Observation of the Radical Anion Intermediates in the Photolyses of 4-Cyano- and 4-Nitro-azobenzene in MTHF at 77 K

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Steady-state photolyses of 4-methoxy-4′-cyanoazobenzene and 4-methoxy-4′-nitroazobenzene have been studied in rigid matrices. The radical anions of these azobenzenes have been observed for the first time by the 266 nm and 355 nm light irradiation in 2-methyltetrahydrofuran at 77 K.

Azobenzene derivatives with an electron-attracting substituent linked to the side chain of various kinds of polymers have been developed extensively for the liquid crystals, optical switching devices and nonlinear optical materials.[1] This kind of azobenzene with substituents such as *p*-cyano or *p*-nitro group has a highly delocalized π-electron system because of the charge transfer property from the azobenzene moiety to substituents. In the course of our studies on the photophysics of polysilane with *p*-nitro- or *p*-cyano-azobenzene groups in the side chain, the formation of radical anions of azobenzene derivatives has been suggested in 2-methyltetrahydrofuran (MTHF) at 77 K. Now we investigate the formation of radical anions of substituted azobenzenes by UV-light photolysis and radiolysis. In this letter, we report for the first time the photochemical formation of radical anions of 4-methoxy-4′-cyano- and 4-methoxy-4′-nitro-azobenzenes by the steady-state photolysis in MTHF at 77 K.

Previously, it has been shown that photolyses of azobenzene and 4-amino-4′-nitroazobenzene in ethanol and hydrocarbon solvents involve hydrogen abstraction from solvents by the excited-state molecules.[2] Hydrazyl radicals have been suggested as intermediates in these reactions. Furthermore, the laser flash photolysis of 4-methoxy-4′-nitroazobenzene in cyclohexane only gives rise to a transient species assigned to the *cis*-form.[3] Therefore, it is understood that solvents play important roles in photochemistry of azobenzene derivatives.

4-Methoxy-4′-cyanoazobenzene and 4-methoxy-4′-nitroazobenzene were synthesized and purified by column chromatography with silica gel using acetone–petroleum ether as eluant followed by recrystallization from acetone. Nearly all *trans*-azobenzene derivatives were obtained, and the amount of *cis*-isomer was estimated to be less than 5%.[4] Steady-state photolysis was carried out by using light outputs (266 nm and 355 nm light) from an Nd^{3+}:YAG laser. Before UV-irradiation, there are an intense absorption band at 380 nm and a very weak shoulder around 460 nm, which are attributed to π-π^* and n-π^* transition of *trans*-4-methoxy-4′-cyanoazobenzene, respectively.[4] Figures 1a and b show the spectral change of 4-methoxy-4′-cyanoazobenzene observed upon irradiation in MTHF at 77 K, and differential absorption spectra before and after irradiation with 355 nm light, respectively. After UV-light irradiation, three new peaks were observed at 475, 560, and 630 nm. The absorbance of these new bands increase with increasing irradiation time.

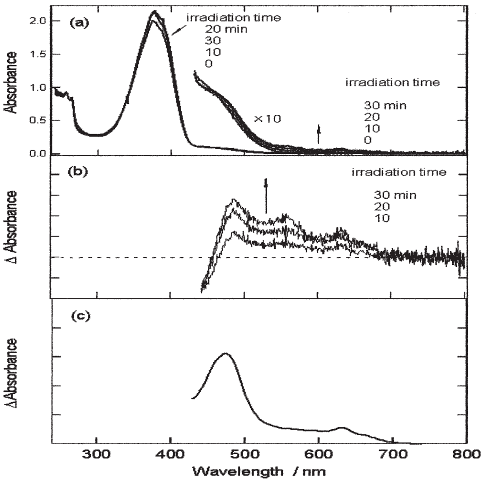

Figure 1. The spectral change of 4-methoxy-4′-cyanoazobenzene observed upon irradiation in MTHF at 77 K (a), and the differential absorption spectra before and after irradiation with 355 nm light (b), and with ^{60}Co γ-ray (dose: 5 Gy) (c).

However, the absorption peaked at 380 nm increases slightly at first due to *cis*→*trans* isomerization, and then decreases due to photolysis of *trans*-isomer. The same result was obtained by the 266 nm light irradiation. When the sample was warmed up to room temperature, these three new peaks disappeared with a recovery of the absorption of *trans*-4-methoxy-4′-cyanoazobenzene.

It is well known that γ-irradiation of organic molecules in MTHF at 77 K is available for preparing their radical anions.[5] In order to identify the present obtained species, the sample in MTHF at 77 K was irradiated by ^{60}Co γ-ray with a dose of 5 Gy, and the result is shown in Figure 1c. The absorption spectrum is very similar in feature to that of the radical anion of azobenzene.[6] The comparison of Figures 1b and 1c shows that these bands are assigned to radical anions of *trans*-4-methoxy-4′-cyanoazobenzene. But the absorption intensity around 560 nm in Figure 1b is higher than that in Figure 1c. It has been reported that the hydrazyl radical of *trans*-azobenzene shows an absorption around 540 nm.[6] Therefore, it is considered that the absorption band due to the hydrazyl radical of *trans*-4-methoxy-4′-cyanoazobenzene may overlap with that of the radical anion around 560 nm.

In the steady-state photolysis of 4-methoxy-4′-nitroazobenzene, similar results to the case of 4-methoxy-4′-cyanoazobenzene were obtained in the 450–700 nm region by the UV-light irradiation in MTHF at 77 K. Figures 2a and b show the spectral change of 4-methoxy-4′-nitroazobenzene observed upon irradia-

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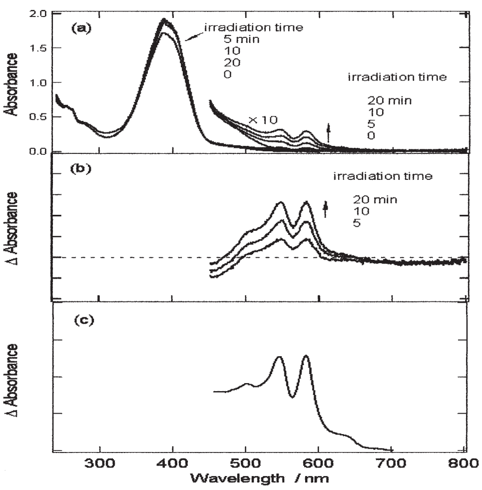


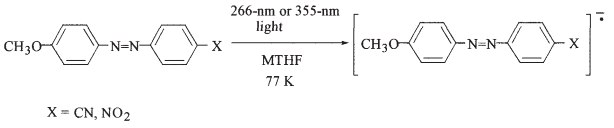
Figure 2. The spectral change of 4-methoxy-4′-nitroazobenzene observed upon irradiation in MTHF at 77 K (a), and the differential absorption spectra before and after irradiation with 355 nm light (b), and with ^{60}Co γ-ray (dose: 5 Gy) (c).

tion in MTHF at 77 K, and differential absorption spectra before and after irradiation with 355 nm light, respectively. In the 350–450 nm region, the absorption change is complex because of the *cis→trans* photoisomerization and photoreduction of the *trans*-isomer. Two new peaks were observed at 545 and 580 nm. These bands increased simultaneously with increasing the irradiation time. The same results were obtained by the 266 nm light irradiation. Figure 2c shows the differential absorption spectrum of 4-methoxy-4′-nitroazobenzene irradiated by ^{60}Co γ-ray with a dose of 5 Gy in MTHF at 77 K. These two spectra are very similar to each other in the 500–650 nm region. Monti et al. reported that the radical anion of *p*-nitroazobenzene produced by the pulse radiolysis shows the broad absorption band around 470 nm in 2-propanol.[7] The difference in the absorption region of the radical anion in MTHF and 2-propanol is attributable to the solvent effect similar to that observed for azobenzene radical anions.[6] Thus, the steady-state photolysis of 4-methoxy-4′-nitroazobenzene with 266 nm or 355 nm light produces the radical anion of *trans*-4-methoxy-4′-nitroazobenzene in MTHF at 77 K.

This kind of new absorption band was not observed for *p*-cyano- and *p*-nitro-azobenzenes in ethanol and methylcyclohexane, and for other azobenzenes without electron-attracting substituents in MTHF, even irradiated with the 266 nm or 355 nm light at 77 K. This indicates that the solvent with low ionization energy and the electron-attracting substituents play decisive roles in the photoreduction of azobenzene derivatives. This kind of photoreduction was repeoted by Inoue et al.; photoreduction of 2, 2′-pyridyl was initiated by the electron transfer from tetrahydrofuran.[8] The difference in the absorption spectra in Figures 1 and 2 might be explained by the difference in degree of delocalization of the singly occupied MO and/or unoccupied MO in the radical anions.[9]

Fluorescence emission of *p*-cyano- and *p*-nitro-azobenzene were not observed in MTHF at 77 K, but the broad phosphorescence spectra were observed with emission around 530 nm for 4-methoxy-4′-cyanoazobenzene and around 540 nm for 4-methoxy-4′-nitroazobenzene. Nanosecond transient absorption measurements were carried out for these two azobenzenes at room temperature, but no absorption band due to the radical anion was observed. This suggests that the excited singlet state is not responsible for the formation of these radical anions, and as a result triplet state is considered to play an essential role in this photoreduction. Therefore, the formation of radical anions is ascribable to the electron transfer from the solvent MTHF to the triplet state of substituted azobenzenes. The possibility that the intramolecular CT state is a precursor for the radical anion is, however, not excluded.

In conclusion, it is found out for the first time that the radical anions of *trans*-4-methoxy-4′-cyano- and *trans*-4-methoxy-4′-nitro-azobenzenes are formed by the 266 nm or 355 nm light irradiation in MTHF at 77 K as illustrated below.



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