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Simultaneous Observation of Spin Polarized Anion and Cation Radicals in Solution by Flash Photolysis ESR

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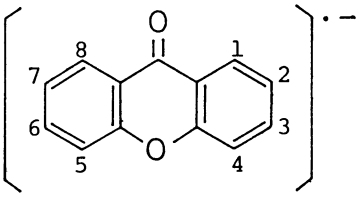
Time-resolved ESR studies have shown that UV irradiation of a mixture solution of xanthone and 1,4-diazabicyclo[2.2.2]octane generates corresponding radical anions and radical cations at the same time; their unpaired electrons are emissively spin polarized at the initial stage of radical creation as a result of the action of the triplet mechanism of CIDEP.

The usefulness of time-resolved ESR technique to study the radical reactions: an electron transfer and a molecular dissociation by flash photolysis or pulse radiolysis, has been recognized because the method has fast sub-microsecond response time.[1)] This fact allows to detect short-lived radicals showing spin polarization effect on the microsecond time scale as a result of the triplet mechanism (TM) and the radical-pair mechanism (RPM).[2)] Similar to conventional ESR, this technique has also the advantage of high sensitivity and selectivity to identify definitely the unknown radicals which cannot themselves be isolated.



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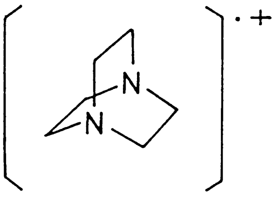

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Recently, we have reported[3)] the observation of emission enhanced CIDEP (E-CIDEP) signals of p-benzoquinone and of its derivatives radical anions as a result of the electron trnasfer from benzophenone radical anions which formed on flash photolysis in the presence of tripropylamine (TPA). However, no signal of counter cation radicals derived from the amine was detected. McLauchlan and Ritchie studied on flash photolysis of 1,2,4,5-benzenetetracarboxylic anhydride in *t*-alkylamine containing solutions.[4)] It has shown that H-abstraction occurred from the alkyl group in the amines, and spin polarized neutral α-aminoalkyl radicals were detected. However, none of cation radicals of their amines were found. Here we report the direct evidence that irradiation of xanthone (XT) and 1,4-diazabicyclo[2.2.2]octane (Dabco) mixture in the deoxygenated water/acetonitrile solution with an UV laser has generated XT radical anions **1** and Dabco radical cations **2** ; the both ion radicals with E-CIDEP have been detected at the same time using a time-resolved ESR at the early stage of the photoreactions.

The method of observation was substantially similar to one of those by McLauchlan and Stevens;5) the CIDEP spectrum of transient radicals was obtained with a boxcar integrator (NF; BX-531) by creating the radicals repetitively on flash photolysis as the magnetic field of a spectrometer (JEOL; JES-FE-3X) was swept continuously. The light source for photolysis was a nitrogen laser (Molectron; UV24, λ=337.1 nm, 10 ns pulse duration, 16 Hz repetition rate). The XT was selected because it has a high intersystem crossing (ISC) yield6) and a high extinction coefficient at 337.1 nm. As an electron donor the Dabco was chosen because it has smaller ionization energy compared with other amines.7)

In Fig. 1-(a) is shown the spectrum observed. A gate of the boxcar integrator was opened from 0.1 to 1.1 μs after each laser shot. The spectrum apparently consists of superposition of two transient species with the same emissive spin polarization. The calculated composite spectrum is shown in Fig. 1-(b) with the stick spectrum underneath.8) No contribution of the RPM was included for the simulation. Deviation from unity in the total intensity ratio of the two radicals is mainly attributed to the different relaxation time (T_A and T_D) of the respective spin states. Good agreement between the simulated and the experimental spectrum is found. Obtained ESR parameters of the respective radical are given in Table 1 with those derived previously with conventional ESR.9,10) The results show that the TM dominantly contributes to the E-CIDEP of both radicals. No CIDEP spectrum was observed with use of aerated solutions. It is considered that the triplet states of the XT were effectively quenched by O_2 of ground states.11) The fact of no apparent O_2 effect on the CIDEP in a similar experiment by McLauchlan and Ritchie4) might be attributed to higher content of the amines compared with O_2 concentration in the sample solutions. The photochemical reaction we observed could be represented as shown in the following scheme where the asterisk denotes an electron spin polarized molecule or exciplex.

Table 1. ESR parameters of xanthone anion radicals ($XT^{\cdot -}$) and 1,4-diazabicyclo-[2.2.2]octane ($Dabco^{\cdot +}$) (Hyperfine coupling constants in G : 1 G = 10^{-4} T.)

Radical	g Value	a(1H,3H,6H,8H)	a(2H,7H)	a(4H,5H)	Ref.
$XT^{\cdot -}$	2.00344	3.90	0.99	0.79	This work
$XT^{\cdot -}:Na^+$	2.0036	3.88	0.88	0.20	a)
		a(H)	a(N)		
$Dabco^{\cdot +}$	2.00477	7.49	16.91		This work
$Dabco^{\cdot +}$	-----	7.34	16.96		b)

a) Obtained by reduction with Na metal in ethereal solvents.10) 0.98 G to a(Na) is also given.

b) Generated by electrolytic oxidation in acetonitrile.9)

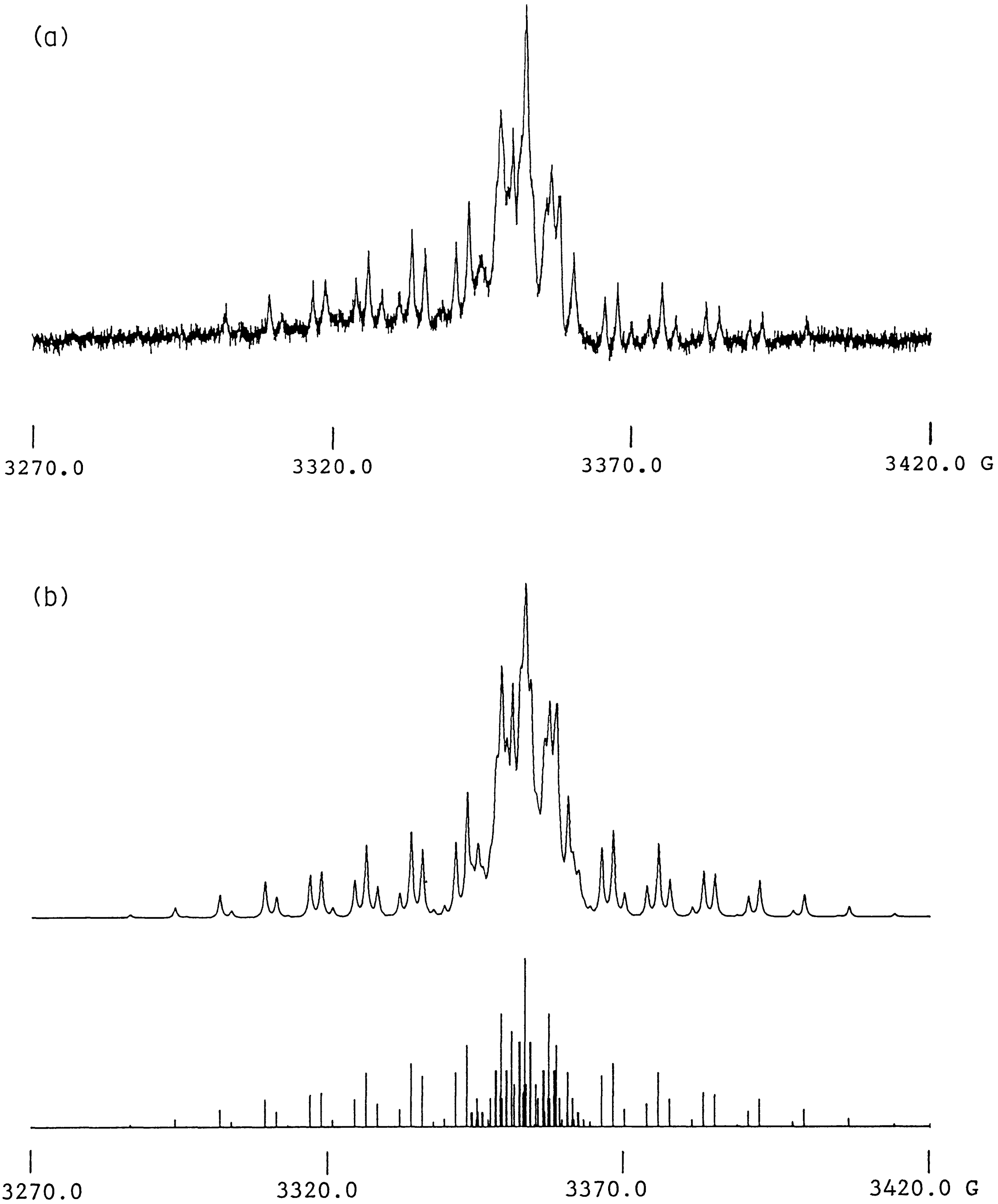
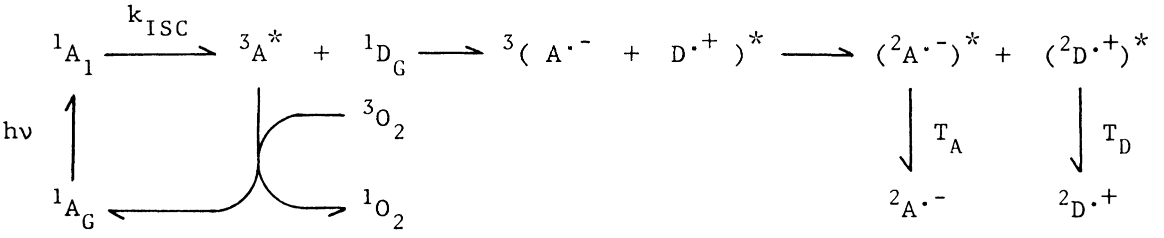


Fig. 1. (a) The superposed CIDEP spectrum of xanthone (XT) radical anions 1 and 1,4-diazabicyclo[2.2.2]octane (Dabco) radical cations 2 observed on photolysis of 2 mM XT and 50 mM Dabco solution in water/acetonitrile (1/1 in v/v) at room temperature. The signal was integrated from 0.1 to 1.1 µs after the laser flash with no field modulation; power and freq. of the microwave were 0.1 mW and 9.40088 GHz; the emissive signal was recorded upwardly.
(b) The composite CIDEP spectrum calculated by a computer simulation using the ESR parameters of the respective radicals given in Table 1. Lorentzian line shape was used for the individual h.f. component of the radical; line width ΔH(m.s.l.) of 1 and 2 were 0.4 and 0.3 G, respectively; intensity ratio 1/2 was 1.0/0.7 . No contribution of the radical pair mechanism (RPM) was included in the simulation. The stick spectrum was shown underneath.



A: electron acceptor (XT). D: electron donor (Dabco).

It is confirmed that the both ion radicals were formed as a result of photo-induced electron transfer from the donor D (Dabco) to the acceptor $^3A^*$ ($^3XT^*$) ; it is directry shown here that the Dabco radical cations surely exist as transient intermediates and a role of the Dabco as a good reducing agent or quencher for photo-excited carbonyls[12)] has been clarified. However, any corresponding cation radicals of the amines have not been observed in a similar experiment with *t*-alkylamines including the TPA instead of the Dabco. Kaim reported simultaneous detection of N-silicified 1,4-dihydropyrazine radical cation and TCNQ radical anion[13)] in solution with conventional ESR. They were formed by a single electron transfer reaction between their parent molecules. His detection of both ion radicals is a rare event among solution ESR. Further studies with other triplet sensitizers are now in progress to investigate more detailed mechanism of charge transfer photoreactions which involve ion radicals with spin polarization.

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8) In a computer simulation, Lorentzian line shape with the same proper line width was used for individual h.f. component of respective CIDEP spectrum because supurious sidebands were negligible under our experimental condition with low microwave power and the calculated spectrum well reproduced the observed one. For more detailed analytical expression of CIDEP spectra, see: S. Basu, K.A. McLauchlan, and G.R. Sealy, Mol. Phys. 52, 431 (1984).
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