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Photoinduced reduction of $W_{10}O_{32}^{4-}$ by organic compounds in aqueous solution

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Abstract

The photoreduction of decatungstate anion ($W_{10}O_{32}^{4-}$, DTA), a representative polyoxotungstate, was studied in the presence of several types of organic substrate in aqueous solution. The complete conversion of DTA to DTA^{2-} was observed on steady irradiation in the presence of certain organic substrates in aqueous solution. Colour-selective irradiation showed that the formation of DTA^{2-} is due to the photoinduced reduction of excited DTA^{-} by organic molecules. Laser flash photolysis with benzyl alcohol, phenol and terephthalaldehyde exhibited different time profiles of electron transfer. Prompt formation and second-order decay of DTA^{-} at the rate of the diffusion limit were observed. The quantum yield of reduction changed as a function of the amount of substrate, indicating the formation of a complex with organic molecules before photoexcitation. Proton nuclear magnetic resonance (NMR) measurements supported complex formation. DTA was suggested to play a major role in the photoinduced reactions of aqueous colloidal WO_3.

Keywords: Photoreduction; Decatungstate anion; Polyoxotungstate; Organic compounds

1. Introduction

Colloidal WO_3 particles have been used as a photocatalyst [1-3] in water detoxification by sunlight. This colloid can store electrons [4] and has electrochromic properties [5]. Moreover, ultrasmall particles of WO_3, having the chemical formula $W_{10}O_{32}^{4-}$ (decatungstate anion, DTA), have also been investigated for catalytic activity [5-12]. On irradiation, DTA catalyses the oxidation of alcohols [7], dehydrogenation of alkanes [8], bond cleavage of thioethers [9], and other reactions [10-12]. It suffers a two-step reduction and develops a blue colour. Applications in microlithography, as well as the photocatalytic oxidation of organic substrates, are of interest [5]. The mechanism of the reaction between excited DTA and organic molecules is also of interest in connection with investigations of photoinduced reactions at solid surfaces. The photochemical investigations reported so far involve reactions in organic solvents such as acetonitrile. Since the use of photocatalysts in environmental applications is based on the photochemistry in aquatic media, we report here the photocatalytic processes in aqueous solution. By comparison with the photoelectrochemistry of colloidal WO_3 [1-3], DTA is suggested to play a major role in the reactions of aqueous colloidal WO_3.

2. Materials and methods

DTA in aqueous solution was prepared according to Ref. [13] and used for both steady light irradiation and laser flash photolysis. A solid powder of DTA as $Na_4W_{10}O_{32}\cdot xH_2O\cdot yCH_3CN$ was prepared from $Na_2WO_4\cdot 2H_2O$ (purchased from Junsei Chemical Co., Ltd.) according to the method of synthesis for the potassium salt [14]. The formation of $W_{10}O_{32}^{4-}$ was confirmed by the UV-visible spectra by dissolving the powder in water. The concentration of DTA in the sample for photolysis was 0.075 mM. The organic substrates for photocatalytic oxidation in aqueous solution included terephthalaldehyde (TPA), *p*-xyleneglycol (PXG) and diphenyl methanol (DPM), which were purchased from Tokyo Kasei, Ltd., and benzaldehyde (BzA), terephthalaldehydic acid (TPAA), terephthalic acid (TPAC), phthalimide (PI), benzyl alcohol (BzOH), phenol (PhOH), ethanol (EtOH) and methanol (MeOH), which were obtained from Nacalai Tesque, Ltd. The organic substrates used were selected mainly because of the possible formation of transient species showing absorption in the visible region.

Steady light photolysis was performed for deaerated 4 ml sample solutions in a Pyrex glass cell with a water jacket at 25 °C. The light source was a 500 W high-pressure Hg lamp (Ushio, USH-500). Selective irradiation was performed at

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313 and 365 nm. A blue glass filter (Toshiba UV-D33S) with a 1.39 mM K_2CrO_4 solution filter and a blue glass filter with a 350 nm cut-off filter (UV-35) were used for 313 and 365 nm irradiation respectively. The incident photon density estimated by a power meter (Gentech, TPM-310) was 7 μM s^{-1} for a sample of 4 ml at 313 nm. Electronic spectra were recorded with a Hitachi U-3210 spectrophotometer.

Laser flash photolysis was performed with the third harmonics (355 nm) of a *Q*-switched laser (Spectron, SL-803). The time response of the system was as slow as 200 ns to obtain a better sensitivity for the absorbance change after laser pulse irradiation of 30 ns duration. The absorbed photon density was calculated from the triplet–triplet (T–T) absorption of anthracene in hexane as described previously [15].

Nuclear magnetic resonance (NMR) spectra were recorded with a JEOL GX-270 spectrometer for powdered DTA dissolved in 0.5 ml of dimethylsulphoxide (DMSO) solution. In order to examine the interaction of organic substrates with DTA^{2-}, sodium hydrosulphide (SHS, Junsei Chemical Co., Ltd.) was added to the solution after deaeration by argon bubbling in the NMR sample tube.

3. Results and discussion

3.1. Steady light photolysis

Fig. 1 shows the process of formation of DTA from WO_4^{2-} with decreasing pH. The absorption peak at 320 nm is attributed to DTA and the shoulder at 260 nm is due to $H_2W_{12}O_{40}^{6-}$ which is in equilibrium with DTA [13]. At pH 2.5, 80% of WO_4^{2-} changes to DTA [13]. The molar absorption coefficient ϵ of DTA was calculated from the spectrum in Fig. 1 and is shown in Table 1. The ϵ value of DTA at 320 nm agrees with the reported value [13]. The value at 360 nm was used to estimate the concentration of DTA^-.

Table 1
Extinction coefficients of decatungstate anion (DTA) and the reduced species

Species	ϵ (10^3 M^{-1} cm^{-1})			
	320 nm	360 nm	630 nm	780 nm
DTA ($W_{10}O_{32}^{4-}$)	13.2 13.0 [a] 13.5 (323 nm) [b]	3.3	–	–
DTA^- ($W_{10}O_{32}^{5-}$)	–	6.9 6.7 [c]	2.4	9.5 7.0 [c] 9.8 [a] 11.0 [b]
DTA^{2-} ($H_2W_{10}O_{32}^{4-}$)	–	–	12.9 12.5 [d] 18.0 [b] 14.0 [c]	5.9

[a] From Ref. [13].
[b] From Ref. [16].
[c] From Ref. [17].
[d] From Ref. [18].

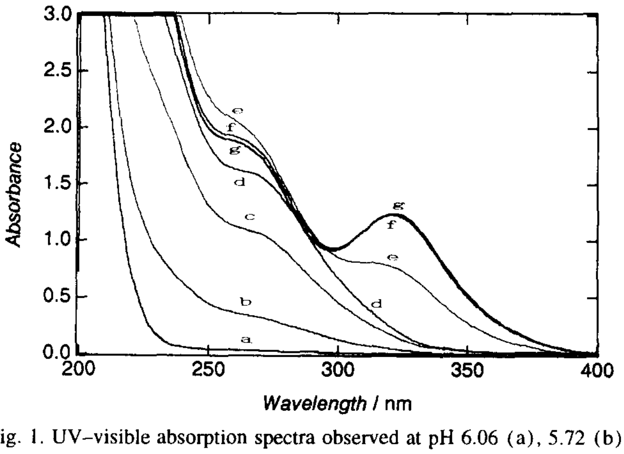

Fig. 1. UV–visible absorption spectra observed at pH 6.06 (a), 5.72 (b), 5.33 (c), 4.96 (d), 4.08 (e), 2.47 (f) and 1.87 (g), showing the formation of $H_2W_{12}O_{40}$ with a peak at 260 nm and $W_{10}O_{32}$ (DTA) at 320 nm.

Fig. 2 shows the change in the absorption spectra of DTA in the presence of 0.75 mM BzOH. The absorption bands at 360 and 780 nm are attributed to DTA^- and that at 630 nm to DTA^{2-}. Although the molar absorption coefficients ϵ at each peak have been reported [10,13,16,17], the two bands at 630 and 780 nm overlap. In order to calculate the concentrations of the two species from the absorbance at the two wavelengths, the ϵ values at each wavelength must be known. Since these values have not been reported, even in acetonitrile, the sets of ϵ values were measured as follows. The initial increase in absorbance at 630 and 780 nm concomitant with the decrease in absorbance at 320 nm allowed ϵ of DTA^- to be calculated. The value of ϵ at these wavelengths for DTA^{2-} was calculated as an average value from the spectra obtained after sufficient irradiation of DTA^- in the presence of TPA, TPAA or DPM. In Table 1, the values of ϵ thus obtained are shown with the reported values for DTA, DTA^- and DTA^{2-}.

By using the two pairs of ϵ values for DTA^- and DTA^{2-} at 630 and 780 nm, the concentrations of both reduced species were calculated at each period of irradiation time. For the reaction with BzOH, DTA^- is formed at an initial rate of 0.148 μM s^{-1} and reaches a maximum value of 40 μM after 7 min of irradiation (Fig. 3). At the same time, DTA^{2-} increases at a rate of 0.013 μM s^{-1} and reaches 52 μM after 400 min of irradiation. Since the initial concentration of DTA was 75 μM, yields of DTA^- and DTA^{2-} were calculated to be 54% and 69% respectively. For certain organic substrates, the sequential reduction of DTA was observed. The formation rate and maximum conversion for DTA^- and DTA^{2-} are summarized in Table 2. Although the formation rate in Table 2 depends on the excitation intensity, the differences between the organic molecules are significant. The redox potential or ionization potential cannot explain the difference in the formation rate and maximum yield of the different organic substrates. Thus the oxidation mechanism may depend on the chemical nature of the substrate, such as the deprotonation ability.

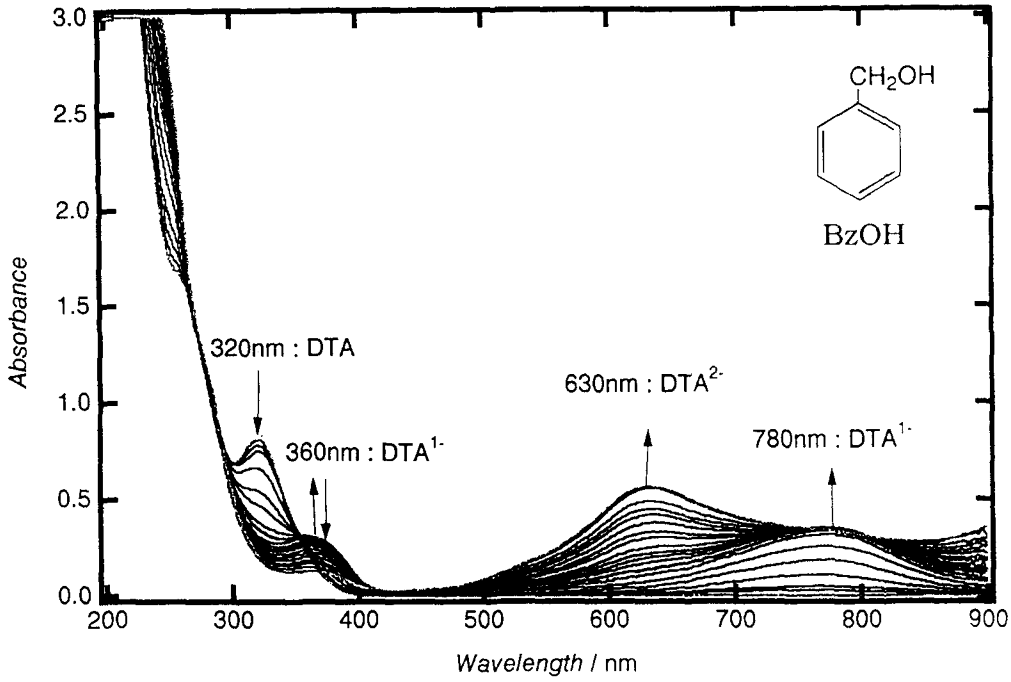

Fig. 2. Change in the UV–visible spectra with steady light irradiation (greater than 310 nm) for 0.075 mM DTA and 0.75 mM BzOH aqueous solution.

The squares in Fig. 3 are plots of the concentrations of DTA$^-$ and DTA^{2-} calculated from the spectral change obtained for the BzOH–DTA system by irradiation through a blue glass filter (310–380 nm). The maximum yield of DTA^{2-} decreases when the glass filter is used because of the decrease in the excitation rate. Since the absorption band at 360 nm of DTA$^-$ overlaps with the 320 nm band of DTA, the excitation light in the above experiment may be absorbed by both DTA and DTA$^-$. In order to determine the reaction scheme, selective excitation was performed. DTA was

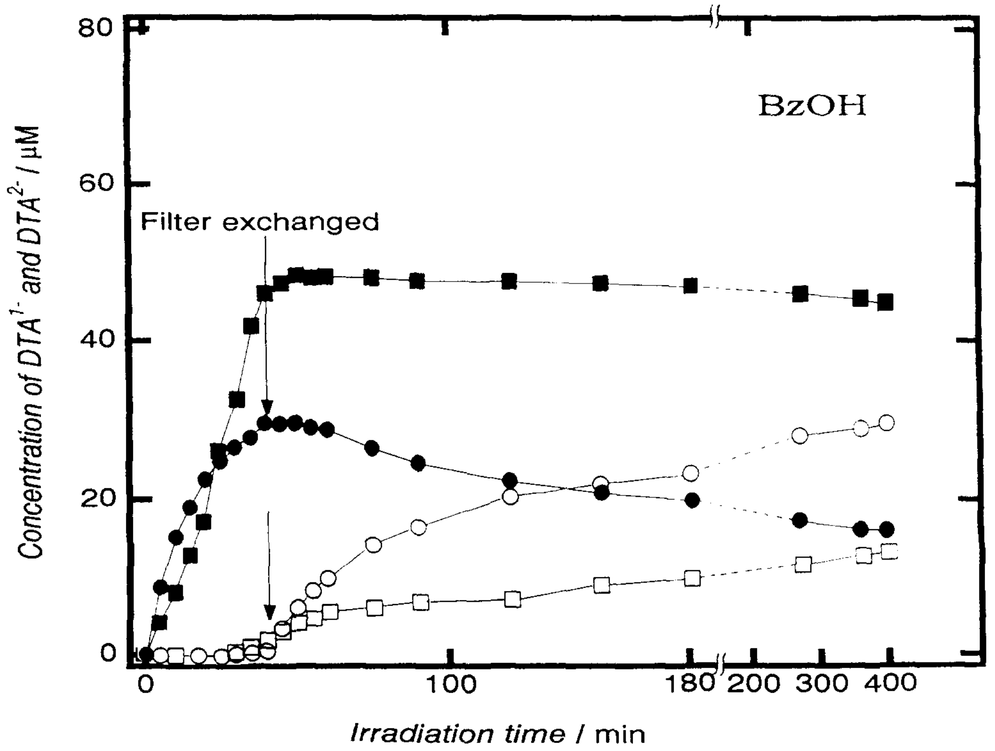

Fig. 3. Selective excitation of an aqueous solution of 0.075 mM DTA containing 0.75 mM BzOH. The concentrations of DTA$^-$ (●, ■) and DTA^{2-} (○, □), calculated from the absorbance at 630 and 780 nm, are plotted as a function of the irradiation time. The light wavelength was restricted with a blue glass filter throughout the period (■, □), or 313 nm light was applied for 40 min followed by 365 nm light (●, ○).

Table 2
Formation rates and maximum yield of reduced decatungstate anions formed by steady light irradiation of DTA in the presence of various organic substrates

Organic substrate	Formation rate (10^{-9} M s^{-1})		Maximum yield (%)[a]	
	DTA^-	DTA^{2-}	DTA^-	DTA^{2-}
Benzaldehyde (BzA)	23	1	53	7
Terepthalaldehyde (TPA)	536	133	49	100
Terephthalaldehydic acid (TPAA)	56	8	48	100
Terephthalic acid (TPAC)	4	0	35	1
Phthalimide (PI)	3	0	28	0
Benzyl alcohol (BzOH)	148	13	54	69
p-Xyleneglycol (PXG)	50	4	54	34
Diphenyl methanol (DPM)	20	4	54	92
Phenol (PhOH)	2	0	42	0
Ethanol (EtOH)	37	5	53	49
Methanol (MeOH)	22	2	52	35

[a] Obtained during irradiation up to 240 min.

excited at 313 nm for up to 40 min and successively at 365 nm for several hours. The circles in Fig. 3 show the concentration of DTA^- and DTA^{2-} as a function of time. When only DTA^- is excited, the amount of DTA^- decreases with increasing DTA^{2-}. This observation shows that the excitation of DTA^- causes the formation of DTA^{2-} in the presence of organic substrates, although DTA^{2-} has been reported to be formed by the disproportionation of DTA^- [19].

3.2. *Transient absorption measurements*

The organic substrates used in this work were selected mainly because of the possible formation of transient coloured species. However, no transient absorption after laser pulse excitation was observed other than that of DTA^- and DTA^{2-}. On the basis of the experimental results for steady light excitation, the following three organic substrates were used in flash photolysis investigations: PhOH with the slowest DTA^- formation and very small yield of DTA^{2-}; BzOH with fast DTA^- formation but no absorption at 355 nm; TPA with the fastest formation of DTA^- and complete conversion to DTA^{2-}.

For the PhOH–DTA system, the absorption change for DTA^- was measured immediately after pulse excitation at various wavelengths. The absorption change at 380 nm for the formation of phenoxyl radical [20] was not observed. The yield of DTA^{2-} was less than the detection limit of 0.005 at the highest laser intensity used. When the solution was saturated with air, the yield of DTA^- decreased by a factor of 0.7. The time profile of the decay, however, showed no significant change.

Fig. 4 shows the time profile of the concentrations of DTA^- and DTA^{2-} after the laser pulse. Similar profiles were measured at pH values of 1.7, 2.5, 3.1 and 5.1. The inverse of the concentration of DTA^- changes linearly with time after laser excitation, showing a decay based on second-order kinetics. The rate constants and maximum amount of DTA^- are obtained from the slope and cross-section of the plot. The quantum yield calculated from the maximum amount of DTA^- is independent of pH. The decay rate for DTA^- increases at pH 5.1. At pH < 3.1, the second-order rate constant is $(4.1 \pm 1.9) \times 10^9$ M^{-1} s^{-1} and is close to that of the diffusion limit (approximately 10^{10} M^{-1} s^{-1}). The second-order reaction does not take place between DTA^- species, because the expected product DTA^{2-} is not formed as a function of the decay of DTA^-. Thus the reaction may occur with undetected chemical species accompanied by the formation of DTA^-.

Fig. 5 shows the quantum yield of DTA^- as a function of the concentration of photons absorbed per laser pulse. The quantum yield increases from 0.09 to 0.16 with increasing intensity of the excitation light. This observation is similar to that found for the dimerization of olefins [19], and in contrast with that found for colloidal particles. In the electron transfer from an irradiated colloidal semiconductor to molecules at the surface, the quantum yield decreases with increasing light intensity. Thus the reaction of DTA can be described as a molecular process rather than electron–hole recombination in the particle [15].

When the concentration of the substrate was increased, the quantum yield increased and levelled off at 20 mM, indicating that an association process between PhOH and DTA is involved in the reaction mechanism. The apparent association constant obtained from the plot is 260 M^{-1}. This association constant is equal for both aerated and deaerated conditions.

For BzOH–DTA, fast formation of DTA^- is observed, similar to PhOH–DTA. The formation of DTA^{2-} is observed immediately after pulse excitation, in contrast with the result for PhOH. This observation is consistent with the experimental results of steady light photolysis, where the yield of DTA^{2-} was 19% for BzOH, but 2% for PhOH. The quantum yields of DTA^- and DTA^{2-} immediately after laser excitation were measured and are plotted in Fig. 6 as a function of the BzOH concentration. The apparent association constant

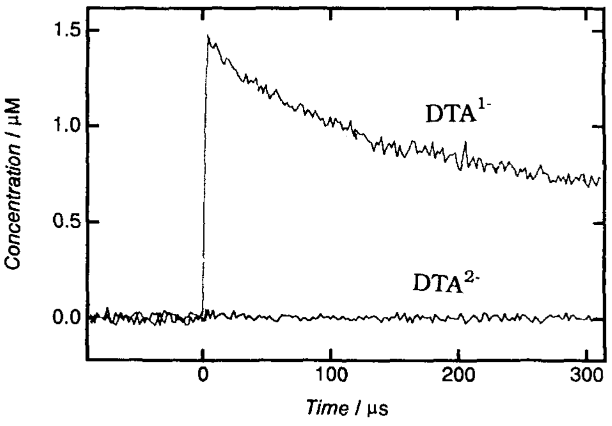

Fig. 4. Time profile of the concentrations of DTA^- and DTA^{2-} recalculated from the absorbance at 620 and 780 nm after laser pulse irradiation of an aqueous solution containing 0.075 mM DTA and 0.5 M PhOH at pH 2.5.

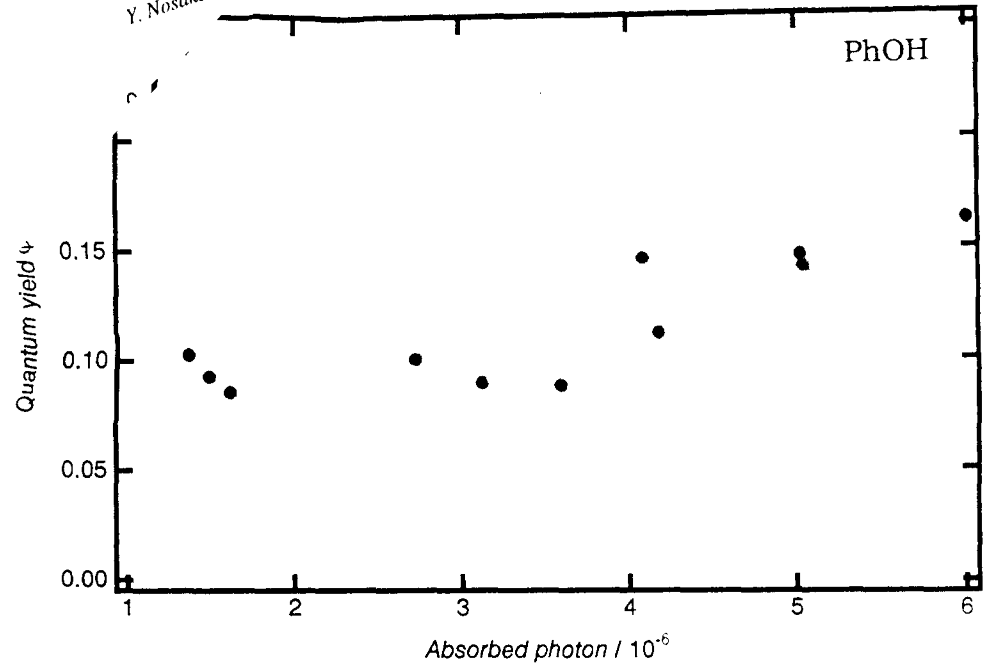

Fig. 5. Quantum yield of DTA$^-$ obtained after pulsed laser irradiation plotted as a function of the light intensity in terms of the concentration of photons absorbed by DTA.

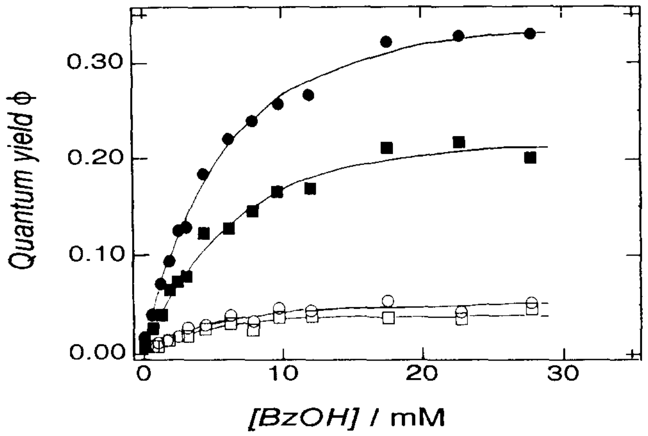

Fig. 6. Dependence of the quantum yield of DTA$^-$ (●, ■) and DTA^{2-} (○, □) obtained after pulsed laser irradiation on the concentration of BzOH in deoxygenated (●, ○) and aerobic (■, □) 0.075 mM DTA aqueous solution.

obtained from the plot is 240 M^{-1}. In the presence of oxygen in air, the quantum yield decreases by a factor of 0.6. However, the apparent association constant obtained (230 M^{-1}) is almost the same as for the deaerated sample. This observation is similar to the results for PhOH–DTA.

Picosecond laser photolysis has been reported for colloidal WO_3 in EtOH [4]. The formation of a similar spectrum with a peak at 630 nm was measured to have a rate of 10^{10} s^{-1}. Although the particle size of colloidal WO_3 has been reported to be less than 50 Å, the spectrum is almost identical to that of DTA^{2-}. Furthermore, the report showed a decrease in absorption at 320 nm with a reduction in the "WO_3 colloid". The 320 nm peak is attributable to DTA as shown in Fig. 1.

Thus DTA is suggested to play a major role in the reactions of aqueous colloidal WO_3.

For the TPA–DTA system, a slow increase in the absorbance at 780 nm is observed (Fig. 7(a)). The transient spectrum in Fig. 8 shows that the species responsible for this increase in absorbance is DTA$^-$. The concentration of DTA$^-$

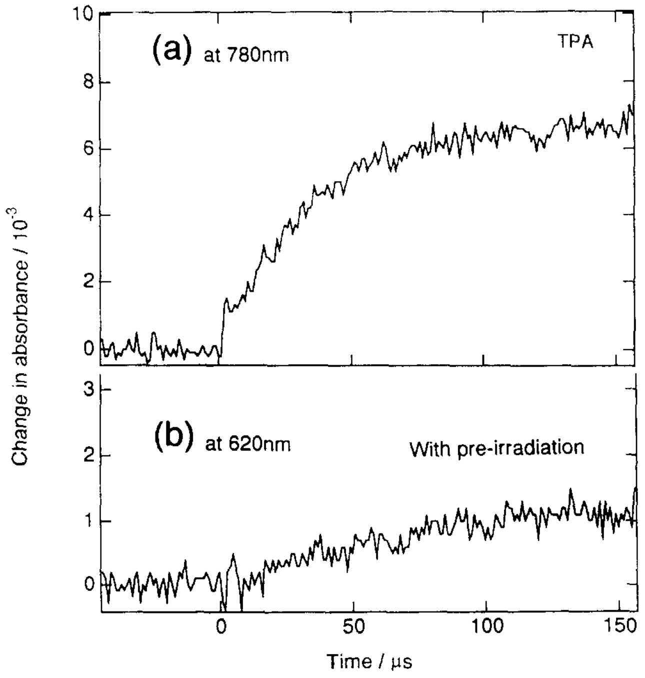

Fig. 7. Change in the absorbance after pulsed laser irradiation of 0.075 mM DTA in the presence of 0.75 mM TPA: (a) recorded at 780 nm; (b) observed in the presence of DTA$^-$ formed by the pre-irradiation of DTA before the laser pulse.

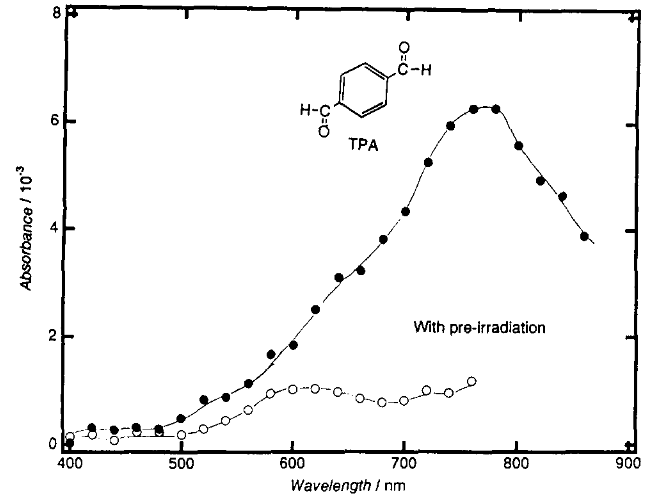

Fig. 8. Transient spectra obtained 150 μs after the laser pulse with the same experimental conditions as in Fig. 7: without pre-irradiation (●); with pre-irradiation (○).

during this increase in absorbance was calculated from the absorbance at 780 and 630 nm. The increase can be analysed using first-order reaction kinetics with a rate constant of $(5.2 \pm 0.3) \times 10^4$ s^{-1} as the average value for TPA concentrations between 0.9 and 3.3 mM. The rate constant in air was $(5.9 \pm 0.8) \times 10^4$ s^{-1}, i.e. similar to that under deaerated conditions. The yield of DTA^- in the presence of oxygen is a factor of 0.87 lower. Although the triplet state of TPA can reduce DTA energetically, the present observation indicates that this reaction process is not dominant in DTA^- formation.

The reduction of DTA^- to DTA^{2-} is observed when the sample is pre-irradiated with steady light. Fig. 7(b) shows the increase in absorbance at 620 nm. The transient difference spectrum in Fig. 8 shows that the increase at 620 nm represents the formation of DTA^{2-}. This observation is consistent with that during steady light irradiation, where selective two-colour excitation showed the growth of DTA^{2-} concomitant with the decay of DTA^-.

3.3. Evidence for complex formation

The formation of a complex between organic substrates and DTA was examined by proton NMR spectroscopy. Although the photochemical investigations were performed in aqueous solution, NMR measurements were conducted in DMSO solution because the signals of the OH proton could not be observed in D_2O solution. Various amounts of powdered DTA ($Na_4W_{10}O_{32} \cdot xH_2O \cdot yCH_3CN$) were added to DMSO-$d_6$ solutions (3 mM) of the organic substrates. The integrated area and chemical shifts of the NMR signals for the organic substrates were analysed. In order to examine the interaction with DTA^{2-}, an excess amount (approximately 10 mM) of SHS was added.

For PhOH, the NMR signal of the OH proton shifts to lower magnetic fields with the addition of DTA, while the signal intensity remains unchanged. The shifts are 0.07 and 0.15 ppm when th [PhOH]) are 0.59 an ive a proton indicates the form spective oxygen of DTA. Since H_2O is f a hyd TA OH proton of the organic mole nt in pow ([DTA]/ exchange with H_2O protons. In a se may possib experiment, ever, the addition of H_2O instead of D ate caused no shift i the proton signal. In the presence of SHS here DTA gives DTA^{2-}, no shift in the OH signal was obser d for DTA^{2-}–PhOH, indicating that PhOH is free from interaction with DTA^{2-}. Since the two oxygen atoms in the DTA^{2-} molecule are occupied by protonation, these specific oxygen atoms in the DTA molecules may form hydrogen bonds with PhOH.

For BzOH, the signal intensity of the OH proton decreases with the addition of DTA as shown in Fig. 9(a). The decrease in the signal intensity is not due to the presence of H_2O molecules in powdered DTA. Since no decrease in the OH signal was observed for PhOH, a stronger interaction with DTA is suggested for BzOH. When SHS is present, the OH signal of BzOH does not decrease, similar to that observed for PhOH–DTA. Thus the oxygen atoms in DTA resulting in complexation with BzOH are located in the DTA^{2-} molecule.

No change in the signal intensity of the aldehyde protons of TPA was observed in the presence of DTA (Fig. 9(b)). However, the signal intensity decreased in the presence of DTA^{2-}. The decrease in the signal intensity for the aldehyde protons suggests the decomposition of aldehyde to carboxylate. The formation of carboxylate was confirmed by the NMR spectra.

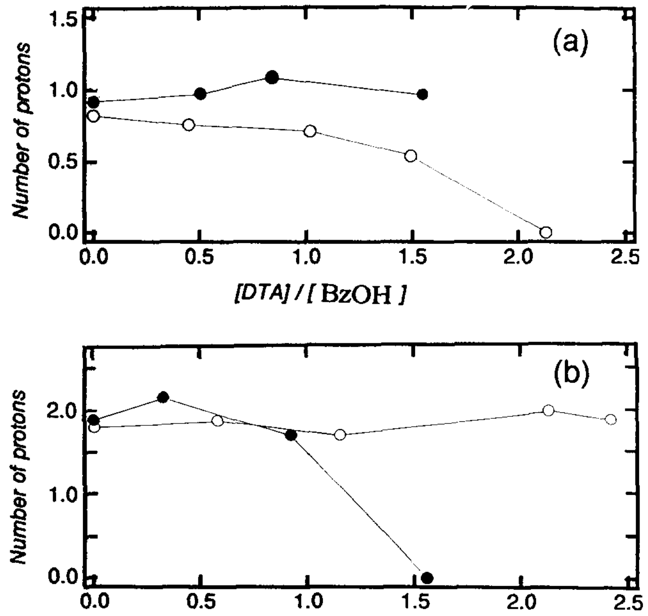

Fig. 9. Number of protons in the substrate molecule (BzOH (a) and TPA (b)) observed by NMR spectroscopy vs. the amount of DTA in DMSO solution. An excess (●) and zero (○) amount of SHS were added to prepare DTA^{2-}.

4. Concluding remarks

During steady irradiation with an Hg lamp, the complete conversion of DTA to DTA^{2-} is observed for certain organic substrates in aqueous solution. The decay profile of DTA$^-$ corresponds to the growth of DTA^{2-}, and the apparent reaction rate differs for the different substrates. Although the photoinduced disproportionation of DTA$^-$ has been reported for the formation of DTA^{2-}, the photoinduced reduction of excited DTA$^-$ with organic molecules is suggested from the results of colour-selective irradiation.

In laser flash photolysis, different time profiles of electron transfer were observed for selected substrates (benzyl alcohol, phenol and terephthalaldehyde). The quantum yields of DTA$^-$ and DTA^{2-} observed after the laser pulse at different substrate concentrations indicate that the organic molecules form a complex with DTA before photoexcitation. The complex formation in the ground state was confirmed by proton NMR measurements for these substrates in the presence of DTA.

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