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Ionization of Aromatic Molecules *via* σ-Complex with Aluminum Chloride in Solid Phase

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While Perkampus and Kranz[1] observed the formation of σ-complex of aromatic molecules on an evaporated film of aluminum chloride, Terenin *et al.*[2] observed that of aromatic cation radical on it. The condition of formation of these two species does not seem to have been clarified. We would like to show that the formation of tetracene cation radical takes place by way of a σ-copmlex. For anthracene, an additional intermediate was found between the σ-complex and the cation radical.

Procedure. Aluminum chloride was prepared from aluminum and silver chloride by the procedure described in an earlier report.[3] The cell assembly used in this study was similar to that shown in it. A break-off seal containing aluminum chloride was fused to the cell assembly. After evacuation (10^{-3} mmHg), the sublimed film of aromatic molecule was prepared on the inside wall of the cell. The break-off seal was then broken and aluminum chloride vapor was brought into contact with the sublimed film of aromatics.

Primary Step: σ-Complex Formation. The absorption spectra of colored products given by the contact of aromatics and aluminum chloride vapor were essentially in accordance with those of Perkampus and Kranz,[1] and can be interpreted in terms of σ-complex formation, as discussed by them (π-v complex in their notation).

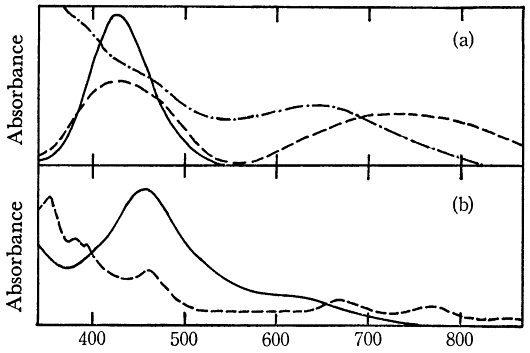

Fig. 1. Absorption spectra of anthracene- and tetracene-aluminum chloride system.
(a): anthracene–aluminum chloride
—— aluminum chloride in excess
–·–· anthracene in excess (before heating)
---- anthracene in excess (after heating)
(b): tetracene–aluminum chloride
—— before heating, ---- after heating.

TABLE 1. ABSORPTION SPECTRA OF TETRACENE– AND ANTHRACENE–ALUMINUM CHLORIDE SYSTEM
(Positions of Bands, nm)

Aromatic Molecule	Before Heating	After Heating
Tetracene	354	355, 385
	450	395, 670
	650	760, 850
Anthracene		
Aluminum chloride in excess	420	420
Anthracene in excess	420 665	730

Cation Radical Formation on Heating. The colored σ-complex was heated over a free flame. In the cases of anthracene and tetracene, the spectra changed into those which have the characteristics of cation radical. These spectra are shown in Fig. 1. The positions of bands are shown in Table 1. The spectra of cation radicals of these molecules are well-established.[4,5] Anthracene cation has absorption maximum at 735 nm, and tetracene cation at 348, 397, 667, 752, 833 nm.[5] The spectra of the heated products are quite similar to those of the cation radical. The samples gave ESR signals which were structureless and broad. The values of ΔH_{msl} were 7.2 G for anthracene, 5.6 G for tetracene. These findings seem to support the formation of aromatic cation radical in these systems.

In producing tetracene cation radical, no excess aromatics was necessary (in contrast with anthracene, *vide infra*). An approximate isosbestic point was obtained in its reaction from σ-complex into cation. Thus, this cation seems to arise from the σ-complex. In the case of anthracene the reaction was more complex.

Cation Radical Formation in Anthracene. The yellow σ-complex of anthracene did not change into its cation radical on heating, without the presence of an excess of anthracene. When the σ-complex was brought into contact with an excess of anthracene (supplied from another break-off seal), the yellow color changed into deep green. No heating was necessary, but a little warming accelerated the reaction. The deep green material (hereafter called species 665) showed an absorption maximum at 665 nm, and when it was heated over a free flame the color changed to

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[1] H. H. Perkampus and Th. Kranz, *Z. Phys. Chem.*, *N. F.*, **34**, 213 (1962); *ibid.*, **38**, 295 (1963).

[2] a) A. N. Terenin, V. A. Barachevsky, E. I. Kotov, and V. A. Holmogorov, *Spectrochim. Acta*, **19**, 1797 (1963). b) A. N. Terenin, *Advan. Catal.*, **15**, 227 (1964).

[3] H. Sato, K. Hirota, and S. Nagakura, This Bulletin, **38**, 962 (1965).

[4] W. I. Aalversberg, G. J. Hoijtink, E. L. Makor, and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3049, 3055.

[5] D. Distler and G. Hohlneicher, *Ber. Bunzenges. Phys. Chem.*, **74**, 960 (1970). Numerals are read from the figure.

dark brown. This dark brown material has an absorption maximum at 730 nm, and gave the ESR signal mentioned above. 9,10-Dimethylanthracene and 9,10-diphenylanthracene gave corresponding σ-complexes (λ_{max} at 425 and 430 nm, respectively). However, addition of excess aromatics did not give any species corresponding to species 665, and no cation radical was given on heating. When an excess of 9,10-disubstituted anthracene was added to anthracene σ-complex (with $AlCl_3$ in excess), neither species 665 nor cation formation was observed. When an excess of anthracene was added to 9,10-disubstituted anthracene σ-complex (with $AlCl_3$ in excess), species 665 was formed and anthracene cation was obtained on heating. These findings seem to show that cation radical is formed only *via* species 665, the latter not being obtained for 9,10-disubstituted anthracene. Thus, cation radical is not derived directly from a σ-complex, but from an additional intermediate, species 665. The presence of this species is reported. Actually it almost always appears when ionization of anthracene is found on solid Lewis acid.[2,6] However, its true nature has not been assigned, neither has its relation to ionization been noted. Hall[6] once assigned it tentatively to the dication but without any reasoning at all. On the other hand, Aalversberg *et al.*[4] remarked that anthracene is peculiar in the point that it is more liable than expected from its ionization potential to form cation radical on contact with Lewis acid in solution. The presence of species 665 as an ionizing intermediate may clarify these points.

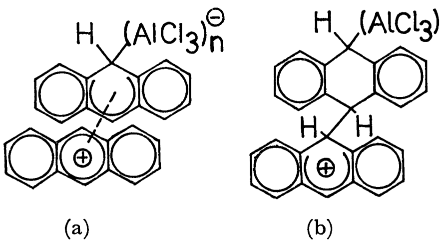

Fig. 2. Expected structures for the "665 species."
(a): a π-complex, (b): a σ-complex.

In order to determine the structure of species 665, an attempt was made to measure its NMR spectrum in solution. However, the attempt failed, because it decomposed on contact with the solvent used (dry chloroform, dimethyl sulfoxide, benzene, *etc.*). Thus we cannot give any definite molecular structure to this species, but we might say that it is either a π-complex or a σ-complex as shown in Fig. 2, considering that anthracene can dimerize at 9,10-position and that steric hindrance of 9,10-substituents prevents its formation.

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[6] W. K. Hall, *J. Catal.*, **1**, 53 (1962).