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Evidence of phenoxymethyl radical formation in laser photolyses of anisole in solution

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Abstract

Transient absorption spectrum of anisole in acetonitrile was observed by a 248-nm laser photolysis. In addition to the structured band observed at 400 nm, which was assigned to phenoxyl radical, a broad absorption band appeared at around 440 nm. The lifetime of the unknown species was not affected by oxygen. By means of acetone photosensitization reaction, photolysis of 1,2-diphenoxyethane, and ESR measurements, it is demonstrated that the transient is phenoxymethyl radical. The formation mechanism of the phenoxymethyl radical is discussed.

Keywords: Phenoxymethyl radical; Laser photolysis; Anisole; ESR; 1,2-Diphenoxyethane

1. Introduction

Photolysis of anisole and phenol in the gas phase is well known to generate phenoxyl radical [1–3]. Absorption spectrum of phenoxyl radical was reported by Porter and Wright [1] in flash photolysis studies of phenol and anisole for the first time. Kajii et al. [2] studied the reaction mechanism by ArF laser flash photolysis of phenol and anisole. The photodissociation is explained in terms of predissociation. Bayrakçeken et al. [3] reported that phenoxyl radical decays with bimolecular recombination.

In the condensed phase, primary photochemical and photophysical processes of excited phenol were extensively studied [4–6]. Köhler et al. [4] found that a non-radiative process different from intersystem crossing occurs during the S_1 decay of phenol. Kajii and Fessenden [5] proposed a reaction model with solvated electrons for excited phenol in ethanol. However, there have been few reports for photolysis of anisole so far. In addition to the absorption spectrum resulting from phenoxyl radical, a broad one was observed in water [7,8]. According to the results of product analysis, Joschek and Grossweiner [7] speculated the production of phenoxymethyl radical. In this article, we report the photochemical processes of excited anisole studied by laser flash photolysis, ESR, and photosensitization techniques.

2. Experimental

Transient absorption spectra were measured with the conventional laser flash photolysis system [9]. A KrF excimer laser (Lambda Physik COMPex102; 248 nm, 10–50 ns pulse duration) or a XeCl excimer laser (Lambda Physik COMPex102; 308 nm) was used as an excitation light source. The laser power was monitored with a silicon photodiode (Hamamatsu S1336-5BQ) calibrated with a pyroelectric detector (Gentec ED-100). An analyzing light of a pulsed xenon flash

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lamp (Ushio UXL-300DO; 300 W), passing through a flow cell (NSG T-59FL-UV-10; 10 mm light path length), was detected by a monochromator (Nikon P-250)/photomultiplier tube (Hamamatsu R928) system. The signals were averaged over 30 shots. Sample solution was flowed in the cell to eliminate the influence of photoproducts. All measurements were carried out at room temperature. Absorption spectra were measured with a double beam spectrometer (Jasco Ubest V-550).

ESR signals were detected by X-band ESR spectrometer (JEOL RE2X) with 100 kHz magnetic field modulation at 77 K.

Anisole (Kanto Chemical, GR grade), which contains a trace of phenol as an impurity, was purified [10]. To remove phenol, liquid anisole was shaken with half volume of aqueous solution of NaOH (2 M) for four times. Then, the anisole was washed twice with distilled water, dried with $CaCl_2$, filtered, dried with sodium wire, and finally distilled. Phenol (Kanto Chemical, GR grade) was purified by recrystallization twice from hexane. 1,2-Diphenoxyethane, acetonitrile, 2-propanol, and acetone (Kanto Chemical, GR grade) were used as received.

3. Results and discussion

Fig. 1 shows transient absorption spectra of anisole in acetonitrile obtained with a 248 nm laser excitation under the aerated condition. Similar spectra were obtained with a 266 nm laser excitation. A broad absorption band at around 440 nm and a sharp absorption band at 400 nm appeared. The solid line in Fig. 1 shows a transient absorption spectrum of phenol in acetonitrile obtained at 1 μs after the 248 nm laser excitation under the aerated condition. The sharp absorption band observed at around 400 nm is identical to the reported one of a phenoxyl radical. Therefore, the broad band does not result from phenoxyl radical.

Fig. 2 shows the time profile of the transient absorption of anisole in acetonitrile monitored at 440 nm under the aerated or deaerated condition. The time profile under the aerated condition shows fast and slow components. Under the deaerated condition, lifetime of the fast component became longer. It is known that oxygen in the solution should quench excited triplet state species. The quenching rate constant can be approximately determined to be $1.2 \times 10^7\ s^{-1}$ with quenching rate constant ($6.3 \times 10^9\ M^{-1}\ s^{-1}$) of the excited triplet state of anisole by oxygen in water (pH 8.5) and oxygen concentration in acetonitrile (1.9 mM) [11]. The agreement of the decay rate constant ($4.0 \times 10^7\ s^{-1}$) implies that the fast component should be attributed to the excited triplet state of anisole. However, the longer-lived species, which has a broad absorption band at around 440 nm, was not influenced by oxygen. A reciprocal plot of the time profile under the aerated condition (Fig. 2 inset) shows a good linear relation, suggesting that the longer-lived species should disappear with bimolecular reaction.

Fig. 3 shows transient absorption spectra of anisole in acetonitrile under the aerated condition obtained by the 248 nm laser excitation. The broad spectrum of phenoxyl radical was reported in the similar red spectral region [5]. However, the transient absorption at around 630 nm almost disappeared in 100 ns (see Fig. 3). The absorption coefficient of phenoxyl radical is reported to be $300 \pm 150\ M^{-1}\ cm^{-1}$ at 580 nm and $3000\ M^{-1}\ cm^{-1}$ at 400 nm and the decay time of phenoxyl radical is also reported to be several μs [5]. In Fig. 3, therefore, we can safely ignore the contribution of phenoxyl radical.

It is known that solvated electron has absorption in the wavelength region as shown in Fig. 3 [12]. The report sug-

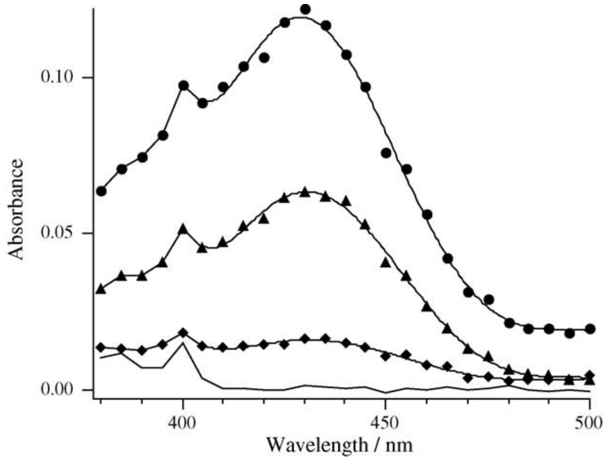

Fig. 1. (a) Transient absorption spectra of anisole in acetonitrile under the aerated condition obtained at 60 ns (●), 150 ns (▲) and 1 μs (◆) after the 248 nm excitation. The solid line is transient absorption spectra of phenol in acetonitrile obtained at 1 μs after the 248 nm excitation under the aerated condition.

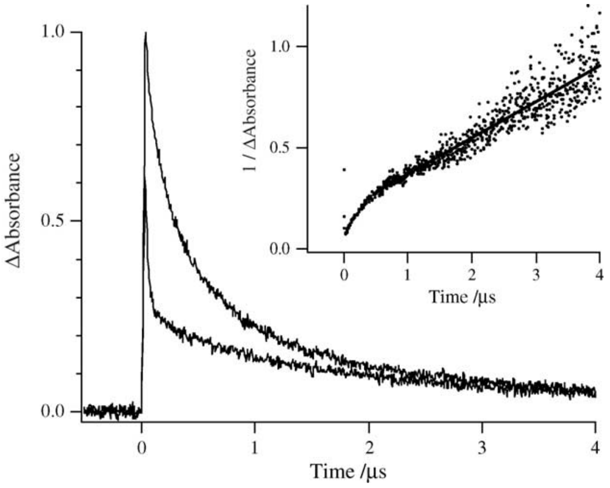

Fig. 2. Time profiles of transient absorption signal of anisole in acetonitrile under the deaerated (upper) and aerated (lower) condition monitored at 440 nm. Inset: reciprocal plot of the time profile of transient absorption signal of anisole in acetonitrile under the aerated condition monitored at 440 nm.

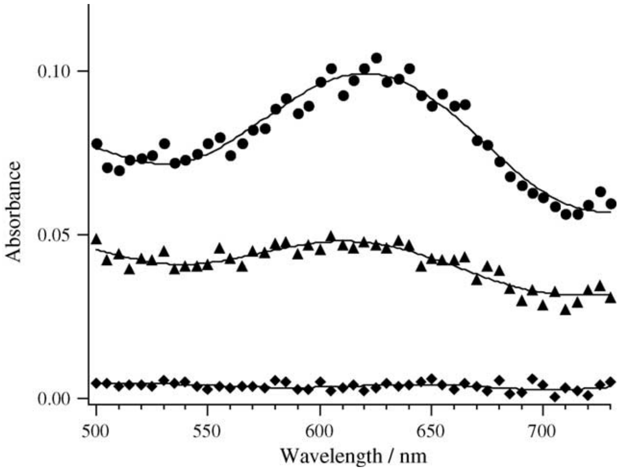

Fig. 3. Transient absorption spectra of anisole in acetonitrile under the aerated condition obtained at 30 ns (●), 45 ns (▲) and 100 ns (♦) after the 248 nm excitation.

gests that the broad absorption band at around 630 nm (Fig. 3) should be due to solvated electron. After addition of water to the sample solution (the volume ratio of water to the acetonitrile was 4:1), the absorption band peak was red-shifted to 700 nm. Since the hydrated electron is reported to have a broad absorption band at around 700 nm [12], the fact should reveal the existence of solvated electron in this system. One thing to note here is that in acetonitrile solution ejected electron by excited anisole should give rise to the formation of solvated electron with a trace of water contained in acetonitrile. It was reported that the solvated electron and several solvating molecules form a solvation shell [13]. The reason why the absorption band peak is red-shifted to 700 nm after addition of water to the sample solution may be explained by the different environment of the solvation shell of the hydrated electron between in acetonitrile and water-acetonitrile solution.

We also observed transient absorption spectrum of anisole in methanol under the aerated and deaerated conditions. The spectra had broad absorption bands at around 440 nm and around 620 nm. The broad absorption band at around 620 nm is in good agreement with that reported for solvated electron in methanol [12]. Under the aerated solution the solvated electron was quenched by the presence of oxygen. Furthermore, calculated rate constant ($4.4 \times 10^7\ \mathrm{s}^{-1}$) [11,12] for reaction of solvated electron with oxygen in methanol is in good agreement with estimated decay rate constant ($3.3 \times 10^7\ \mathrm{s}^{-1}$) from the experiment. Accordingly, it is confirmed that the broad absorption band at around 630 nm in Fig. 3 should be due to solvated electron.

The existence of solvated electron should imply the formation of counter cation. The longer-lived species, namely, the slow component observed in Fig. 2 under the aerated condition, which has a broad absorption band at around 440 nm, may be anisole cation. Anisole cation was reported to have a broad absorption band at 440 nm [14]. However, the lifetime of the species did not depend on the solvent polarity. The experimental fact suggests that anisole cation would not be appropriate.

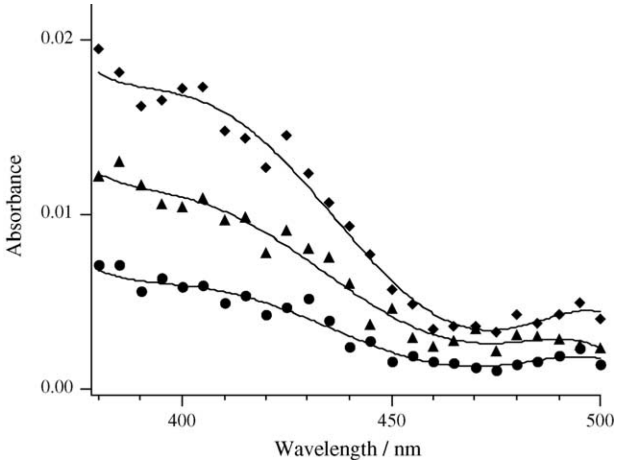

Fig. 4. Transient absorption spectra of anisole in acetonitrile with acetone under the deaerated condition obtained at 70 ns (●), 120 ns (▲) and 230 ns (♦) after the 308 nm excitation.

We measured transient absorption spectrum of anisole in acetonitrile with acetone as a hydrogen abstractor by a XeCl excimer laser excitation under the deaerated condition. New absorption band rose up at around 440 nm (see Fig. 4). The obtained spectrum is excellently identical to that of the longer-lived species in Fig. 1, and absorption due to 2-propanol radical would be overlapped below 400 nm [15]. Accordingly, the experimental results suggest the probable reaction mechanism as shown in Scheme 1. Formed triplet acetone by 308 nm excitation abstracts hydrogen of anisole to yield phenoxymethyl radical and 2-propanol radical. Triplet-triplet energy transfer would not take place because the triplet energy of anisole is higher than that of acetone (approximately $10\ \mathrm{kJ\ mol}^{-1}$ [11]).

Furthermore, we measured transient absorption spectra of 1,2-diphenoxyethane in acetonitrile under the aerated and deaerated conditions. A broad absorption band at around 440 nm was observed under the aerated condition (see Fig. 5). The inset shows a time profile monitored at 440 nm, which has fast and slow components. Because lifetime of the fast component became longer under the deaerated condition, the fast component should result from the excited triplet state of 1,2-diphenoxyethane. The spectral profile obtained at 1 μs after the 248 nm excitation (Fig. 5) is similar to that of the longer-lived species generated by photolysis of anisole (Fig. 1). And formation of phenoxymethyl radical was confirmed by cw-ESR measurement of 1,2-diphenoxyethane, as will be described below. These results of acetone photosensitization reaction, photolysis of 1,2-diphenoxyethane, and cw-ESR

$$\text{acetone} \xrightarrow[308\ \text{nm}]{h\nu} {}^{3}(\text{acetone})^{*}$$

$${}^{3}(\text{acetone})^{*} + \text{anisole} \xrightarrow{\text{hydrogen abstraction}} \text{2-propanol radical} + \text{phenoxymethyl radical}$$

Scheme 1.

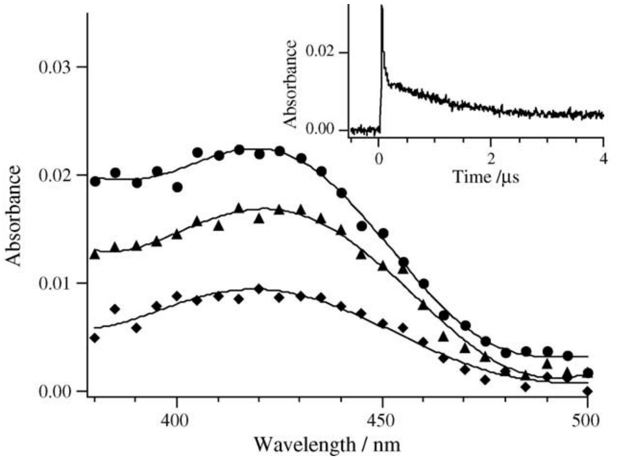

Fig. 5. Transient absorption spectra of 1,2-diphenoxyethane in acetonitrile under the aerated condition obtained at 90 ns (●), 130 ns (▲) and 1 μs (◆) after the 248 nm excitation. Inset: time profile of transient absorption signal of 1,2-diphenoxyethane in acetonitrile under the aerated condition monitored at 440 nm.

measurements strongly suggest that the longer-lived species, which has a broad absorption band at around 440 nm in Fig. 1, should be phenoxymethyl radical.

Time-resolved ESR measurements were carried out by direct irradiation of anisole at 266 nm at room temperature [16]. But no transient signal was observed. This is probably due to inefficient spin polarization creation in photocleavage processes to yield phenoxymethyl radical. No observation of time-resolved ESR signal and the quenching of the excited triplet state by oxygen for the transient absorption measurement prove that the contribution of the initial process in photolysis of anisole should be via the singlet state.

We carried out low temperature cw-ESR experiments at 77 K. Sample solutions were irradiated by pulsed laser for 10 min at 10 Hz. Fig. 6(a) shows the ESR spectrum of anisole in 2-propanol that consists of broad 10 peaks. The lines of the lower and higher magnetic fields show characteristic lines due to 2-propanol radical. The observed spectra were isotropic, so that simulated spectrum of 2-propanol radical was calculated with the hyperfine coupling constants ($H_{\mathrm{CH_3}} = 2.0$ mT, $H_{\mathrm{OH}} = 0.06$ mT [17]) and with line width of 0.2 mT (hwhm) for each line, as also shown in Fig. 6 (a). The simulated spectrum of 2-propanol radical is in good agreement with the observed signal in lower and higher magnetic fields. Fig. 6(b) shows the residual spectrum obtained by subtracting the simulated spectrum from the one obtained experimentally. Simulated spectrum of phenoxymethyl radical ($H_\mathrm{o} = 0.54$ mT, $H_\mathrm{m} = 0.27$ mT, $H_\mathrm{p} = 0.49$ mT and $H_{\mathrm{CH_2}} = 1.77$ mT [18]) with line width of 0.2 mT (hwhm) for each line was also presented in Fig. 6(b). Since the subtracted spectrum is in good agreement with the simulated phenoxymethyl radical spectrum, phenoxymethyl radical formation by the direct irradiation of anisole is concluded. It is expected that 2-propanol radical was formed by hydrogen abstraction of phenoxymethyl radical from 2-propanol. The ESR spectrum of 1,2-diphenoxyethane at 77 K was also observed. The sample was prepared in a similar fashion to the anisole. The residual spectrum, which was obtained by subtracting the simulated spectrum of 2-propanol radical from the one obtained experimentally, was in good agreement with the simulated spectrum of phenoxymethyl radical. Accordingly, photolysis of 1,2-diphenoxyethane would produce phenoxymethyl radical.

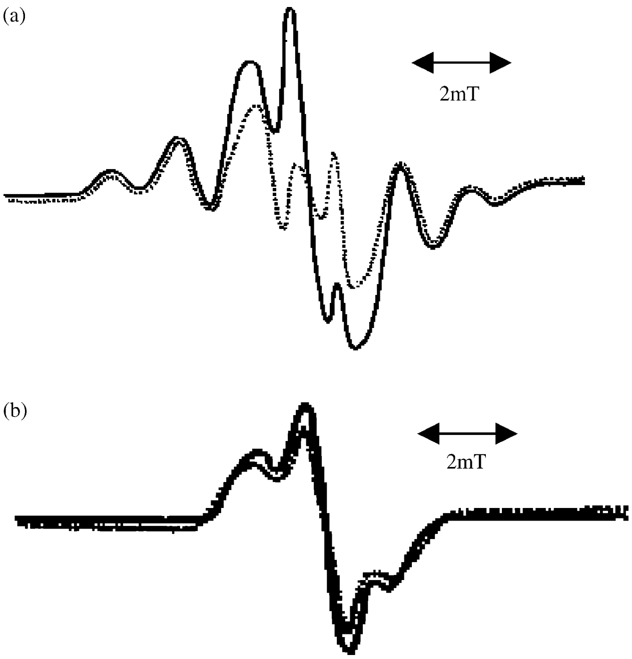

Fig. 6. cw-ESR spectra of (a) anisole (solid line) in 2-propanol after the laser irradiation of 266 nm for 10 min at 10 Hz and simulation spectrum of 2-propanol radical (dotted line). (b) Residual spectrum obtained by subtraction from simulation spectrum of 2-propanol radical (solid line) and simulation spectrum of phenoxymethyl radical (dotted line).

We examined the laser power dependence of absorption intensity of phenoxymethyl radical under the aerated condition. Fig. 7 shows the log–log plot of the laser power dependence at 1 μs after the 248 nm laser excitation monitored at 430 nm.

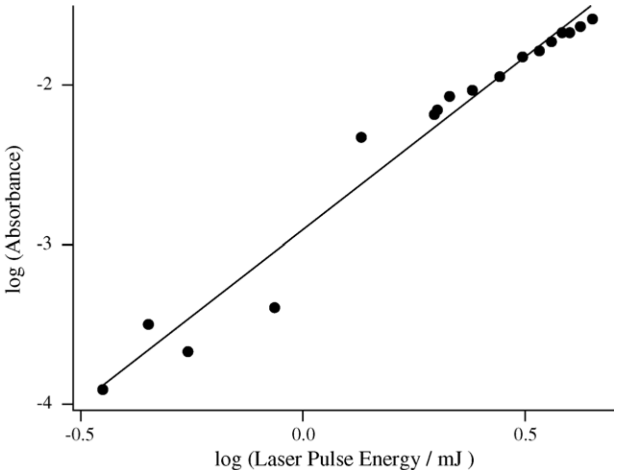

Fig. 7. Log–log plot of the laser power dependence at 1 μs after the 248 nm laser excitation monitored at 430 nm.

$$\text{anisole} \xrightarrow[\text{248 nm or 266 nm}]{2h\nu} \text{anisole cation + solvated electron}$$

$$\text{anisole cation} \xrightarrow[\text{- H}^+]{\text{deprotonation}} \text{phenoxymethyl radical}$$

Scheme 2.

The slope of this plot is 2.2. Thus, phenoxymethyl radical is formed with two-photon absorption. The two-photon energy of 248 nm and 266 nm light is 10.0 eV and 9.32 eV, respectively, that is higher than the IP of anisole (8.21 eV in gas phase [19]) and the C–H bond energy of methyl group of anisole (approximately 4 eV estimated from ethyl methyl ether and toluene [20]). Thus, phenoxymethyl radical will be produced by two-photon absorption of anisole to form anisole cation and consecutive deprotonation of the cation (see Scheme 2).

In conclusion, transient absorption spectra of anisole were measured and the longer-lived species, which has a broad absorption band at around 440 nm, was observed. The hydrogen abstracting reaction by acetone, photolysis of 1,2-diphenoxyethane, and the cw-ESR measurements were also carried out. The species was assigned to phenoxymethyl radical, produced with two-photon absorption through the S_1 state of anisole to form anisole cation and consecutive deprotonation of the cation.

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