CHEMISTRY LETTERS, pp. 1651-1654, 1988.

Kinetic Pressure Effect on Photoreduction of 2,4,6-Trinitrobenzoic Acid as Studied by Time-Resolved ESR

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Kinetic time-resolved ESR study was carried out on Photoreduction of 2,4,6-trinitrobenzoic acid (TNA). The CIDEP signal decayed in a biphasic manner, and the activation volumes for the fast and the slow decays were 26 and 11 cm^3 mol^{-1}, respectively.

The photoreduction of nitro-compounds in the 2-propanol-water mixture containing hydrochloric acid has been investigated by several workers,[1,2] and two radical mechanisms for the primary chemical process have been proposed. One involves the electron transfer from the chloride ion to the nitro-compound in the $n\pi^*$ triplet state,[1] and the other involves the hydrogen abstraction from 2-propanol.[2] Akiyama et al.[3] carried out the CIDEP measurements for the photoreduction of nitrobenzene derivatives in 2-propanol in the presence of triethylamine as efficient electron donor. The mechanism of the HCl-catalyzed photoreduction has not been well-established so far. Pressure effects on the reaction rate would provide important information regarding the reaction mechanisms, however, ESR study on kinetic pressure effects has been rarely done.[4] In the present paper, measurements of CIDEP in the HCl-catalyzed photoreduction of nitro-compound at high pressures were carried out and kinetic pressure effects on photoreduction were examined.

The commercially obtained 2,4,6-trinitrobenzoic acid (Ishizu Seiyaku Co.) was recrystallized from ethanol. The concentration of TNA was kept at 0.05 mol dm^{-3}. Sample solution was deoxygenized by bubbling nitrogen. CIDEP measurements were

performed using a home-made spectrometer at X-band without field modulation. A nitrogen laser was used as a light source. The time response of the detection system was ca. 35 ns. The high pressure technique and procedure were the same as described elsewhere.[5] The sample cell for CIDEP measurements was a quartz capillary (o.d. 4 mm, i.d. 1 mm). The pressure cell could be used up to 490 bar (1 bar = 0.1 MPa). All experiments were performed at room temperature.

The time-resolved ESR spectrum observed in the photoreduction of TNA in a 2-propanol-water mixture (9:1 v/v) containing hydrochloric acid is shown in Fig. 1. The emissive CIDEP spectrum consists of nine lines, and its intensity decreased with time. In the absence of hydrochloric acid, no CIDEP signal was observed. Further, the similar signal was observed in the presence of LiCl in 2-propanol-water mixture although the signal was not observed when HCl was replaced with H_2SO_4. These facts suggest that the chloride ion is a reactant in the formation of the radical species. The signal pattern shows the large spin-density distribution in 4-nitro-group, and the hyperfine structure (hfs) was ascribed to a nitrogen nucleus in 4-nitro-group and the two hydrogen nuclei in the benzene ring; the nitrogen coupling constant A_N = 1.2 mT and the hydrogen coupling constant A_H = 0.32 mT. Ward[6] has estimated a hyperfine coupling constant for the hydrogen atom bonded to an oxygen atom in the $ArNO_2H\cdot$ radical to be 0.038 mT. Thus, CIDEP spectra of $ArNO_2^{\cdot-}$ and $ArNO_2H\cdot$ are almost similar and not distinguished to each other.

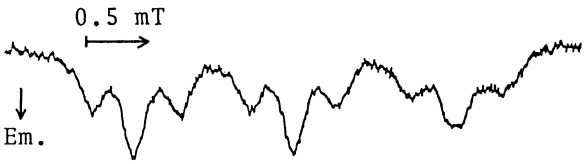

Fig. 1. CIDEP spectrum of TNA in a 2-propanol-water mixture; time delay 0.2 μs, gate width 0.2 μs.

The CIDEP signal clearly decays in a biphasic manner, as can be seen in Fig. 2. The rates of the two decays considerably differ each other and hence the rate constant for each decay process can be evaluated independently. In order to explain the biphasic decay curve, two possible mechanisms may be proposed; One is a consecutive reaction involving two radical species and the other a parallel reaction of two radical species. The result that the electron transfer from the chloride ion contributes to the formation of the anion radical suggests the consecutive reaction.[1] When the rate constant k_f^{obsd} of the fast decay is sufficiently greater than that k_s of the proceeding process, the time dependence

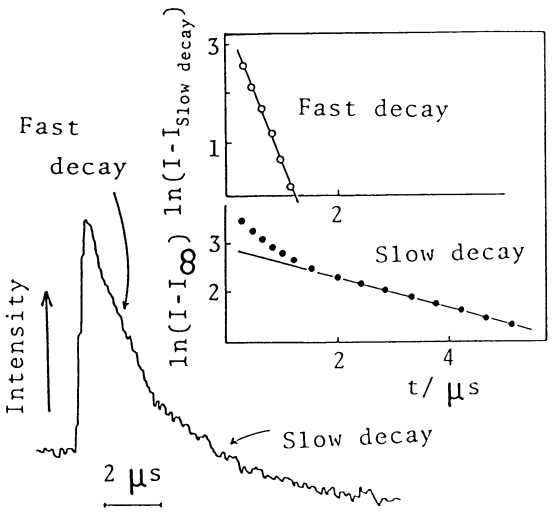

Fig. 2. Time profile of the central line in the hfs of CIDEP signal. A logarithmic plot of the intensity against time is shown in the inset.

of the CIDEP signal could be expressed by the following equation ;

i) Fast decay

$$P_{(t)}-P_{(t)\text{Slow decay}} \approx (P_1-P_2)\exp(-k_f^{obsd}t) \quad (1)$$

ii) Slow decay

$$P_{(t)} \approx P_2\exp(-k_s t) \quad (2)$$

where P_1 and P_2 are constants proportional to the number of radicals and in the present case $P_1 > P_2$. At the initial period of the signal decay, the decay curve was approximated by a single exponential function with the rate constant k_f^{obsd}. Then, the succeeding exponential decay with the rate constant k_s was found as seen in Fig. 2. The decay curve was fitted to eqs 1 and 2 with $k_f^{obsd} \approx 10^6$ s^{-1} and $k_s \approx 10^5$ s^{-1} at the microwave power of 1.4 mW in 1.2 mol dm^{-3} HCl solution, as shown in the inset of Fig. 2.

The influence of the microwave power on the decay rate of the faster component was not observed, while the rate of the slower component increased with increasing the microwave power. These findings suggest that the fast decay is due to a chemical reaction and the slow decay is associated with the relaxation of spin polarization by spin-lattice relaxation process.[7)]

Kinetic studies at high pressures permit the estimation of activation volumes $\Delta V^{\ddagger}$ of the reactions, and give useful information on the structure of transition state and the reaction mechanism.

$$RT(\partial \ln k/\partial p)_T = -\Delta V^{\ddagger}, \quad (3)$$

where $\Delta V^{\ddagger}$ is the difference in molar volume between the activated complex and reactant. As shown in Table 1, the fast decay is remarkably retarded as external pressure increases. The activation volume estimated from the slope of the linear plot of $\ln k_f^{obsd}$ against p was 26±1 cm^3 mol^{-1} for the reaction associated with the fast decay. The pronounced pressure dependence observed indicates that the fast decay involves a step of charge neutralization.

The rate of electron spin-lattice relaxation depends on the microwave power

and effective time constants $T_{1,eff}^{-1}(=k_s)$ are given by following relation.[8)]

$$T_{1,eff}^{-1} = T_1^{-1} + \omega_1^2(T_{2,ex}^{-1} - T_1^{-1})^{-1} \quad (4)$$

where notations have their usual meanings. The relaxation rate constants $T_1^{-1}(=k_s^0)$ of radicals are obtained from extrapolation to zero microwave power and are given in Table 1. The relaxation rates are also found to be retarded as external pressure increases. The activation volume estimated for the spin-lattice relaxation process was 11±2 cm^3 mol^{-1}.

Taking the informations obtained into account, the following reaction scheme is tentatively proposed.

$$TNA^{\cdot-} + H^+ \xrightarrow{\text{fast}} TNAH\cdot \xrightarrow{\text{slow}} \text{Stable product}$$

Mechanistic details of photoreduction of TNA on the basis of the activation volume will be reported elsewhere.

Table 1. Rate constants (s^{-1}) and activation volumes (cm^3 mol^{-1}) for CIDEP signal decay of photoreduction of TNA (probable errors in parentheses)

p/bar	1	98	198	245	294	392	$\Delta V^{\ddagger}$
Fast decay $10^{-6}k_f^{obsd}$	2.38	2.14	1.88		1.72	1.58	26
	(0.25)	(0.10)	(0.11)		(0.02)	(0.11)	(1)
Slow decay $10^{-5}k_s^0$	1.66	1.49		1.45		1.37	11
	(0.11)	(0.07)		(0.19)		(0.08)	(2)

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(Received July 15, 1988)