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Isopolyanions of Molybdenum and Tungsten as Photocatalysts for Hydration of Acetylene

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It has been reported that photoirradiation of aqueous solutions containing alkylammonium polymolybdates(VI) results in the oxidation of water to $\dot{O}H$ with an accompanying reduction of Mo^{VI} to Mo^{V} [1–3]. For example, the photoredox reaction between $[Mo_7O_{24}]^{6-}$ and water (eqn. 1) as a main process, has been evidenced by e.s.r. spectroscopic studies.

$$[Mo_7O_{24}]^{6-} + H_2O \xrightarrow{h\nu} [Mo_7O_{23}(OH)]^{6-} + \dot{O}H \qquad (1)$$

The mechanism of initial steps induced by LMCT at a terminal Mo=O bond has been interpreted in terms of the charge-transfer complex, which is capable of oxidizing water and which is photochemically produced by a proton transfer from an alkylammonium cation to a bridging oxygen atom at an octahedron site of polymolybdate(VI) [1, 2].

Similar mechanisms could be applicable to the photolysis in the presence of acetic acid [3]. In these two cases, alkylammonium cations and acetic acid have been considered to serve mainly as electron relays for the photoredox reaction (eqn. 1), although they were oxidized in only a minor way [1, 3]. Recently, we found that acetylene also was an electron relay for the photoredox reaction of eqn. 1. This paper describes the photohydration of acetylene in the presence of polyoxometallate(VI) anions as a photocatalyst, in which one can understand the involvement of hydroxyl radicals generated from the photoredox reaction between polymetallate anions and water.

Experimental

Sample solutions were prepared by adjusting the pH of aqueous solutions of 96 m*M* Na_2MoO_4 or 0.16 *M* Na_2WO_4 with $HClO_4$ and saturating acetylene gas in the solutions. The concentration of acetylene was calculated with Bunsen's absorption coefficient of 0.97 (at 23 °C) [4]. A 500-W super-high pressure mercury lamp in conjunction with filters was used as a light source and photoirradiation was carried out with $\lambda \geqslant 313$ nm light to avoid the excitation of acetylene. Light intensities were measured using a potassium ferrioxalate actinometry method [5].

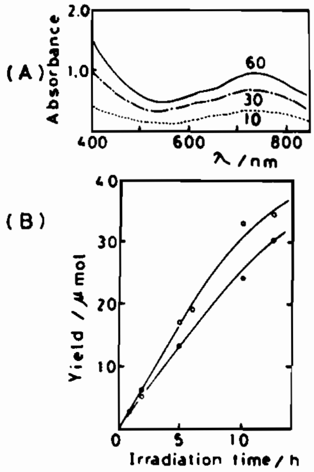

Fig. 1. Absorption spectral changes (A) during 313-nm irradiation (1.4×10^{18} photon min^{-1}) and the formation (B) of Mo^{V} (●) and acetaldehyde (○), when irradiated with $\lambda \geqslant 330$ nm light. Numbers in Fig. 1(A) indicate the irradiation time (min). Absorbance indicates the value for an optical path length of 1 cm.

Analysis of Mo^{V} or W^{V} in the photolyte was made at room temperature by the titration of $KMnO_4$ under nitrogen atmosphere, which resulted in the disappearance of the blue color due to Mo^{V} or W^{V} [3]. Gas chromatography (Hitachi 164 instrument) and mass spectrometry (Hitachi M80 GC/MS spectrometer) were employed for analyses of acetaldehyde and hydrogen. Acetaldehyde and hydrogen were analyzed using PEG 1000 or flusin T and carbosieve S columns respectively. Acetaldehyde was also determined by means of the oxalhydrazide–cupric acetate procedure [6]. All procedures for the colorimetric analysis were done after decoloration of the blue color due to Mo^{V} or W^{V} by admitting oxygen, and blanks were prepared with solutions kept in the dark.

Results and Discussion

On exposing sample solutions containing 42 m*M* acetylene and polymolybdate (96 m*M* in total Mo^{VI})

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at pH 5.0 to $\lambda \geqslant 330$ nm light, a blue color (λ_{max} = 730 nm) due to Mo^V developed, accompanied by a formation of acetaldehyde as shown in Fig. 1.* The quantum yields (ϕ) for the formation of Mo^V and acetaldehyde under 313 nm-light excitation (1.4×10^{18} photon min^{-1}, 3 h) of the solutions were 1.3×10^{-2} and 1.4×10^{-2}, respectively. In the absence of acetylene, there was no photolysis. Optimum pH for the photoreaction was observed around 5, where $[Mo_7O_{24}]^{6-}$ is a principle polymolybdate(VI) species [7]. This can be explained by $[Mo_7O_{24}]^{6-}$ susceptible to the photoredox reaction of eqn. 1. The absorption spectrum of the blue species and its e.s.r. signal (g = 1.93) were quite similar to those for the photolytes containing alkylammonium cations or acetic acid as electron relays [1, 3]. In connection with the Brönsted acid properties (pK_a = 25) of acetylene [8], therefore, it was suggested that the photolysis in the presence of acetylene proceeded *via* the charge transfer complex between $[Mo_7O_{24}]^{6-}$ and acetylene, which was similar to the complex proposed for the photolysis in the presence of alkylammonium cations and acetic acid [1,3].

The aerobic sample solution saturated by acetylene/air = 4/1 (v/v) gas exhibited a decrease in the quantum yield ($\phi_{Mo^V} = 1.7 \times 10^{-3}$ and $\phi_{CH_3CHO} = 1.1 \times 10^{-3}$ under 313 nm-light excitation). The lack of participation of oxygen molecules in the acetaldehyde formation implies that the formation of acetaldehyde results from an addition of hydroxyl radicals to triple bonds. The hydration of acetylene has also been observed for the reaction with Fenton's reagent [9]: Hydroxyl radicals generated from $Fe^{2+}-H_2O_2$ add readily to acetylene and the resulting vinyl radicals are readily reduced by Fe^{2+}, the principle overall reaction thus being hydration of acetylene.

In order to confirm the involvement of hydroxyl radicals in the photolysis, the effect of isopropylammonium cations on yields of photoproducts was investigated, since $[Pr^iNH_3]^+$ served mainly as an electron relay for eqn. 1 with the formation of propylene in only a minor way [1, 3]. The result is shown in Fig. 2: each yields Mo^V and acetaldehyde, and propylene increases with the concentration of $[Pr^iNH_3]^+$. This supports the involvement of hydroxyl radicals in the formation of acetaldehyde, if we consider that ϕ_{Mo^V} (<0.03) in the presence of acetylene is very small compared with the values (0.3 ~ 1.0) for the $[Pr^iNH_3]^+$ system [1]. Thus, the photochemical steps outlined in eqns. 2–6 were proposed based on the mechanism of the photolysis in the presence of $[Pr^iNH_3]^+$ or acetic acid [1,3].

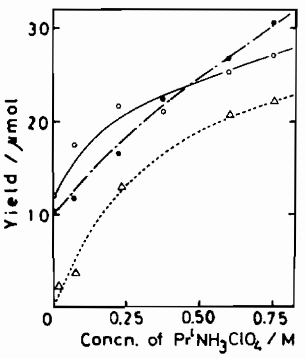
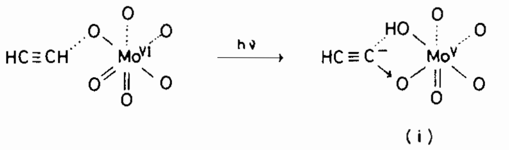
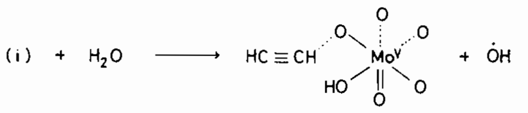
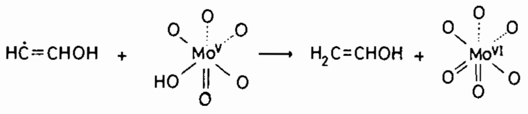


Fig. 2. Effect of $[Pr^iNH_3]^+$ on the yields of Mo^V (●), acetaldehyde (○), and propylene (△) as photoproducts. Each of yields of photoproducts was measured after 5-h irradiation of $\lambda \geqslant 330$ nm light. There was no effect of ClO_4^- on the photolysis [1].


(2)


(3)

$$HC{\equiv}CH + \dot{O}H \longrightarrow H\dot{C}{=}CHOH \quad (4)$$


(5)

$$H_2C{=}CHOH \longrightarrow CH_3CHO \quad (6)$$

Photoexcitation of LMCT band (⩾3.1 eV) in a terminal Mo=O bond causes the creation of the charge-transfer complex (i) being capable of oxidizing water to $\dot{O}H$ (eqn. 3), which is photochemically produced by a proton transfer (eqn. 2) from acetylene to a bridging oxygen atom at an octahedron site of $[Mo_7O_{24}]^{6-}$. β-hydroxyvinyl radicals, produced by the addition of $\dot{O}H$ to acetylene (eqn. 4), are reduced by the photoreduced octahedral Mo^V site (Mo^V–OH) to give acetaldehyde (eqns. 5, 6). This indicates the reductive route of β-hydroxyvinyl intermediate, leading to a decrease in ϕ_{Mo^V}.

Observed values of ϕ_{Mo^V} suggest the occurrence of other reaction pathways for intermediate radicals such as $\dot{O}H$, $H\dot{C}{=}CHOH$, and $HC{\equiv}\dot{C}$. The latter radicals, $CH{\equiv}\dot{C}$, would be produced by an intra-

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*The prolonged irradiation of the sample solution containing acetylene and polymolybdate in D_2O resulted in the appearance of a singlet line due to acetaldehyde with a chemical shift of 2.53 ppm relative to $SiMe_4$ in ^1H NMR spectrum.

electron-transfer from $CH{\equiv}C^-$ to a terminal oxygen in (i), which competes with the inter-electron-transfer from water to (i) (eqn. 3). In reality, the unidentified photoproduct obtained was insoluble in water, showing $\nu = 1710$ and 1715 cm^{-1} due to C=O stretching in its IR spectrum. There was no glycolaldehyde or CO_2 detected.

The photoreaction could be extended to the polytungstate(VI) solution. Exposure of the solution containing 16 m*M* $[W_{10}O_{32}]^{4-}$ and 42 m*M* acetylene at pH 2 to $\lambda \geqslant 330$ nm light resulted in the formation of hydrogen in addition to acetaldehyde and W^V as photoproducts. The absorption spectra ($\lambda_{max} = 630$ and 780 nm) of the blue species containing W^V were quite similar to those for the photolyses of $[NBu_4]_4$-$[W_{10}O_{32}]$ in acetonitrile or $[W_{10}O_{32}]^{4-}$ in a water/alcohol mixture. the photoreduced decatungstate anions were considered to be $[W_{10}O_{32}]^{5-}$ and $[H_2W_{10}O_{32}]^{4-}$ [10, 11]. H_2-evolution for the polytungstate(VI) system could be explained by the fact that the oxidation potential of the photoreduced polytungstate was more negative than the reduction potential of water [10–12].

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