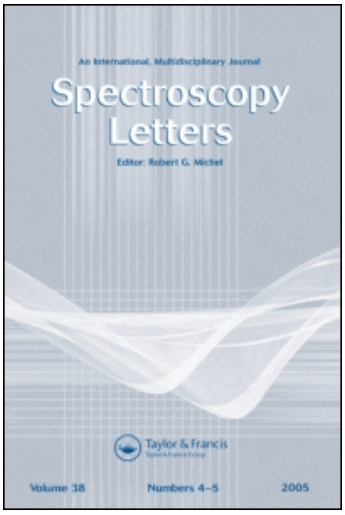


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Proton Exchange Effects in Laser Photolystic P-Benzosemiquinone Spin Polarized Radicals

Gao Jun[a]
[a] Department of Chemistry, Chinese University of Hong Kong, Shatin, N.T., HONG KONG

To cite this Article Jun, Gao(1996) 'Proton Exchange Effects in Laser Photolystic P-Benzosemiquinone Spin Polarized Radicals', Spectroscopy Letters, 29: 7, 1459 — 1468
To link to this Article: DOI: 10.1080/00387019608007137
URL: http://dx.doi.org/10.1080/00387019608007137

SPECTROSCOPY LETTERS, 29(7), 1459-1468 (1996)

PROTON EXCHANGE EFFECTS IN LASER PHOTOLYSTIC P-BENZOSEMIQUINONE SPIN POLARIZED RADICALS

Key words: CIDEP, p-benzosemiquinones radical, TRESR, proton exchange

Lu T. X.
Department of Physics, Anhui Normal University,
WUHU 241000, Anhui, PRC
and
Gao Jun
Department of Chemistry, Chinese University of Hong Kong,
Shatin,N.T,HONG KONG

Abstract

The TRESR spectra of benzosemiquinone radical and the ethylene glycol ketyl radical formed from laser photolysis of P-benzoquinone in ethylene glycol or ethylene glycol/water systems are presented. The photon exchange between p-benzosemiquinone radicals $PBQH^{\bullet}$ and their protonated forms $PBQH^{+}$ is studied by adding H_2SO_4 to the solution . The experimental results show that different hyperfine lines for $PBQH^{+}$ have different time-dependence which depend upon the fraction of the overall number of nuclear spin states, and that the lines with smaller fraction are decay fast.

1. INTRODUCTION

Time-resolved ESR spectroscopy (TRESR) of the chemically induced dynamic electron polarization (CIDEP) are proved of great value in the investigation of the mechanism and kinetics of photochemical reactions. The work by K. A. Mclanchlan and the co-workers shows that the CIDEP spectra of transient radicals formed in the flash-photolystic are unusually sensitive to the occurrence of chemical exchange processes[1-3]. Ian C.P.Smith et al have studied the semiquinone radicals derived from hydroquinone in aqueous solution by using cw-ESR spectroscopy, and observed that the ESR spectra changed drastically with pH. they attributed these effects to the protonation of the semiquinones, the rate which depended on the pH [4-5]. Therefore, it will be very interesting to see what kinds of TRESR are to be expected if the spin polarized p-benzosemiquinones radical in the acidic condition are studied. In this paper, we report the investigation of TRESR spectra of p-benzosemiquinone radicals formed from laser photolysis of p-pbenzoquinone in ethylene glycol and ethylene glycol/water systems respectively, and the effect of the acid on the CIDEP of flash photolytic benzosemiquinone radicals.

2.EXPERIMENTAL

The experiments are performed using a homemade X-band time-resolved ESR spectrometer with balanced zero frequency mixer, whose detail is described otherwhere[6], the main structure is as follows. Two signals from two balanced mixer diodes have opposite phases and each is amplified by the same amplifier with 50 ns time response. Then the signals are sent to opposite inputs of a wideband differential amplifier, where TRESR signal is further amplified and noise is offset. The output signal from differential amplifier is fed to a computer controlled digital oscilloscope(PM3350) and a boxcar(SRS256). An excimer laser(Lambda Physik LPX-105, XeCl, λ =308nm) with repetition rates of 20-40 Hz is used

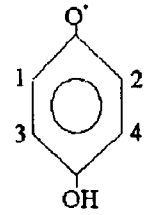
as photolysis source. The time origin is determined by a trigger pulse from a mini-controller. The sample solution is flowed through a flat quartz cell (0.3mm light path) after deoxygenating by bubbling the pure nitrogen gas.

The TRESR measurements are made at room temperature with a 0.3μs of boxcar gate and different time delay after laser excitation. The commercial grade p-benzoquinone is purified by sublimation before use, the ethylene glycol and other materials are analytical grade reagents without further purification. The concentration of p-benzoquinone in solvent is 0.01 M.

3. RESULTS

3.1 CIDEP spectra of p-benzoquinone in the unmixed ethylene glycol

Fig.1 shows the CIDEP signal of P-benzoquinone in the unmixed ethylene glycol solvent observed at 0.4-0.7μsand 1.2-1.5μs of time windows after the laser excitation, respectively. As can be seen in Fig.1, the whole spectrum shows a total emission pattern of the microwave. At an early stage after the laser excitation, the spectrum can be resolved into two superimposed signals, a stronger signal and a weaker one. The stronger signal which has the hyperfine coupling constants of 0.48mT and 0.17mT can be assigned to p-benzosemiquinone radical, PBQH$^{\bullet}$. The photolystic process can be shown as:



$$PBQ \xrightarrow{h\nu} {}^1PBQ^{\bullet} \xrightarrow{ISC} {}^3PBQ^{\bullet}$$

$${}^3PBQ^{\bullet} + RH \rightarrow PBQH^{\bullet} + R^{\bullet}$$

where PBQ, $^1PBQ^{\bullet}$, and $^3PBQ^{\bullet}$, represent the p-benzoquinone molecule, and their single and triplet excited states, respectively, and RH represents ethylene glycol molecules.

The larger hyperfine splitting(0.48mT) is attributed to the two equivalent protons of p-benzosemiquinones radicals at 1,2 positions, and the smaller

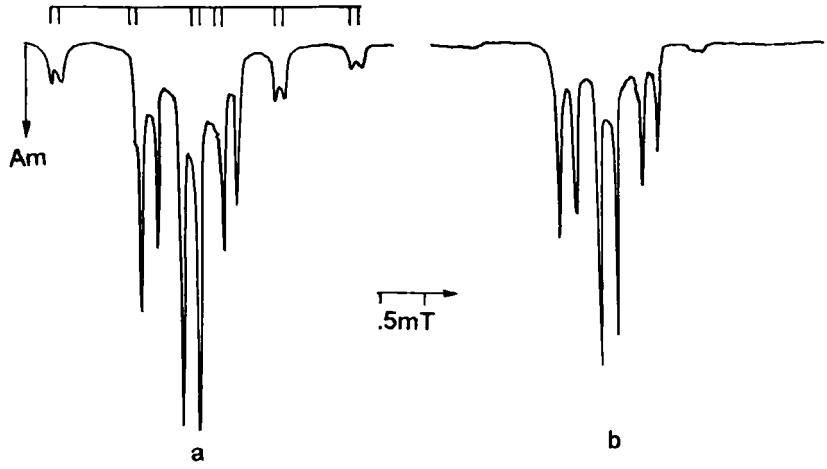
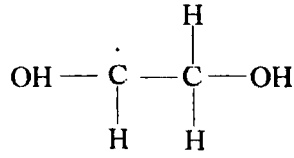


Fig.1 TRESR spectra of p-benzoquinone in the unmixed ethylene glycol solvent. at delay times 0.4μs (a) and 1.2μs (b) after the laser excitation.

hyperfine splitting(0.17mT) is attributed to its OH radical, while the hyperfine splitting pertaining to the other two protons at 3,4 positions are not resolvable.

The weaker signal appears as three doublet peaks, but by comparing the spectrum in the Fig.1b with that in the Fig.1a, it may lead to the conclusion that the additional peaks should be attributed to this signal. We consider that this signal contains six doublet peaks, which are indicated by the solid stick in the top of Fig 1a. We assign this signal to the ethylene glycol ketyl radical $R^{\bullet}$ with a g-values of 2.0037 ± 0.0002.



The observed total emission spectrum after laser excitation is apparently due to the transfer of the spin polarization of $^3PBQ^*$ to radicals $PBQH^{\bullet}$ and $R^{\bullet}$, namely, the triplet mechanism(TM). For the occurrence of the TM, the

spin polarization phase for the $PBQH^{\bullet}$ and $R^{\bullet}$ are same. Therefore, $PBQH^{\bullet}$ and $R^{\bullet}$ radicals should exhibit the same emissive polarization pattern just as observed in the experiment.

The TRESR signal duration for ethylene glycol radical $R^{\bullet}$ is very short. Fig.2 shows the time-profile for one component of the central line of $PBQH^{\bullet}$ signal and one of outside lines of $R^{\bullet}$ signal at the high field side, respectively. It is can be seen that the rising rate and the decay rate of the TRESR signal for $R^{\bullet}$ radical are faster than that for $PBQH^{\bullet}$ signal. In the condition of 4 mw microwave power, rising time for $PBQH^{\bullet}$ radical from zero to its peak is ~ 0.8 μs and decay time from the peak to zero is ~ 10μs after laser excitation, while for $R^{\bullet}$ radical the values are ~ 0.4μs and ~ 1.5μs, respectively. Therefore, in the spectrum diagram obtained at a time delay longer than 1.5μs(Fig.1b), the TRESR signal of $R^{\bullet}$ radical. disappears completely. That is to say, the lifetime of $R^{\bullet}$ radical is probably also short.

3.2 Proton exchange effects in laser photolysic p-benzosemiquinone radicals

The above mentioned CIDEP spectral lines of $PBQH^{\bullet}$ radical start to broaden and coalesced, when H_2SO_4 is added to ethylene glycol solvent. As shown in Fig.3A, when H_2SO_4 amount in solvent is increased to 1.26% in volume, the CIDEP spectral lines change to five sharp peaks. It's hyperfine coupling constant is 0.22mT. This signal should be assigned to $PBQH^{+}$. In ethylene glycol/water mixed solution the CIDEP spectral lines are broaden as H_2SO_4 amount increases. When H_2O is added in solvent and its amount increased, the similar effect that, the spectral lines change from six peaks becomes first to three wide peaks and then to five peaks appears, only now H_2SO_4amount in solvent is very small. Therefore acid amount can be represented by the pH value of the solution, instead of using direct volume amount. Fig.3B shows spectrum lines at some pH values when ethylene glycol / water = 1:1 in volume.

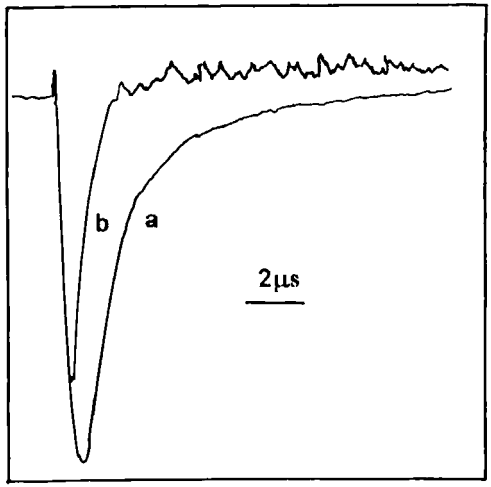


Fig.2 Time-profile of TRESR spectrum lines of p- benzoquinone in the unmixed ethylene glycol solvent with 4 mw microwave power a. for a central line of $PBQH^{\bullet}$ signal b. for a outside line of $R^{\bullet}$ signal

It is noted that, the effect of line coalesce appears at a much smaller H_2SO_4 amount in ethylene glycol / water mixed solvent, in comparison with the unmixed ethylene glycol solvent. This is understandable because the viscosity of ethylene glycol / water solution is much smaller that of pure ethylene glycol. In high viscous solution with great the molecular motion is inhibited and the slow rate of protons exchange is expected.

The TRESR spectra of $PBQH^{+}$ at different time after laser excitation are presented in Fig.4. As seen from this figure that two outside lines with $M_I = \pm 2$ appear to decay first, followed by the decay of central line with $M_I = 0$ and, eventually the second and fourth lines with $M_I = \pm 1$.

4. Discussion

It is known that, the semiqunone radical $PBQH^{\bullet}$ is unstable because of asymmetry of its structure. There are two thermodynamically equivalent

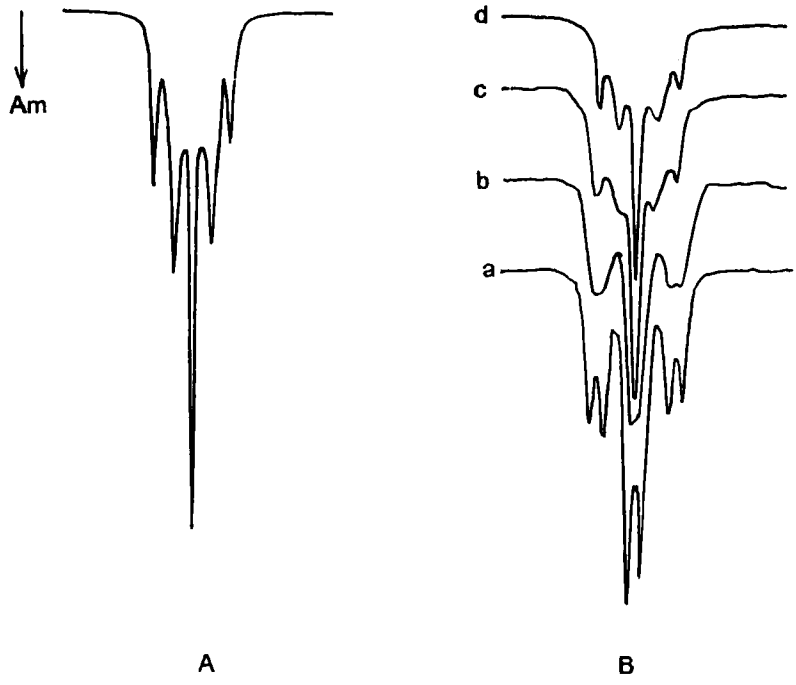
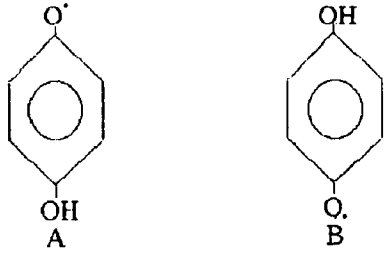


Fig.3 TRESR spectrum of p-benzoquinone at delay times 0.8μs after the laser excitation in ethylene glycol solvent with H_2SO_4 1.26% in total volume(A),. in ethylene glycol/water=1:1 mixed solution (B) at pH=5.5(a), pH =2.9(b), pH 2.65(c) and pH 2.02(d).

figuration, A and B, i.e. states of the same energy in $PBQH^{\bullet}$ radicals which can be written as:



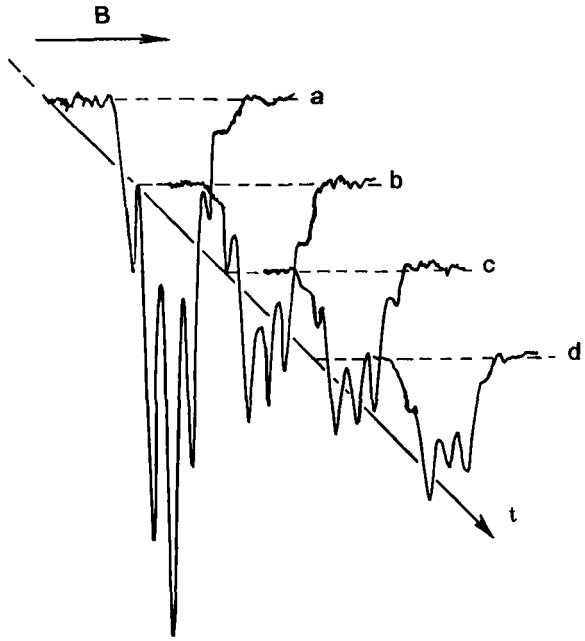
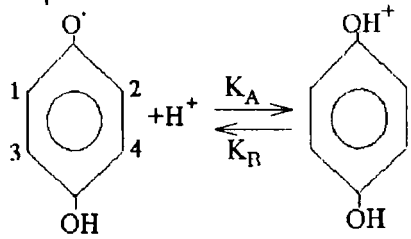


Fig.4 The TRESR spectra of $PBQH^+$ in ethylene glycol/water=1:1 mixed solution at different delay times after the laser excitation, 1.2μs(a), 1.6μs(b), 2.0μs(c), 2.4μs(d).

In acidic conditions there is a proton exchange between p-benzosemiquinone radicals $PBQH^{\bullet}$ and their protonated form $PBQH^+$, which can be expressed as :



Therefore the inter-conversion from A to B or from B to A by $PBQH^+$ is occurred. We first note that wherenever in the forms A or B, 1 and 2 are

completely equivalent, so are protons 3 and 4. The protons different pairs are not completely equivalent. The completely equivalent protons of $PBQH^+$ at 1, 2, or 3, 4 positions can be taken as nuclei with 1 spin. The two nuclei with 1 spin are not instantaneously equivalent, and that leads to an alternating linewidth effect.

The rate of proton exchange increases with increase of H^+ concentration. In the region of slow exchange, one would observed the spectrum in character with neutral monoprotonic radical $PBQH^{\bullet}$, as shown in Fig.1, namely, TRESR spectrum is a strong emissive signal with six hyperfine components. As the exchange rate increases, the lines will appear to broaden and coalesce, the spectrum lines are coalesced to three broad peaks are obtained. As the exchange rate further increases, the lines will also coalesce to five sharp lines with intensities ratio 1:4:6:4:1.

To explain the time-dependence of the spectra in Fig.4, it is necessary to analyze the contribution of individual nuclear spin states of the protons at the positions 1,2,3and 4 to the composite line. The two outside lines with $M_I = \pm 2$ of spectrum in Fig.3A and four lines with $M_I = 0$(the central line in Fig.3A) will be unaffected by the exchange processes. The widths of all $M_I = \pm 1$ lines (second and fourth lines in Fig.3, made up of contribution from eight proton nuclear spin states) and of two of the $M_I = 0$ lines (center line in Fig.3A) are affected by the exchange processes. Therefore, the time-dependence of spectra presented in Fig.4 is an interesting behavior. The different behavior of the different hyperfine lines depends upon the fraction of the overall number of nuclear spin states which contribute to them which change their resonance position on exchange processes. The lines with smaller fraction from nuclear spin states decay faster. For the hyperfine lines from radical $PBQH^{\bullet}$, the fractional contribution of individual nuclear spin states to each line is given by 0,1,1/3,1 and 0 in turn. That is, two outside lines with $M_I = \pm 2$ decay first, followed by the central $M_I = 0$ line, finally $M_I = \pm 1$ lines decay.

References

1. S. Basu, K.A. Mclauchlan, J.A.D. Ritchie, Time-resolved electron spin resonance with electron spin polarization(CIDEP) as a sensitive probe of degenerate exchange reactions, Chem.Phys.Lett., 1984; 105: 447.
2. K.A. Mclauchlan, J.A.D. Ritchie, A flash-photolysis electron spin resonance study of radicals formed from carboxylic acids; exchange effects in spin- polarized radicals, Mol.Phys., 1985; 56: 141.
3. K.A. Mclauchlan, J.A.D. Ritchie, A flash-photolysis electron spin resonance study of radicals derived from anhydrides of carboxylic acids; spin-polarized (CIDEP) spectra under conditions of fast electron exchange, Mol.Phys., 1985; 56: 1357.
4. Iso Yamazaki, L.H. Piette, Electron paramagnetic resonance of undissociated p-benzosemiquinones J. Am. Chem. Soc., 1965; 87: 986.
5. Ian C.P. Smith, A. Carrington, An electron spin resonance study of proton transfer equilibria involving the semiquinone radicals derived from hydroquinone and catechol Mol.Phys., 1967 12 439
6. T.X. Lu, Q.Z. Wei, Q,S. Yu, G.L. He, On 0.2μs time resolution ESR spectrometer, Chin. J. scient. Instrum., 1993 14 263
7. J.B. Pedersen, C.E.M. Hansen, H. Parbo, and L.T. Muss, A CIDEP study of p-benzosemiquinone. J. Chem. Phys. 1975; 63: 2398.

Received: April 9, 1996
Accepted: May 20, 1996