quantitative relationship on the basis of the data obtained since the difference in enthalpy values are not large and not quite outside the range of experimental errors inherent in these types of measurements. The range of entropy values for majority of compounds from 1 to 6 calories per mole per degree indicate no covalent binding in this complex formation.

An examination of Table 2 reveals the fact that the value for stilbene complex is substantially higher than that for the diphenyl complex at the same temperature which in its turn is higher than that for the benzene complex. Thus the observed order of increasing stabilities with increase in the number of benzene rings and the length of the chain is consistent with the observed intensification of the colours of complexes of s-trinitrobenzene with diphenyl polyenes.[5]

Briegleb and Schachowskoy [8] have found the complex stability to increase with an increase in the polarisability of the hydrocarbon component which is in qualitative agreement with the order of

K values observed by the author and also with the order of ΔH values calculated from the K values at 18° and 27°C. Table 3 relates complex stabilities of hydrocarbons with their molar polarisability and total molar polarisation.

The progressive increase in stability with the number of fused rings may also be related to the increase in the degree of delocalisation of the π-electron systems of the component rings in the order.

Benzene   < Naphthalene   < Fluorene
< Acenaphthene   < Anthracene   < Phenanthrene
< Pyrene
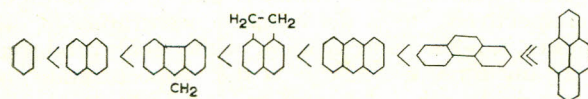
The stability of the pyrene complex was found to be very much higher than that of the rest. The explanation of this high value lies probably in the symmetry of the pyrene molecule and its compactness allowing it to fit well over the picric acid molecule and promoting maximum interaction of the π-electron systems of the donor with the acceptor molecule. The high melting points of the picrates of pyrene and its derivatives compared with those of the other hydrocarbons are an index of their much higher stability.[12]

The above discussion leads to the conclusion that the stability of complexes of this type is governed by polarisability, π—electron systems and size and shape of the donor molecule. However, the interactions are weak in nature involving no charge transfer or bond formation. These views are also supported by Khatavkar, Datar and Khanolkar[13] in the magnetic susceptibility measurements of these complexes. The positive departures from additivity is explained on the basis of electronic polarisation of hydrocarbon whereas the absence of a negative departure from additivity has led the authors to infer the absence of a strong bond of the covalent type.

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