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Intermediates in the Early Events of $Mo_7O_{24}^{6-}$-Catalyzed Photodehydrogenations: A Picosecond–Nanosecond Flash-Photochemical Study[†]

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The polymolybdate-photocatalyzed dehydrogenations of organic substrates have been the matter of considerable interest in recent years.[1-6] A number of the mechanisms proposed for such processes assign either the OH radical or a long-lived excited state as the oxidant.[2,4-6] However, studies about the effect of deuterium labeling on the yields of photoproduct, e.g. acetone from 2-propanol oxidation, cast doubts about the significance of the OH radicals in the photodehydrogenations.[2] Little is known about the short-lived reaction intermediates and/or excited states possessing the required lifetimes and reactivities because time-resolved observations have been restricted to a millisecond–second time domain. In this work, we have investigated the spectra and reaction kinetics of intermediates with picosecond–nanosecond lifetimes.

Results

Flash photolysis, $\lambda_{exc} = 355$ nm, of 5.0×10^{-2} M $Mo_7O_{24}^{6-}$ in aqueous acidic solutions induces optical changes within a 18-ps irradiation (Figure 1). Such transient spectra disappear in a nanosecond time domain (Figure 1) with a first-order kinetics, $k_I = 3.0 \times 10^7\ s^{-1}$. The transient spectra and the rate of decay do not change when ammonia ions are replaced by sodium ions as counterions of $Mo_7O_{24}^{6-}$.[7,8] Moreover, the transient species reacts with organic scavengers, e.g. 2-propanol and AcOH, as is shown in Figure 2. A rate constant, $k = 9.3 \times 10^7\ s^{-1}$, measured from the time-resolved optical changes at $\lambda_{ob} = 400$ nm under a pseudo-first-order kinetics with 0.7 M 2-propanol (Figure 2A) leads to a rate constant for a second-order kinetics, $k_{II} = 1.3 \times 10^8\ M^{-1}\ s^{-1}$. These values of the rate constants for the decay of the transient spectra and for the reaction with 2-propanol show that a fraction of the primary species, $0.756 = k_{II}[\text{2-propanol}]/(k_I + k_{II}[\text{2-propanol}])$, has been trapped with 0.7 M scavenger. This value for the fraction of trapped species is in agreement with one calculated from the 460-nm optical density changes. $\Delta OD_{t=\infty}/\Delta OD_{t=0} = 0.72$ for the quotient of the value at the beginning of the reaction, $\Delta OD_{t=0}$, divided by the value at the end of it, $\Delta OD_{t=\infty}$ (Figure 2B). Moreover, the values of k_I and k_{II} are in agreement with the dependence of the product yield on the 2-propanol concentration (Figure 3).

In a microsecond–millisecond time domain we have observed spectral changes assigned by Yamase et al. to the decomposition of $Mo_7O_{23}(OH)^{6-}$ and to the formation of the "Keggin" 12- and 13-atom molybdates, (Figure 4).[9] Similar optical transformations take place when 0.1 M I^- or 0.1 M $CH_3CO_2^-$ are used as scavengers of the primary species (Figure 5). Despite that similar time-resolved spectra have been recorded with each of the scavengers considered above and that all of them lead to permanent spectral transformations assigned to the "Keggin's polymolybdates",[9] the kinetics of product formation and $Mo_7O_{23}(OH)^{6-}$ decay is specific to the scavenger (Figure 6) contrary to previous assumptions.

Discussion

The observations reported above are not in accord with mechanisms involving a long-lived excited state or any photooxidation of water that leads to OH-radical formation.[10] Indeed, the nanosecond-lived intermediate detected in aqueous solutions, in the absence of scavengers, cannot be identified as an excited

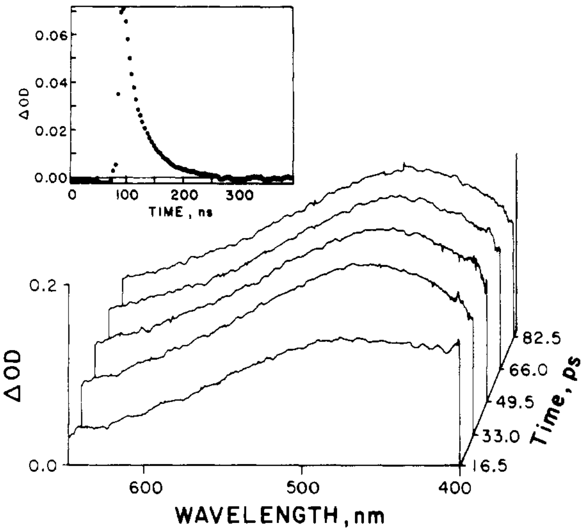

Figure 1. Transient spectra recorded during 355-nm irradiations of 5.0×10^{-2} M $Mo_7O_{24}^{6-}$ in aqueous deaerated solutions. The insert shows a trace recorded during 308-nm irradiations of a 10^{-3} M solution of the polymolybdate complex.

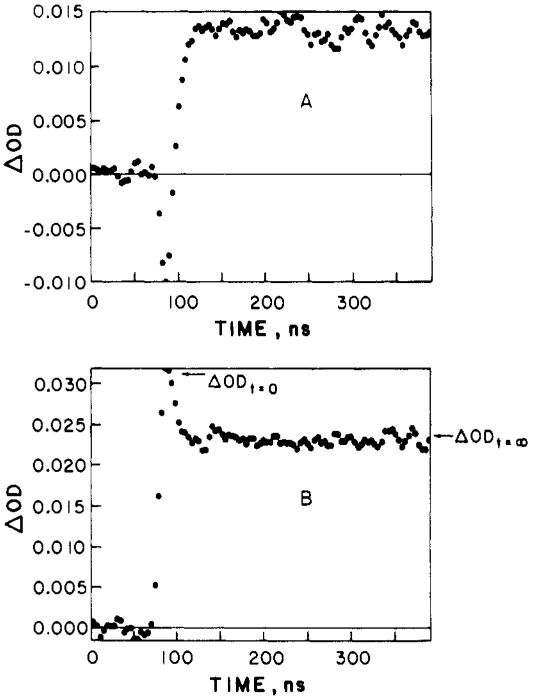

Figure 2. Optical density changes recorded with (A) $\lambda_m = 400$ nm and (B) $\lambda_m = 460$ nm during 308-nm irradiations of 10^{-3} M $Mo_7O_{24}^{6-}$ in 0.7 M 2-propanol. The solution was deaerated with streams of N_2.

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(5) Yamase, T. *J. Chem. Soc., Dalton Trans.* **1985**, 2585.
(6) Yamase, T.; Kurozumi, T. *Inorg. Chim. Acta* **1984**, *83*, L25.
(7) In spite of the reported luminescence of solid MoO_4^{2-}, we have been unable to detect luminescence from the compound in room-temperature aqueous deaerated solutions. Such emission was investigated over the spectral range 300–900 nm in 300-nm steady and flash irradiations, respectively.
(8) Blasse, G. In *Structures and Bonding*; J. D. Dunitz, J. D., et al., Eds.; Springer-Verlag: New York; Vol. 42, pp 22–25.
(9) Yamase, T.; Sasaki, R.; Ikawa, T. *J. Chem. Soc., Dalton Trans.* **1981**, 628.
(10) We have not observed under the experimental conditions of this work conclusive UV-vis spectral evidence supporting the formation of adducts between the polymolybdate and the scavengers.

[†] Document No. NDRL-3157 from the Notre Dame Radiation Laboratory.

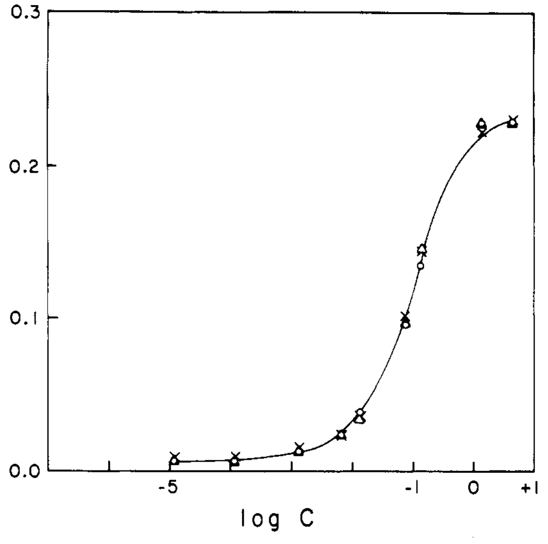


Figure 3. Dependence of the $Mo_7O_{23}(OH)^{6-}$ yield on 2-propanol concentration when such yields are measured by means of the optical density change at λ_m = 360 nm (×), 475 nm (○), and 775 nm (△), respectively. The values of ΔOD measured with λ_m = 360 nm or λ_m = 775 nm have been normalized to the maximum ΔOD-change measured with λ_m = 475 nm. In these measurements, 5.0 × 10^{-4} M $Mo_7O_{24}^{6-}$ deaerated solutions were irradiated at 308 nm with ~100 mJ/pulse flashes.

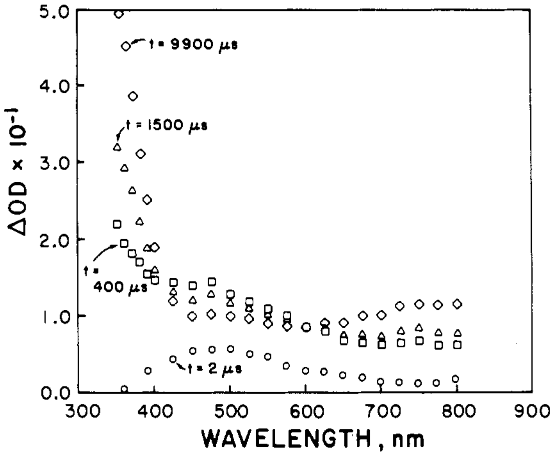


Figure 4. Transient spectra recorded during flash irradiations (λ_{exc} = 308 nm, I_0 ~ 100 mJ/pulse) of 5.0 × 10^{-4} M $Mo_7O_{24}^{6-}$ in 1.7 M 2-propanol.

state and does not behave, from the standpoint of its kinetics of disappearance, as a solvent-caged radical-ion pair.[7,11] Results of the scavenging with 2-propanol indicate that such species must be the common oxidant of the organic substrates. In addition, the small amounts of reduced polymolybdate detected when concentrations of 2-propanol are between 10^{-5} and 10^{-3} M, i.e. concentrations that will determine the total scavenging of OH, show that OH radicals must be photogenerated in very small yields, i.e. cannot be the main oxidant in these reactions. In this regard, a mechanism that accounts for the experimental results must consider that the photogenerated oxidant is able to dissociate only a small concentration of OH radicals. These observations are in accord with literature reports about the effect of deuterium labeling on the product yields[2] and show that the mechanism in eq 1–4 gives the best description of the early events in the $Mo_7O_{24}^{6-}$-catalyzed photodehydrogenations.

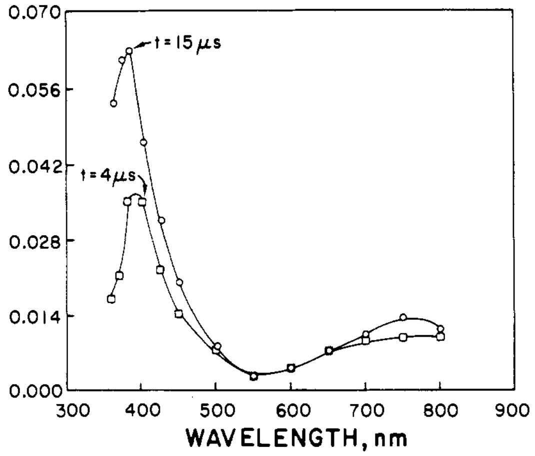
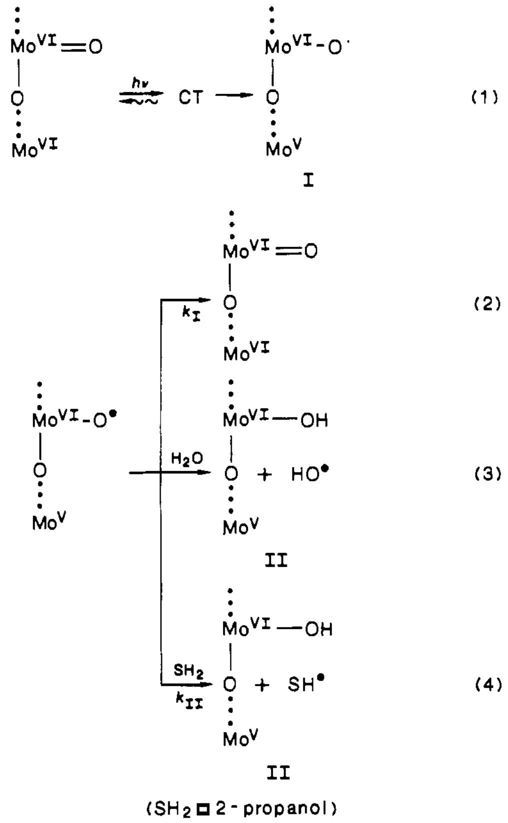


Figure 5. Transient spectra recorded during flash irradiations (λ_{exc} = 308 nm, I_0 ~ 200 mJ/pulse) of 5.0 × 10^{-4} M $Mo_7O_{24}^{6-}$ in 0.1 M KI.



A possible assignment for the nanosecond-lived intermediate is, therefore, that of a mixed-valence polymolybdate with an oxide radical functioning as a ligand, e.g. species I in eq 1. Such a species can be produced from excited states with ligand to metal charge-transfer character, CT in eq 1, and achieve nanosecond stability by charge migration, i.e. from the Mo center attached to the oxide radical to another metal center in the polymolybdate. In accord with the assignments given above, it must be pointed out that similarities in the spectra of the nanosecond- and microsecond-lived intermediates (Figures 1 and 4) are expected if the structures of the Mo chromophore in the species I (eq 1) and II (eq 3 and 4) are nearly the same.

The mechanistic differences between the scavenging of the reaction intermediates with 2-propanol and acetate, respectively, (Figure 6) can be related to the dual ability of the acetate ion

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[11] Ferraudi, G. In *Elements of Inorganic Photochemistry*; Wiley-Interscience: New York, 1988; Chapter 1, pp 21–30.

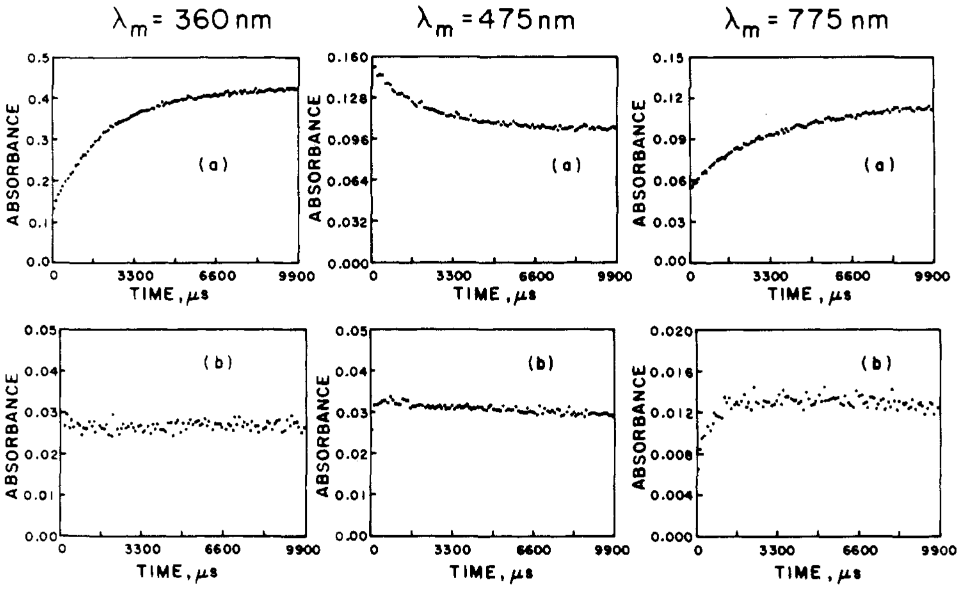
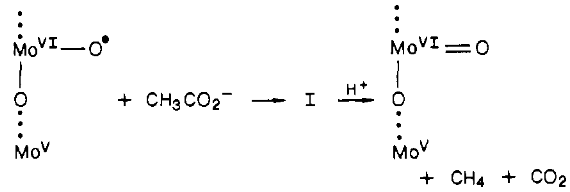


Figure 6. Traces recorded during the formation of the "Keggin's polymolybdates" when (a) 1.7 M 2-propanol or (b) a 2.0 M equimolar mixture of $CH_3CO_2^-$ and CH_3CO_2H are respectively used as scavengers of the primary species generated during 308-nm flash irradiations of deaerated 5.0 × 10^{-4} M $Mo_7O_{24}^{6-}$.

to function like 2-propanol as an hydrogen donor (eq 4) in addition to being an electron donor (eq 5).[12] In eq 5, the intermediate


$$Mo^{VI}{-}O^{\bullet}\,/\,O\,/\,Mo^{V} + CH_3CO_2^- \longrightarrow I \xrightarrow{H^+} Mo^{VI}{=}O\,/\,O\,/\,Mo^{V} + CH_4 + CO_2 \quad (5)$$

I can be a radical–ion pair between the mixed-valence polymolybdate and $CH_3^{\bullet}$ radicals or a short-lived alkyl derivative. The reported formation of CH_4 can be related to the decomposition of I.[13]

Experimental Section

Photochemical Procedures. The flash-photolysis apparatus used for the measurements of spectra and reaction kinetics in picosecond and nanosecond time domains, respectively, have been described elsewhere.[14,15] In these experiments, 355-nm light pulses, ca. 18-ps width, from a mode-locked YAG laser were used for the investigation of transients in a time range covering from 18 ps to 100 ns. Similar observations in 1 ns to 20 μs were carried out in another flash-photolysis set up where an excimer laser delivered pulses of 308-nm light for the irradiation of the photolysis.[16] Aqueous acidic solutions of $Mo_7O_{24}^{6-}$ were deaerated with streams of ultrapure N_2. Continuous-wave emission experiments were carried out in an SLM spectrofluorometer with a 1000–300-nm sensitive detection system, which allows detection of luminescence with $\phi > 10^{-4}$.

Materials. Aldrich's ammonium heptamolybdate, $(NH_4)_2Mo_7O_{24}$, was purified according to literature reports.[17] The sodium salt was synthesized from Na_2MoO_4 according to Yamase's procedure.[17] Other chemicals were reagent grade and were used without further purification.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy.

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[12] It must be noticed that the principal reaction of OH radicals with acetate is hydrogen abstraction: Neta, P.; Simic, M.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 4207.

[13] Yamase, T.; Kurozumi, T. *J. Chem. Soc., Dalton Trans.* **1983**, 2205.

[14] Ebbesen, T. W. *Rev. Sci. Instrum.* **1988**, *59*, 1307.

[15] Muralidharan, S.; Ferraudi, G. *J. Phys. Chem.* **1983**, *87*, 4877.

[16] Van Vlierberge, B.; Ferraudi, G. *Inorg. Chem.* **1987**, *26*, 337.

[17] Yamase, T.; Ikawa, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 746.