612. *Complexes of Aromatic Hydrocarbons with Strong Lewis Acids.*

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The electronic absorption spectra of complexes of 1,2-benzanthracene, anthracene, perylene, tetracene, and 3,4-benzopyrene with strong Lewis acids such as BF_3, PF_5, $SbCl_5$, and SO_3 have been investigated. Two sorts of complex are formed: a covalent complex with the Lewis acid, and a complex in which the hydrocarbon is present as its monopositive ion.

The spectra of the covalent complexes very closely resemble those of the corresponding proton complexes. This implies that, for the hydrocarbons investigated, proton addition and the addition of a Lewis acid take place at the same carbon atom of the hydrocarbon molecule. The competition between the formation of covalent complexes and monopositive ions is discussed on the basis of the basicity constants and oxidation potentials of the aromatic hydrocarbons.

Tetracene in dimethyl sulphate with sulphur trioxide displays a spectrum which is a superposition of the spectra of the mono- and the di-positive ion.

VARIOUS aromatic hydrocarbons form intensely coloured complexes with Lewis acids such as ferric chloride, stannic chloride, and antimony pentachloride.[1] Their structures remained obscure until Weissman, de Boer, and Conradi[2] reported that the solid complex of perylene with antimony pentachloride is paramagnetic. In addition, the solution of the complex in nitrobenzene displays practically the same absorption spectrum as the perylene monopositive ion formed on dissolving the hydrocarbon in concentrated sulphuric acid.[3] We therefore conclude that on addition of a strong Lewis acid, such as antimony pentachloride, to a solution of perylene in nitrobenzene, electron transfer takes place from the hydrocarbon molecule to the Lewis acid and the monopositive ion is formed.

The reaction of a number of highly basic aromatic hydrocarbons with compounds such as BF_3, PF_5, $SbCl_5$, and SO_3 will now be discussed. The experimental results may illuminate the nature of these complexes of aromatic hydrocarbons with strong Lewis acids.

EXPERIMENTAL

Hydrocarbons were from the previous source.[4]

Complexes with Boron Trifluoride and Phosphorus Pentafluoride in 1,2-Dichloroethane.—Most of the solutions were prepared in a Pyrex apparatus to which a quartz cell (optical path 1 cm.) was connected by a graded Pyrex-to-quartz seal. The Pyrex apparatus had no glass joints or stopcocks and was provided with four magnetic break-seals. The whole equipment was baked out at 450° under high vacuum ($\sim 10^{-6}$ mm. Hg) for two days.

Through one break-seal about 100 ml. of 1,2-dichloroethane (prefractionated and carefully dried on P_2O_5 *in vacuo*) was distilled into the equipment. Another break-seal was used to introduce a weighed amount of hydrocarbon. The concentration of the hydrocarbon was about 10^{-4}M. The apparatus was then sealed off and the spectrum of the solution was measured. Next, boron trifluoride (Fluka A.G.; carefully fractionated) or phosphorus pentafluoride was introduced through the third break-seal, while the apparatus was kept in the dark. The pressure was read from a constant-volume manometer. The concentration of BF_3 in 1,2-dichloroethane at 20·0°/1 atm. is $3·7 \times 10^{-2}$M.

After the equipment had been sealed off the spectrum of the solution was recorded. Finally the fourth break-seal could be used for the removal of the gas by freezing the solution in solid carbon dioxide–alcohol and evacuating (3 times).

Phosphorus pentafluoride was prepared by decomposing Phosfluorogen (Ozark-Mahoning Co.),

[1] (a) Hilpert and Wolf, *Ber.*, 1913, **46**, 2215; (b) Radulescu, *Ber.*, 1931, **64**, 2223.
[2] Weissman, de Boer, and Conradi, *J. Chem. Phys.*, 1957, **26**, 963.
[3] Hoijtink and Weijland, *Rec. Trav. chim.*, 1957, **76**, 836.
[4] Aalbersberg, Hoijtink, Mackor, and Weijland, preceding paper.

a substituted benzidinediazonium salt of phosphorus hexafluoride, at about 100°. It was purified by freezing (−180°), evacuating, and distilling (3 times).

The spectra were recorded on a Cary spectrophotometer (Model 11 or 14).

Complexes with Antimony Pentachloride and Sulphur Trioxide.—No special precautions were taken in the preparation of solutions of tetracene and perylene in nitrobenzene with $SbCl_5$ or in dimethyl sulphate with SO_3. In nitrobenzene the complexes with $SbCl_5$ slowly decompose and the extinctions were calculated by extrapolation to zero time. The extrapolated values obey the Beer–Lambert law in the concentration range $0·01$—$0·5 \times 10^{-4}$M.

The spectra were measured on a Unicam SP.500 spectrophotometer.

Results.—The spectra of the complexes of anthracene, perylene, tetracene, and 3,4-benzopyrene with BF_3 (1 atm.) in 1,2-dichloroethane, and with $SbCl_5$ in nitrobenzene, are shown in Figs. 1, 2, 3, and 4, respectively. The spectrum of a solution of tetracene in dimethyl sulphate

FIG. 1.

FIG. 2.
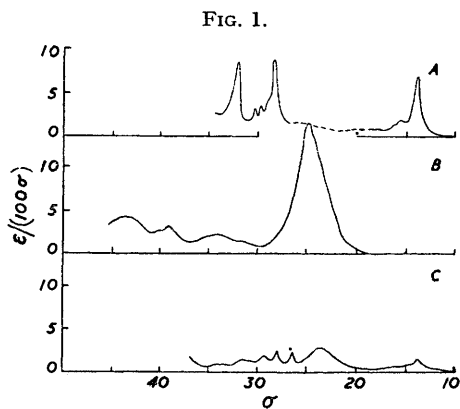
A, Monopositive ion of anthracene (solvent $CF_3·CO_2H$–BF_3,H_2O in contact with air, by extrapolation); *B*, Proton complex of anthracene (solvent HF); *C*, Anthracene + BF_3 in 1,2-dichloroethane in the dark.
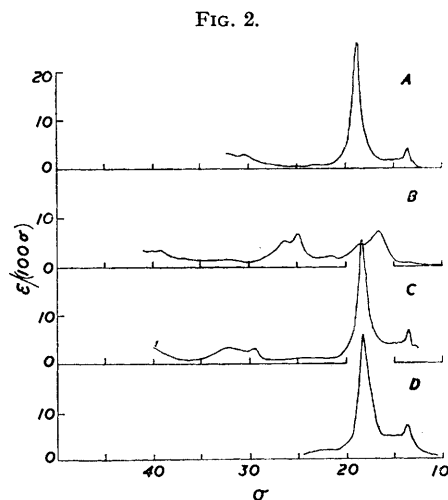
A, Monopositive ion of perylene (solvent $CF_3·CO_2H$–BF_3,H_2O in contact with air); *B*, Proton complex of perylene (solvent HF); *C*, Perylene + BF_3 in 1,2-dichloroethane after irradiation; *D*, Perylene + $SbCl_5$ in nitrobenzene.

In all diagrams the function ε/σ is plotted against σ, where ε is the molar absorption coefficient and σ is the wave number (in kK).

with SO_3 is given in Fig. 5C. The spectrum of perylene in dimethyl sulphate in the presence of SO_3 is identical with that of Fig. 2D. For comparison the spectra of the monopositive ions [4] and the proton complexes [5] of anthracene,* perylene, tetracene, and 3,4-benzopyrene are also represented in Figs. 1—4. The spectrum of the tetracene dinegative ion [6] is given in Fig. 5B.

Complexes with BF_3 and PF_5. The reaction of BF_3 and PF_5 with the hydrocarbons in 1,2-dichloroethane appears to be perfectly reversible. If the gas is removed from the solution by freezing and evacuation or if an excess of water is added, the original spectrum of the hydrocarbon reappears. No decomposition was observed after short exposure to ultraviolet radiation (medium-pressure mercury arc).

Water must be rigorously excluded since BF_3 and PF_5 with water form strong proton acids, *e.g.*, BF_3,H_2O. These acids might react with the strongly basic hydrocarbons to give their proton complexes.[5]

* Anthracene in $CF_3·CO_2H$–BF_3,H_2O (22 moles %) containing oxygen [4] is present as an equimolar mixture of proton complex and monopositive ion. This spectrum of the anthracene monopositive ion of Fig. 1A has been obtained by extrapolation to 100% conversion.

[5] Dallinga, Mackor, and Verrijn Stuart, *Mol. Phys.*, 1958, **1**, 123; Verrijn Stuart and Mackor, *J. Chem. Phys.*, 1957, **27**, 826.

[6] Balk, de Bruijn, and Hoijtink, *Mol. Phys.*, 1958, **1**, 151.

In view of the extreme care taken to exclude water it is highly improbable that proton complexes should be formed.* Nevertheless in nearly all cases the solutions, at least initially, display spectra remarkably similar to those of the proton complexes. In particular the more basic hydrocarbons show this behaviour, as Fig. 4C shows for 3,4-benzopyrene. Since water is absent, these spectra are probably due to the formation of covalent BF_3–hydrocarbon complexes.

The covalent complex of 3,4-benzopyrene appears to be very stable; exposure to ultraviolet
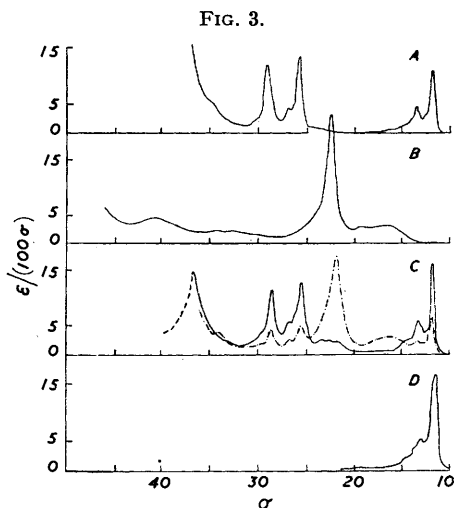
FIG. 3.

FIG. 4.

A, Monopositive ion of tetracene (solvent $CF_3 \cdot CO_2H$–BF_3,H_2O in contact with air); *B*, Proton complex of tetracene (solvent HF); *C*, Tetracene $+ BF_3$ in 1,2-dichloro-ethane, — · — · — before irradiation, ⎯⎯ after irradiation; *D*, Tetracene $+ SbCl_5$ in nitrobenzene.
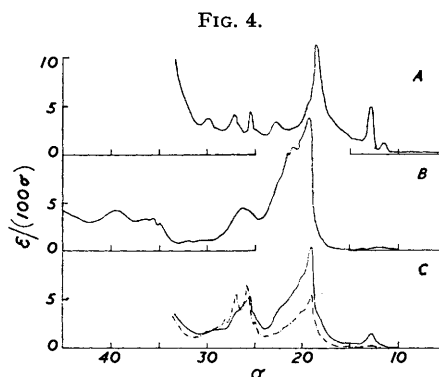
A, Monopositive ion of 3,4-benzopyrene (solvent $CF_3 \cdot CO_2H$–BF_3,H_2O in contact with air); *B*, Proton complex of 3,4-benzopyrene (solvent HF); *C*, 3,4-benzo-pyrene in 1,2-dichloroethane; — · — · — with BF_3 in the dark, ⎯⎯ with PF_5 after irradiation.

radiation hardly affects the spectrum. The solutions of the other hydrocarbons mentioned in Table 1, on the other hand, are not stable and the spectra of the solutions change slowly. This reaction is photo-catalysed; on exposure of the solutions to ultraviolet radiation the spectra

TABLE 1. *Percentages of hydrocarbon present as molecule, covalent complex, and mono-positive ion for different hydrocarbons in 1,2-dichloroethane at 1 atm. of BF_3.*

	Before irradiation			After irradiation		
Hydrocarbon	M	M,BF_3	M⁺	M	M,BF_3	M⁺
1,2-Benzanthracene	⩾98	⩽2 ‡	⩽1 ‡	92 *	⩽3 ‡	⩽1 ‡
Anthracene	55	25	20	35 *	35 *	30 *
Perylene	100	⩽1	⩽1	⩽1	⩽1	⩾98
Tetracene	⩽5	70	25	⩽2 †	⩽5 †	⩾93
3,4-Benzopyrene	58	40	⩽2	56	40	~5

   * On irradiation the solute is partly precipitated.
   † Could not be analysed accurately.
   ‡ The spectrum (not recorded in the Figures) shows very weak absorption bands at 18·80 and 21·75 kK similar to the bands of the proton complex. The spectrum of either monopositive or mono-negative ion is not known. By comparison with the spectra of the monopositive ion of anthracene [4] and of the mononegative ion of dibenzanthracene, measured by Paul, Lipkin and Weissman,[12] it seems certain that the mononegative as well as the monopositive ions of 1,2-benzanthracene should have a fairly strong absorption band at frequencies lower than 15 kK. Below 16 kK no absorption was observed and we conclude that less than 1% of the molecule is converted into its monopositive ion.

display absorption bands of the monopositive ions.[4] For tetracene this is illustrated in Fig. 3C. After irradiation the spectrum is practically identical with that of the monopositive ion.[4]†

   * No water could be detected in the solution by the Karl Fischer titration. This means that the concentration of BF_3 in our experiment is at least 40 times that of water.
   † In nitromethane the formation of the positive ion proceeds much faster. In this case, however, the spectra alter with time, owing to side reactions with the solvent.

It is clear that the spectra displayed by the solutions of these hydrocarbons in 1,2-dichloro-ethane in the presence of BF_3 are superpositions of the spectra of the uncomplexed molecules, the covalent complexes, and the monopositive ions. Table 1 gives the compositions of the solutions in the presence of BF_3 before and after irradiation. In general, bands to be assigned to covalent complexes and monopositive ions are easily recognized. The bands of the un-complexed molecules are weaker than those of the corresponding complexes and partly coincide with the latter. Fractions of uncomplexed molecules below 10% cannot be analysed accurately.

The preliminary results obtained with PF_5 are similar to those with BF_3.

DISCUSSION

From the spectra in Figs. 1, 2, 3, and 4 and the data in Table 1 it appears that two different species are formed by the reaction of aromatic hydrocarbons with strong Lewis acids, *viz.*, covalent complexes and monopositive ions.

Covalent Complexes.—The spectra of the complexes of the hydrocarbons with BF_3 (or PF_5) in 1,2-dichloroethane before irradiation closely resemble the spectra of the proton complexes.[5] Recent investigations [5,7,8] have firmly established Gold and Tye's [9] idea that in proton complexes the proton is linked to one of the carbon atoms by a covalent bond. From proton spin resonance [8] it appeared that the methylenic group (formed by proton addition to one of the carbon atoms) has an aliphatic character. The positions and

intensities of the absorption bands in the visible and near ultraviolet regions have been shown to be representative of the conjugated part of the proton complex.[5] Since the spectra of the proton complexes and the corresponding covalent BF_3 complexes are closely similar (cf. Figs. 1—4), we conclude that the BF_3 molecule is added to the same carbon atom of the aromatic hydrocarbon as the proton. Thus the structures of the covalent complexes of anthracene, tetracene, and 3,4-benzopyrene (perylene in the presence of BF_3 does not form a covalent complex) must be comparable with the structures of the corresponding proton complexes.[5] For instance the proton complex and the covalent complex with BF_3 of anthracene should have the structures (I) and (II).

TABLE 2. *Basicity constants, oxidation potentials, relative values of* $\log K$ *of reaction* (4) *and other experimental values in 1,2-dichloroethane at 1 atm.* BF_3.

Hydrocarbon	$\log K_b$ [a]	$\log \dfrac{[MBF_3]}{[M]}$	ε_{ox} [b]	$\log \dfrac{[M^+]}{[M]}$ [d]	const. $+ \log K$	$\log \dfrac{[MBF_3]}{[M^+]}$ [d]
1,2-Benzanthracene ...	2·3	$< -1·7$	0·92	$< -1·7$	17·9	—
Anthracene	3·8	$\sim -0·3$	0·84	$\sim -0·0$	18·0	$\sim 0·0$
Perylene	4·4	$< -1·7$	0·63 [c]	$\geqslant 1·7$	15·1	$< -1·7$
Tetracene	5·8	$\sim +1·4$	0·54	$\geqslant 1·7$	15·0	$\sim -1·0$
3,4-Benzopyrene	6·5	$\sim -0·2$	0·76	$\sim -1·0$	19·4	$\sim +0·9$

[a] From ref. 7. [b] In volts against the Ag–0·1N-Ag+ electrode in acetonitrile; solvent: acetonitrile. Taken from ref. 10a. [c] The oxidation potential of perylene has been calculated from its reduction potential by using the linear relation between reduction and oxidation potentials of alternant hydro-carbons (cf. ref. 10b). [d] Values obtained after irradiation.

The stability of the covalent complex is governed by the constant K_c of the equilibrium between uncomplexed molecule M plus Lewis acid A and the covalent complex MA:

$$M + A \rightleftharpoons MA \qquad \ldots \ldots \ldots \ldots \ldots (1)$$

[7] Mackor, Hofstra, and van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.
[8] MacLean, van der Waals, and Mackor, *Mol. Phys.*, 1958, **1**, 247.
[9] Gold and Tye, *J.*, 1952, 2173, 2181.
[10] (a) Lund, *Acta Chem. Scand.*, 1957, **11**, 1323; (b) Hoijtink, *Rec. Trav. chim.*, 1958, **77**, 555.

One would expect the basicity constant K_b (Table 2, column 1) to be a qualitative measure of the constant K_c for these hydrocarbons. In Table 2 values of log K_b and log $\{[MBF_3]/[M]\}$ (taken from Table 1) are compared. The hydrocarbons are arranged in sequence of increasing basicity. 1,2-Benzanthracene (a hydrocarbon with a relatively low basicity) does not form complexes with BF_3, whereas tetracene and 3,4-benzopyrene, both having much higher basicity constants, do form covalent complexes. Deviations from the basicity sequence as occurring in Table 2 are probably due to the fact that steric factors are more important in BF_3 addition than in proton addition.

Monopositive Ions.—In nitromethane and in nitrobenzene (solvents with a relatively high dielectric constant) or in 1,2-dichloroethane on irradiation the aromatic hydrocarbons may be partly or completely converted into their monopositive ions. The spectra of the hydrocarbons anthracene, tetracene, and perylene in the presence of strong Lewis acid such as BF_3, PF_5, and $SbCl_5$ closely resemble those of the monopositive ions reported previously.[4] Here the Lewis acid may act as electron acceptor. The experiments have shown that these reactions are perfectly reversible. If the Lewis acid is assumed to take up one electron from the hydrocarbon the following equilibrium exists: *

$$M + A \rightleftharpoons M^+ + A^- \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For a given Lewis acid the oxidation potentials of the hydrocarbons [10] (Table 2) will give a qualitative measure of the stability of the monopositive ions. If we assume that after irradiation of the solution of the hydrocarbon in 1,2-dichloroethane in the presence of BF_3 the equilibrium of reaction (2) is reached, the value of log $\{[M^+]/[M]\}$ (Table 2) should run parallel with the corresponding value of ε_{ox}. From Table 2 it appears that 3,4-benzo-pyrene and 1,2-benzanthracene are much less easily oxidized than either perylene or tetracene. Anthracene seems to be a better electron donor than would be expected on the basis of its oxidation potential.

The experiments have not provided conclusive evidence about the exact nature of the negative counter-ions formed in reaction (2).

The low rate of this reaction in 1,2-dichloroethane may be due to the fact that the negative counter-ion A^- must be stabilized, *e.g.*, by a combination with a second negative ion:

$$2BF_3^- \rightleftharpoons B_2F_6^{2-} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In solvents with a high dielectric constant such as nitromethane or nitrobenzene the ion is probably stabilized by solvation.

Equilibrium between Monopositive Ions and Covalent Complexes.—The formation of mono-positive ions will be favoured by a low oxidation potential and a relatively low basicity. Since, generally, a low oxidation potential corresponds with a relatively high basicity only few hydrocarbons will be converted quantitatively into their monopositive ions on the addition of Lewis acids. The same conclusion was drawn [4] for formation of monopositive ions in strong proton donors. In the latter case a competition occurs between proton addition and the formation of monopositive ions.

The constant for the equilibrium

$$M^+ + A^- \rightleftharpoons MA \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

will give a qualitative measure of the ratio $[MA]/[M^+]$. Steric factors being neglected, this constant follows from the equation: [4]

$$\log K = \log K_b + 16 \cdot 95 \varepsilon_{ox} + \text{constant} \qquad . \quad . \quad . \quad . \quad (5)$$

in which K_b and ε_{ox} stand for the basicity constant and the oxidation potential of the hydro-carbon, respectively. The constant term depends on the choice of the Lewis acid, its concentration, the nature of the solvent, etc.

* In 1,2-dichloroethane especially, the ions M^+ and A^- will be strongly associated.

In Table 2, column 5, the relative values of log K are listed. These values again show a trend similar to that of the rather rough estimates of the ratios [MBF$_3$]/[M$^+$] listed in the last column.

Bivalent Positive Ions.—So far only the formation of monopositive ions was discussed. When, however, SO$_3$ is added to a solution of tetracene in dimethyl sulphate, a mixture of mono- and di-positive ions is formed. In Fig. 5 the spectrum of this solution is compared with the spectra of the tetracene monopositive and dinegative ion.[6] Since according to the theory the spectra of the dipositive and dinegative ions (as well as the spectra of the monopositive and mononegative ions) of alternant hydrocarbons will be practically identical [11] it may be concluded from Fig. 5 that the reaction of tetracene in dimethyl sulphate leads to a mixture of the mono- and the di-positive ion. Under the same conditions perylene gives only the monopositive ion. Apparently the oxidation potential of the perylene monopositive ion is higher than that of the tetracene monopositive ion.

These investigations [4] on the formation of hydrocarbon positive ions as well as previous investigations on the formation of hydrocarbon negative ions [6,12,13,14] suggest that electron
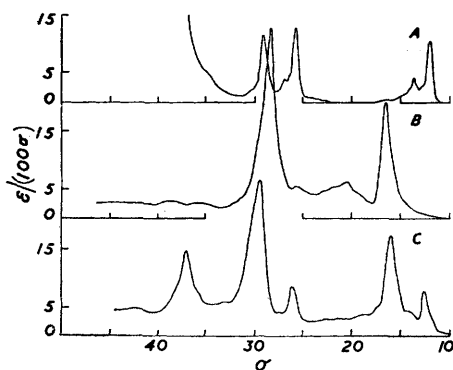

FIG. 5.

A, Monopositive ion of tetracene (solvent CF$_3$·CO$_2$H–BF$_3$,H$_2$O in contact with air); B, Tetracene^{2-} 2(Na$^+$) in tetra-hydrofuran; C, Tetracene + SO$_3$ in dimethyl sulphate.

transfer will be a major step in many organic reactions. This is also demonstrated by investigations by Buck, Lupinski, and Oosterhoff,[15] who found that the highly coloured complexes of substituted diphenyl- and of tetraphenyl-ethylene with acids, halogens, and nitro-compounds are in many cases paramagnetic.

The conclusions drawn in this paper also confirm Wizinger's suggestion [16] that electron transfer takes place in the reaction of aromatic compounds with Lewis acids and Weiss's [17] suggestion that electron transfer is the first step in organic oxidative reactions.

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[11] Weijland, Thesis, Free University, Amsterdam, 1958.
[12] Paul, Lipkin, and Weissman, *J. Amer. Chem. Soc.*, 1956, **78**, 116.
[13] de Boer and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 4549, and related papers.
[14] Balk, de Bruijn, and Hoijtink, *Rec. Trav. chim.*, 1957, **76**, 907; Hoijtink, de Boer, van de Meij and Weijland, *ibid.*, 1956, **75**, 487, and related papers.
[15] Buck, Lupinski, and Oosterhoff, *Mol. Phys.*, 1958, **1**, 197.
[16] Wizinger, *Organische Farbstoffe*, 1933, 48—51.
[17] Weiss, *J.*, 1942, 245; *Proc. Roy. Soc.*, 1954, *A*, **222**, 128.