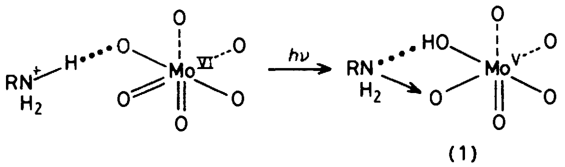
Photoreduction of Polymolybdates(VI) in Aqueous Solutions containing Acetic Acid †

Toshihiro Yamase * and Tadatoshi Kurozumi
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

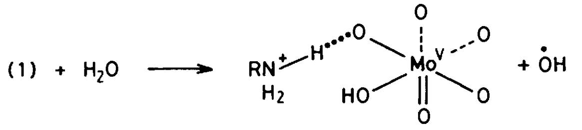
Polymolybdates(VI) have been photochemically reduced to Mo^V in aqueous solutions containing acetic acid. Carbon dioxide, methane, and succinic acid were isolated as decomposition products of the acetic acid but the quantum yield of their formation was *ca.* 20 times smaller than that of Mo^V formation. E.s.r. spin-trapping experiments exhibited the presence of spin-adducts of hydroxyl radical as an oxidation product of water. The photoredox reaction of the polymolybdate(VI) with water was a main process. The reaction mechanism discussed is based on the similarity with the photochemistry for an alkylammonium polymolybdate(VI). The photoredox reaction of the polymolybdate(VI) with water or acetic acid proceeds *via* the photoinduced formation of a charge-transfer complex between the polymolybdate(VI) and acetic acid, which is preceded by the transfer of an acetic acid proton to an oxygen atom at a photoreducible octahedral site in the polymolybdate(VI).

It was recently reported that photoirradiation of aqueous solutions containing alkylammonium polymolybdates(VI) brought about the oxidation of water to $\dot{O}H$ with an accompanying reduction of Mo^{VI} to Mo^V.[1] The mechanism of the initial steps [equations (i) and (ii)] induced by a ligand-to-metal charge-transfer reaction (l.m.c.t.) at a terminal Mo=O bond was interpreted in terms of the charge-transfer complex (1) being capable of oxidizing water, which was photochemically produced by a proton transfer from an alkylammonium cation to a bridging oxygen atom at an octahedral site of the polymolybdate(VI).[1,2] Oxidation [equation (iii)] of alkylammonium cations could compete with that [equation (ii)] of water but the relative rate of the former was considered to be small, since the quantum yield for the oxidation of alkylammonium cations (for example, the quantum yield of the formation of propylene and acetone for isopropylammonium cations) was extremely low compared with that of Mo^V formation.[1] A photoreducible octahedral site in $[Mo_7O_{24}]^{6-}$ was determined by electron spin resonance (e.s.r.) studies of a single crystal of hexakis(propylammonium) heptamolybdate(VI) trihydrate.[3]

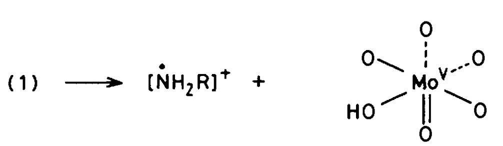


(i)

(1)



(ii)



(iii)

To extend the scope of photo-oxidation of substrates by the use of polymolybdates(VI) we investigated the oxidation of the carboxylates (the Kolbe reaction) which was observed at irradiated n-type semiconductors in a heterogeneous system.[4,5] This paper describes the photo-Kolbe decarboxylation of acetic acid in a homogeneous polymolybdate(VI) system, which competes with water oxidation to the $\dot{O}H$ radical as a main process. The present programme on the photoredox reaction of polymetalates may provide insight into the molecular level for interfacial charge-transfer processes on irradiated oxide-semiconductors, since the l.m.c.t. (oxygen ⟶ metal) state of the polymetalates can be regarded as the electron–hole pair photogenerated on ultrafine particles of n-type oxide-semiconductors.

Experimental

Hexakis(isopropylammonium) heptamolybdate(VI) trihydrate $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$ was synthesized using a published method.[1,6] 2-Methyl-2-nitrosopropane (menp) and *N*-benzylidene-t-butylamine *N*-oxide (bbao), which were used for e.s.r. spin-trapping techniques, were prepared as described by Emmons.[7] Trideuterioacetic acid (CD_3CO_2H, >99% D, Merck Co.) and deuteriated water (D_2O, 99.9% D_2, Merck Co.) were used without further purification. All other reagents were at least analytical grade and were used as supplied. Sample solutions were prepared by mixing $Na_2MoO_4\cdot 2H_2O$ (96 mmol dm^{-3}) in aqueous solutions (10 cm^3) containing a constant total concentration (1 mol dm^{-3}) of acetic acid–sodium acetate. The ratio of acetic acid to sodium acetate was used to obtain the pH of the solution in the pH range 7.0—3.4. More acidic solutions were prepared by acidifying the aqueous acetic acid solutions with a known amount of $HClO_4$. The concentration of acetic acid was calculated using $pK(CH_3CO_2H) = 4.76$.[8]

The evacuation of solutions was carried out by several freeze-pump-thaw cycles to 10^{-4} Torr. A 500-W super-high pressure mercury lamp in conjunction with filters was used as the light source and photoirradiation was carried out with light of $\lambda \geqslant 313$ nm to avoid the excitation of acetic acid. Light intensities were measured using the potassium ferrioxalate actinometry method.[9] The sample cell for irradiation

---

† *Non-S.I. units employed:* 1 Torr = (101 325/760) Pa; 1 G = 10^{-4} T; 1 eV ≈ 1.60 × 10^{-19} J; 1 E (Einstein) = 1 mol of photons.

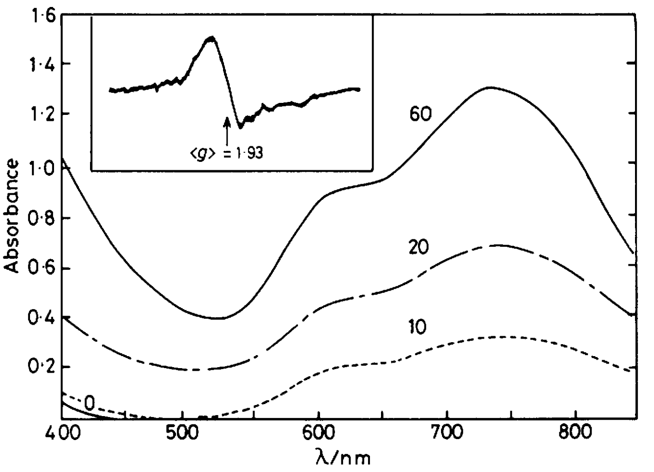


Figure 1. Absorption spectra of the deaerated solution (at pH 5.0) irradiated with 313-nm light. Time (min) is indicated on spectra. $[Mo^{VI}]$ = 96 mmol dm^{-3}. Total concentration of acetic acid–sodium acetate = 1 mol dm^{-3}. Insert: e.s.r. spectrum of the photolyte (60 min of irradiation time) at room temperature

Table. Quantum yields * for the formation of Mo^V, CO_2, CH_4, and succinic acid (H_2succ) from deaerated solutions at room temperature

Incident light (313 nm) intensity/photon min^{-1}	Irradiation time/h	φ_{Mo^V}	$10^3\varphi_{CO_2}$	$10^3\varphi_{CH_4}$	$10^3\varphi_{H_2succ}$
1.4×10^{18}	1	0.12	6.2	3.9	
	3	0.08	4.5	3.0	2.8
	6	0.06	3.6	2.4	
7.3×10^{17}	3	0.11	6.0	3.6	
5.4×10^{17}		0.17	6.3	4.3	
4.0×10^{17}		0.17	7.7	6.5	
0.9×10^{17}		0.20	8.8	6.1	

* φ_{Mo_V}, φ_{CO_2}, φ_{CH_4}, and φ_{H_2succ} indicate quantum yields of the formation of Mo^V, CO_2, CH_4, and succinic acid, respectively, under 313-nm light excitation. Sample solution (at pH 5.0) consists of polymolybdate(VI) (96 mmol dm^{-3} in total Mo^{VI}) and 1 mol dm^{-3} of acetic acid–sodium acetate.

was a 1-cm quartz cell connected to a gas sampling valve, allowing for both gas analysis and absorbance readings during short interruptions in the photolysis. Analysis of Mo^V in the photolyte was made at room temperature by the titration of $KMnO_4$ under a N_2 atmosphere, which resulted in the disappearance of the blue colour due to Mo^V. Gas chromatography of reaction gases was done on a Porapak N column with a Hitachi 164 instrument. Mass spectroscopy was performed using a Hitachi M80 GC/MS spectrometer. Concentrations of carbon dioxide and methane in aqueous solutions were calculated by using Bunsen's absorption coefficients of 0.88 and 0.033 (at 20 °C), respectively.[10] Succinic acid was determined by esterifying with diazomethane and chromatographing on Porapak T. The formation of succinic acid was also confirmed by colorimetric quantitative analysis (at 490 nm).[11] All procedures for the colorimetric analysis were carried out after decolouration of the blue colour due to Mo^V by admitting oxygen gas. ^1H N.m.r. spectra were recorded on a JEOL-PS-100 spectrometer with $SiMe_4$ as the external standard.

Samples for the spin-trapping method were prepared in the dark and under nitrogen. The irradiation in the cavity of a Varian E12 e.s.r. spectrometer was carried out with a 100-W high-pressure mercury lamp. Concentrations of menp and bbao were *ca.* 0.01—0.02 mol dm^{-3}. In order to remove the coloured impurity from 5,5-dimethylpyrroline 1-oxide (dmpo), sample solutions containing *ca.* 0.3 mol dm^{-3} dmpo were shaken with activated charcoal and were filtered through glass wool prior to photolysis.[12] This purification procedure tended to remove a small amount (*ca.* 10%) of the spin trap itself. In the dark, sample solutions gave exceedingly weak signals with dmpo which were not sufficiently strong to interfere with any of the experiments.

Results

Isolated Photoproducts.—Light irradiation (at 313 nm) of the deaerated solutions (at pH 7.0—3.4) containing the polymolybdate(VI) (96 mmol dm^{-3} in total Mo^{VI}) and a constant total concentration (1 mol dm^{-3}) of acetic acid–sodium acetate led to the appearance of a mixed-valence blue complex, with accompanying formations of carbon dioxide, methane, and succinic acid. In the absence of acetic acid–sodium acetate there was no observable photoreaction at various pH levels. The mixed-valence blue complex was not photosensitive to visible light. Prolonged photolysis ($\geqslant$15 h) of the solution gave a trace of ethane. The formation of succinic acid was also evidenced by ^1H n.m.r. investigation. Prolonged photolysis ($\geqslant$10 h) of the sample solution (at pD 5.0) by use of D_2O as solvent resulted in the appearance of a single line due to succinic acid with a chemical shift of 3.07 p.p.m. relative to $SiMe_4$.

The electronic spectra of the solution at pH 5.0 are shown in Figure 1 together with the e.s.r. spectrum of the photolyte. The absorption spectrum of the blue species and the e.s.r. signal ($\langle g \rangle = 1.93$) due to Mo^V are similar to the results obtained for the photolyzed solutions of $[NH_3Pr^i]_6[Mo_7O_{24}]$, allowing us to evaluate the Mo^V concentration by photometry at $\lambda_{max.}$ = 730 nm instead of using the $KMnO_4$-titration method, as in the case of the $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution.[1] There was no difference in Mo^V concentration within experimental error between the two methods for short-duration ($\leqslant$1 h) photolytes.

The quantum yield (φ) for the formation of volatile and non-volatile products decreased with increasing duration of irradiation time. This may be caused by an absorbance of the blue complex. The results under 313-nm light excitation of the solutions (pH 5.0) are shown in the Table. The quantum yield of Mo^V formation (φ_{Mo_V}) is *ca.* 20 times larger than that of the formation of CO_2, CH_4, or succinic acid. Each quantum yield decreases with increasing light intensity. A decrease in the 313-nm light intensity from 1.4×10^{18} photon min^{-1} to 0.9×10^{17} photon min^{-1} increased φ by a factor of *ca.* 2.

The mass spectrum of methane (*m/e*, relative intensity/%) for a 8 h-photolyte ($\lambda > 330$ nm) with the trideuterioacetic acid system $[CD_3CO_2H\text{-}Na(O_2CCD_3)]$ consisted of signals at 20 (CD_4, 7), 19 (CHD_3, 55), 18 (17), 17 (20), and 16 (1), while the experiment with the undeuteriated acetic acid system exhibited signals at 16 (CH_4, 54), 15 (39), 14 (6), and 13 (2). Comparison between the two mass spectral patterns indicates that the ratio of CHD_3 to CD_4 of methane products for the trideuterioacetic acid system can be estimated to be at least 8 : 1. This result eliminates a mechanism for the methane formation involving hydrogen abstraction from the acetic acid methyl by a methyl radical ($\dot{C}H_3$) which is produced by the Kolbe process ($CH_3CO_2^- - e^- \longrightarrow CH_3CO_2^\cdot \longrightarrow \dot{C}H_3 + CO_2$).[5]

The pH dependence of φ is shown in Figure 2 where each φ

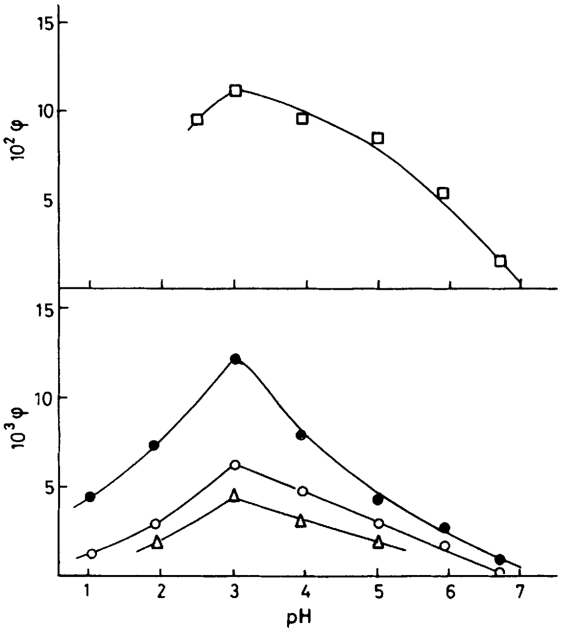


Figure 2. pH Dependence of the quantum yields (φ) of Mo^V, CO_2, CH_4, and succinic acid formation for the deaerated solution containing $[Mo^{VI}]$ = 96 mmol dm^{-3} and 1 mol dm^{-3} acetic acid–sodium acetate at room temperature: Mo^V (□); CO_2 (●); CH_4 (○); succinic acid (△). φ is measured under irradiation for 3 h with 313-nm light (1.4×10^{-4} E h^{-1})

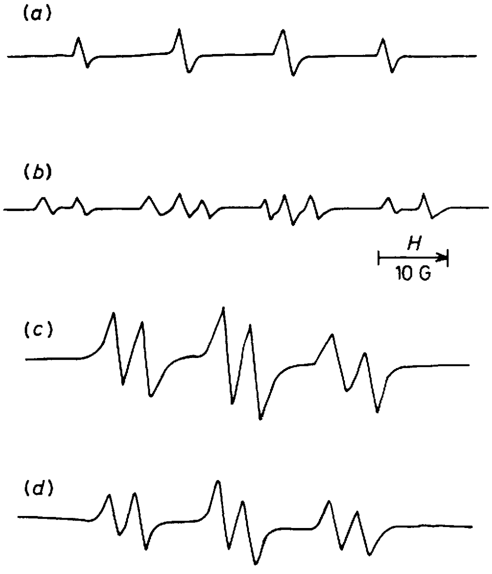


Figure 3. E.s.r. spectra of trapped radicals in the irradiated sample solution (at pH 4.0) containing $[Mo^{VI}]$ = 96 mmol dm^{-3} and 1 mol dm^{-3} acetic acid–sodium acetate at room temperature. (a) $\dot{O}H$ radical trapping by dmpo, $a_N = a_H = 15.0$ G. (b) Combination of $\dot{O}H$ and $CH_3\dot{C}HOH$ radical trappings by dmpo in the presence of ethanol, $a_N = 15.8$, $a_H = 22.8$ G. (c) Spin-adduct of menp, $a_N = 16.0$, $a_H = 4.0$ G. (d) Spin-adduct of bbao, $a_N = 15.6$, $a_H = 3.6$ G

was measured for 3-h photolytes. Optimum pH for the photoreaction is around 3. It is noted that φ_{Mo^V} is always *ca.* 20 times larger than φ_{CO_2}, φ_{CH_4}, or φ_{H_2succ}.

E.S.R. Spin Trapping.—Light irradiation ($\lambda \geqslant 350$ nm) of the deaerated sample solution (at pH 4.0) in the presence of spin traps resulted in the observation of nitroxide radicals. Results for dmpo, menp, and bbao are shown in Figure 3. The 1 : 2 : 2 : 1 quartet signal due to the spin-adduct of dmpo appeared when the solution was exposed to the light for a short time (within a few minutes) and exhibited the coupling parameters of $a_N = a_H = 15.0$ G [Figure 3(*a*)]. When irradiation was stopped, the signal decayed rapidly. Continued irradiation resulted in the disappearance of the signal. When acetic acid was excluded from the solutions, the signal was hardly observed. The signal at $a_N = a_H = 15.0$ G [Figure 3(*a*)] is comparable to the spectrum which has been attributed to the hydroxyl radical ($\dot{O}H$) spin-adduct of dmpo.[13] It is well known that hydrolytic reactions of dmpo can also be a source of artificial radicals, leading to the erroneous assumption that the $\dot{O}H$ radical is being trapped.[14] One method of verifying that $\dot{O}H$ radical trapping has occurred is to utilize the ability of spin trapping to distinguish between different radical species. If the production of the dmpo–OH adduct is due to the spin trapping of $\dot{O}H$ radicals, the addition of ethanol should result in the appearance of a new signal ($a_N = 15.8$, $a_H = 22.8$ G) due to trapping of the α-hydroxyethyl ($CH_3\dot{C}HOH$) radical, since $\dot{O}H$ reacts with ethanol to produce $CH_3\dot{C}HOH$ radicals.[14–16] This is demonstrated in Figure 3(*b*). Figure 3(*b*) revealed a combination of $\dot{O}H$ and $CH_3\dot{C}HOH$ radical adducts generated by photolysis ($\lambda \geqslant 350$ nm) of a sample solution in the presence of ethanol. Thus, the signal in Figure 3(*a*) indicated the presence of the $\dot{O}H$ radical. Adducts of dmpo–OH were also obtained for the photolysis of $[NH_3Pr^i]_6[Mo_7O_{24}]$ solutions, which were considered to give the $\dot{O}H$ radical.[1]

Photolysis of the sample solution in the presence of menp resulted in the formation of an menp–OH adduct [Figure 3(*c*)] with $a_N = 16.0$ and $a_H = 4.0$ G, which was the same as for the photolysis of the $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution.[1] Furthermore, photolysis of the sample solution in the presence of bbao gave an e.s.r. spectrum [Figure 3(*d*)] consisting of a triplet of doublets with $a_N = 15.6$ and $a_H = 3.6$ G. This six-line spectrum is slightly different from the signal which has been assigned to the bbao–OH adduct ($a_N = 16.0$, $a_H = 4.0$ G) for the photolysis of $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution.[1] The coupling parameters are similar to those obtained ($a_N = 15.85$, $a_H = 3.4$ G) for the $\dot{C}H_3$ adduct of bbao in the photo-Kolbe reaction of CH_3CO_2H on oxide–semiconductor particles.[17] Thus, the signal in Figure 3(*d*) is likely to be due to the adduct of the $\dot{C}H_3$ radical formed by the acetic acid oxidation but the possibility of a bbao–OH adduct cannot be excluded.

Discussion

In considering a photoreaction mechanism for the polymolybdate(VI) in the presence of acetic acid, salient points from the experimental results that must be accommodated include the following: $\varphi_{Mo^V} \gg \varphi_{CO_2} > \varphi_{CH_4}$ and φ_{H_2succ}; acidic proton as an origin of one of the methane hydrogens; and the formation of the $\dot{O}H$ radical as the water oxidation product. The results provide a similarity to the photochemistry of the $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution with respect to three points:[1] (*a*) $[Mo_7O_{24}]^{6-}$ as a predominant polymolybdate(VI) in aqueous solutions at pH 7—3[18] and formation of mixed-valence blue species due to Mo^V; (*b*) $\varphi_{Mo^V} \gg$ quantum yield of the $[NH_3Pr^i]^+$ oxidation; and (*c*) formation of $\dot{O}H$ radical.

The addition of acetic acid–sodium acetate to the $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution, keeping the solution pH constant, brought about a decrease in the rate of u.v.-induced formation of propylene as an oxidation product of $[NH_3Pr^i]^+$ with an

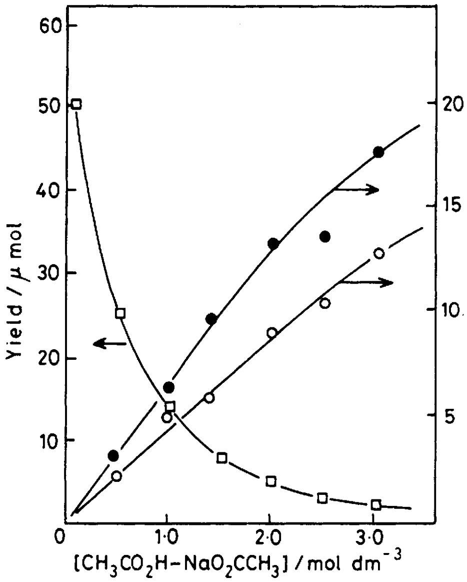
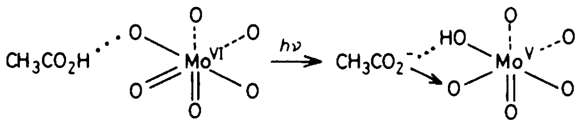


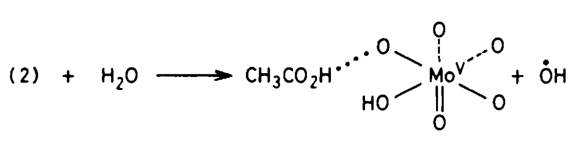
Figure 4. The effect of acetic acid–acetate on propylene formation by the photolysis for 5 h (λ > 330 nm light) of deaerated $[\mathrm{NH_3Pr^i}]_6[\mathrm{Mo_7O_{24}}]$ (14.2 mmol dm^{-3}) solution (at pH 5.4) at room temperature: propylene (□); $\mathrm{CO_2}$ (●); $\mathrm{CH_4}$ (○)

accompanying increase in the rate of the formation of $\mathrm{CO_2}$ and $\mathrm{CH_4}$, as shown in Figure 4. From the similarity between acetic acid and $[\mathrm{NH_3Pr^i}]^+$ concerning the photoreduction of the polymolybdate(VI), therefore, it is reasonable to assume that the mechanistic behaviour of acetic acid in the photoreduction of the polymolybdate(VI) is similar to that of the alkylammonium cation.[1-3] Thus, the steps outlined in equations (iv)—(vi) are suggested.

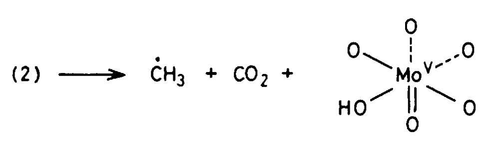


(iv)

(2)



(v)



(vi)

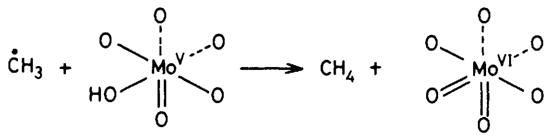
Light of energy greater than the l.m.c.t. band (≥3.1 eV) in a terminal Mo=O bond causes the formation of a $\mathrm{Mo^V}$–hole (free electron centre generated on the oxygen atom) pair, whose recombination is partially prevented probably by the transfer of an acetic acid proton to a bridging oxygen at the $\mathrm{MoO_6}$ site of the polymolybdate(VI).* Thus, the creation of a hypothetical charge-transfer complex (2) resulting from an interaction between acetate anion and the hole on the oxygen atom will be governed by two factors: the polymolybdate(VI) species and the value $\mathrm{p}K(\mathrm{CH_3CO_2H}) = 4.76$. The pH dependence of φ, showing an optimum pH around 3 (Figure 2), can be interpreted in terms of susceptibility to formation of (2). The $[\mathrm{Mo_7O_{24}}]^{6-}$ species, which are predominant at pH 7—3, are converted into $[\mathrm{Mo_8O_{26}}]^{4-}$ at pH <3.[18] Therefore, a decrease in φ at pH < 3 may be due to the structural change of the polymolybdate anions, if we assume that $\varphi_{\mathrm{Mo^V}}$ for $[\mathrm{Mo_8O_{26}}]^{4-}$ is lower than for $[\mathrm{Mo_7O_{24}}]^{6-}$. An increase in pH in the range $3 \leqslant \mathrm{pH} \leqslant 7$, leading to a decrease in the rate of the proton transfer from acetic acid, results in a decrease in φ. In addition, the predominance of non-photoactive $\mathrm{MoO_4^{2-}}$ species at pH levels exceeding 7 results in no observable photoreaction.[18,19] Complex (2) leads to the oxidation of water ($\dot{\mathrm{O}}\mathrm{H}$ formation) or acetate (the Kolbe process). The rapid decomposition of the $\mathrm{CH_3CO_2}\cdot$ radical, leading to the $\dot{\mathrm{C}}\mathrm{H_3}$ radical and $\mathrm{CO_2}$, prevents any reverse reaction.[5] The quantum yield trend of $\varphi_{\mathrm{Mo^V}} \gg \varphi_{\mathrm{CO_2}}$ reflects an occurrence of equation (v) to a large extent [equation (vi) to a small extent] and a slight decrease in φ with increasing light intensity suggests the occurrence of back reactions for equations (iv) and (v). There was no detection of $\mathrm{H_2O_2}$, $\mathrm{O_2}$, or diperoxoheptamolybdate(VI).[20] This implies the predominance of the reaction between $\dot{\mathrm{O}}\mathrm{H}$ and the polymolybdates(VI) probably leading to the condensed polymolybdate(VI). However, further speculation is inappropriate, since the OH adduct of polymolybdate is not isolated at present.

The isotopic labelling experiments excluded the possibility of hydrogen abstraction from the acetic acid methyl by $\dot{\mathrm{C}}\mathrm{H_3}$ radicals. Therefore, the formation of succinic acid indicates that $\dot{\mathrm{O}}\mathrm{H}$ radicals abstract the acetic acid methyl hydrogen to yield $\dot{\mathrm{C}}\mathrm{H_2CO_2H}$-$\dot{\mathrm{C}}\mathrm{H_2CO_2^-}$ radicals,[21] resulting in dimerization [equations (vii) and (viii)].

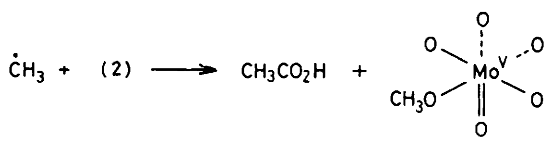
$$\dot{\mathrm{O}}\mathrm{H} + \mathrm{CH_3CO_2H}\ (\text{or } \mathrm{CH_3CO_2^-}) \longrightarrow \mathrm{H_2O} + \dot{\mathrm{C}}\mathrm{H_2CO_2H}\ (\text{or } \dot{\mathrm{C}}\mathrm{H_2CO_2^-}) \quad \text{(vii)}$$

$$2\dot{\mathrm{C}}\mathrm{H_2CO_2H}\ (\text{or } \dot{\mathrm{C}}\mathrm{H_2CO_2^-}) \longrightarrow (\mathrm{CH_2CO_2H})_2\ [\text{or } (\mathrm{CH_2CO_2^-})_2] \quad \text{(viii)}$$

Ethane, the usual Kolbe product from acetic acid electrolysis,[4] was formed in trace yield. Furthermore, the presence of propionic acid, methanol, and formaldehyde, likely products from $\dot{\mathrm{C}}\mathrm{H_3}$ radicals, was not verified experimentally. Although the redox potential of $\dot{\mathrm{C}}\mathrm{H_3}$ radicals in aqueous surroundings



(ix)



(x)

---

* In the $\mathrm{MoO_6}$ site where six oxygen atoms are bonded to molybdenum, there is sharing of the metal *d*π orbitals among the oxygens and so the extent of π bonding between molybdenum and any one oxygen is less. On l.m.c.t. photoexcitation, such *d*π electrons may move toward the positive hole on the oxygen atom because of the latter's attraction, and the repulsion set up by the relative preponderance of the negative charge on the $\mathrm{Mo^V}$ atom. This may result in the stabilization of the hole generated on the oxygen atom.

is not known,[5] it is possible to say that the formation of methane results from the reductive route of $\dot{C}H_3$ radicals. Thus, further follow-up processes [equations (ix) and (x)] of $\dot{C}H_3$ radicals are proposed as shown on the previous page. The reoxidation [equation (ix)] of the photoreduced octahedral site by the $\dot{C}H_3$ radical will result in a decrease of φ_{Mo^V} and compete with photoalkylation [equation (x)]. The photoalkylation process, which has been reported in a study of the photoreduction of tetrabutylammonium dichromate(VI),[22] may be supported by the fact that $\varphi_{CO_2^{\cdot}} > \varphi_{CH_4}$.

References

1 T. Yamase, Y. Sasaki, and T. Ikawa, *J. Chem. Soc., Dalton Trans.*, 1981, 628.
2 T. Yamase, *J. Chem. Soc., Dalton Trans.*, 1978, 283.
3 T. Yamase, *J. Chem. Soc., Dalton Trans.*, 1982, 1987.
4 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1977, **99**, 7729.
5 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 2239, 5985.
6 T. Yamase and T. Ikawa, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 746.
7 W. D. Emmons, *J. Am. Chem. Soc.*, 1957, **79**, 5739, 6522.
8 ‘ Lange's Handbook of Chemistry,’ 11th edn., ed. J. A. Dean, McGraw-Hill, New York, 1973, pp. 5—15.
9 C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1953, **220**, 104.
10 Ref. 8, pp. 10—16.
11 F. Feigl, ‘ Spot Tests in Organic Analysis,’ 7th edn., Elsevier, Amsterdam, 1966, p. 115.
12 P. R. Marriott, M. J. Perkins, and D. Griller, *Can. J. Chem.*, 1980, **58**, 803.
13 G. R. Buettner and L. W. Oberley, *FEBS Lett.*, 1980, **121**, 161.
14 E. Finkelstein, G. M. Rosen, and E. J. Rauckman, *Arch. Biochem. Biophys.*, 1980, **200**, 1.
15 E. G. Adams and P. Wardman, ‘ Free Radicals in Biology,’ ed. W. A. Prylor, Academic Press, New York, 1977, vol. 3, p. 53.
16 C. S. Lai and L. H. Piette, *Biochem. Biophys. Res. Commun.*, 1977, **78**, 51.
17 B. Krauetler, C. D. Jaeger, and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 4903.
18 W. P. Griffith and P. J. B. Lesniak, *J. Chem. Soc. A*, 1969, 1066; J. Aveston, E. W. Anacker, and J. S. Johnson, *Inorg. Chem.*, 1965, **3**, 735.
19 T. Yamase and T. Ikawa, *Inorg. Chim. Acta*, 1980, **45**, L55.
20 I. Larking and R. Stomberg, *Acta Chem. Scand.*, 1972, **26**, 3708.
21 ‘ Free Radicals,’ ed. J. K. Kochi, John Wiley, New York, 1973, vol. 1, p. 82.
22 D. Rehorek, W. Winkler, R. Wagener, and H. Hennig, *Z. Chem.*, 1982, **22**, 112.

Received 17*th January* 1983; *Paper* 3/063