

Catalytic Photooxidation of some Secondary Alcohols by Decatungstate Isopolyanion and Keggin-type Dodecatungstophosphate Heteropolyanion in Homogeneous System under Excess of Oxygen and the Effect of Counterions on Redox Cycle of Polyanions

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Abstract

Under excess of oxygen, catalytic photooxidation of secondary alcohols to ketones, initiated by irradiation of charge-transfer bands of polyanions such as decatungstate isopolyanion and Keggin-type heteropolytungstophosphate, has been investigated. Photooxidation of organic substrates proceeds in conjunction with photoreduction of polyanions and the catalytic cycle is attained by reoxidation of reduced polyanions by the reaction with O_2 , where consumed O_2 is converted to water. Polyanions studied are $H_3[PW_{12}O_{40}]$ and $K_4[W_{10}O_{32}]$ which are soluble in water, and $(TBA)_3[PW_{12}O_{40}]$ and $(TBA)_4[W_{10}O_{32}]$ (TBA = tetrabutylammonium) which are soluble in acetonitrile. Organic substrates studied are secondary alcohols such as isopropyl alcohol, cyclohexanol and ethyl lactate. Catalysis by the Keggin polyanion is based on the redox cycle between the one-electron (1e) reduced species and the oxidized form, whereas that by the decatungstate is based on the redox cycle between the 2e-species and the oxidized form. These two cycles are strongly influenced by the counterion. This is interpreted in that some of the TBA cations are binding with the polyanions in acetonitrile solution.

Introduction

A homogeneous solution containing some molybdo- and tungstopolyanions shows a photochromism in the presence of appropriate organic substrates, which is based on the photooxidizing function of the polyanions. Utilizing this property, the catalytic photooxidation of organic substrates by polyanions has been realized [1–3], where the reoxidation of the reduced forms of the polyanion is performed either by reaction with O_2 or by evolution of H_2 . Especially from a viewpoint of light-to-

chemical energy conversion, an interest has been taken in the catalytic H_2 evolution from alcohols by Keggin- and Dawson-tungstoheteropolyanions and the decatungstate isopolyanion, the reactions of which have been achieved under anaerobic conditions by using some co-catalysts such as colloidal platinum, RuO_2 and IrO_2 for the reoxidation of reduced polyanions [4–6]. On the other hand, from a viewpoint of catalytic organic synthesis, we have focussed on the catalytic photooxidation of alcohols by reoxidation of reduced polyanion by O_2 without any co-catalysts. There are only a few precedents for the catalysis by polyanion under O_2 , although it is well-known phenomenologically [2]. Recently we have described that $(TBA)_4[W_{10}O_{32}]$ in CH_3CN shows a higher catalytic activity than the Keggin tungstophosphate for photooxidation of *i*-PrOH to acetone under excess of O_2 and that prolonged irradiation also gives rise to an oxidation of the TBA cation, even if substrate remains [7]. The difference in catalytic activity of the two polyanions has been attributed to the velocity of the redox cycle and to the form of reduced species participating in 2e-oxidation of the alcohol, *i.e.* 2e-reduced species of $[W_{10}O_{32}]^{4-}$ and 1e-species of $[PW_{12}O_{40}]^{3-}$. Our preliminary experiments have shown that the relative velocity of the redox cycle is markedly influenced by the counterions of the polyanion. In this work, we have examined the effect of the counterion on the redox cycle and the relation of it with the catalytic activity for photooxidation of *i*-PrOH using two sets of polyanion, $Y_3[PW_{12}O_{40}]$ ($Y = H, TBA$) and $Y'_4[W_{10}O_{32}]$ ($Y' = K, TBA$).

Experimental

All chemical used were analytical grade. Apparatus of the photoreaction comprised a 75-W mercury lamp (SHL-100UV, Toshiba Corporation) with a 5 cm cold water filter to cut off the thermal effect of an external light source and a 75 cm³ Pyrex reaction-

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flask which can be attached to an O₂-filled balloon of ca. 5000 cm³. During irradiation ($\lambda > 300$ nm), the solution was well-stirred. The procedure has been described elsewhere [7]. Actinometry was performed by irradiation with 2-hexanone and the light intensity was 8.5×10^{-5} einstein h⁻¹. A typical solution for the photoreaction was prepared as 50 cm³ CH₃CN solution containing TBA salt (5×10^{-3} mol dm⁻³), i-PrOH (0.4 mol dm⁻³) and benzene (0.128 mol dm⁻³) as an internal reference for gas chromatography. For the substrates of cyclohexanol and ethyl lactate, *o*-xylene and decalin were used as an internal reference, respectively. For the catalysts of H₃[PW₁₂O₄₀] and K₄[W₁₀O₃₂], the 1:1 mixture of CH₃CN and water (pH 2.5, H₂SO₄) was used as a solvent. Substrates and reaction products were analyzed by TCD gas chromatography (Shimadzu GC-8A) on a PEG 20M column. A blank test showed that irradiation without the catalyst gave no product. The formation process of reduced species of polyanions under N₂ and the reoxidation process of them under O₂ were monitored by a spectrophotometer (Hitach-340). Since the reoxidation rate changed according to the way of introducing air or O₂ to the reaction vessel, the same work-up was performed.

Preparation of Compounds

The compounds H₃[PW₁₂O₄₀]·*x*H₂O [8], (TBA)₃[PW₁₂O₄₀] [8] and (TBA)₄[W₁₀O₃₂] [9] were

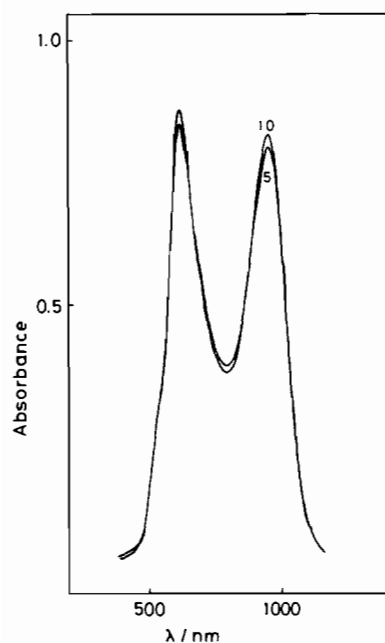


Fig. 1. Absorption spectra of photoreduced species of [W₁₀O₃₂]⁴⁻ under N₂. Irradiation is performed for K₄[W₁₀O₃₂]·4H₂O (7×10^{-5} mol dm⁻³) and i-PrOH (0.4 mol dm⁻³) in the 1:1 mixed media of CH₃CN and water (pH 2.5, H₂SO₄). Figures on the curves show irradiation time (min).

prepared as previously described. The TBA salts were recrystallized twice from CH₃CN.

K₄[W₁₀O₃₂]·4H₂O was prepared by modifications of the previously described method [10]. Into the boiling aqueous solution of Na₂WO₄·2H₂O (33 g 0.1 mol) in 200 cm³ water, 200 cm³ of 1 mol dm⁻³ HCl was added. After boiling for about 10 s, the solution was separated to two portions of 1000 cm³-conical beakers, which were quickly ice-cooled. The KCl saturated aqueous solution kept below 0 °C was poured into the above solutions until yellowish white precipitates were produced. On standing in the refrigerator overnight, white precipitates and pale yellow crystals were separated. Pale yellow crystals were collected, washed with small amounts of ice-cold water, then cold alcohol and ether, and dried. Absorption maxima measured in aqueous solution of pH 2.5 (H₂SO₄): 324 nm (ϵ 13 900), 264 nm (ϵ 16 100) and 218 nm (ϵ 45 700). IR bands measured with KBr disk: 1000(w), 976(s), 955(s), 940(w), 912(m), 890(m), 796(vs), 595–510br(w) and 425(m) cm⁻¹. This compound is soluble only in water. It should be noted that the compound is stable in acidic conditions of pH 2.5, but above pH 3 it is converted to ψ -metatungstate [10].

Results and Discussion

The Effect of Counterions on the Redox Cycle

A cycle of the photooxidation catalysis of the polyanion consists of two processes; one is the oxidation of alcohol by the excited polyanion ($P^* \rightarrow P_{red}$) and the other the reoxidation of the reduced polyanion by the reaction with O₂ ($P_{red} \rightarrow P_{ox}$). The redox cycle can be monitored by spectral changes of the formation of reduced polyanion under anaerobic conditions and the reoxidation of it by O₂. The influence of the counterions of [W₁₀O₃₂]⁴⁻ on the redox cycle was observed in the K salt in the 1:1 mixed media of CH₃CN and water (pH 2.5, H₂SO₄) and in the TBA salt in CH₃CN solution under excess of the secondary alcohol. It appears that both decatungstate systems produce 2e-species (blue) directly from the oxidized form (pale yellow) without stepwise reduction under N₂. The spectral changes are presented in Figs. 1 and 2. End point spectra consist of two absorption maxima in the visible and near-IR absorption region; 960 nm (ϵ 11 700) and 620 nm (ϵ 12 300) in the K salt, and 910 nm (ϵ 12 000) and 620 nm (ϵ 14 000) in the TBA salt. These are in good agreement with the data of the electrochemical 2e-reduced sample; 970 nm (ϵ 10 000) and 630 nm (ϵ 14 000) in DMF [9]. However, the formation of 2e-species in the K salt is completed within 10 min, whereas that in the TBA salt takes about 4 h until the absorbance becomes unchanged. On the contrary, the reoxidation by O₂

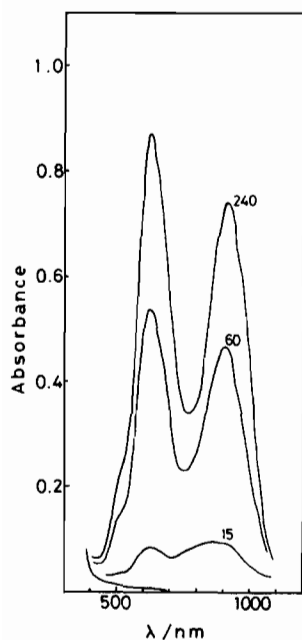


Fig. 2. Absorption spectra of photoreduced species of $[\text{W}_{10}\text{O}_{32}]^{4-}$ under N_2 . Irradiation is performed for $(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]$ ($6.3 \times 10^{-5} \text{ mol dm}^{-3}$) and cyclohexanol ($5.3 \times 10^{-3} \text{ mol dm}^{-3}$) in CH_3CN . Figures on the curves show irradiation time (min).

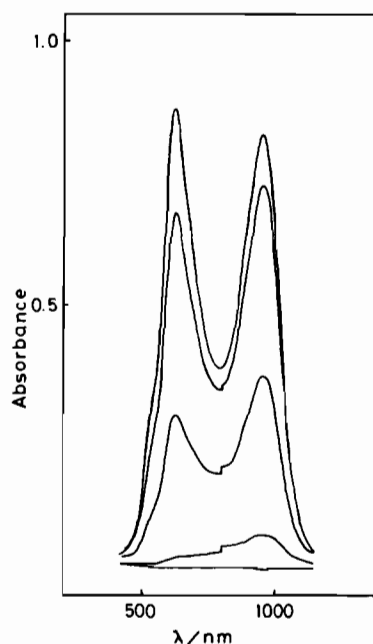


Fig. 3. Spectral change of the reoxidation process of reduced species of $[\text{W}_{10}\text{O}_{32}]^{4-}$ by reaction with O_2 . The absorption spectra are recorded with repeated scanning in the wavelength region between 1200 and 400 nm after the exposure to air of the solution of saturated photoreduced species obtained in the experiment in Fig. 1. Total time for complete decolouring takes about 40 min after the exposure. Drop of absorbance at 800 nm comes from the occurring reoxidation during automatic changeover of the light source.

in the K salt is much slower than that in the TBA salt. The spectral change in the former is shown in Fig. 3. The rapid process in the latter cannot be monitored by the usual scanning of the spectrophotometer. These facts strongly suggest that an ion-pairing or an outer-sphere association between decatungstate and TBA cations takes place in both the photooxidation and reoxidation processes. Since the rate-determining step of the redox cycle becomes the reoxidation in the K salt and is the formation process of the 2e-species in the TBA salt, the actual reaction under excess of O_2 proceeds apparently with a pale blue colour in the K salt and with a pale yellow in the TBA salt. However, in spite of such a difference, the

conversion of *i*-PrOH to acetone and the catalytic turnover were almost unchanged (Table I). These results suggest that with respect to the catalysis the redox cycle of the K salt comprising the fast oxidation and the slow reoxidation becomes comparable with that of the TBA salt consisting of the slow oxidation and the fast reoxidation. The K salt as a catalyst has one merit; the prolonged irradiation does not provide any by-products due to the photooxidation of the counterion as observed in the TBA salt [7].

TABLE I. Results by Gas Chromatographic Analysis for Photooxidation of Secondary Alcohols^a

Substrate	Catalyst	Rate constant ^b (s^{-1})	Product	Conversion ^c (%)	Turn-over ^d
<i>i</i> -PrOH	$\text{H}_3[\text{PW}_{12}\text{O}_{40}]^{\text{e}}$	4.9×10^{-8}	acetone	2.2 ^g	1.8 ^g
<i>i</i> -PrOH	$\text{K}_4[\text{W}_{10}\text{O}_{32}] \cdot 4\text{H}_2\text{O}^{\text{e}}$	2.7×10^{-6}	acetone	23.4 ^h	19.6 ^h
<i>i</i> -PrOH	$(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]^{\text{f}}$	2.2×10^{-6}	acetone	23 ^h	18 ^h
cyclohexanol	$(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]^{\text{f}}$	1.6×10^{-6}	cyclohexanone	22 ^h	17 ^h
ethyl lactate	$(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]^{\text{f}}$				

^aConditions: [catalyst] = $5 \times 10^{-3} \text{ mol dm}^{-3}$ and [substrate] = 0.4 mol dm^{-3} in 50 cm^3 solution containing an internal reference for gas chromatography. ^bRate constant of decreasing substrate determined by first-order kinetics. ^cMolar ratio of substrate to product. ^dMolar ratio of catalyst to product. ^eSolvent: 1:1 mixed media of CH_3CN and water (pH 2.5, H_2SO_4).

^fSolvent: CH_3CN . ^gResult from 100 h-irradiation. ^hResult from 30 h-irradiation.

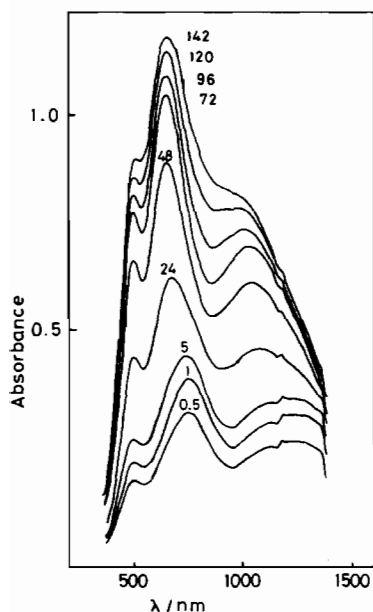


Fig. 4. Absorption spectra of photoreduced species of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ under N_2 . Irradiation is performed for $\text{H}_3\text{-}[\text{PW}_{12}\text{O}_{40}]$ ($2.25 \times 10^{-4} \text{ mol dm}^{-3}$) and $i\text{-PrOH}$ (0.4 mol dm^{-3}) in aqueous solution with no other acids added. Small peaks at *ca.* 1180 nm account for the absorptions of water. Figures on the curves show irradiation time (h).

On the other hand, the effect of counterions in the Keggin-type $[\text{PW}_{12}\text{O}_{40}]^{3-}$ polyanion is quite different from that in the $[\text{W}_{10}\text{O}_{32}]^{4-}$ described above. For the photoreduction of the free acid in acidic aqueous solution under N_2 , the 1e-species is observed as the absorbance increases until 1 h-irradiation, then the 2e-species begins to be formed, and its absorbance is saturated after 140 h-irradiation. The 1e- and 2e-species are identified by the previously reported spectra of samples electrochemically prepared [11]. Two reduced species are produced stepwise. These aspects are commonly observed with and without addition of other acids (H_2SO_4). A typical spectral change is shown in Fig. 4, which results from no addition of H_2SO_4 . On the other hand, $(\text{TBA})_3[\text{PW}_{12}\text{O}_{40}]$ in CH_3CN solution containing $i\text{-PrOH}$ could not generate any reduced species by irradiation under N_2 . Only by addition of another acid is formation of the reduced species possible. This is in contrast to the case of $(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]$. Although the addition of acid is essential for such a formation, the spectral change does not depend upon the acid concentration studied (H_2SO_4 $2.25 \times 10^{-4} - 4.5 \times 10^{-3} \text{ mol dm}^{-3}$). A typical example is shown in Fig. 5, which results from the added acid of $4.5 \times 10^{-3} \text{ mol dm}^{-3}$. Two prominent absorption maxima after 15 min-irradiation are observed at 960 and 620 nm. A broad band may also exist at 1150–1180 nm, but it is obscured by the absorption of water. Until 1 h-

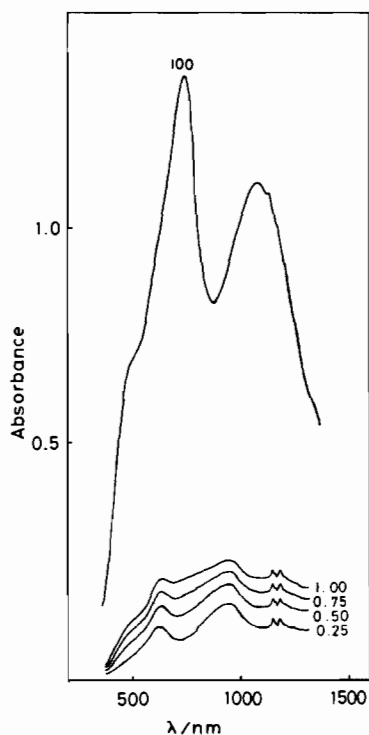


Fig. 5. Absorption spectra of photoreduced species of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ under N_2 . Irradiation is performed for $(\text{TBA})_3\text{-}[\text{PW}_{12}\text{O}_{40}]$ ($2.25 \times 10^{-4} \text{ mol dm}^{-3}$) and $i\text{-PrOH}$ (0.4 mol dm^{-3}) in CH_3CN solution containing aqueous H_2SO_4 ($4.5 \times 10^{-3} \text{ mol dm}^{-3}$). Small peaks at *ca.* 1180 nm account for the absorptions of water. Figures on the curves show irradiation time (h).

irradiation, a new band at 490 nm appears and the band at 960 nm increases its absorbance at that position, but the band at 620 nm shifts to the lower energy region with increasing absorbance. By further irradiation, these spectra change to the saturated one with absorption maxima at 1090, 745 and 500 nm given after 100 h-irradiation. These spectra cannot be tentatively assigned to discrete 1e- and 2e-species as observed in the free acid, or to their mixture, because the 1250 nm band characteristic of the 1e-species and the 650 nm-band of the 2e-species are not seen. However, these facts suggest that (1) the formation of the reduced species of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ accompanies the protonation, (2) some of the TBA cations are binding with the polyanion to form an ion-pair or an outer-sphere association species during the photooxidation and (3) the protonated and TBA-binding species of the reduced polyanion shows different spectra from those of the protonated and TBA non-binding reduced species. The last point differs markedly from the case of $[\text{W}_{10}\text{O}_{32}]^{4-}$.

The effect of the counterions is also observed in the reoxidation of the reduced species of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ by O_2 . The spectral changes are recorded just after the exposure to air of the solution containing the

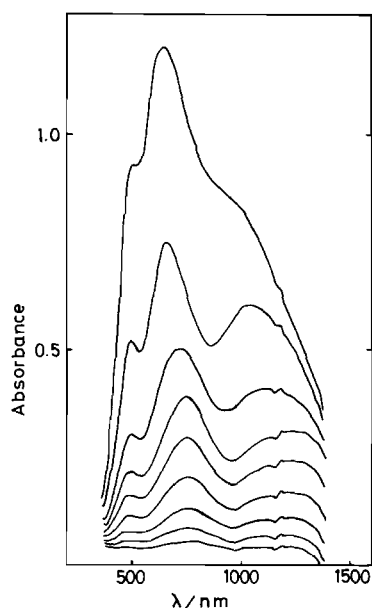


Fig. 6. Spectral change of the reoxidation process of reduced species of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ by reaction with O_2 . The absorption spectra are recorded with repeated scanning in the wavelength region between 1400 and 400 nm just after the exposure to air of the aqueous solution of saturated photo-reduced species obtained in the experiment in Fig. 4. Small peaks at ca. 1180 nm account for the absorptions of water. Total time for complete decolouring takes about 3 h after the exposure.

saturated reduced species. The reoxidation of the TBA salt is very rapid and could not be monitored by usual scanning of the spectrophotometer, while in the case of the free acid the fast oxidation of the 2e-species to the 1e-species and mild oxidation of the 1e-species to the original oxidized form can be observed (Fig. 6). Recently Ioannidis and Papaconstantinou have demonstrated H_2 evolution with and without Pt co-catalyst under anaerobic conditions, which is based on the reoxidation of the 2e-species to the 1e-species by H^+ [12]. However, in the actual photooxidation of i-PrOH by the free acid under excess of O_2 , the 2e-species will be difficult to form and it will be short-lived even if produced.

Although the counterions studied here affect the redox cycles of the two tungstopolyanions, they do not essentially change the higher activity of $[\text{W}_{10}\text{O}_{32}]^{4-}$ over $[\text{PW}_{12}\text{O}_{40}]^{3-}$; about 50 times with respect to the rate constant of substrate consumption and about 35 times with respect to the conversion per hour and the catalytic turnover per hour.

Photooxidation of Secondary Alcohols

The results given by gas chromatographic analysis are listed in Table I. In the photooxidations of i-PrOH

by $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ and $\text{K}_4[\text{W}_{10}\text{O}_{32}]$, i-PrOH is catalytically photooxidized to acetone under excess of O_2 and the decrease of substrate follows the first-order kinetics at constant concentration of catalyst. Since more than 90% of consumed substrate becomes acetone, the stoichiometry between them is retained within the experimental error. During irradiation, these catalysts promote the reaction without decomposition and deactivation. In the photooxidation of cyclohexanol by $(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]$ in CH_3CN , the molar amounts of produced cyclohexanone were about 80% of that of consumed substrate. It follows that some by-products can be produced. In fact, a few minor products were observed as very small broad peaks in the gas chromatograms. One of them could be collected as yellowish oil. Its IR spectrum was very similar to that of the peroxide of cyclohexanol which is obtained from the reaction of cyclohexanol with hydrogen peroxide. Akid and Darwent have recently reported the formation of superoxide HO_2^\cdot in the electron-transfer reaction of 1e-reduced polyanion $[\text{XW}_{12}\text{O}_{40}]^{(n+1)-}$ with O_2 by flash photolysis [5]. The observed minor product implies the reaction of cyclohexanol with superoxide or peroxide ion, which may be produced in the reoxidation of the 2e-species of $[\text{W}_{10}\text{O}_{32}]^{4-}$ by O_2 . The photooxidation of ethyl lactate, which contains the adjacent carboxylic group, to ethyl pyruvate could not be achieved. The electron-withdrawing group presumably interferes with the dehydrogenation [13]. In this reaction, only the photooxidation of the TBA cation was observed.

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