Observation of Triplet-Triplet Absorption Spectra of Nitronaphthalenes by Means of Flash Excitation Technique

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Aromatic hydrocarbons with the nitro group are known to have some peculiar characteristics in electronic structure and photochemical reactivity. Phosphorescence life times of nitrosubstituted aromatics are considerably shorter than those of non-substituted aromatics in spite of the nature of π-π^* type of the lowest triplet states of the aromatics having the nitro group.[1-4] Nitrobenzene is the only exception whose lowest triplet state is assigned to n-π^* type.[2,3] In order to obtain further information on characteristics of the triplet states of nitroaromatics, it seems important to measure their triplet-triplet (T-T) absorption spectra. So far, no reports have been published on T-T absorption spectra of nitroaromatics. This might be attributed to the short life times of their lowest triplet states and also to their reactivities. We report for the first time the T-T absorption spectra of some nitroaromatics obtained with a flash spectroscopic technique.[5]

Flash experiments of 1- and 2-nitronaphthalenes were carried out with various deaerated solutions (in n-hexane, liquid paraffin, ethanol, ether, and tetrachloromethane) at room temperature, and also with an ether–isopentane–alcohol (EPA, 5:5:2) glass at 77°K, giving transient absorption spectra in all cases. It was found that the transient absorption spectra are almost independent of the solvents. Typical spectra obtained with ethanol solutions of 1- and 2-nitronaphthalenes (1×10^{-4}M) are shown in Fig. 1. Each of the transient absorption spectra could be ascribed to only one sort of intermediate in either 1- or 2-nitronaphthalene. Life times of the transient absorptions in various solutions at room temperature were too short for an accurate measurement of decay curves. Intrinsic life times of the transient absorptions seem to be at most about 10 μsec at room temperature. It should be mentioned that the addition of oxygen remarkably reduces the intensities of the transient absorptions.

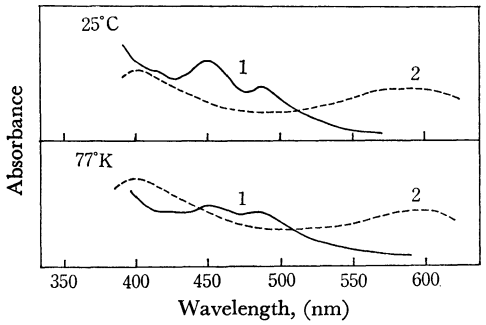

Fig. 1. Transient absorption spectra observed immediately (~0 μsec) after the flash irradiation of 1-nitronaphthalene (curve 1) and of 2-nitronaphthalene (curve 2) in deaerated ethanol solutions at room temperature and in EPA glasses at 77°K.

Transient absorption spectra obtained in the EPA glass at 77°K which are very similar to those obtained at room temperature are compared in Fig. 1. The decay curves of the transient absorptions observed at 77°K could be analyzed in terms of 60 ± 10 msec and 242 ± 10 msec for 1- and 2-nitronaphthalenes respectively in EPA at 77°K.

In order to compare the life time of the transient absorptions with that of phosphorescence under the same conditions, we also measured the phosphorescence life time for 1- and 2-nitronaphthalenes in EPA at 77°K with a Hitachi MPF-2A fluorescence spectrophotometer. As a result, we obtained a phosphorescence life time of 50 ± 2 msec for 1-nitronaphthalene, which is in good agreement with the reported values of 50 msec[1] and 47 msec[3], while a life time of 240 ± 6 msec was obtained for the phosphorescence of 2-nitronaphthalene.[6] Since the phosphorescence life times we obtained are in agreement with those of the transient absorptions within experimental limits of error, we conclude that the transient absorption spectra observed at room temperature as well as at 77°K can be assigned to the absorption spectra due to T-T transitions of 1- and 2-nitronaphthalenes.

1) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
2) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 1949 (1968).
3) R. Rusakowicz and A. C. Testa, *Spectrochim. Acta*, **27A**, 787 (1971).
4) E. C. Lim and J. Stanislaus, *Chem. Phys. Lett.*, **6**, 195 (1970).

5) The duration times of photolysisflash and spectroflash lamps are 5.0 and 3.5 μsec, respectively, quartz cells 10 cm long and 1 cm long being used at room temperature and 77°K, respectively. The output energy was about 400 joules. Transient absorption spectra were recorded photographically and their decay curves were followed photoelectrically.

6) The value 240 ± 6 msec differs somewhat from that reported by Rusakowicz and Testa who obtained a value of 206 msec in EPA at 77°K.[3] The difference might be attributed to the difference in experimental methods: We measured the decay curve of phosphorescence after cutting off stationary exciting light, while they employed the method of flash excitation.[3]