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ON THE OXIDATION MECHANISM OF AROMATIC PROTON COMPLEXES

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Aalbersberg et al.[1] investigated the formation of hydrocarbon positive ions in solution of strong proton donors. As hydrocarbons were chosen perylene, tetracene, pyrene, anthracene and 3,4-benzopyrene. The reactions of these substances when dissolved in sulphuric acid, in oxygenated hydrogen fluoride or in oxygenated mixtures of trifluoroacetic acid and $BF_3.H_2O$ were studied spectroscopically. It appeared that proton complexes (ArH^+) as well as radical ions (Ar^+) were formed. The ratio of their concentrations was interpreted as depending on the basicity constant (K_b) and the standard oxidation potential ($\mathcal{E}_{ox}$) of the hydrocarbon corresponding to the equilibrium:

$$ArH^+ + A \rightleftharpoons Ar^+ + A^- + H^+ \qquad (1)$$

where A is an electron acceptor.
The equilibrium constant is given by the equation:

$$\log K = \log\frac{[ArH^+]}{[Ar^+]} = \log K_b + 16.95\ \mathcal{E}_{ox} + \text{constant} \qquad (2)$$

Theoretical values of the equilibrium constants calculated from the experimentally determined basicity constants and oxidation potentials are given in the last column of the table.

TABLE

hydrocarbon	log K_b	ε_{ox}	log K + C
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	15.1
tetracene	5.8	0.54	15.0

According to Aalbersberg et al.[1] their experiments are in qualitative agreement with equation (2). Perylene and tetracene (in particular perylene) are readily oxidized to their monopositive ions, whereas 3,4-benzopyrene is not. Anthracene and pyrene are in an intermediate position. However, it is also mentioned that tetracene, dissolved in a mixture of trifluoroacetic acid and $BF_3.H_2O$ (H_o= -9.9) containing oxygen, is converted rather slowly, as compared with perylene, into the monovalent positive ion.

We have studied the forward reaction (1) with diphenoquinone in sulphuric acid as oxidizing agent. As has been discussed elsewhere[2] the diphenoquinone molecule dissolves in sulphuric acid as a double protonated conjugate acid, which may also be considered as the double positive ion of 4,4'-dihydroxydiphenyl. The hydrocarbons investigated were 3,4-benzopyrene, anthracene, perylene and tetracene.

The proton complexes of these hydrocarbons in sulphuric acid solution can be obtained by first dissolving the hydrocarbon in e.g. methylcyclohexane which then is extracted with the acid. In the perylene solution, which is the least stable one, a small amount of radical ion is gradually formed. Addition of diphenoquinone in sulphuric acid to these solutions results in the formation of radical ions. Protonated anthracene and perylene react very fast, whereas protonated tetracene and 3,4-benzopyrene react very slowly. In another experiment it could be shown that the proton complex of perylene (Per) reacts under hydrogen transfer with the monopositive ion of tetracene (Tetr):

$$PerH^+ + Tetr^+ \longrightarrow Per^+ + TetrH^+ \qquad (3)$$

Consideration of this reaction suggests that the conversion of ArH^+ to Ar^+ occurs as an electron transfer with a proton as the carrier. It may then be conjectured that the contribution of the oxidation potential is much less important than might be deduced from the table.

The results of the experiments with diphenoquinone in sulphuric acid give rise to the supposition that only about 0.2 to 0.3 of the oxidation potential of the hydrocarbon appears in the transition state. The sequence in the table changes as follows: 3,4-benzopyrene, tetracene, anthracene, perylene, pyrene. This classification also gives a better description of the results of Aalbersberg c.s.

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