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Contribution from the Radiation Laboratory,
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Intermediates in the Early Events of Heteropolymolybdate-Catalyzed Photodehydrogenations: The Picosecond-Nanosecond Reactions of $M(OH)_6Mo_6O_{18}^{n-}$, Where M = Al^{III} (n = 3), Rh^{III} (n = 3), Fe^{III} (n = 3), Cr^{III} (n = 3), and Ni^{II} (n = 4)

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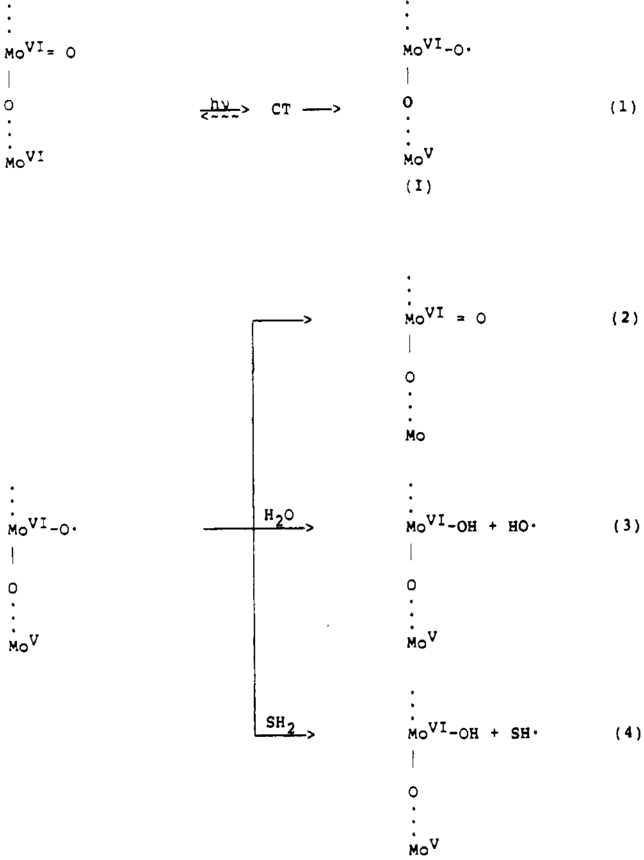
Introduction

The hetero- and isopolymolybdates have been used as photocatalysts in oxidations of organic compounds and a considerable number of studies have been concerned with the mechanism of these processes.[1-8] Recent studies about the photodehydrogenation of alcohols catalyzed by $Mo_7O_{24}^{6-}$ have shown that the oxidant is neither the charge-transfer excited state, CT, nor OH radicals.[3,4] A nanosecond-lived intermediate, detected in flash photolysis with picosecond resolution, has the thermal reactivity expected in a ligand-radical species (I), and the early events in the mechanism of such photodehydrogenations can be described by eqs 1-4.[3]



It is fair to question whether this mechanism, eqs 1-4, will also apply to photodehydrogenations of alcohols catalyzed by heteropolyoxomolybdates. A number of compounds where Mo(VI) ion has been replaced by another metal ion are well-characterized from the stand point of their structure and can be regarded as close relatives of $Mo_7O_{24}^{6-}$.[7,9] In this regard, we have investigated the early events in photodehydrogenations of alcohols catalyzed by $M(OH)_6Mo_6O_{18}^{n-}$; where M = Al^{III} (n = 3), Cr^{III} (n = 3), Fe^{III} (n = 3), Rh^{III} (n = 3), and Ni^{II} (n = 4), and compared the photochemistries of these compounds with that of $Mo_7O_{24}^{6-}$.

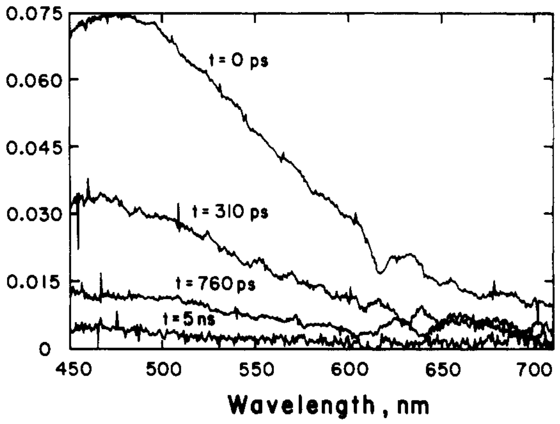


Figure 1. Transient absorption spectra recorded in 266-nm flash irradiations of 10^{-3} M $(NH_4)_3Cr(OH)_6Mo_6O_{18}$ in aqueous, 5 < pH < 6, deaerated solutions.

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.[10,11] In these experiments, 355- or 266-nm light pulses with ca. 18 ps width from a mode-locked YAG laser were used for the investigation of transients in a time range from 18 ps to 20 ns while observations in 10 ns to 20 μs were carried out in another flash-photolysis apparatus with an excimer laser on a YAG laser respectively used as an excitation source. Aqueous solutions of the heteropolymolybdates, 5 ≤ pH ≤ 6, were always 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. Quantum yields of formaldehyde were determined by measuring the concentration of formaldehyde at various irradiation times. The polymolybdate concentration, ca. 3.0×10^{-3} M, was adjusted for a complete absorption of the respective 300 and 254-nm light. These experiments were carried out with solutions deaerated with streams of ultrapure N_2 and conversions to products limited to less than 4% of the polymolybdates concentration. The light intensity at 254 or 300 nm was measured, respectively, with tris(oxalato)ferrate(III).[12] Formaldehyde concentrations were determined with chromotropic acid.[13]

Materials. $(NH_4)_3Cr(OH)_6Mo_6O_{18}$,[14,15] $Na_3Cr(OH)_6Mo_6O_{18}$,[15,16] $(NH_4)_3Al(OH)_6Mo_6O_{18}$,[17] $(NH_4)_4Ni(OH)_6Mo_6O_{18}$,[18] $Na_4Ni(OH)_6Mo_6O_{18}$,[15] $(NH_4)_3Rh(OH)_6Mo_6O_{18}$,[15] and $(NH_4)_3Fe(OH)_6Mo_6O_{18}$[15] were synthesized by literature procedures. These compounds were recrystallized three times from water and their purity established by comparing their UV-vis spectra with literature reports[15,18,19] and by means of their elemental analysis.

Results

Time-Resolved Absorption and Emission Spectra. The 266-nm flash irradiation of 10^{-3} M $Cr(OH)_6Mo_6O_{18}^{3-}$ deaerated aqueous solutions (pH 5-6) produces a transient spectrum (λ_{max} = 470 nm) within the time resolution of the instrument (t ≤ 15 ps),

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(1) Renneke, R. F.; Hill, C. L. *Agnew. Chem., Int. Ed. Engl.* **1988**, *27*, 1526.
(2) Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; William, M. M.; Schmidt, J. A.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 5471.
(3) Kraut, B.; Ferraudi, G. *Inorg. Chem.* **1989**, *28*, 2692.
(4) Ward, M. D.; Brazdill, J. F.; Grasselli, R. K. *J. Phys. Chem.* **1984**, *88*, 4210.
(5) Yamase, T. *Polyhedron* **1986**, *5*, 79.
(6) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347.
(7) Pope, M. T. In *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
(8) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 31 and references therein.
(9) Tsigdinos, G. A. In *Aspects of Molybdenum and Related Chemistry*; Springer-Verlag: Berlin, 1978.
(10) Ebbesen, T. *Rev. Sci. Instrum.* **1988**, *59*, 1307.
(11) Muralidharan, S.; Ferraudi, G. *J. Phys. Chem.* **1983**, *87*, 4877.
(12) Parker, C. A.; Hatchard, G. E. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.
(13) Muralidharan, S.; Ferraudi, G. *Inorg. Chem.* **1981**, *20*, 2306.
(14) Brauer, G. In *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1965; Vol. 2.
(15) Tsigdinos, G. A. Thesis, Boston University, Boston, MA, 1961.
(16) Perloff, A. *Inorg. Chem.* **1970**, *9*, 2228.
(17) Baker, L. C. W.; Foster, G.; Tan, W.; Scholnick, F.; McCutcheon, T. L. *J. Am. Chem. Soc.* **1955**, *77*, 2136.
(18) Matijevic, E.; Kerker, M.; Beyer, H.; Theubert, F. *Inorg. Chem.* **1963**, *2*, 581.
(19) Shimura, Y. *J. Chem. Soc. Jpn.* **1954**, *75*, 560.

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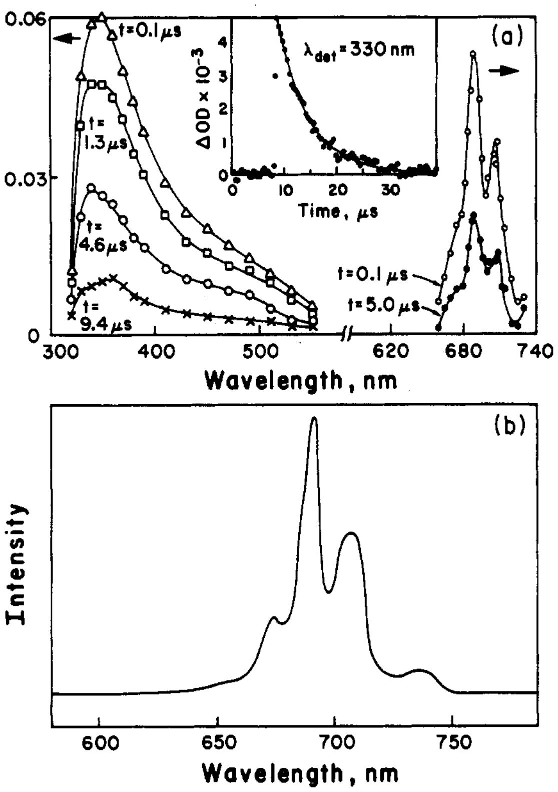

Figure 2. (a) Long-lived transient absorption (left) and emission spectra (right), recorded in 308-nm flash irradiations of 10^{-3} M $(NH_4)_3Cr(OH)_6Mo_6O_{18}$. The inset shows a typical trace for the decay of the 466-nm optical density change at 330 nm under experimental conditions. (b) Emission spectrum recorded in 325-nm continuous-wave irradiations of 3.0 10^{-3} M $(NH_4)_3Cr(OH)_6Mo_6O_{18}$ at 3 °C.

Figure 1. In less than a nanosecond the optical density change, ΔOD, decreases to near 16% of the prompt value, i.e. with first-order rate constant $k = (2.4 \pm 0.5) \times 10^9$ s^{-1}, without any significant change in the shape of the transient spectrum. The 16% residual ΔOD disappears in less than a microsecond with a first-order rate constant, $k = (1.7 \pm 0.3) \times 10^5$ s^{-1}, Figure 2a. We have observed in flash fluorescence experiments that emission of red light (λ_{max} = 690 nm) is simultaneous with the second step in the decay of the optical density, Figure 2a. Such a luminescence of the compound was confirmed in continuous-wave excitations, Figure 2b.

The nanosecond–microsecond optical transients respectively determined with 308- or 355-nm flash irradiations of 10^{-3} M deaerated solutions of the chromium(III) heteropolymolybdate were similar to the spectra and reaction rates described above despite an order of magnitude difference in the flash-induced concentration of intermediates. The emission intensity increases almost 5 times from 20 to 2.5 °C a fact that is reflected on the values of the quantum yields of emission, i.e. 2.2×10^{-2} at 2.5 °C and 4.4×10^{-3} at 20 °C.

The nature of the processes described above was investigated by flash photolysis (λ_{exc} = 308 nm) of heteropolymolybdate solutions where 2-propanol, in concentrations between 5×10^{-4} and 1×10^{-4} M, was used as an hydrogen donor for the polymolybdate-induced photodehydrogenation. Such a photodehydrogenation leads to the formation of a product with $\lambda_{max} \sim 460$ nm whose yield increases with the concentration of 2-propanol, Figure 3. It must be noted that the optical spectrum and stability ($\tau > 100$ ms) of the product are similar to those of the primary product, $Mo_7O_{23}(OH)^{6-}$, in flash photolysis of $Mo_7O_{24}^{6-}$ and it must, therefore, be assigned as $Cr(OH)_6Mo_6O_{17}(OH)^{3-}$. A rate constant, $k = 1.3 \times 10^9$ M^{-1} s^{-1}, for the formation of this product has been determined from the dependence of the overall rate constant on 2-propanol concentration. In these experiments, we have also observed that the respective rates of the 350-nm optical density decay in a nanosecond–microsecond time domain and the 690-nm emission are not affected by 1 M 2-propanol.

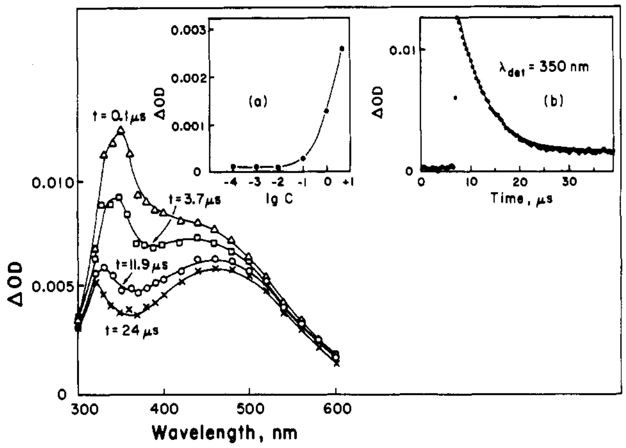

Figure 3. Transient spectra recorded in the scavenging of the Mo(V)–ligand-radical intermediate with 2.6 M 2-propanol in 308-nm flash photolysis of 2.0×10^{-3} M $Na_3Cr(OH)_6Mo_6O_{18}$. Inset a shows the 460-nm absorbance changes, measured 350 ns after the flash, as a function of 2-propanol concentration. Inset b shows a typical trace recorded under the same experimental conditions used for the determination of the transient spectra.

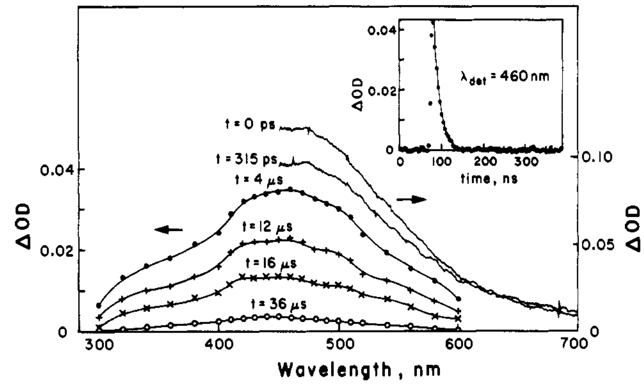

Figure 4. Spectral changes, in a picosecond–nanosecond time domain, induced by 266-nm excitations of 10^{-3} M $(NH_4)_3Al(OH)_6Mo_6O_{18}$ deaerated aqueous solutions and a trace (inset) recorded under the same experimental conditions.

Table I. Rate Constants for the Disappearance (k_d) and Reaction with 2-Propanol (k_R) of Ligand-Radical Intermediates[a]

polymolybdate	$k_d/10^9 \times$ s^{-1}	$k_R/10^9 \times$ M^{-1} s^{-1}	α[b]
$Mo_7O_{24}^{6-}$	0.030 ± 0.002	0.17 ± 0.01	0.15
$Al(OH)_6Mo_6O_{18}^{3-}$	0.059 ± 0.003	0.30 ± 0.02	0.16
$Cr(OH)_6Mo_6O_{18}^{3-}$	2.5 ± 0.6	1.3 ± 0.2	0.66
$Ni(OH)_6Mo_6O_{18}^{4-}$	2.0 ± 0.6	1.0 ± 0.9	0.67
$Fe(OH)_6Mo_6O_{18}^{3-}$	5.0 ± 0.7	1.0 ± 0.9	0.83
$Rh(OH)_6Mo_6O_{18}^{3-}$	2.0 ± 0.6	1.0 ± 0.9	0.66

[a] Reactions followed at 450 nm in flash irradiations of deaerated aqueous solutions, 5 ≤ pH ≤ 6, of the polymolybdates. [b] Fraction of intermediate undergoing back electron transfer in reactions with 1 M 2-propanol, e.g. $\alpha = k_d/(k_R + k_d)$.

Flash photolysis (λ_{exc} = 266 nm) of 10^{-3} M $Al(OH)_6Mo_6O_{18}^{3-}$ in aqueous deaerated solutions resulted in the prompt formation ($t < 15$ ps) of a transient spectrum, $\lambda_{max} \sim 450$ nm, which disappears by a first-order process, Figure 4. Moreover, flash irradiations of the heteropolymolybdate in solutions having 2-propanol in concentrations equal to or less than 1 M produce a species whose spectrum (λ_{max} = 480 nm) and stability resembles those of the product of the $Mo_7O_{24}^{6-}$-induced 2-propanol photodehydrogenation, Figure 5 and Table I. This observation suggests that the species with λ_{max} = 480 nm must be assigned as $Al(OH)_6Mo_6O_{17}(OH)^{3-}$, i.e. the first stable product of the hydrogen abstraction. The dependence of the product yield on the concentration of 2-propanol is in accord with this proposition, Figure 5.

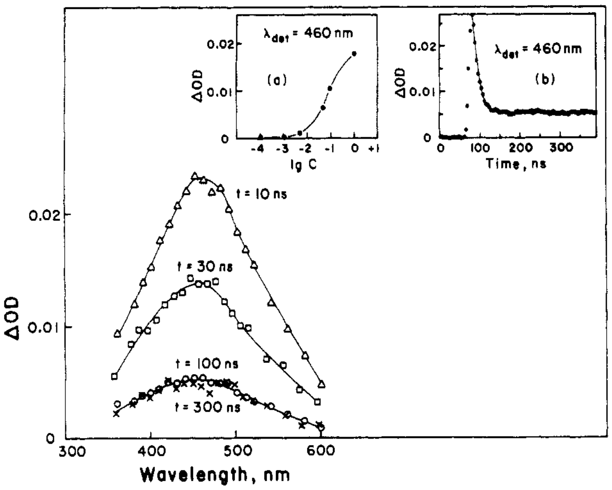

Figure 5. Time-resolved spectral changes in the interception of a Mo(V)-ligand radical in flash photolysis of 10^{-3} M $(NH_4)_3Al(OH)_6Mo_6O_{18}$ in deaerated 0.05 M 2-propanol and 460-nm optical density changes (inset a) determined 350 ns after the 266-ns laser flash as a function of 2-propanol concentration. Inset b shows a typical trace recorded in deaerated 0.05 M 2-propanol.

Table II. Quantum Yields of Formaldehyde from the Photodehydrogenation of Methanol with Polymolybdates[a]

	$\phi \times 10^2$ [b]	
polymolybdates	λ_{excit} = 254 nm	λ_{excit} = 300 nm
$Mo_7O_{24}^{6-}$	25 ± 1	43 ± 1
$Al(OH)_6Mo_6O_{18}^{3-}$	16 ± 1	34 ± 1
$Cr(OH)_6Mo_6O_{18}^{3-}$	6.7 ± 0.6	7.0 ± 0.4
$Ni(OH)_6Mo_6O_{18}^{4-}$	5.9 ± 0.3	6.1 ± 0.5
$Fe(OH)_6Mo_6O_{18}^{3-}$	3.1 ± 0.4	3.3 ± 0.4
$Rh(OH)_6Mo_6O_{18}^{3-}$	5.1 ± 0.4	5.0 ± 0.5

[a] Photolyses were carried out with aqueous deaerated solutions, $5 \le pH \le 6$, of the polymolybdates. The concentration of methanol, [MeOH] = 1.0 M, was the same in all the experiments. [b] Values are an average of 2–4 determinations. In each determination the concentration of formaldehyde was measured at four different times in irradiations, $I_0 \sim 10^{-5}$ einstein/(dm^3 s), where conversions to products were less than 3%.

The spectra observed in flash irradiations (λ_{exc} = 266 nm or 308 nm respectively) of the $M(OH)_6Mo_6O_{18}^{n-}$, where M = Ni^{II} (n = 4), Fe^{III} (n = 3), or Rh^{III} (n = 3), in deaerated aqueous solutions were similar to one generated in flash irradiations of $Al(OH)_6Mo_6O_{18}^{3-}$ and exhibited lifetimes dependent on the transition metal ion, Table I. Moreover, rate constants for the abstraction of hydrogen from 2-propanol in the order of 10^9 M^{-1} s^{-1} were determined for these heteropolymolybdates, Table I.

Product Quantum Yields. In order to determine the effect of the hetero metal ion on the photoinduced dehydrogenation of methanol, irradiations of the polymolybdates investigated by flash photolysis (see above) were respectively carried out in aqueous solutions where methanol concentrations ([MeOH] ≤ 3 M) allowed us to intercept a known fraction of the shortest lived intermediate detected in our time-resolved experiments.[20] Quantum yields for the formaldehyde formation were measured in 254- and 300-nm photolyses respectively, Table II. The values in Table II reveal that quantum yields from 300-nm irradiations are almost 2 times larger than the corresponding yields from irradiations at 254 nm in the Al(III) and heptamolybdate compounds.

Discussion

The experimental observations reported above show that early events in the photochemistry of the heteropolymolybdates $M(OH)_6Mo_6O_{18}^{n-}$, where M = Ni^{II} (n = 4), Al^{III} (n = 3), Fe^{III} (n = 3), Cr (n = 3), or Rh^{III} (n = 3) is more complex than those previously investigated with $Mo_7O_{24}^{6-}$. Indeed, one the primary species detected in flash photolysis of $Cr(OH)_6Mo_6O_{18}^{3-}$ ($\tau_{formation}$ < 20 ps) disappears in less than a nanosecond while another remains as a microsecond-lived product. The decay of the longest lived transient is simultaneous with luminescence having a spectrum similar to the emission spectrum of the $(^2T_1,{}^2E)Cr_2O_3$ in ruby and must be assigned, therefore, as a mixture of the $^2T_1$ and ^2E ligand field excited states, $^*Cr(OH)_6Mo_6O_{18}^{3-}$, whose relative populations are probably determined by a rapid thermal equilibrium.[21,22] In addition, a comparison of the spectral changes and chemical reactions of the intermediate observed in a picosecond time domain with those of the Mo(V)-ligand radical generated in photolyses of $Mo_7O_{24}^{7-}$, suggests that a similar species, i.e. $Cr(OH)_6Mo_6O_{17}(O^\bullet)^{3-}$, is a precursor of the photodehydrogenation induced by the chromium(III) heteropolymolybdate. On the basis of the kinetics of the spectral transformations described above, it is necessary to have this ligand-radical intermediate photogenerated together with the emissive ligand field states, i.e. by parallel processes as shown in eqs 5 and 6 or nearly simultaneously generated by rapid conversion from the CT state to the LF states as is shown in eqs 7–8. Since

$$Cr(OH)_6Mo_6O_{18}^{3-} \xrightarrow{h\nu} \xrightarrow{\phi_1} CT \tag{5}$$

$$Cr(OH)_6Mo_6O_{18}^{3-} \xrightarrow{h\nu} \xrightarrow{\phi_2} {}^*Cr(OH)_6Mo_6O_{18}^{3-} \tag{6}$$

$$CT \longrightarrow Cr(OH)_6Mo_6O_{18}^{3-} \tag{7}$$

$$CT \longrightarrow Cr(OH)_6Mo^VMo^{VI}{}_5O_{17}(O\cdot)^{3-} \tag{8}$$

$$CT \longrightarrow {}^*Cr(OH)_6Mo_6O_{18}^{3-} \tag{9}$$

$$Cr(OH)_6Mo^VMo^{VI}{}_5O_{17}(O\cdot)^{3-} \xrightarrow[k_d]{} Cr(OH)_6Mo_6O_{18}^{3-} \tag{10}$$

$$Cr(OH)_6Mo^VMo^{VI}{}_5O_{17}(O\cdot)^{3-} \xrightarrow[k_R]{SH_2} Cr(OH)_6Mo^VMo^{VI}O_{18}(OH)^{3-} + SH\cdot \tag{11}$$

$${}^*Cr(OH)_6Mo_6O_{18}^{3-} \longrightarrow Cr(OH)_6Mo_6O_{18}^{3-} + h\nu \tag{12}$$

$${}^*Cr(OH)_6Mo_6O_{18}^{3-} \rightsquigarrow Cr(OH)_6Mo_6O_{18}^{3-} \tag{13}$$

flash-photolyses of the nickel(II), rhodium(III), and iron(III) heteropolymolybdates show that these compounds also generate short-lived ligand-radicals, $M(OH)_6Mo^VMo^{VI}{}_5O_{17}(O^\bullet)^{n-}$, where M = Ni ($n$ = 4), Rh (n = 3), or Fe (n = 3), it is possible that the alcohol photodehydrogenation can be described by mechanisms similar to the one proposed for the Cr(III) compound, eqs 5–13. In terms of this mechanism, the optical transformations observed in less than a nanosecond are described by eqs 7–10 while eqs 11–13 account respectively for the scavenging of the ligand-radical intermediate and the LF state decay via radiative and nonradiative paths. It must be also noted that competition between eq 8 and eq 9 does not change the lifetime of the phosphorescence in accord with our experimental results. Moreover, the dependence of the emission quantum yield on the temperature can be consequence of a change in the rate of the radiationless relaxation of the Cr(III) emissive states and/or a change in the efficiency of formation of such states, eqs 6, 9, 12, and 13.

The rate constants for the decay of the Ni(II), Cr(III), Rh(III), and Fe(III) ligand-radical intermediates, eq 10, and their reactions with alcohols, eq 11, have been used in calculations which show that quantum yields in Table II have been determined under conditions where nearly 70% of the intermediate undergoes back-electron-transfer. Under similar experimental conditions,

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(20) Rate constants for the abstraction of hydrogen from methanol by the heteropolymolybdate ligand radicals have been found to have values close to those determined with 2-propanol.

(21) Foster, L. S. *Transition Met. Chem. (N.Y.)* **1969**, *5*, 1.

(22) Flint, C. D.; Matheous, A. P. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 379.

the respective scavengings of $Al(OH)_6Mo_6O_{17}(O^\bullet)^{3-}$ and $Mo_7O_{23}(O^\bullet)^{6-}$ are nearly complete. Corrections of the Cr(III), Ni(II), Rh(III), and Fe(III) quantum yields in Table II for incomplete scavenging of the ligand-radical intermediates give values that are very close to those determined with $Al(OH)_6Mo_6O_{18}^{3-}$. This observation suggests that population of the dd states by various paths, eqs 6 and 9, does not appear to diminish, to a large extent, the yield of the ligand-radical formation. In this regard, the 2-fold difference between the quantum yields measured respectively at 300 and 254 nm, Table II with $Mo_7O_{24}^{6-}$ and $Al(OH)_6Mo_6O_{18}^{3-}$ is likely related to an intrinsic dependence of ϕ_1, eq 5, on λ_{exc}.[23]

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[23] Preliminary results (Kraut, B.; Ferraudi, B., Work in progress) from extended Huckel MO calculations suggest that there are several LMCT excited states with close energies but centered on different metal ions. These states can be populated with photonic energies within those of the absorption bands in the spectra of the polyoxomolybdates and have characteristic photochemistries, eqs 7–9. These results also indicate that the thermal stability of the intermediates listed in Table I may also be related to the characteristics of the LUMO in such species.

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Reaction of Bis(trimethylphosphine)–Tetraborane(8) with Trimethylphosphine

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Smaller boranes undergo fast, primary reactions with trimethylphosphine. Diborane(6), tetraborane(10), and pentaborane(11) undergo rapid cleavage reactions at low temperatures to give BH_3, B_3H_7, and B_4H_8 adducts of $P(CH_3)_3$, respectively.[1,2,3] Pentaborane(9) and hexaborane(10) readily form adducts with $P(CH_3)_3$.[4,5] All of these adducts, except $BH_3\cdot P(CH_3)_3$, further react with $P(CH_3)_3$ to finally give cleavage products which are electron precise. Thus, eqs 1–4 have been established.[3,6,7]

$$B_3H_7\cdot P(CH_3)_3 + 2P(CH_3)_3 \rightarrow BH_3\cdot P(CH_3)_3 + B_2H_4\cdot 2P(CH_3)_3 \qquad (1)$$

$$B_5H_9\cdot 2P(CH_3)_3 + 3P(CH_3)_3 \rightarrow B_2H_4\cdot 2P(CH_3)_3 + B_3H_5\cdot 3P(CH_3)_3 \qquad (2)$$

$$B_6H_{10}\cdot 2P(CH_3)_3 + 4P(CH_3)_3 \left\{ \begin{array}{ll} \rightarrow B_2H_4\cdot 2P(CH_3)_3 + B_4H_6\cdot 4P(CH_3)_3 & (3) \\ \rightarrow 2B_3H_5\cdot 3P(CH_3)_3 & (4) \end{array} \right.$$

Similarly, $B_4H_8\cdot 2P(CH_3)_3$, the primary cleavage product of B_5H_{11}, was known to further undergo reactions with $P(CH_3)_3$.[3] However, the exact nature of the reaction products was not established; one of the possible products, $B_3H_5\cdot 3P(CH_3)_3$, had not been known, and the ^{11}B NMR signals of the products were too broad and close together to be resolved by the instruments that were commonly used at that time. Now that higher field NMR instruments are available, the unequivocal identification of the reaction products is possible. Therefore, the reaction of $B_4H_8\cdot 2P(CH_3)_3$ with $P(CH_3)_3$ was reinvestigated, and the results of the study are reported in this note.

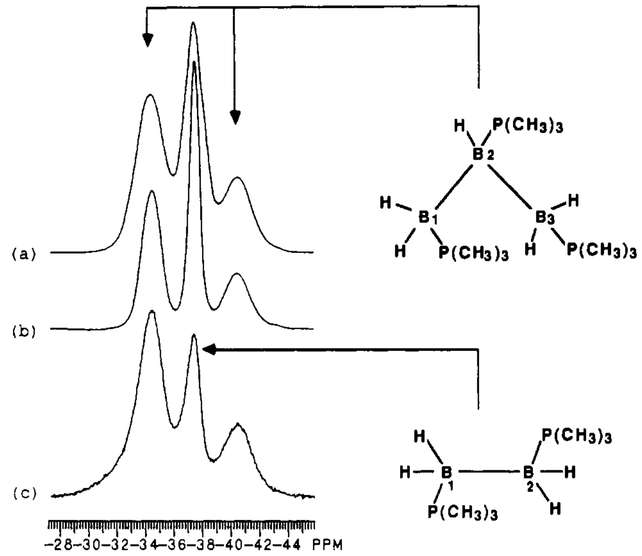

Figure 1. ^{11}B NMR spectra of a 1:1 mixture of $B_3H_5\cdot 3P(CH_3)_3$ and $B_2H_4\cdot 2P(CH_3)_3$ in dichloromethane at +20 °C: (a) normal spectrum; (b) proton-spin-decoupled spectrum. (c) $^{11}B\{^1H\}$ NMR spectrum of the products from the reaction of $B_4H_8\cdot 2P(CH_3)_3$ with excess $P(CH_3)_3$ in dichloromethane at −30 °C. $BH_3\cdot P(CH_3)_3$ had been removed from the product mixture.

Results and Discussion

A. ^{11}B NMR Spectrum of $B_3H_5\cdot 3P(CH_3)_3$. The reaction of $B_5H_9\cdot 2P(CH_3)_3$ with a large excess of $P(CH_3)_3$ gives a 1:1 mixture of $B_2H_4\cdot 2P(CH_3)_3$ and $B_3H_5\cdot 3P(CH_3)_3$.[4] The 96.2-MHz ^{11}B NMR spectra of this mixture are shown in parts a and b of Figure 1. Unlike those in the 32.1-MHz spectra that were reported earlier,[4] the signals of $B_3H_5\cdot 3P(CH_3)_3$ at −34.5 and −40.5 ppm in a 2:1 intensity ratio are seen to be clearly separated from the signal of $B_2H_4\cdot 2P(CH_3)_3$ at −37.5 ppm. The two signals of $B_3H_5\cdot 3P(CH_3)_3$ are assigned to the $B_{1,3}$ and B_2 atoms, respectively.

B. Cleavage of $B_4H_8\cdot 2P(CH_3)_3$ with $P(CH_3)_3$. When B_5H_{11} was dissolved in $P(CH_3)_3$, a cleavage reaction of B_5H_{11} occurred immediately at −80 °C, thus producing $BH_3\cdot P(CH_3)_3$ and $B_4H_8\cdot 2P(CH_3)_3$ as reported earlier.[3] Then, the second reaction proceeded at room temperature, and the framework of the B_4H_8 moiety was cleaved by $P(CH_3)_3$ according to eqs 5 and 6. This cleavage reaction was slow, requiring more than 24 h but less than 50 h for completion when ~0.5-mmol samples of $B_4H_8\cdot 2P(CH_3)_3$ were used. No products other than those indicated in eqs 5 and 6 were produced. Shown in Figure 1c is the $^{11}B\{^1H\}$ NMR spectrum of the products from the reaction of B_5H_{11} with $P(CH_3)_3$. Prior to the spectrum recording, $BH_3\cdot P(CH_3)_3$, one of the reaction products, was removed from the product mixture for spectrum clarity. The relative intensities of the signals indicated that the molar ratio of $B_3H_5\cdot 3P(CH_3)_3$:$B_2H_4\cdot 2P(CH_3)_3$ in the product mixture was approximately 10:7, or the reactions shown in eqs 5 and 6 proceeded in a 10:3.5 ratio.

$$B_4H_8\cdot 2P(CH_3)_3 + 2P(CH_3)_3 \left\{ \begin{array}{ll} \rightarrow BH_3\cdot P(CH_3)_3 + B_3H_5\cdot 3P(CH_3)_3 & (5) \\ \rightarrow 2B_2H_4\cdot 2P(CH_3)_3 & (6) \end{array} \right.$$

C. Conclusion. The trimethylphosphine adduct of tetraborane(8), $B_4H_8\cdot 2P(CH_3)_3$, was found to undergo clean cleavage reactions with trimethylphosphine to finally give the electron-precise borane adducts $BH_3\cdot P(CH_3)_3$, $B_2H_4\cdot 2P(CH_3)_3$ and $B_3H_5\cdot 3P(CH_3)_3$. Thus, the behavior of $B_4H_8\cdot 2P(CH_3)_3$ is reconciled with those of the $P(CH_3)_3$ adducts of other lower boranes.

Experimental Section

Chemicals and Equipment. Conventional high-vacuum line techniques were used throughout for the handling of air-sensitive volatile compounds.

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(1) Burg, A. B.; Wagner, R. I. *J. Am. Chem. Soc.* **1953**, *75*, 3872.
(2) Edwards, L. J.; Hough, W. V. U.S. Patent 3 281 218 (Cl.23–358), Oct 25, 1966.
(3) Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302.
(4) Fratini, A. V.; Sullivan, G. W.; Denniston, M. L.; Hertz, R. K.; Shore, S. G. *J. Am. Chem. Soc.* **1974**, *96*, 3013.
(5) (a) Kameda, M.; Kodama, G. *Inorg. Chem.* **1981**, *20*, 1072. (b) Mangion, M.; Hertz, R. K.; Denniston, M. L.; Long, J. R.; Clayton, W. R.; Shore, S. G. *J. Am. Chem. Soc.* **1976**, *98*, 449.
(6) Kameda, M.; Kodama, G. *Inorg. Chem.* **1980**, *19*, 2288.
(7) Kameda, M.; Kodama, G. *Polyhedron* **1983**, *2*, 413.

0020-1669/90/1329-4837$02.50/0