SHORT COMMUNICATIONS

The Formation of the Anion Radicals of Pyromeritonitrile and Tetracyanoethylene by Flash Irradiation

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It is well known that pyromeritonitrile (1, 2, 4, 5-tetracyanobenzene)[1] and tetracyanoethylene[2] are strong electron-acceptors. Furthermore, these electron acceptors are known to give stable anion radicals by reduction with alkalimetals in appropriate solvents.[3,4] In the course of their study of the effect of flash light upon charge-transfer-type complexes, the present authors have found that pyromeritonitrile and tetracyanoethylene can produce anion radicals by the irradiation of flash light, even in the absence of a definife electron donor.

Pyromeritonitrile.—Pyromeritonitrile was dissolved in purified acetonitrile in a concentration of 10^{-2}—10^{-3} M; the resulting solution was thoroughly degassed and used as the sample. As a flash-light source, a flash photolysis apparatus provided with argon flash lamps was utilized. An electric charge of 10—15 kV. in a 10 μF condenser was discharged through the lamps, and the light pulse generated (500—1200 joule/flash) was irradiated to the degassed sample solution contained in a quartz reaction vessel.

After the irradiation with flash light, the solution showed new absorption bands at 270, 375 and 462 mμ (see Fig. 1),* and an ESR spectrum with a hyperfine structure of 9 lines.** The electronic absorption spectrum and ESR spectrum observed with the irradiated solution

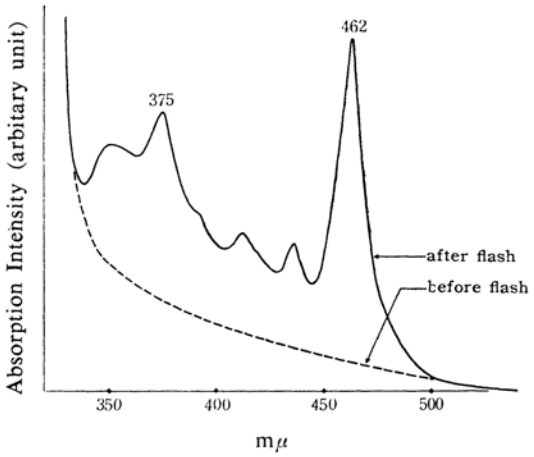

Fig. 1 Ultraviolet absorption spectrum of pyromeritonitrile before and after flash irradiation.

1) S. Iwata and S. Nagakura, to be published.
2) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).
3) A. Ishitani and S. Nagakura, to be published.
4) W. D. Phillips, J. C. Rowell and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

* The electronic spectra were measured with a Cary recording spectrophotometer, Model 14 M.

** The ESR spectra were measured with a Hitachi ESR spectrometer, Model MPV-2B (X-band, 100 kc. modulation).

are completely identical with those of the pyromeritonitrile anion produced by the alkali metal reduction method.[3] Thus, it was confirmed that the pyromeritonitrile anion radical was produced by the irradiation of the acetonitrile solution of the parent molecule with an intence flash light.

The electronic absorption spectrum of the anion radical solution slowly decreased in intensity in vacuo and returned to that of the original neutral molecule. The lifetime was estimated to be 5 hr. This anion vanishes quickly if oxygen was introduced into the system.

Similar results were obtained with the ethanol and ethyl ether solutions. The lifetimes of the anions formed in these solvents were estimated to be 40 min. and 3 hr. respectively.

Tetracyanoethylene.—A degassed solution of tetracyanoethylene in acetonitrile, when irradiated with an intense flash light, showed a new absorption band at 250—400 mμ (see Fig. 2), and the sample solution turned pale yellow. The new absorption band was completely identical with that of the tetracyanoethylene anion produced by the alkali metal reduction method; therefore, the formation of the anion was confirmed.

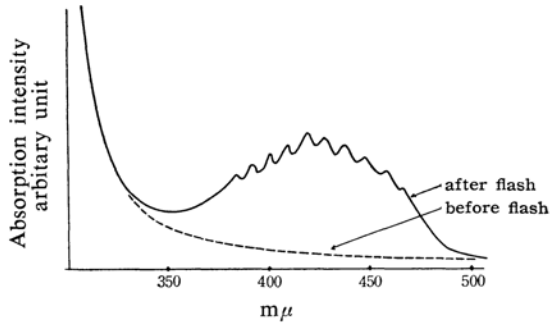

Fig. 2 Ultraviolet absorption spectrum of tetracyanoethylene before and after flash irradiation.

In the cases described above, no counter cations, which may be presumed to be produced simultaneously with the anions, could be detected.

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