Note on the Oxidation of Perylene in Strong Acids

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The color reaction in concentrated sulfuric acid is one of the characteristic properties of polycyclic aromatic hydrocarbons and quinones, and has been used by organic chemists for their identification. Handa has measured the absorption spectra of a number of aromatic compounds dissolved in sulfuric acid of various concentrations, and attempted to estimate their basicities[1]. On the other hand, it has been pointed out by several authors that aromatic hydrocarbons in sulfuric acid show ESR absorption[2,3]. The paramagnetic species has been assigned by Weissman as a positive ion formed by oxidation. Hoijtink and Weijland have reported that the visible spectrum of a perylene solution in sulfuric acid resembles very closely that of a mononegative ion of this hydrocarbon[4].

In order to elucidate the nature of the species existing in sulfuric acid we attempted to study the oxidation of perylene by the optical and ESR methods. We examined the absorption spectrum of perylene dissolved in 70 per cent perchloric acid and observed two bands, at 503 and 530 mμ, which are located at nearly the same position as the one in sulfuric acid (see Fig. 1a and c.). We attempted also the oxidation of perylene in perchloric acid using potassium ferricyanide and the isolation of the product. Weiss reported in 1941 that the salts of some other aromatic hydrocarbons were prepared by oxidation in strongly acidic media[5]. The black reaction mixture was washed with a slightly diluted perchloric acid, in which the oxidized perylene was found to be only very sparingly soluble, and examined by an ESR spectrometer at a frequency of 9 kMc./sec. and at room temperature. A sharp line with a width of about 2.4 gauss at a half power was found. The g-value corresponding to the center of the line was estimated, by comparison with DPPH, to be 2.0025 ± 0.0003. The solubility of the product in 70 per cent perchloric acid was found to be much higher than that of the original hydrocarbon, so the main product seems to be ionic, probably the hydrocarbon perchlorate as described by Weiss. Unfortunately the solubility is still not high enough to examine ESR absorption in the dissolved state.

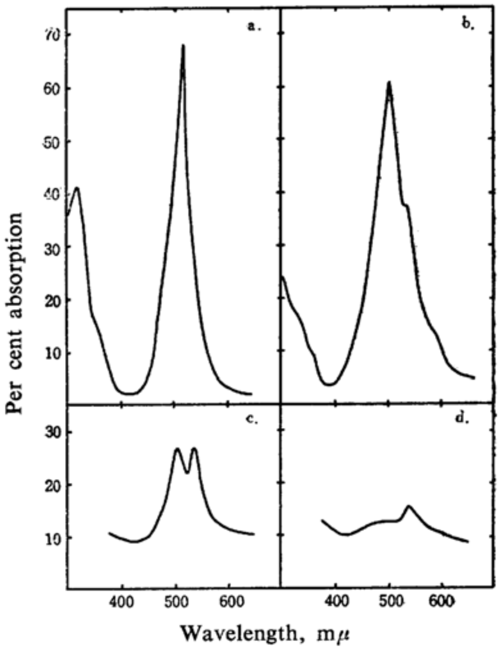

Fig. 1. Absorption spectrum of perylene in strong acids.
a, Dissolved in concentrated sulfuric acid
b, Oxidized perylene in 70 per cent perchloric acid
c, Dissolved in 70 per cent perchloric acid
d, After warming of c for a short time

The spectrum of the oxidized perylene has two bands which are located exactly at the same positions as those obtained by the direct dissolution of the hydrocarbon in perchloric acid. However, as shown in Fig. 1b, after oxidation the intensity of the band at lower wavelength became appreciably higher than the other. Although Dallinga and others have observed a similar spectrum of perylene by the dissolution in hydrogen fluoride and by the contact with oxygen, the band at higher wave-

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[1] T. Handa, This Bulletin, 28, 483 (1955).

[2] Y. Yokozawa and I. Miyashita, *J. Chem. Phys.*, 25, 796 (1956).

[3] S. I. Weissman, E. de Boer and J. J. Conradi, ibid., 26, 963 (1957).

[4] G. J. Hoijtink and W. P. Weijland, *Rec. trav. chim.*, 76, 836 (1957).

[5] J. Weiss, Nature, 147, 512 (1941).

length was found to be stronger in their case[6]. It seems to be evident that the band at lower wavelength is due to the paramagnetic ion formed by oxidation and the other is due to some other species derived from perylene. It is unlikely that the latter species is the protonated perylene, because no strong band was observed in this region of the spectrum of perylene in oxygen-excluded hydrogen fluoride[6]. The oxidation of perylene without the addition of an oxidizing reagent seems to be due to the presence of molecular oxygen dissolved in perchloric acid or combined with the hydrocarbon**. An attempt to accelerate the oxidation reaction of perylene in perchloric acid was made by warming. However, the band at 503 mμ decreased its intensity quickly (see Fig. 1d.). This observation shows that the band at the low wavelength side is due to a unstable species and seems to be not inconsistent with the above conclusion.

As it is convincing that only a part of perylene dissolved in concentrated sulfuric acid is paramagnetic[2,7], there must be again two or more species derived from perylene. Therefore, it seems likely that, as shown by the presence of a shoulder on the low wavelength side, the band due to the monopositive ion in sulfuric acid overlaps the band due to some other species.

The author attempted also the oxidation of tetracene in perchloric acid using ferricyanide and obtained a deep green solution and an unstable black precipitate. The absorption spectra of tetracene oxidized in perchloric acid and tetracene dissolved in sulfuric acid are rather complicated and the intensity ratios of bands depend on the time. Although the complete assignment has not yet been made, it appeared that there are three or more common species in these two solutions.

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[6] G. Dallinga, E. L. Mackor and A. A. Verrijn Stuart, *Mol. Phys.*, 1, 123 (1958).

** Although we have no direct evidence that perylene molecule combines with oxygen, mesonaphthodianthrene, which has a similar molecular structure to perylene, was found to give a paramagnetic molecular complex with oxygen, see Y. Matsunaga, *Can. J. Chem.*, 38, 323 (1960).

[7] Y. Matsunaga, This Bulletin, 31, 776 (1958).