Molecular Complex between the Cation Radicals of Perylene and Tetracene

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A spectroscopic study of a molecular complex formed between two kinds of Würster's cations in solution has been reported by Takemoto *et al.*[1] Recently, Kimura *et al.*[2] have studied the reversible dimerizations of (perylene)$^+$ and (tetracene)$^+$ in concentrated sulfuric acid from an electronic-absorption study. In the present work, we have first established, spectroscopically, the existence of an interesting 1 : 1 complex between the cation radicals of cata-condensed hydrocarbons in concentrated sulfuric acid. The (perylene)$^+$-(tetracene)$^+$ complex may be one of the typical examples of radical-radical complexes.

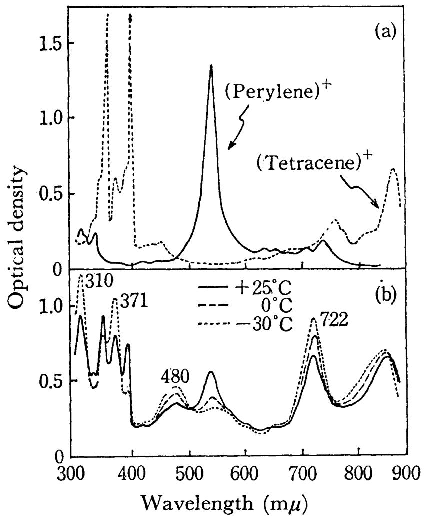

Fig. 1. (a) Electronic absorption spectra of (perylene)$^+$ (2.38×10^{-5}M) and (tetracene)$^+$ (2.21×10^{-5}M) in concentrated sulfuric acid at room temperature.
(b) Temperature dependent spectra of a mixed solution containing the two cations, whose concentrations are almost the same as above.

Perylene and tetracene are readily soluble in concentrated sulfuric acid; they thus form stable cation radical.[3] The absorption measurements were carried out under conditions in which none of the cations dimerized in a dilute concentrated-sulfuric acid solution. In Fig. 1, the electronic absorption spectra of the mixed solutions of (perylene)$^+$ and (tetracene)$^+$ measured at room temperature and also at lower temperatures are shown. Upon the mixing of the two cations, new several absorption bands appear at 264, 310, 371, 480, and 722 mμ, in addition to their own absorption bands, which become weak upon the mixing; several isosbestic points also exist.

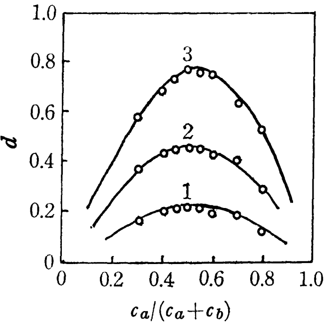

Fig. 2. Plots of $\bar{d}$ against $c_a/(c_a+c_b)$ in the continuous-variation method for different wavelengths.
Curve 1: 310 mμ, 2: 371 mμ, and 3: 538 mμ.
$c_a+c_b=5.0 \times 10^{-5}$M.

In order to identify this new species, we attempted to analyze the changes in the absorption intensity by using a method of continuous variation, in which concentrations of the two cations were selected so as to be constant. In Fig. 2, the increments of the optical densities, $\bar{d}=d-(c_a\varepsilon_a+c_b\varepsilon_b)$, are plotted aganst $c_a/(c_a+c_b)$ for three different wavelengths. Here, d is the optical density; c_a and c_b are the concentrations of (perylene)$^+$ and (tetracene)$^+$ respectively and ε_a and ε_b are the molar extinction coefficients of the absorption peaks of (perylene)$^+$ and (tetracene)$^+$ respectively. From Fig. 2 it can be seen that the maximum of each curve is located at 0.5. Therefore, it may reasonably be concluded that the (perylene)$^+$ and (tetracene)$^+$ in the solutions are in equilibrium with the 1:1 complex. This result was also supported by another analysis of the present absorption data by using the mole-ratio method, in which c_b was changed from 1.0×10^{-5} to 4.5×10^{-5}M, while c_a was kept constant (3.0×10^{-5}M). Furthermore, it was confirmed that the observed electronic absorption spectrum of the mixed solution can not be explained in terms of a mixture of (perylene)$^{2+}$ and tetracene, or of perylene and (tetracene)$^{2+}$; no absorption bands due to these species appear upon the mixing of the two cations.

The electronic absorption spectra were measured by a Cary Model 15 spectrophotometer, quartz cells with a pathlength of 1 cm being used. Commercial materials of perylene and tetracene were purified by vacuum sublimation. Concentrated sulfuric acid of a high purity ("Wako" 98.08%) was used without further purification.

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[1] K. Takemoto, S. Nakayama, K. Suzuki, and Y. Ooshika, This Bulletin, **41**, 1974 (1968).

[2] K. Kimura, T. Yamazaki, and S. Katsumata, to be published.

[3] W. I. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3049.