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SPIN-POLARIZED TRANSIENT RADICALS FROM p-BENZOQUINONE AND DI-t-BUTYL-p-QUINONES BY PHOTO-EXCITATION OF BENZOPHENONE IN A MAGNETIC FIELD

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In the photochemical electron transfer reactions of t-alkylamine and p-benzoquinone in liquid, emissively spin-polarized transient anion radicals from p-benzoquinone(PBQ) and 2,5- or 2,6-di-t-butyl-p-quinone(25Q or 26Q) are exclusively produced by photo-excitation of benzophenone(BP) in a magnetic field. Transient radicals of quinones with different unpaired spin distribution are obtained at the onset of photolysis.

It has been confirmed that an electron is transferred from tertiary alkyl or aromatic amines to triplet BP in the photo-reaction of aromatic carbonyl compounds with amines.1) In the ESR study, a duroquinone anion radical has been detected by UV-laser photolysis of a substrate in an alcoholic solution in the presence of triethylamine as an electron donor.2) By the method of time-resolved ESR,3) polarized ESR spectra of duroquinone anion are shown to arise via triplet mechanism(TM) of chemically induced dynamic electron polarization (CIDEP).4)

We report here that emissively spin-polarized transient radicals from PBQ and 25Q or 26Q are efficiently obtained by photo-excitation of BP in the solution containing quinones and tri-propylamine(TPA), and their emission enhanced CIDEP (E-CIDEP) spectra with considerable intensities could be successfully observed even in non-alcoholic solvents different from other studies.5-8)

The ESR apparatus without magnetic field modulation coupled with nitrogen laser (λ = 337.1 nm) was used in these studies.

All of our measurements show that coexistence of BP and elimination of oxygen from the solution are indispensable conditions to get those transient radicals with

E-CIDEP of considerable intensity. If PBQ or its derivatives have not contained in the solution, the anion radical of BP with E-CIDEP is observed. There is, however, another report$^{9)}$ with the result that the BP ketyl radical is produced by the use of N,N-diethylaniline as an electron donor.

Measurement of PBQ in a solvent of 2-propanol with TPA resulted in the detection of a feeble E-CIDEP of PBQ^- different from Trifunac et al.$^{8)}$ They have not observed PBQ^- but detected E-CIDEP of p-benzosemiquinone radical ($PBQH^\cdot$) with a_{OH} = 0.18 mT. When BP is added in the solution, however, a considerably intensive E-CIDEP spectra of PBQ are obtained. Measured spectra with non-alcoholic solvent, dimethylformamide(DMF), are given in Fig. 1. The signal is readily assigned to PBQ^- $^{10)}$ (g = 2.0050, a_H = 0.24 mT : see Fig. 2.). If 25Q is used instead of the PBQ, the E-CIDEP spectra with a triplet h.f. of 1:2:1 intensity ratio are obtained (g = 2.0050, a_H = 0.23 mT), which can be assigned to $25Q^-$ (Fig. 3.). If triphenylene is used as a substitute of BP, neither conventional ESR signal nor E-CIDEP of corresponding quinone anion radical is observed. This fact shows that T-T energy transfer dose not contribute to the production of quinone anion radical.

It is known that photo-excited BP, $^3BP^*$, exhibits a dominant $n\pi^*$ character and its primary reactions are electron abstraction at first to produce BP anion radical, and successive proton abstraction of BP^-, i.e., creation of BP ketyl radical ($BPH^\cdot$). The possibility of the latter reaction is depends on the electron or proton donating character of the surrounding medium.$^{11)}$ In the photo-CIDEP study of BP with triethylamine in alcoholic solvent, $BPH^\cdot$ was detected.$^{12)}$ However, neither $BPH^\cdot$ nor BP^- is observed in our BP and PBQ or 25Q containing DMF/TPA solution, and PBQ^- or $25Q^-$ with E-CIDEP is detected instead.

The results obtained here are interpreted that the abstracted electron by $^3BP^*$ from TPA is efficiently and emissively polarized in a magnetic field, and transferred fast into quinones within the electron spin-lattice relaxation time, which leads to the formation of the spin-state population inverted anion radicals of quinones, i.e., PBQ^- or $25Q^-$. It is known that the zero-field splitting parameter(D) is negative for the ^3BP,$^{13)}$ the ISC rate under the magnetic field is spin-state selective and the zero-field spin sublevel(T_z : z designates C=O bond direction of BP molecule) is populated predominantly,$^{14)}$ which results in the overpopulation of upper spin-state of the radical even in liquid. It is reasonable to assume that spin polarized electrons are transferred from BP^- to quinones, different from McLauchlan et al.$^{15)}$ in photosensitized reactions.

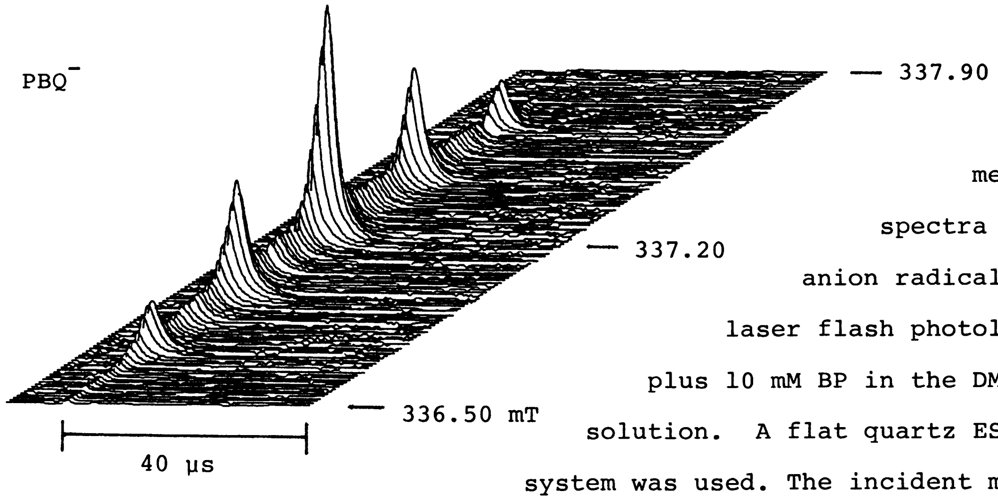

Fig. 1. The three dimensional CIDEP spectra of the transient anion radical of PBQ created by laser flash photolysis of 5 mM PBQ plus 10 mM BP in the DMF/TPA (20/1; v/v) solution. A flat quartz ESR cell with flow system was used. The incident m.w. power was 1 mW and individual I(t) signal was obtained by 128 times accumulation. The emission is indicated upward.

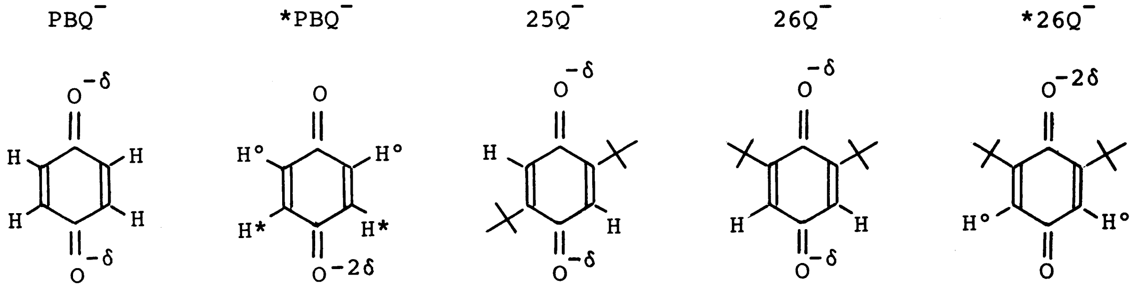

Fig. 2. The anion radicals of p-Benzoquinone(PBQ⁻), 2,5-Di-t-butyl-p-quinone (25Q⁻), and 2,6-Di-t-butyl-p-quinone(26Q⁻). (a_H = 0.24 - 0.21 mT, $a_{H°}$ = 0.00 mT, a_{H*} = 0.48 - 0.42 mT; δ indicates the unpaired electron spin density on oxygen atoms.)

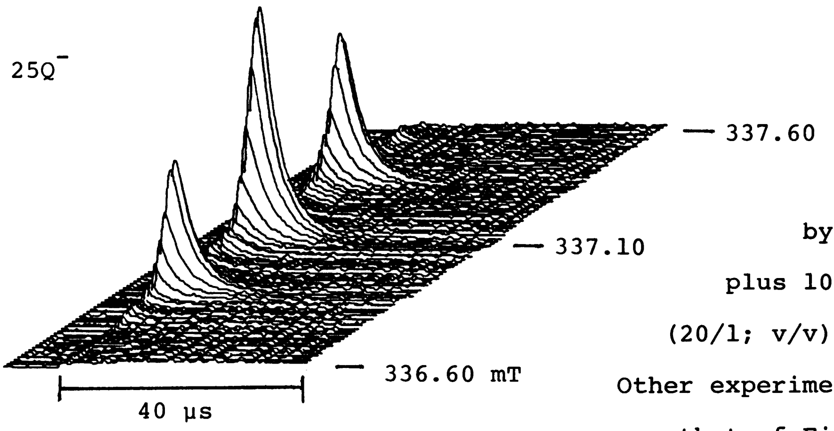

Fig. 3. The three dimensional CIDEP spectra of the anion radical of 25Q by photolysis of 10 mM 25Q plus 10 mM BP in the DMF/TPA (20/1; v/v) solution. Other experimental conditions were the same as that of Fig. 1.

When 26Q is used instead of 25Q, E-CIDEP spectra with a triplet h.f. of 1:6:1 intensity ratio (g = 2.0050, a_H = 0.23 mT) are observed, and E-CIDEP spectra of a triplet h.f. of 1:2:1 intensity ratio are obtained (g = 2.0050, a_{H*} = 0.46 mT, $a_{H°}$ = 0.0 mT : see Fig. 2.) by the photolysis of PBQ and BP with TPA in a benzene solvent. These results show that anion radical with lopsided unpaired spin density on oxygen atoms are prduced with E-CIDEP even in liquid ($*PBQ^-$ and $*26Q^-$ + $26Q^-$ in Fig. 2.). There is a similar report for the cation radical of PBQ at 77 K,16) where it is concluded that the unpaired electron is confined largely to one oxygen atom. It is found that PBQ derivatives including duroquinone have also yielded the corresponding anion radicals with E-CIDEP in a similar experiment with BP.

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