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Simultaneous Formation of Perylene Cation and Anion by Flash Excitation of Perylene in Solutions

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Formation of transient cations and anions from the electron donor-acceptor interactions in the excited states was confirmed by using the flash technique in polar solutions for the first time by Leonhardt and Weller[1] and recently by Koizumi and Yamashita[2] and by us.[3]

In this note, we report a simultaneous formation of positive and negative ions of perylene revealed by the flash technique.

An acetonitrile solution of perylene (8×10^{-5}M) was used as a sample solution. It was carefully de-aerated by the usual freeze-pump-thaw method, and placed in a quartz cylindrical cell, 1.5 cm in diameter and 20 cm in length. The instrument used for the flash illumination has been described elsewhere.[4] The electric energy of a flash was about 430 J. The profile of the flash is shown in Fig. 2. A concentrated aqueous solution of sodium nitrate was used as a filter solution, which absorbed the light in the region shorter than 340 mμ, so that the perylene was excited only in the region of its ^1L_a band.

Flash illumination of the sample through the filter solution gave a transient absorption spectrum consisting of two overlapping bands at 576 mμ and 538 mμ and two others near 490 mμ and 480 mμ

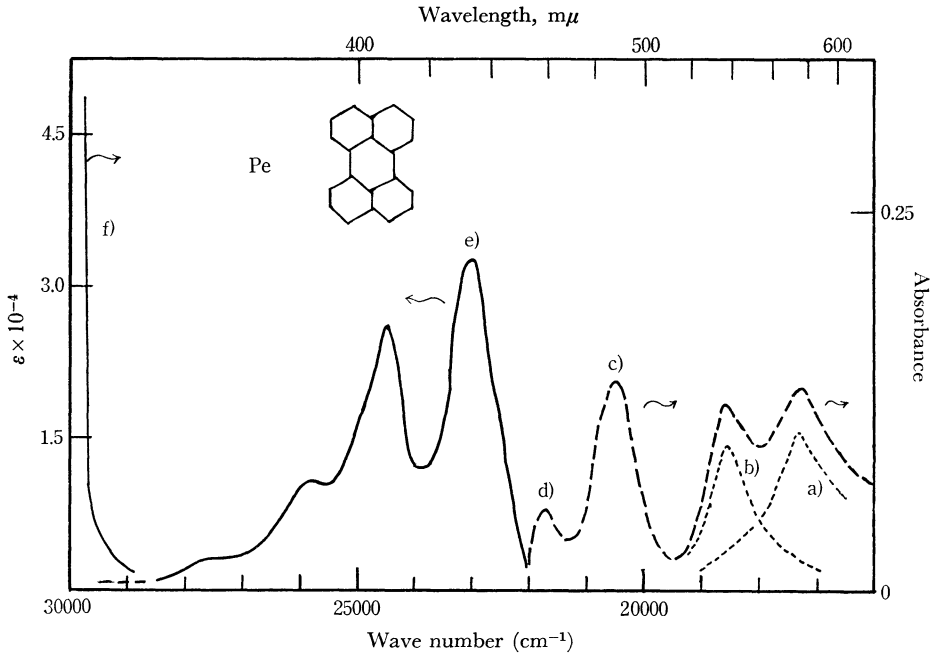

Fig. 1. Transient absorption spectrum caused by the flash illumination of perylene (8×10^{-5}M) in an acetonitrile solution. It was measured 10 μsec after illumination. Bands a) and b) correspond to perylene negative and positive ion respectively. Bands c) and d) indicate the T–T′ absorption of perylene. Spectrum e) indicates absorption of perylene in the ground state. Spectrum f) is that of the filter solution.

1) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

2) M. Koizumi and H. Yamashita, *Z. Phys. Chem. N. F.*, **57**, 103 (1968).

3) K. Kawai, N. Yamamoto and H. Tsubomura, This Bulletin, **42**, 369 (1969).

4) N. Yamamoto, Y. Nakato and H. Tsubomura, *ibid.*, **39**, 2603 (1966).

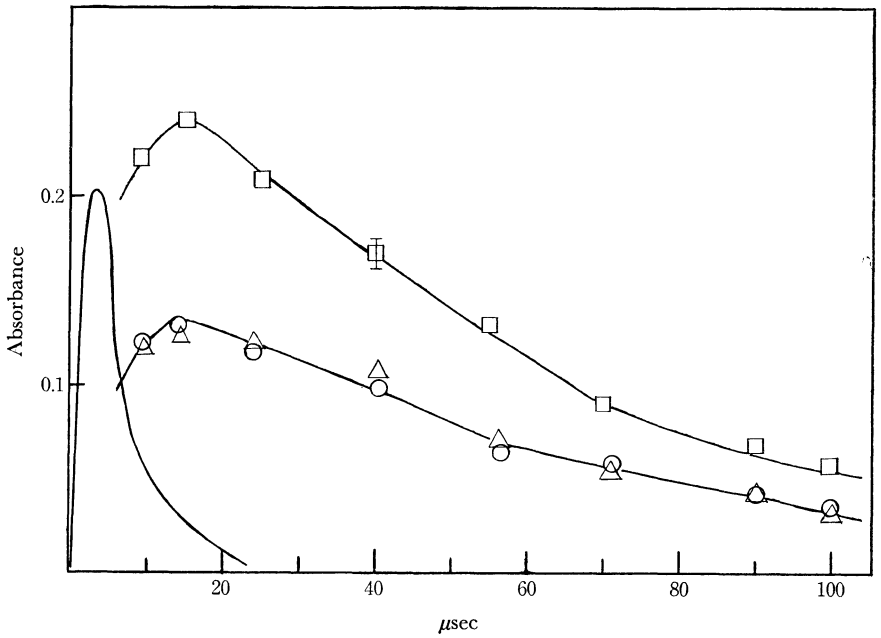

Fig. 2. The formation and decay curves of transient absorption spectra caused by flash illumination of acetonitrile solution of perylene.
-□-□- perylene in the triplet state.
-○-○- perylene anion
-△-△- perylene cation
——— flash profile.

(Fig. 1). Only two bands at 480 and 490 mμ appeared in the case where nonpolar solvents such as benzene or methylcyclohexane were used. When the acetonitrile solution of perylene was saturated with oxygen, the flash illumination of the solution resulted in the appearance of only the 538 mμ absorption band. From these results, it is highly probable that the 480—490 mμ bands are T—T′ absorption bands and the 576 mμ band is due to a negative ion.

The 576 mμ band may be ascribed to perylene mononegative ion, because it nearly agrees in position and shape with the spectrum of the perylene anion (λ_{max}: 581 mμ) formed by the action of sodium metal in a tetrahydrofuran solution.[5] The 538 mμ band is also attributed to the perylene cation, because it approximately agrees with the absorption peak at 543 mμ of perylene oxidized by antimony pentachloride in nitrobenzene.[6] The 490—480 mμ bands can be identified with the triplet-triplet absorption of perylene which Porter and Windsor found on flash illumination of perylene in solution.[7] The initial concentrations of perylene anion and cation formed at a flash energy of about 430 J was estimated to be about 2×10^{-7}M from the absorbances obtained and the molecular extinction coefficients, 4.3×10^{4} for the anion and 4.9×10^{4} for the cation.[5,6]

The absorbances of the transient species were followed in detail as the function of time. Some of the results obtained are given in Fig. 2. It was found that the ion concentrations increased during the flash illumination which continued for about 15 μsec. The decay of the ions nearly followed the second-order kinetics ($k=7\times10^{10}$M^{-1} sec^{-1}). This result suggests that the decay of the ions is mainly due to recombination of the cations and anions and is a diffusion-controlled process.

Three mechanisms may be set up as possible routes for the simultaneous formation of perylene cation and anion:

1) *Auto-ionization* from perylene excimer.

$$^1Pe^* + Pe \longrightarrow (Pe \cdots Pe)^* \rightsquigarrow Pe^+_{solv.} + Pe^-_{solv.}$$

2) T-T annihilation.

$$^3Pe + {}^3Pe \rightsquigarrow Pe^+_{solv.} + Pe^-_{solv.}$$

3) Two-step (bi-photonic) excitation.

$$Pe + h\nu_1 \longrightarrow {}^1Pe^* \rightsquigarrow {}^3Pe$$

$$^3Pe + h\nu_2 \longrightarrow {}^3Pe' \rightsquigarrow Pe^+_{solv.} + e_{solv.}$$

$$e_{solv.} + Pe \longrightarrow Pe^-_{solv.}$$

5) P. Balk, G. T. Hoijtink and J. W. H. Schreurs, *Rec. Trav. Chim. Pays-Bas*, **76**, 813 (1957).
6) J. Hoijtink and W. P. Weijland, *ibid.*, **76**, 836 (1957).
7) G. Porter and W. H. Windsor, *Proc. Roy. Soc., Ser A*, **245**, 238 (1958).

The life time of perylene in the lowest singlet excited state (^{1}Pe) is 5×10^{-9} sec and, from this short life and low concentration of perylene in our experiment, it is unlikely that collisions of ^{1}Pe* and ground state perylene (Pe) occur to any appreciable degree. Therefore, mechanism (1) may be discarded. Also, the probability of formation of higher excited singlet state of perylene by the S—S′ absorption is very small.

The second mechanism, T–T annihilation, was assumed by Kawada and Jarnagin[8] for the explanation of photo-current of anthracene and phenanthrene in solutions. In such a process, ions need collisions of two triplet molecules. As the concentration of triplet perylene in our experimental condition is in the order of 10^{-6}M, the T–T annihilation process must be rather slow and the maximum of the ion concentration should appear at a time considerably later than that of the triplet molecules as seen in the case of Kawada and Jarnagin's work. Our experimental result shows that the concentrations of the ions increase almost in the same way as the triplet perylene and reach their maxima already at about 15 μsec after the start of the flash. Therefore, the second mechanism is also unlikely.

The third mechanism is consistent with the experimentally obtained rate of production of the ions. The ionization potential of perylene has been determined to be 7.15 eV[9] in the gas phase. Although the phosphorescence spectrum of perylene has not been observed, the lowest triplet state of perylene is estimated to be *ca.* 1.6 eV from MO calculations. As the filter solution used in the present experiment allows entrance of light having energy up to 3.6 eV, perylene can be excited to a level as high as *ca.* 5.2 eV by the T–T′ transition. This value seems to be a little too low for ionization of perylene even in a solution, based on our experience in the photo-ionization of aromatics in condensed environments.[10] In spite of this, mechanism (3) seems to be the most probable at the moment, as there is no other strong alternative. Stevens and Walker[11] have studied the photo-ionization of perylene in the rigid glass and conclude that the ionization potential of perylene is *ca.* 5.0 eV in liquid paraffine at 77°K. Photo-electron emission may then occur from the higher triplet states.

Once an electron is emitted from a highly excited perylene molecule, the electron can be captured by another perylene molecule leading to the formation of perylene anion.[10]

8) A. Kawada and R. C. Jarnagin, *J. Chem. Phys.*, **44**, 1919 (1966).

9) G. Briegleb and J. Czekalla, *Z. Electrochem.*, **63**, 6 (1959).

10) N. Yamamoto, Y. Nakato and H. Tsubomura, This Bulletin, **40**, 451 (1967).

11) B. Stevens and M. S. Walker, *Chem. Commun.*, **1965**, 8.