611. *The Formation of Hydrocarbon Positive Ions in Strong Proton Donors.*

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The electronic spectra were measured of solutions of highly basic aromatic hydrocarbons in concentrated sulphuric acid, in oxygenated anhydrous hydrogen fluoride, and in oxygenated mixtures of trifluoroacetic acid and BF_3,H_2O. In the last, the spectra of solutions of perylene, tetracene, pyrene, anthracene and 3,4-benzopyrene resemble those of the corresponding mononegative ions. Similar observations were made with solutions of perylene, tetracene, and anthracene in the other solvents. We conclude that under these conditions the monopositive ions of these hydrocarbons are formed by electron transfer.

The solutions of anthracene in sulphuric acid as well as in hydrogen fluoride in the presence of oxygen display the spectra of the proton complex and of the anthracene monopositive ion. 3,4-Benzopyrene forms only proton complexes in these acids.

This difference in behaviour is discussed on the basis of the relative stabilities of monopositive ion and proton complex calculated from their oxidation potentials and basicity constants.

Yokozawa and Miyashita[1] discovered that a solution of perylene in concentrated sulphuric acid is paramagnetic. Weissman, de Boer, and Conradi[2] found that its electron spin resonance spectrum is nearly identical with the characteristic spectrum of the perylene mononegative ion. The electronic absorption spectra of perylene in sulphuric acid and its mononegative ion are also strikingly similar.[3] In the light of current quantum-chemical

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[1] Yokozawa and Miyashita, *J. Chem. Phys.*, 1956, **25**, 796.

[2] Weissman, de Boer, and Conradi, *J. Chem. Phys.*, 1957, **26**, 963; de Boer and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 4549; de Boer, Thesis, Free University, Amsterdam, 1957.

[3] Hoijtink and Weijland, *Rec. Trav. chim.*, 1957, **76**, 836.

theories these and other experimental results point to the formation of the perylene monopositive ion.[2,3,4] Gold and Tye,[5] on the other hand, demonstrated that anthracene in sulphuric acid forms a proton complex. Apparently, when aromatic hydrocarbons dissolve in strongly proton-active and oxidizing media both proton complexes and positive ions may be formed. This is confirmed by recent investigations on perylene in anhydrous hydrogen fluoride.[6] In absence of oxygen, perylene dissolves in the acid as the proton complex. When the solutions come into contact with oxygen, however, the absorption bands of the proton complex become very weak and a spectrum appears which closely resembles that of perylene in sulphuric acid.

The absorption spectra [42—10 kK (K, Kaiser ≡ cm.$^{-1}$)] of strongly basic aromatic hydrocarbons dissolved in concentrated sulphuric acid as well as in anhydrous hydrogen fluoride and a mixture of trifluoroacetic acid and BF_3,H_2O containing oxygen have been measured. On the basis of the results the relative stabilities of monopositive ions and proton complexes in strong proton donors with oxidizing properties are discussed.

EXPERIMENTAL

Hydrocarbons in Sulphuric Acid (with R. VAN HARDEVELD and J. VAN DER REE).—In the preparation of the solutions of aromatic hydrocarbons in sulphuric acid (" AnalaR " 96%) no special precautions were taken to exclude air and moisture. The hydrocarbons were from the same source as previously.[7,8]

The spectra were measured on a Unicam SP.500 spectrophotometer. Solutions of perylene and tetracene (0·01—0·5 × 10^{-4}M) obeyed the Beer–Lambert law.

Hydrocarbons in Anhydrous Hydrogen Fluoride and in Mixtures of Trifluoroacetic Acid with BF_3,H_2O.—Carefully purified samples of the hydrocarbons were used.[8]

The equipment for use with hydrogen fluoride was made of monel and nickel. It comprised a vessel with calibrated Kel-F windows, and the absorption cell, which has been described elsewhere,[6] mounted together on a panel. A weighed amount of hydrocarbon was placed in the calibrated vessel and hydrogen fluoride (I.C.I., pure grade) was distilled in *in vacuo*. By rotating the panel the solution was made to flow into the evacuated cell, which had a variable thickness (0·2—2 mm.). The cell was detached from the assembly, and the spectrum measured. Oxygen could be introduced into the system at pressures of up to 3 atm.

No special precautions were taken in handling the solutions in mixtures of CF_3CO_2H–BF_3,H_2O, since they do not attack either quartz or Pyrex. The solvent was prepared by saturating trifluoroacetic acid (Matheson Inc., redistilled) containing 22 moles % of water with boron trifluoride (Fluka AG; carefully fractionated) at atmospheric pressure. Finally, the solutions of the hydrocarbons in $CF_3{\cdot}CO_2H$–BF_3,H_2O were saturated with air.

The spectra were measured on a Cary spectrophotometer, model 11 or 14 (thermostatted at 25°).

Results.—The results obtained with perylene, tetracene, anthracene, 3,4-benzopyrene, and pyrene are in Figs. 1—5. Our remarks apply to the individual observations.

For comparison, the spectra of the mononegative ions of perylene (Fig. 1*A*), tetracene (Fig. 2*A*), anthracene (Fig. 3*A*), 3,4-benzopyrene (Fig. 4*A*), and pyrene (Fig. 5*A*) have been included. The spectrum of the 3,4-benzopyrene mononegative ion is new; the others have been reported.[7]

Solutions in sulphuric acid. Pyrene is readily soluble in sulphuric acid but decomposes within a few minutes, the colour of the solution changing from green to yellow. The green solution clearly displays the strong absorption of the proton complex at 22 kK. The solution of anthracene is slightly more stable than that of pyrene; its absorption spectrum can be measured with reasonable accuracy (Fig. 3*C*).

Perylene, tetracene, and 3,4-benzopyrene give stable solutions. On dilution with water and extraction with benzene the original hydrocarbons are recovered. When perylene dissolves in

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[4] Kon and Blois, jun., *J. Chem. Phys.*, 1958, **28**, 743.

[5] Gold and Tye, *J.*, 1952, 2173, 2181.

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

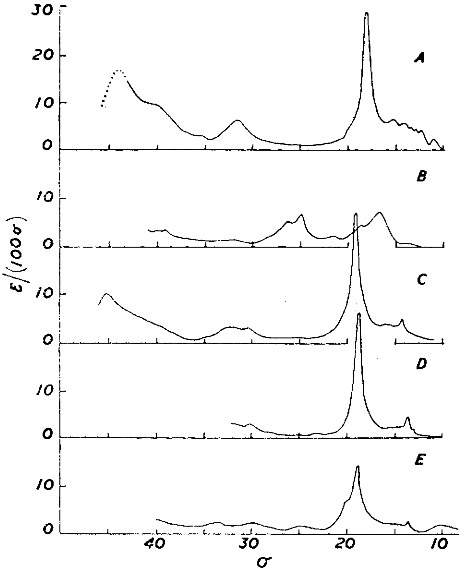
[7] Balk, Hoijtink, and Schreurs, *Rec. Trav. chim.*, 1957, **76**, 813.

[8] Mackor, Hofstra, and van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.

sulphuric acid a green colour is observed which after a few seconds changes to violet. The spectrum does not alter when the violet solution is kept for several days (Fig. 1*C*).

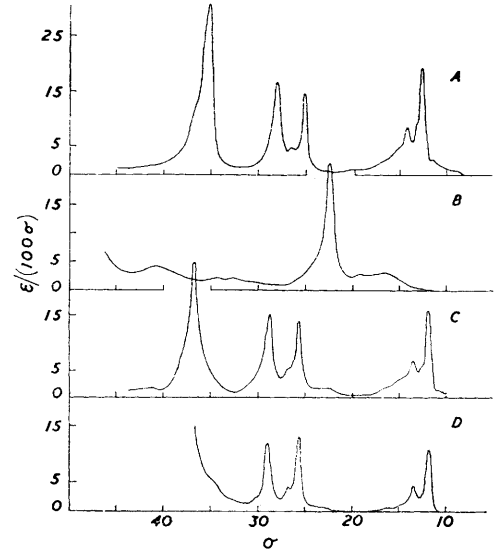
The spectrum of tetracene in sulphuric acid is a superposition of the spectra of two species. When the solution is kept for a few hours, a strong absorption band at 23 kK disappears and the bands of the positive ion become stronger; exposure to ultraviolet radiation for one minute has the same effect. The spectrum of the positive ion in sulphuric acid afterwards remains unaltered for several days (Fig. 2*C*) if the solution is kept in darkness. It is very likely that the strong absorption band at 23 kK is due to the initial formation of the proton complex.[6]

FIG. 1.



A, Perylene$^-$ Na$^+$ in tetrahydrofuran; *B*, Perylene in HF; *C*, Perylene in H_2SO_4; *D*, Perylene in $CF_3{\cdot}CO_2H–BF_3,H_2O$ in contact with air; *E*, Perylene in HF in contact with air.

FIG. 2.



A, Tetracene$^-$ Na$^+$ in tetrahydrofuran; *B*, Tetracene in HF; *C*, Tetracene in H_2SO_4; *D*, Tetracene in $CF_3{\cdot}CO_2H–BF_3,H_2O$ in contact with air.

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).

3,4-Benzopyrene in sulphuric acid displays a spectrum which very closely resembles that of the proton complex in hydrogen fluoride.[6] The spectra are represented in Fig. 4*C* and 4*B* respectively.

Naphthalene, phenanthrene, and chrysene were insoluble in concentrated sulphuric acid (see ref. 4). 1,2-Benzanthracene and 1,2:5,6-dibenzanthracene are only sparingly soluble and the solutions decompose rapidly. These hydrocarbons were not further investigated.

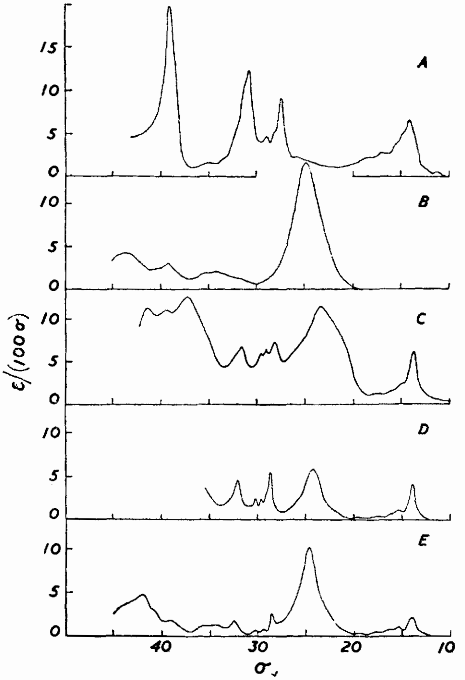
Solutions in anhydrous hydrogen fluoride. The spectra displayed in HF in the absence of oxygen by the proton complexes of perylene, tetracene, anthracene, 3,4-benzopyrene, and pyrene are in Figs. 1*B*—5*B*. The assignment of the spectral bands has been given.[6] In presence of oxygen the absorption bands of the proton complexes of perylene, tetracene, and anthracene rapidly become less intense while the absorption bands of their monopositive ions become more intense; no change was observed for 3,4-benzopyrene and pyrene when oxygen was introduced at 1 atm. The spectra of the solutions in oxygen-containing HF of perylene and anthracene are in Figs. 1*E* and 3*E*, respectively.

A few hours after introduction of oxygen at low pressures, and more rapidly at higher oxygen pressures, the spectra of the solutions, except perhaps for perylene, begin to change markedly. Dark precipitates are formed. Nevertheless, the formation of the monopositive ions appears to be reversible. For solutions of anthracene which have been in contact with oxygen for

1 hr., the original spectrum of the proton complex reappears when oxygen is eliminated by cooling and evacuating. In another experiment, at least 85% of the anthracene could be recovered from a solution in HF after it had been kept for 1 hr. in contact with oxygen at 45 atm. at 20° c.

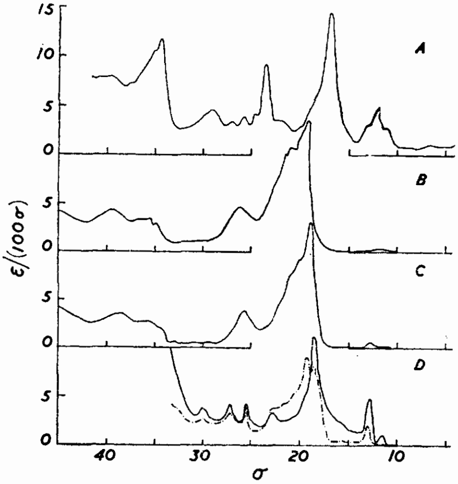
Solutions in trifluoroacetic acid with 22 *moles* % *of* BF_3,H_2O. If more than about 5 moles % of an equimolar mixture of BF_3 and H_2O are added to trifluoroacetic acid, the more highly basic hydrocarbons will dissolve in the mixture as their proton complexes. In absence of oxygen the solutions display spectra resembling those in anhydrous HF. A mixture with 22 moles % of BF_3,H_2O was used. The Hammett acidity function of this mixture, determined spectroscopically by use of picramide ($pK_a = -9{\cdot}22$) as indicator, is $H_0 = -9{\cdot}9$. When oxygen is introduced into these solutions of perylene, tetracene, anthracene, 3,4-benzopyrene, and pyrene the spectra are drastically changed. In all cases these spectra, which are in Figs. 1*D*—4*D* and 5*C*, respectively, are very similar to those of the corresponding mononegative ions.

FIG. 3.



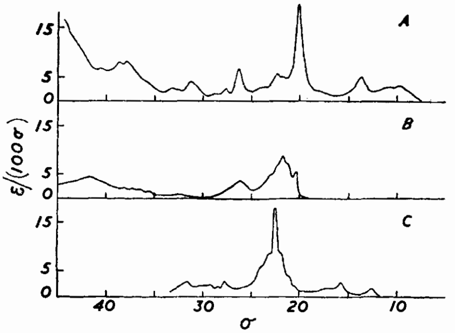
A, Anthracene⁻ Na⁺ in tetrahydrofuran; *B*, Anthracene in HF; *C*, Anthracene in H_2SO_4; *D*, Anthracene in $CF_3{\cdot}CO_2H-BF_3,H_2O$ in contact with air; *E*, Anthracene in HF, in contact with oxygen at 3 atm.

FIG. 4.



A, 3,4-Benzopyrene⁻ Na⁺ in tetrahydrofuran; *B*, 3,4-Benzopyrene in HF; *C*, 3,4-Benzopyrene in H_2SO_4; *D*, 3,4-Benzopyrene in $CF_3{\cdot}CO_2H-BF_3,H_2O$ in contact with air: ——·—— after 30 min.; —— after 24 hr

FIG. 5.



A, Pyrene⁻ Na⁺ in tetrahydrofuran; *B*, Pyrene in HF; *C*, Pyrene in $CF_3{\cdot}CO_2H-BF_3,H_2O$ in contact with air.

The solutions of perylene, tetracene, and 3,4-benzopyrene are stable. For the last two the reaction with oxygen is rather slow; after 1 hr. the reaction is only 50% complete. For anthracene and pyrene, too, the reaction was incomplete after 1 hr., but solutions of these hydrocarbons were not stable; after 24 hr. they had decomposed.

The broken line of Fig. 4*D* shows that the proton complex of 3,4-benzopyrene after 30 minutes' contact with oxygen is only partly (*ca.* 50%) converted into the monopositive ion. After 24 hr. the bands of the proton complex have disappeared; the new spectrum (full line) is very similar to that of the mononegative ion of Fig. 4*A* (the first absorption band of the proton complex is at 19·20 kK, while the strong absorption band of the positive ion is at 18·35 kK). In comparison with the absorption bands of the mononegative ion the bands of the monopositive ion are shifted a few kK towards the blue region.

Similar observations can be made for pyrene. The spectrum of Fig. 5*C* is a superposition of the spectrum of proton complex (*ca.* 10%) and that of its monopositive ion.

DISCUSSION

One may expect theoretically that the electronic spectra of the monopositive and mononegative ions of alternant hydrocarbons are practically identical.[9] One must therefore conclude that on dissolving perylene, tetracene, anthracene, 3,4-benzopyrene, and pyrene in $CF_3\cdot CO_2H-BF_3,H_2O$, containing oxygen, their monopositive ions are formed, because the electronic spectra of these solutions are very similar to those of the corresponding mononegative ions. Apparently, electron transfer may occur when strongly basic hydrocarbons are dissolved in strongly acidic oxidizing solvents. The oxygen molecule in strongly acidic solvents acts as an electron acceptor, probably giving rise to the protonated forms of O_2^- or O_2^{2-}.

Similar phenomena are observed when these hydrocarbons are dissolved in concentrated sulphuric acid, where SO_3 may act as an electron acceptor [10] and in hydrogen fluoride containing oxygen.[6] The oxidizing properties of the latter solvents, however, must be less strong than those of oxygen in $CF_3\cdot CO_2H-BF_3,H_2O$ mixtures. This may be demonstrated from the results for perylene and 3,4-benzopyrene. In this mixture both hydrocarbons are almost quantitatively oxidized to their monopositive ions. In sulphuric acid and in HF with oxygen, on the other hand, only perylene forms a monopositive ion whereas 3,4-benzopyrene dissolves as its proton complex.

Our results indicate that in strong oxidising acids an equilibrium exists between the proton complex MH^+ and the monopositive ion M^+. Compared with the concentrations of MH^+ and M^+ the concentration of hydrocarbon molecules M is negligible. If one assumes that the acceptor adds one electron the equilibrium can formally be written as:

$$M^+ + A^- + H^+ \rightleftharpoons MH^+ + A \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The constant for this equilibrium follows from the equation:

$$\ln K = \ln K_b + \varepsilon_{ox} \times \frac{F}{RT} + \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or in decadic logarithms:

$$\log K = \log K_b + 16{\cdot}95\ \varepsilon_{ox} + \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which K_b and ε_{ox} stand for the basicity constant and the standard oxidation potential of the hydrocarbon, respectively. The constant in eqn. (3) depends on the natures and the concentrations of proton donor and electron acceptor.

The relative values of the equilibrium constant K can be calculated for a great number of aromatic hydrocarbons by using known basicity constants [8] and Lund's oxidation

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[9] Weijland, Thesis, Free University, Amsterdam, 1958; Hoijtink, Colloque International sur le Calcul des Fonctions d'Ondes Moléculaires; Ed. C.N.R.S., Paris, 1958, 237.

[10] Aalbersberg, Hoijtink, Mackor, and Weijland, following paper.

potentials.[11] The values of K for the hydrocarbons studied by us, which combine a high value of K_b and a low value of ε_{ox}, are in the Table. If the formal eqn. (1) corresponds to reality, the values of K are a relative measure of the concentration ratio between proton complex and monopositive ion.

Basicity constants, oxidation potentials, and relative values of log K, *of reaction* (1).

Compound	log K_b [a]	E_{ox} [b]	log K + const.
3,4-Benzopyrene	6·5	0·76	19·4
Anthracene	3·8	0·84	18·0
Pyrene	2·1	0·86	16·7
Perylene	4·4	0·63 [c]	15·1
Tetracene	5·8	0·54	15·0

[a] Taken from ref. 8. [b] In volts against the silver–0·1N-Ag^+ electrode in acetonitrile; solvent: acetonitrile; taken from ref. 11. [c] The oxidation potential of perylene has been calculated from its reduction potential, by use of the linear relation between reduction and oxidation potentials of alternant hydrocarbons (Hoijtink, *Rec. Trav. chim.*, 1958, **77**, 555).

From the Table one must expect that (under equal conditions) the ratio of the concentrations $(MH^+)/(M^+)$ will be largest for 3,4-benzopyrene and smallest for perylene or tetracene. This is confirmed by the experiments, which show that the latter compounds (in particular perylene) are readily oxidized to their monopositive ions, whereas 3,4-benzopyrene is not. Anthracene and pyrene, which according to the values in the Table must have intermediate values of $(MH^+)/(M^+)$, are indeed less easily oxidized than perylene. Anthracene is only partially oxidized in HF by O_2 under conditions that cause complete oxidation of perylene. Similar observations were made in concentrated sulphuric acid, showing that anthracene is intermediate between perylene and 3,4-benzopyrene in its properties as an electron donor.

It is difficult to draw more quantitative conclusions. On the one hand solutions of anthracene and pyrene in strong oxidizing acids are not stable and on the other the formation of the monopositive ions is in several cases slow and may be photocatalysed. One does not know therefore whether equilibrium has been established. The present investigations make it clear that the paramagnetism found for anthracene, pyrene, and 3,4-benzopyrene in concentrated sulphuric acid by Kon and Blois [4] is due to a small fraction of the hydrocarbon dissolved; especially for 3,4-benzopyrene only a very small fraction can be present as the monopositive ion.

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[11] Lund, *Acta Chem. Scand.*, 1957, **11**, 1323.