

Vanadium-Sensitized Photochemistry of Heteropoly Compounds. Mixed Molybdo- and Tungstovanadates

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Received January 2, 1986

Incorporation of vanadium into 1:12 heteropoly compounds (HPC) shifts the absorption to higher wavelengths, thus allowing photochemistry to be performed well into the area of high-intensity solar light. $PV_2Mo_{10}O_{40}^{5-}$ ($V^V_2Mo_{10}$) and $PV_2W_{10}O_{40}^{5-}$ ($V^V_2W_{10}$) were selected, for stability reasons, for this purpose. The improved photosensitivity toward the visible region, however, was not accompanied by an improvement of results. Quantum yield (qy) of the one-electron-photoreduced product, obtained at the O-V^V CT bands, was about 4 times less (2-3%) for tungstovanadates, and about 10 times less (0.1-0.3%) for molybdovanadates relative to the qy at the O-W^{VI} and O-Mo^{VI} CT bands, respectively. Irradiation with $\lambda > 400$ nm, i.e. at the O-V^V CT bands, would place a maximum of two electrons only on vanadium ions. Under these conditions no hydrogen was produced. For irradiation with $\lambda < 400$ nm, i.e. at the O-Mo^{VI} and O-W^{VI} CT bands, tungstovanadate was not further reduced and no hydrogen was evolved contrary to the case for 1:12 tungstates; molybdovanadate, on the other hand, was reduced past two electrons, and hydrogen was evolved with a qy < 0.01.

Introduction

One aspect of solar energy research in the last few years has been the photocatalytic splitting of water into hydrogen and oxygen. Several systems have been used employing, mainly, Ru-(bpy)₃²⁺ as photosensitizer and MV²⁺ as relay, whereas EDTA and or triethanolamine are used as sacrificial reagents in the production of hydrogen with Pt catalyst.²

We have indicated,³ and subsequently shown, among others, that heteropoly compounds (HPC) of the 1:12 and 2:18 structure and isopoly compounds are photosensitive in the near-visible and UV areas, producing stepwise multielectron reduction products,⁴ and that these products, depending on thermodynamics, are able to produce hydrogen with and without Pt catalyst.⁵ The production of H₂ and the concomitant oxidation of organic compound are catalytic in nature. Under carefully controlled conditions HPC have worked for over 30 cycles without signs of decomposition. Quantum yields for H₂ production have been shown to be of the order of 1-2%.^{5e} In the presence of O₂, photoreduced HPC, again depending on thermodynamics, are reoxidized, the net reaction being the photocatalytic oxidation of organic compounds.⁶

There is an advantage in using HPC in solar energy conversion and storage as hydrogen, in that one compound works as photosensitizer, relay, and catalyst. In reality, apart from the sacrificial reagent it is a one-component system. However, the light of excitation is limited to near-visible and UV light essentially below 400 nm, at least for tungstates. Hence these compounds, while being shown to be good relays, are not effective photosensitizers.

Our efforts have been directed to incorporate chromophores to move the absorption toward visible light. The most obvious and least troublesome was to incorporate vanadium in HPC by using the known mixed heteropolyvanadates, known to absorb considerably in the visible region.

This paper reports on the photochemistry of mixed molybdo- and tungstovanadates $\{PV_2Mo_{10}O_{40}\}^{5-}$ and $\{PV_2W_{10}O_{40}\}^{5-}$ designated for simplicity as $V^V_2Mo_{10}$ and $V^V_2W_{10}$. It also reports,

either verifying literature and/or presenting new data, on their basic chemistry, i.e. electrolytic reduction, spectra, and stability under conditions of different pH and concentration of organic compounds. These compounds were chosen because of their relative stability vs. other mixed HPC. As far as photochemistry is concerned, it examines the effect of various organic compounds in connection with λ , pH, and intensity of radiation. It also deals with attempts made to produce H₂ from photoreduced mixed HPC.

While this work was in progress Ganelina et al. have reported on the photoreduction of isopolyvanadates and a series of tungstovanadates.⁷ Generally their results, wherever there is an overlap of investigation, are in good agreement with ours.

Experimental Section

$V^V_2W_{10}$ and $V^V_2Mo_{10}$ were prepared according to well-established literature procedures.⁸ Analysis performed by atomic absorption spectroscopy on V, Mo, and W and gravimetric methods on P and Mo has given the following results. Calcd for tungstovanadate $H_5PV_2W_{10}O_{40} \cdot 10H_2O$: V, 3.64; W, 65.74. Found: V, 3.73; W, 64.12. Calcd for molybdovanadate $H_5PV_2Mo_{10}O_{40} \cdot 34H_2O$: V, 4.34, Mo, 40.81; P, 1.32. Found: V, 4.37; Mo, 40.60; P, 1.29. They were also analyzed by polarography and spectra although the latter are not so well-defined. Polarography was performed with a Princeton Applied Research Model 174A polarograph employing a glassy-carbon electrode. Solutions of 1×10^{-3} M $H_5[PV_2W_{10}O_{40}]$ in 2 M 2-propanol buffered to pH 4.5-5.0 with NaH₂PO₄ (0.1 M) and Na₂HPO₄ (0.36×10^{-2} M), which served as supporting electrolyte as well, revealed two well-defined one-electron waves at $E_{1/2} = 0.34$ and 0.04 V vs. SCE, in agreement with the literature,¹⁶ followed by a large, pH-dependent wave beginning at -0.9 V vs. SCE. In the absence of tungstovanadate the above solution gave a large hydrogen wave beginning at -1.2 V vs. SCE. Solutions of 7×10^{-4} M $H_5[PV_2Mo_{10}O_{40}]$ in 7 M 2-propanol, pH 2.7, in NaH₂PO₄ (0.12 M) and HClO₄ (0.09 M) were also reduced stepwise at $E_{1/2} = 0.36, 0.02, -0.06,$ and -0.24 V vs. SCE, again in accordance with literature data.⁹

ESR spectra were obtained with a Bruker ER 2000D-SRC spectrometer using a Suprasil flat cell.

The UV-vis spectra of tungstovanadate, of oxidized and reduced forms by one and two electrons, were according to the literature;¹⁰ see Figures 1 and 2.

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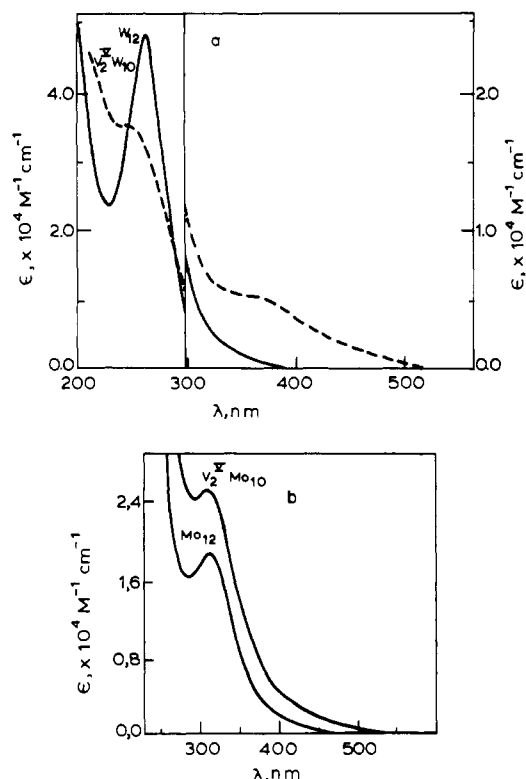


Figure 1. Spectra of nonreduced HPC showing the shift in absorbance toward the visible region with incorporation of V^{5+} ions. $W_{12} = PW_{12}O_{40}^{3-}$, $V^2W_{10} = PV_2W_{10}O_{40}^{5-}$, $Mo_{12} = PMo_{12}O_{40}^{3-}$, and $V^2Mo_{10} = PV_2Mo_{10}O_{40}^{5-}$.

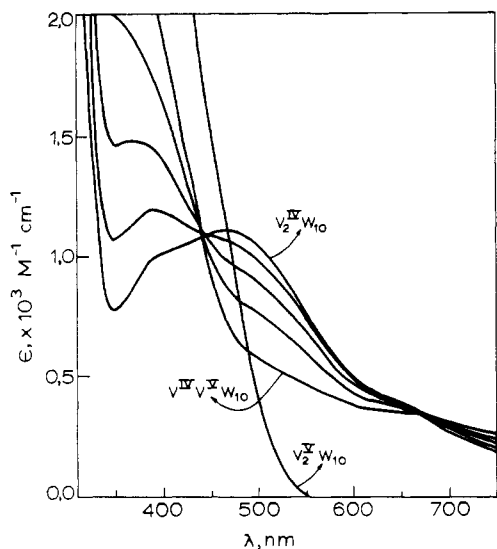


Figure 2. Spectra of $PV_2W_{10}O_{40}^{5-}$ (V^2W_{10}) photoreduced by one ($V^{IV}V^VW_{10}$) and two ($V^{IV}V^2W_{10}$) electrons.

The spectra of one- and two-electron-reduction products of molybdovanadate are not reported in the literature. The spectra were obtained by adding stoichiometric amounts of Cr^{2+} and are shown in Figures 1 and 3. The corresponding spectra of products obtained photochemically were identical.

Photolysis was performed with a 100-W Hanovia Hg arc lamp and a 150-W Xe illuminator, employing monochromators and filters. Limited work was also done with a 300-W Xe illuminator. Actinometry was performed with iron(III) oxalate and monitored with a selenium photocell; details have been presented elsewhere.^{5c} Solutions were deaerated with Ar scrubbed with V^{2+} or alkaline pyrogallol.

Results

Stability of Mixed HPC. Our aim has been to work under strict conditions at which the compounds in question are stable so that

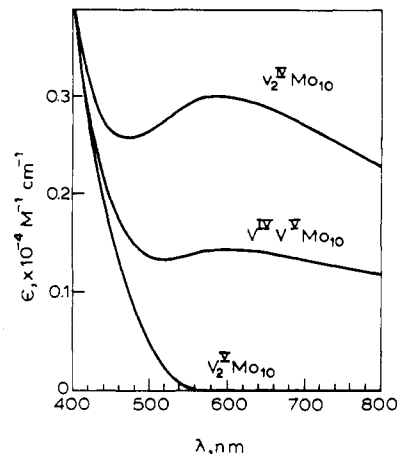


Figure 3. Spectra of $PV_2Mo_{10}O_{40}^{5-}$ (V^2Mo_{10}) reduced by one ($V^{IV}V^V$ - Mo_{10}) and two ($V^{IV}V^2Mo_{10}$) electrons after stoichiometric addition of Cr^{2+} . The photoreduced spectra were identical.

we could address basic questions with certainty.

Pope et al.¹⁰ have reported that V^2W_{10} is stable up to pH ~ 5 , whereas $V^{IV}V^VW_{10}$, i.e. reduced by one electron, is stable between pH 4–11 and $V^{IV}V^2W_{10}$ (i.e. reduced by two electrons) is unstable below pH 8.

We have worked in the pH range 4.5–5.0 adjusted with phosphate buffer. Under these conditions solutions of reduced tungstovanadates (1×10^{-3} M, as indicated above) were stable for days, whereas an aqueous solution of the nonreduced form (1×10^{-3} M) was kept for several months with no signs of decomposition.

As far as V^2Mo_{10} is concerned, it has been reported to be stable up to pH 3–3.5.^{11,12} The reduced form, according to Polotebnova et. al. lacks vanadium,¹³ whereas Matveev et al. have reported that this is a function of pH.¹⁴ It has also been reported that dioxane stabilizes both oxidized and reduced species.⁹

We have worked with solutions of molybdovanadates in 8 M isopropyl alcohol, pH 2. Under these conditions V^2Mo_{10} is stable and $V^{IV}V^VMo_{10}$ seems to return to V^2Mo_{10} without decomposition. When reduction proceeds beyond 1e molybdovanadates become less and less stable.

It should be pointed out, as suggested by one of the reviewers, that V_2W_{10} and V_2Mo_{10} are not discrete compounds but are mixtures of stereoisomers.

Spectra. According to Courtin¹⁵ the spectra of V^2W_{10} are characterized by an absorption band at ~ 250 nm and a shoulder at ~ 360 nm. The 250-nm band exists also in the corresponding compound $PW_{12}O_{40}^{3-}$ (W_{12}), i.e. without vanadium. From our spectra we estimate $\epsilon(250) \sim 3.5 \times 10^4$ $M^{-1} cm^{-1}$ and $\epsilon(360) \sim 4.5 \times 10^3$ $M^{-1} cm^{-1}$. Pope et al.¹⁶ have published the spectra of PV_xW_{12-x} with $x = 0, 1, 4-6$ but not with $x = 2$. Figure 1a shows the spectra of V^2W_{10} and W_{12} for comparison. Absorption bands, ϵ , and assignments of reduced tungstovanadates have been reported.¹⁰ The spectra we have obtained with photoreduction are in good agreement with those reported in the literature.

Figure 1b shows the spectra of V^2Mo_{10} and Mo_{12} for comparison. It can be seen that the tail of the absorption of V^2Mo_{10} extends well into the visible area.^{8a,17}

Spectra of reduced V^2Mo_{10} have not been reported in the literature. It has been shown by ESR that the first two electrons are located on vanadiums, i.e. the species that are formed are $V^{IV}V^VMo_{10}$ and $V^{IV}V^2Mo_{10}$.¹⁸ We have obtained the spectra of

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Table I. Quantum Yields for the One-Electron-Photoreduced Products of Mixed HPC in the Presence of Organic Compounds at Various Wavelengths

organic compd	λ , nm	assignt	$\Phi(V^{IV}V^VW_{10})^a$	$\Phi(V^{IV}V^V-Mo_{10})^b$
alcohols ^c	509	O-V ^V ¹⁰	0.02–0.03	0.001–0.003
alcohols	436	O-V ^V	0.002–0.03	0.001–0.003
alcohols	365	O-V ^V	0.02–0.03	0.001–0.003
alcohols	252	O-W ^{VI}	0.08	0.02
ethanoic acid	<i>d</i>		0.0	0.0

^a Conditions: $[V_2W_{10}] = 1 \times 10^{-3}$ M and [organic compd] ~ 2 M, at pH 4.5–5.0 with phosphate buffer. ^b Conditions: $[V_2Mo_{10}] = 5 \times 10^{-4}$ M, and [organic compd] ~ 8 M, pH ~ 2.7 with HClO₄. Solutions were deaerated with Ar. ^c Alcohols studied were isopropyl alcohol, ethanol, and glycol. ^d At all above wavelengths.

$V^{IV}V^VMo_{10}$ and $V^{IV}V^VMo_{10}$ by stoichiometric addition of Cr²⁺, for which we have obtained $\epsilon(600) \sim 1370$ M⁻¹ cm⁻¹ and $\epsilon(585) \sim 2900$ M⁻¹ cm⁻¹, respectively. Figure 3 shows the photochemically reduced species, which are similar to those stoichiometrically produced by Cr²⁺.

Photolysis of V_2W_{10} . Solutions of V_2W_{10} in presence of a variety of organic compounds at pH ~ 4.5 –5.0 adjusted with phosphate buffer, as indicated above, are photoreduced in the visible and UV regions with concomitant oxidation of the organic compounds. In case of 2-propanol the main oxidation product was acetone. Quantum yields for the one-electron-reduction product, i.e. $V^{IV}V^VMo_{10}$, as is discussed below, are shown in Table I.

Photolysis with monochromatic radiation at the O–V^V charge-transfer bands, shown in Table I, and 252 nm (O–W^{VI} CT band) did not proceed beyond the addition of one electron. On the other hand, on irradiation with the full strength of the lamps with and without a Pyrex (300 nm cutoff) filter, photoreduction proceeded up to addition of two electrons as shown in Figure 2. As can be seen, the spectra present the overall characteristics of reduced HPC, i.e. a gradual increase in absorbance around 700 nm and a decrease in absorbance at lower wavelengths, with, in addition, two isosbestic points at 450 and 680 nm.

As will be discussed below, the first two electrons are placed on vanadiums. No electrons could be placed on tungsten under the conditions used.

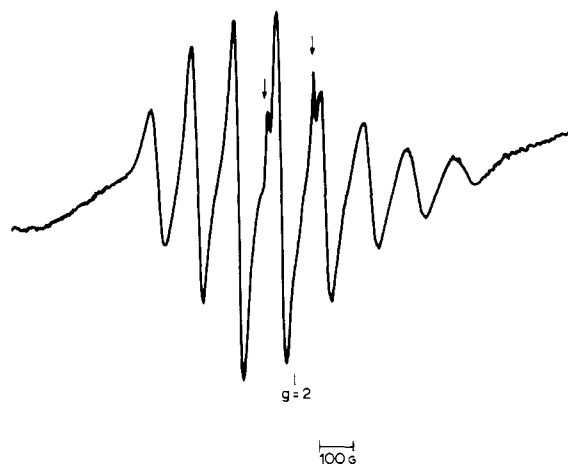
When V_2W_{10} was allowed to stand in the absence of oxygen there was no change in absorbance and, of course, no hydrogen was detected. Irradiation of the above species at the V^{IV} –W^{VI} CT bands, i.e. 576 and 509 nm, had no effect. V_2W_{10} in presence of oxygen returns slowly (hours) to $V^{IV}V^VMo_{10}$, which is not oxidized further.

Photolysis of V_2Mo_{10} . This species is also photosensitive in the presence of a variety of organic compounds, resulting in photoreduction of molybdovanadate and oxidation of the organic compound. Again the main product of 2-propanol oxidation was acetone. Quantum yields for addition of one electron at various wavelengths are shown in Table I.

Irradiation with a 400-nm cutoff filter proceeded to addition of up to two electrons whereas that with a Pyrex filter proceeded beyond the addition of two electrons.

As will be discussed below, the first two electrons are added on vanadium atoms, whereas further reduction involves molybdenum atoms. Reduction beyond two electron favors, from a thermodynamic point of view, reduction of hydrogen, which is observed. However no hydrogen was produced with a 400-nm cutoff filter, as photoreduction did not proceed beyond two electrons, as indicated above.

Photoreduced species were fully reoxidized in the presence of atmospheric oxygen. This reaction was also slow requiring a few hours for complete reoxidation.

**Figure 4.** ESR spectrum, at room temperature, of an aqueous solution of photochemically produced $\sim 1 \times 10^{-4}$ M $V^{IV}V^VMo_{10}$ in the presence of ~ 8 M 2-propanol, pH 2.8, with HClO₄.

It should be remembered, here, that the instability of molybdovanadate increased with the extent of reduction, as was indicated earlier.

Discussion

(a) V_2W_{10} . Under the conditions described above, tungstovanadate was able to accept photochemically up to two electrons, which have been shown to add on vanadiums. Further irradiation produced no further reduction.

One notes that polarographic reduction similarly produces $V^{IV}V^VMo_{10}$ and $V^{IV}V^VMo_{10}$ successively, for which $E_{1/2}$ values are 0.34 and 0.04 V vs. SCE, respectively, followed by further reduction located on tungsten, beginning at ~ -0.9 V vs. SCE. This is considerably more negative, as has been mentioned earlier, in accordance with the literature.¹⁶

This provides, to begin with, a reasonable qualitative explanation as to why photoreduction proceeds to addition of electrons only on vanadium. It should be recalled that the extent of reduction depends also on the intensity of radiation. Thus under monochromatic irradiation in the area of O–V^V CT bands at 508 and 436 nm and even at the O–W^{VI} CT band at 252 nm, as has been mentioned before, reduction did not proceed beyond one electron. This tends to suggest that the extent of reduction is also a matter of the intensity of the radiation and not only of wavelength.

Since no more than two electrons, located on vanadiums, could be added photochemically, under any circumstances, hydrogen was not produced in agreement with thermodynamics.

It has been reported that the absorption band around 500 nm is the V^{IV} –W^{VI} CT band.¹⁰ We thought, then, that irradiation of tungstovanadate at the V^{IV} –W^{VI} CT band would promote the electron to tungsten atoms, thereby favoring reduction of H⁺. However, the results were negative.

Another point that is worth mentioning is the inability of the one-electron-reduced product, $V^{IV}V^VMo_{10}$, to be oxidized by oxygen, contrary to the corresponding molybdovanadate with a similar half-wave potential. The difference may be attributed to kinetic reasons since, generally, reoxidation of reduced HPC by oxygen is H⁺ dependent.^{5f,23,24} It should be remembered that tungstovanadate and molybdovanadate experiments were performed at pH 4.5–5.0 and 2.7, respectively, for stability reasons. Investigation of the effect of pH on tungstovanadate reoxidation is not trivial due to the instability of the reduced forms at lower pH.

(b) V_2Mo_{10} . Photoreduction of V_2Mo_{10} under the condition described before, proceeds stepwise with the first two electrons located on vanadium atoms. Figure 4 shows the ESR spectrum of photochemically reduced, by one electron, molybdovanadate. The well-defined eight-line hyperfine structure (^{51}V , $I = 7/2$),

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superimposed on a slightly seen 15-line component, indicates that the electron is located on vanadium ions, as is the case when reduction is obtained by chemical means.¹⁸ However, one of the reviewers has pointed out that the "narrow" lines and large hyperfine splitting constant (estimated ~ 120 G) suggests that the ESR spectrum is almost certainly not of $V^{IV}V^{V}Mo_{10}$, rather it is of VO^{2+} , and that the extra lines do not indicate a 15-line component.

Further reduction involves molybdenum atoms. $E_{1/2}$ for successive addition of electrons reported in the literature and verified by this laboratory are 0.36, 0.02, and -0.24 V vs. SCE, respectively.⁹

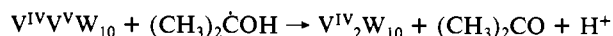
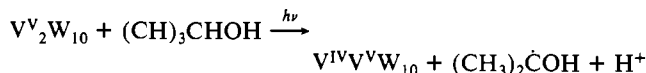
One could observe that much less energy is required to place electrons on molybdenum than on tungsten. This provides a qualitative argument as to the ability of V_2Mo_{10} to accept photochemically more electrons than the corresponding tungstate. When photoreduction proceeded over the addition of two electrons, in the absence of atmospheric oxygen, hydrogen was produced. It has been reported, and is observed here, that instability of reduced molybdovanadates increases with the extent of reduction, thus making the picture not as clear.

Reduced molybdovanadates are fully reoxidized by atmospheric oxygen. The mechanism has been discussed by Matveev and co-workers.²³

Conclusions

Incorporation of vanadium into HPC of molybdenum and tungsten has shifted the absorption to higher wavelengths thus allowing photoreduction of HPC with concomitant oxidation of organic compounds to be performed well into the area of high-intensity solar light; see Figure 1. This however was not without cost: (a) Generally incorporation of vanadium into HPC, mainly tungstates, makes the reduced HPC less stable than the corresponding "classical" heteropoly blues of the Keggin (1:12) and Dawson (2:18) structures.¹⁹ Similar instability has been observed during photolysis. However this may not be a serious problem, from a practical point of view, since catalysts of this kind operate effectively in thermal reactions.²⁰ An equilibrium is established between the mixed HPC and the decomposition products, thus allowing the system to operate despite partial decomposition. (b) Quantum yields of the one-electron-photoreduced product obtained at the O-V^V CT bands are about 4 times less for tungstovanadates and about 10 times less for molybdovanadates relative to quantum yields at the O-W^{VI} and O-Mo^{VI} CT bands respectively; see Table I. (c) Irradiation with a 400-nm cutoff filter, i.e. in the area of O-V^V CT bands, would place a maximum of only two electrons on vanadium atoms. No further reduction that would place electrons on molybdenum or tungsten, as has been shown elec-

trochemically, was observed on prolonged irradiation. Under these conditions, no hydrogen was produced. As far as V_2W_{10} was concerned, reduction did not proceed beyond the addition of two electrons on vanadium atoms even with UV irradiation and no hydrogen was produced under any circumstances. On the other hand V_2Mo_{10} would be reduced past two electrons when photolyzed with $\lambda < 400$ nm (O-Mo^{VI} bands). Under these circumstances hydrogen was evolved. (d) It has been suggested⁶ and verified²¹ that photoreduction of HPC in the presence of at least alcohols proceeds by hydrogen transfer through formation of free radicals, which are known to thermally reduce HPC.²² A similar stepwise reduction mechanism seems to operate here. If for instance, isopropyl alcohol is used, the following reactions take place:



No further photochemistry takes place upon irradiation with $\lambda > 250$ nm.

A similar stepwise mechanism is proposed for V_2Mo_{10} . Here photoreduction with $\lambda < 400$ nm proceeds beyond addition of two electrons on vanadium ions, placing electrons on molybdenum ions. Under these circumstances hydrogen is evolved, as has been stated earlier, with quantum yield < 0.01 .

It has been reported that 1:12 tungstates produce hydrogen with an efficiency of about one molecule of hydrogen per 100 photons.^{5e} No reasonable direct comparison with the hydrogen produced by those tungstates can be made because of the specificities that are represented with molybdovanadates: (a) the part of the absorption in the visible area due to incorporation of vanadium is useless as far as hydrogen production is concerned; (b) instability involved with higher reduction products makes the picture not so clear.

Acknowledgment. We thank M. Z. Hoffman and G. Pneumatikakis for helpful discussions and comments and G. Papacostidis and V. Petrouleas for assistance with polarography and ESR respectively. E.P. and M.Z.H. acknowledge financial support from NATO.

Registry No. $PV_2W_{10}O_{40}^{5-}$, 58071-94-6; $PV_2Mo_{10}O_{40}^{5-}$, 60440-70-2; $V^{IV}V^{V}Mo_{10}$, 57127-16-9; $V^{IV}_2Mo_{10}$, 104574-62-1; $V^{IV}V^{V}W_{10}$, 56188-76-2; $V^{IV}_2W_{10}$, 56188-74-0; H_2 , 1333-74-0; isopropyl alcohol, 67-63-0; ethanol, 64-17-5; glycol, 107-21-1.