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One-Electron Oxidation of Alcohols by the 1,3,5-Trimethoxybenzene Radical Cation in the Excited State during Two-Color Two-Laser Flash Photolysis

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One-electron oxidation of alcohols such as methanol, ethanol, and 2-propanol by 1,3,5-trimethoxybenzene radical cation ($TMB^{\bullet+}$) in the excited state ($TMB^{\bullet+}*$) was observed during the two-color two-laser flash photolysis. $TMB^{\bullet+}$ was formed by the photoinduced bimolecular electron-transfer reaction from TMB to 2,3,5,6-tetrachlorobenzoquinone (TCQ) in the triplet excited-state during the first 355-nm laser flash photolysis. Then, $TMB^{\bullet+}*$ was generated from the selective excitation of $TMB^{\bullet+}$ during the second 532 nm laser flash photolysis. Hole transfer rate constants from $TMB^{\bullet+}*$ to methanol, ethanol, and 2-propanol were calculated to be $(5.2 \pm 0.5) \times 10^{10}$, $(1.4 \pm 0.3) \times 10^{11}$, and $(3.2 \pm 0.6) \times 10^{11}$ M^{-1} s^{-1}, respectively. The order of the hole transfer rate constants is consistent with oxidation potentials of alcohol. Formation of TCQH radical ($TCQH^{\bullet}$) with a characteristic absorption peak at 435 nm was observed in the microsecond time scale, suggesting that deprotonation of the alcohol radical cation occurs after the hole transfer and that TCQ radical anion ($TCQ^{\bullet-}$), generated together with $TMB^{\bullet+}$ by the photoinduced electron-transfer reaction, reacts with H^+ to give $TCQH^{\bullet}$.

Introduction

Organic radical cations and anions are important reactive intermediates in chemistry, physics, and biology. Because of the higher excitation energy of radical ions in the excited states than that in the ground state, high reactivities of radical ions in the excited states are expected.[1−3] Because the redox potential of radical ions in the excited-state is larger than that in the ground state,[3−5] the electron transfer (ET) reaction that cannot occur in the ground state can be expected in the excited states.[5,6] Therefore, the investigation of the properties and reactions of radical ions in the excited states have been an attractive subject for a long time.[7] Recently, the lifetimes of diimide radical anions in the excited states have been reported to be shorter than 600 ps.[6] The lifetime of zinc(II) tetraphenylporphine radical cation in the excited states has been found to be 17 ps using a combination of controlled potential coulometry and femtosecond transient absorption measurement.[8] It is very important to be sure that only radical ion is generated and selectively excited as Fox and Breslin pointed out.[3] Two-color two-laser flash photolysis is a powerful tool for studying the properties and reactions of radical ions in the excited state.[9] The radical ions can be generated by photoinduced bimolecular ET reaction during the first laser flash photolysis.[10] With a short-time delay after the first laser flash, the radical ions can be selectively excited by the second laser flash with the wavelength tuned to the absorption of the radical ions.

The oxidation of alcohols such as methanol and ethanol to corresponding aldehydes or ketones is one of important reactions in chemistry and biology.[11−13] However, because of the high oxidation potentials of alcohols, the oxidation of alcohols have been realized only by a strong oxidant or efficient catalyst.[13−17] As a photochemical method, the oxidation of alcohols by TiO_2 photocatalysts is well-known.[13,15,18] During the UV- or visible-light irradiation of TiO_2 or modified TiO_2, positive charges (holes) with high oxidation potential at the surface of TiO_2 or modified TiO_2 are produced. Hole transfer to the alcohols adsorbed on these TiO_2 photocatalysts caused the oxidation of alcohols.[13,15,18]

Here, we report that one-electron oxidation of alcohols such as methanol, ethanol, and 2-propanol using 1,3,5-trimethoxybenzene radical cation ($TMB^{\bullet+}$) in the excited state ($TMB^{\bullet+}*$) as an oxidant during the two-color two-laser flash photolysis. The reaction of the hole transfer from $TMB^{\bullet+}*$ to alcohols can be initiated by the selectively excitation of $TMB^{\bullet+}$ in solution using the two-color two-laser flash photolysis technique.

Experimental Methods

Materials. 1,3,5-Trimethoxybenzene and 2,3,5,6-tetrachlorobenzoquinone were purchased from Aldrich Chemical Co. (purity >99%) and used without further purification. Acetonitrile, methanol, ethanol, and 2-propanol (spectral grade from Nacalai Tesque) were purchased from Nacalai Tesque Inc. Sample solutions were freshly prepared before irradiation. All experiments were carried out at room temperature.

Two-Color Two-Laser Flash Photolysis. The two-color two-laser flash photolysis system has been described previously.[19] Briefly, the third harmonic oscillation (355 nm) from a Nd:YAG laser (Brilliant, Quantel; 5 ns full width at half-maximum (fwhm)) was used as the first excitation light. The second harmonic oscillation (532 nm) from another Nd:YAG laser (Continuum, Surelite II-10; 5 ns fwhm) was used as the second excitation light. Two laser flashes were synchronized by a pulse generator with a delay time of 10 ns to 10 μs. The probe light was obtained from a 450 W Xe-lamp (Osram XBO-450). The transmitted probe light was focused on a monochromator (Nikon G250). The output of the monochromator was monitored using

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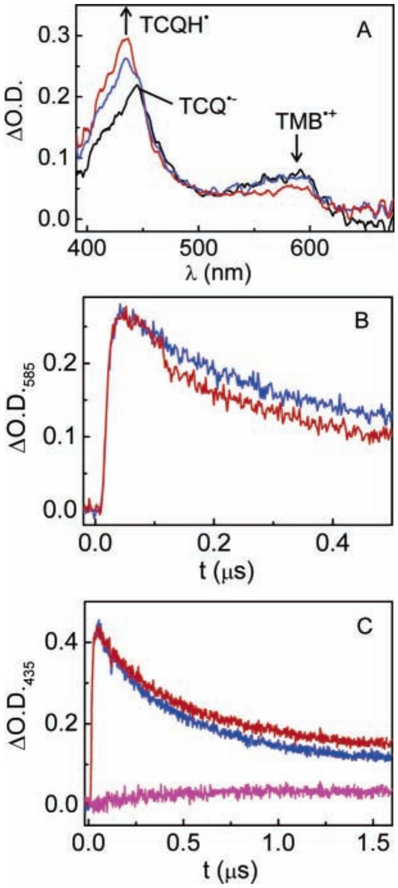


Figure 1. (A) Transient absorption spectra obtained 1.1 μs after the first 355 nm laser flash in the absence (black line) and presence of alcohols 0.4 M (blue line). The red line shows the spectral changes at 1 μs after the second 532 nm laser flash in the presence of alcohols (0.4 M) during the two-color two-laser flash photolysis of a mixture of TMB (1.0×10^{-2} M) and TCQ (5.0×10^{-3} M) in aerated acetonitrile. The delay time of the two lasers was 100 ns. (B) and (C) show the transient absorption time profiles obtained at 585 and 435 nm in the presence of alcohols 0.4 M during one 355 nm laser flash photolysis (blue line) and during the two-color two-laser flash photolysis (red line), respectively. The carmine line in (C) was obtained by the subtraction of blue line from the red line. The slow growth shows the formation of TCQH$^{\bullet}$ during the second laser irradiation, see discussion in text. Alcohols: methanol, ethanol, and 2-propanol.

a photomultiplier tube (PMT, Hamamatsu Photonics, R928). The signal from the PMT was recorded on a transient digitizer (Tektronix TDS 580D). A multichannel analyzer system (Hamamatsu Photonics, C5967) was used for the measurement of the transient absorption spectra. The total system was controlled with a personal computer via GP-IB interface. To avoid any damage of the sample solution by the probe light, a suitable cutoff filter was used in front of the sample.

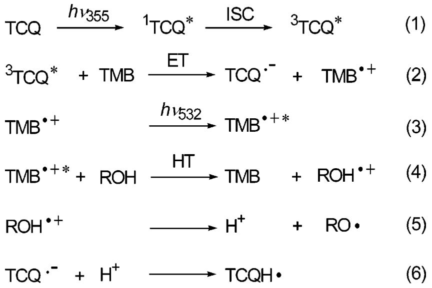
Results and Discussion

During the first 355 nm laser (10 mJ pulse^{-1}) irradiation of a mixture of TMB (1.0×10^{-2} M) and 2,3,5,6-tetrachlorobenzoquinone (TCQ) (5.0×10^{-3} M) in aerated acetonitrile, TCQ was excited to the singlet excited state (^{1}TCQ*), which converts rapidly to the triplet excited state (^{3}TCQ*) through the intersystem crossing with the quantum efficiency of near unity within 30 ps.[20] The ET reaction from TMB to ^{3}TCQ* occurred to give TMB$^{\bullet+}$ with an absorption band around 585 nm ($\epsilon_{585} = 4500$ M^{-1} cm^{-1})[21] and TCQ$^{\bullet-}$ with an absorption band around 450 nm ($\epsilon_{450} = 9700$ M^{-1} cm^{-1})[20,22] (Figure 1A, black line). During the second 532 nm laser (60 mJ pulse^{-1}) irradiation, TMB$^{\bullet+}$ can be selectively excited. No absorption change was observed, because the 532 nm laser pulse duration of 5 ns is much longer than the lifetime of TMB$^{\bullet+*}$ (41 ps of lifetime was directly measured using nanosecond−picosecond two-color two-laser flash photolysis).[23] TMB$^{\bullet+}$ was reproduced through rapid internal conversion from TMB$^{\bullet+*}$. No absorption was observed using the 532 nm laser flash only, because both TMB and TCQ in the ground state have no absorption at 532 nm. It is also suggested that no two-photon excitation of TCQ occurs with the 532 nm laser intensity (60−120 mJ pulse^{-1}).

On the other hand, in the presence of alcohols, such as methanol, ethanol, and 2-propanol in the solution, a new absorption band around 435 nm was observed during the first 355 nm laser irradiation (Figure 1A, blue line), indicating the generation of semiquinone radical (i.e., TCQH$^{\bullet}$) by hydrogen abstraction of ^{3}TCQ* from alcohol. It has been reported that TCQH$^{\bullet}$ has a characteristic absorption band around 435 nm ($\epsilon_{435} = 6600$ M^{-1} cm^{-1}).[24] The hydrogen abstraction of ^{3}TCQ* from alcohol to give TCQH$^{\bullet}$ is known to occur at a rate constant of $\sim 10^{6}$ M^{-1} s^{-1},[24] whereas the ET reaction between ^{3}TCQ* and TMB proceeds at a rate constant of $\sim 10^{10}$ M^{-1} s^{-1}.[20,22] That is, the reaction rate between ^{3}TCQ* and TMB is 100−1000 times faster than that of between ^{3}TCQ* and alcohol under the present experimental conditions. Therefore, ^{3}TCQ* was mainly quenched by TMB to give TMB$^{\bullet+}$ by ET reactions and hydrogen abstraction is a minor process, which is consistent with very a little change of the transient absorption at 585 nm in the presence of alcohols. The apparent peak shift from 450 to 435 nm is due to the overlap of the absorption band of TCQH$^{\bullet}$ with quite small concentration ($\sim 10^{-6}$ M).

During the second 532 nm laser irradiation at 100 ns after the first 355 nm laser irradiation, the bleaching of the absorption band at 585 nm (ΔΔOD$_{585}$) and the growth of the absorption band at 435 nm were observed (Figure 1A, red line). The bleaching at 585 nm occurred within the second 532 nm laser flash duration and no recovery was observed (Figure 1B). On the other hand, the growth at 435 nm, assigned to the formation of TCQH$^{\bullet}$, occurred in the microsecond time scale after the second 532-nm laser irradiation (Figure 1C). The ΔΔOD$_{585}$ and the growth at 435 nm increased with increasing the second 532 nm laser intensity. It is suggested that irreversible reaction occurred during the 532 nm laser excitation of TMB$^{\bullet+}$ to TMB$^{\bullet+*}$ in the presence of alcohols and TCQ$^{\bullet-}$. Because the bleaching at 585 nm occurred in the nanosecond time scale and the growth at 435 nm is in the microsecond time scale, the depletion of TMB$^{\bullet+}$ and the formation of TCQH$^{\bullet}$ can be attributed to different reactions. Because the oxidation potential ($E_{1/2}{}^{\mathrm{ox}}$) of TMB$^{\bullet+*}$ is approximately $\sim +3.5$ V from $E_{1/2}{}^{\mathrm{ox}}$ of TMB (+1.5 V)[25] and the excited-state energy of TMB$^{\bullet+*}$,[21] hole transfer (HT) from TMB$^{\bullet+*}$ to alcohols such as methanol ($\sim +3.2$ V), ethanol ($\sim +3.0$ V), and 2-propanol ($\sim +2.9$ V) can occur to give alcohol radical cation (ROH$^{\bullet+}$).[26] HT from TMB$^{\bullet+*}$ to alcohols was supported by the fact that the ΔΔOD$_{585}$ and the absorption growth at 435 nm increased with increasing the concentration of alcohols (0.1−0.8 M) during the second 532 nm laser irradiation. Therefore, the possible reaction mechanism can be summarized in Scheme 1. During the second 532 nm laser flash, TMB$^{\bullet+}$ was excited to give TMB$^{\bullet+*}$ (eq 3). In the presence of alcohols, HT from TMB$^{\bullet+*}$ to alcohols occurs to give ROH$^{\bullet+}$ (eq 4), from which deprotonation occurs rapidly to give alcohoxyl radical (RO$^{\bullet}$) (eq 5).[13−17] The further reaction between proton (H^{+}) and TCQ$^{\bullet-}$ occurs to give TCQH$^{\bullet}$ (eq 6).[24] To confirm the reactivity of TCQ$^{\bullet-}$ with of H^{+}, 355 nm laser flash photolysis of the mixture of TMB and TCQ in

SCHEME 1: Reaction Mechanisms during the Two-Color Two-Laser Flash Photolysis of a Mixture of TMB and TCQ in the Presence of Alcohols[a]



[a] ROH = CH_3OH, CH_3CH_2OH, and $CH_3CHOHCH_3$. ISC = intersystem crossing. ET = electron transfer. HT = hole transfer.

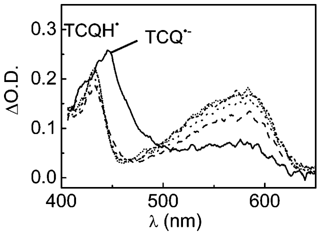


Figure 2. Transient absorption spectra obtained 1 μs after the 355 nm laser flash in the absence (solid line) and presence of various concentrations (0.02, 0.04, 0.06, and 0.08 M, respectively) of CF_3COOH (dash line, dot line, short dash line, and short dot line, respectively) during the 355 nm laser flash photolysis of a mixture of TMB (1.0×10^{-2} M) and TCQ (5.0×10^{-3} M) in aerated acetonitrile.

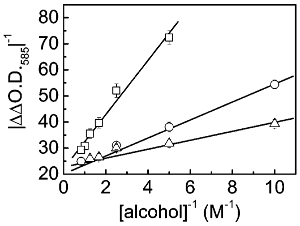


Figure 3. Plots of $\Delta\Delta OD_{585}$ vs the concentration of alcohol such as methanol (square), ethanol (circle), and 2-propanol (triangle).

the presence of various concentration (0.02−0.08 M) of CF_3COOH was carried out (Figure 2). It is known that CF_3COOH is a good H^+ donor. Obvious absorption band shift from 450 nm ($TCQ^{\bullet-}$) to 435 nm ($TCQH^{\bullet}$) was observed. Therefore, the reaction mechanism including one-electron oxidation of alcohols by $TMB^{\bullet+*}$ to give $ROH^{\bullet+}$ and deprotonation of $ROH^{\bullet+}$ to give $RO^{\bullet}$ (eqs 4 and 5, respectively) were reasonable.

Because $\Delta\Delta OD_{585}$ increased with increasing the concentration of alcohols, the HT rate constant (k_{HT}) from $TMB^{\bullet+*}$ to alcohols can be calculated on the basis of the linear plots of $\Delta\Delta OD_{585}$ vs the concentration of alcohols (Figure 3)[27] and the lifetime of $TMB^{\bullet+*}$ ($\tau = 41$ ps), eq 7, where β is a constant indicating the ratio of $TMB^{\bullet+}$ excited during the second 532 nm laser irradiation.

$$\Delta\Delta OD_{585}/\beta = (k_{HT} \times [\text{alcohol}])/(\tau^{-1} + (k_{HT} \times [\text{alcohol}])) \tag{7}$$

The k_{HT} value from $TMB^{\bullet+*}$ to methanol, ethanol, and 2-propanol were calculated to be $(5.2 \pm 0.5) \times 10^{10}$, $(1.4 \pm 0.3) \times 10^{11}$, and $(3.2 \pm 0.6) \times 10^{11}$ M^{-1} s^{-1}, respectively. The k_{HT} value increases in the order methanol < ethanol < 2-propanol, which is consistent with the order of oxidation potentials of the alcohol, i.e., methanol > ethanol > 2-propanol.

When H^+ is produced from $ROH^{\bullet+}$ by deprotonation, the rapid reaction between H^+ and $TCQ^{\bullet-}$ occurs to give $TCQH^{\bullet}$ with an absorption peak at 435 nm. Because the concentration of H^+ can be estimated from the concentration of $TMB^{\bullet+}$ disappeared, the reaction rate constant between H^+ and $TCQ^{\bullet-}$ can be estimated on the basis of the observed growth rate of the $TCQH^{\bullet}$ absorption at 435 nm. The concentration of H^+ was estimated to be 7.6×10^{-6} M in the presence of alcohols (0.4 M) during the second 532 nm laser irradiation of $TMB^{\bullet+}$ from the $\Delta\Delta OD_{585}$ value and $\epsilon_{585} = 4500$ M^{-1} cm^{-1}. The bimolecular reaction rate between H^+ and $TCQ^{\bullet-}$ to give $TCQH^{\bullet}$ was estimated to be $(9.7 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}.

Conclusions

One-electron oxidation of alcohols such as methanol, ethanol, and 2-propanol by $TMB^{\bullet+*}$ was successfully performed during the two-color two-laser flash photolysis. The HT process from $TMB^{\bullet+*}$ to alcohols was monitored by the detection of $TMB^{\bullet+}$ absorption disappeared at 585 nm and the $TCQH^{\bullet}$ absorption appeared at 435 nm. The k_{HT} from $TMB^{\bullet+*}$ to methanol, ethanol, and 2-propanol was calculated to be $(5.2 \pm 0.5) \times 10^{10}$, $(1.4 \pm 0.3) \times 10^{11}$, and $(3.2 \pm 0.6) \times 10^{11}$ M^{-1} s^{-1}, respectively. The k_{HT} order is consistent with that of alcohol oxidation potentials.

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