October, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *59*, *3269—3270 (1986)* 3269

A Time-Resolved ESR Study on the Photochemical Reduction of Nitrobenzene Derivatives in Alcoholic Solution

Kimio Akiyama, Yusaku Ikegami,* Tsuneo Ikenoue, and Shozo Tero-Kubota
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai 980

(Received May 6, 1986)

Synopsis. Time-resolved ESR experiments have been carried out to elucidate the initial process in the photochemical reduction of aromatic nitro compounds. The first observation of CIDEP due to nitrobenzene anion radicals in the presence of an electron donor proved that radical generation takes place through a triplet mechanism.

A number of organic and physicochemical studies on the photoreduction and photosubstitution reactions of aromatic nitro compounds have been reported and various intermediates in these reactions have been detected. Among these, ESR studies revealed several types of intermediates in photochemical reactions involving nitrobenzenes. In the presence of electron donors, the observed ESR spectra could be interpreted as the photoreductive generation of anion radicals of the parent compounds. On the other hand, neutral radicals are generated from excited triplet states of aromatic nitro compounds by hydrogen abstraction and a successive reaction in the presence of hydrogen donors.[1] It is thought that the operative excited state in these reactions is the $n\pi^*$ triplet state by an analogy with the $n\pi^*$ excitation of aromatic carbonyl compounds, regardless of the low quantum yield of the excitation compared with that of the latter.

The present paper reports the initial process of the photoreduction of nitrobenzene derivatives contains the anisotropic intersystem crossing from the $n\pi^*$ singlet state to the triplet state. The study was carried out by means of time-resolved ESR spectroscopy for the photoreduction systems of unsubstituted (**1**), 4-methoxy- (**2**), and 4-chloro-nitrobenzenes (**3**).

Experimental

A transient ESR signal from the preamplifier output of a Varian E-109E EPR spectrometer was taken without any field modulation at arbitrary times after a laser pulse into a two-channel boxcar integrator. A nitrogen laser (5 mJ per pulse, 10-Hz repetition rate) was used as the source of the light pulse.[2] The sample solution was flowed in the ESR cavity in order to prevent any secondary reaction of the photochemical products formed from the nitrobenzene. All sample solutions were deoxygenated by bubbling of pure nitrogen gas before measurements.

Results and Discussion

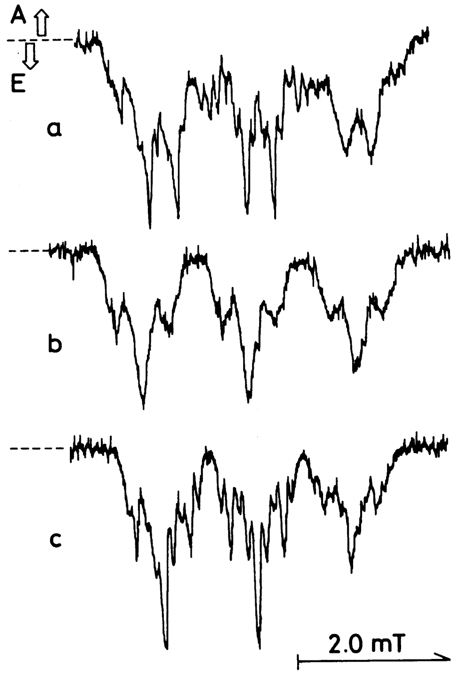

Fig. 1. Transient polarized ESR spectra of the anion radicals generated by photoreduction of unsubstituted (a), 4-methoxy- (b), and 4-chloronitrobenzenes (c) at room temperature. The spectra were taken at 1.0 μs after the laser pulse.

Figure 1 shows the transient ESR spectra observed during the photoreduction of **1**—**3** in the presence of triethylamine (TEA) in 2-propanol. These spectra were confirmed to be due to the anion radicals of the corresponding nitro compounds by comparing them with the steady-state spectra measured under the same condition with continuous light irradiation.[1] The totally emissive CIDEP (chemically induced dynamic electron spin polarization) pattern of the spectra indicated that an electron transfer occurred between the excited triplet state of a nitro compound and the added electron donor. Obeying the interpretation of the CIDEP phenomena,[3] the emissive (E) polarization arises from an anisotropic intersystem crossing of the $n\pi^*$ excited singlet state to the triplet state in which the spin is most populated at the P_+ level; the electron transfer would proceed rapidly prior to a relaxation of the polarization in the excited triplet state.

The same E polarization was observed for the CIDEP spectra of the anion radicals of **1**—**3** in the presence of dimethylamine (DMA) instead of TEA. According to Barltrop and Bunce,[4] the photoreduction products of nitrobenzenes varied depending on the reaction condition; also, the relative ratio of the produced aniline and azobenzene became reversed in the presence of TEA and DMA. However, the time-resolved ESR experiments showed the same CIDEP patterns in the presence of these two amines and gave no signal due to the hydrogen abstraction products. This suggests that the major photoreduction process is initiated by an electron transfer. Hydrogen abstraction from the α position of TEA is relatively slow and the polarization conserved in the hydrogen adduct may be very weak or completely diminished by the fast relaxation of polarization within the excited triplet state of the aromatic nitro compound. Thus, the present behavior obviously differs from the CIDEP observations for the photolysis of aromatic carbonyl compounds in the presence of TEA in an alcoholic solution, which showed the spin polarization in the hydrogen-abstraction products.[5] A relatively lowered reduction potential of the aromatic nitro compounds may cause an efficient electron transfer from TEA to form anion radicals.

Since the ESR spectra of the hydrogen-abstraction products of nitrobenzene derivatives have been observed in photolysis under continuous light irradiation, it is expected that the polarized spectra of the hydrogen adducts can be observed. An examination to observe the polarized spectra of $ArNO_2H^{\cdot}$, however, has been unsuccessful, even for the active 4-chloronitrobenzene, by the use of good hydrogen donors: 2,6-di-*t*-butylphenol, benzhydrol, and cumene. Presumably, the hydrogen-abstraction rate of the triplet state of nitrobenzenes is slower than the rate of spin relaxation within the excited triplet state, even in the presence of reactive hydrogen donors.

The coexistence of hydrogen and electron donors in the above photoreduction systems also resulted in the same CIDEP spectra as that from the anion radicals. If equilibrium between the anion and its conjugated acid ($ArNO_2^{\cdot-}+H^+ \rightleftharpoons ArNO_2H^{\cdot}$) is accompanied by a fast exchange, the appearance of another polarized signal is expected. Referring to the suggestion by Cu and Testa,[6] that the conversion rate between these two radical species should be the order of $10^8\ s^{-1}$ in an acidic solution, the present result suggests that the spin polarization relaxed rapidly before conversion in the present neutral solution.

References

1) For example, see: a) R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963); b) J. K. Brown and W. G. Williams, *J. Chem. Soc., Chem. Commun.*, **1966**, 495; c) D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, **1968**, 201; d) C. Chachaty and F. Forchioni, *Tetrahedron Lett.*, **1968**, 307; e) E. G. Janzen and J. L. Gerlock, *J. Am. Chem. Soc.*, **91**, 3108 (1973); f) S. K. Wong and J. K. S. Wan, *Can. J. Chem.*, **51**, 753 (1973).

2) K. Akiyama, S. Tero-Kubota, Y. Ikegami, and T. Ikenoue, *J. Phys. Chem.*, **89**, 339 (1985).

3) F. J. Adrian, *Rev. Chem. Intermed.*, **3**, 3 (1979).

4) J. A. Barltrop and N. J. Bunce, *J. Chem. Soc. (C)*, **1968**, 1467.

5) K. Miyagawa, H. Murai, and Y. T. I'haya, *Chem. Phys. Lett.*, **118**, 140 (1985).

6) A. Cu and A. C. Testa, *J. Am. Chem. Soc.*, **96**, 1963 (1974).