Inorganica Chimica Acta, *87* (1984) 177–180

Photochemistry of Heteropoly Electrolytes: the 1:12 Tungstates

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Received November 23, 1983

1:12 tungstates are photosensitive in near visible and ultra-violet areas at the oxygen to metal charge transfer bands, in the presence of a great variety of organic reagents. Photosensitivity results in multi-electron reduction of tungstates with concomitant oxidation of organic compounds. Photosensitivitiy follows the order $PW_{12}O_{40}^{3-} > SiW_{12}O_{40}^{4-} > FeW_{12}O_{40}^{5-} > H_2W_{12}O_{40}^{6-}$*, which is the same order with increasing negative redox potentials. Maximum quantum yield ~15% is obtained with high concentrations of organic reagents (1–10 M). The reduced heteropoly compounds (HPC) are easily re-oxidized by atmospheric oxygen. They are also capable of reducing hydrogen ions and this limits the extent of photoreduction.*

Introduction

The photosensitivity of polyoxotungstates and molybdates in the presence of organic reducing reagents has been recognized in the past. Photographic processes based on this phenomenon have been patented [1]. As early as 1916 Rindl observed the photosensitivity of HPC [2]. Subsequent work by Chalkley showed that PW_{12}^{3-} undergoes one-electron reduction when exposed to sunlight in the presence of organic reducing reagents [3]. Chalkley patented this property for possible use in photography [1c, 4].

Recently various Russian workers have investigated the photoreduction of molybdenum and tungsten for analytical purposes [5], whereas Yamase has studied the photochemistry of various alkylammonium salts of isopoly compounds of molybdenum and tungsten [6].

It is well documented that HPC are capable of multi-electron reductions in distinct reduction steps without decomposition [7]. On the other hand, compounds that are multi-electron reducing reagents are recently in demand as potential reductants for nitrogen and carbon dioxide and for splitting water.

We have recently demonstrated that $P_2Mo_{18}^{6-}$ is photosensitive in the presence of a great variety of organic compounds, accepting photochemically up to six electrons [8]. We have also shown that various HPCs function as catalysts in the photochemical oxidation of a great variety of organic compounds with solar radiation [9].

This paper deals with the basic photochemical studies of a series of 1:12 heteropoly tungstates with Keggin structure, namely $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $FeW_{12}O_{40}^{5-}$, and $H_2W_{12}O_{40}^{6-}$ designated for simplicity as PW_{12}^{3-}, SiW_{12}^{4-}, FeW_{12}^{5-} and $H_2W_{12}^{6-}$ respectively.

Experimental

Literature methods were used for the preparation of HPC [11]. All chemicals were of analytical grade.

Deaerated aqueous solutions of HPC in presence of organic compounds were photolysed at time intervals. Photolysis was performed with a high pressure Hg arc and a 150 W Xe lamp using filters or a monochromator. Actinometry was performed with potassium iron(III) oxalate. Details have been presented elsewhere [8].

Results and Discussion

When deaerated solutions of 1:12 tungstates with Keggin structure are exposed to near visible and UV light in the presence of a great variety of organic compounds, they undergo multielectron photoreduction producing heteropoly blue products (HPB), with concomitant oxidation of organic compounds.

The formation of one-electron blue products follows zero order kinetics. The photoreaction could be easily followed by the characteristic spectra of the HPB [10]. As is well known, reduction of HPC is characterized by broad intense absorption around 700 nm, which is generally proportional to the number of added electrons [10]. Figure 1 shows typical formation spectra of some photochemically reduced tungstates.

*Part of Ph.D. Thesis.

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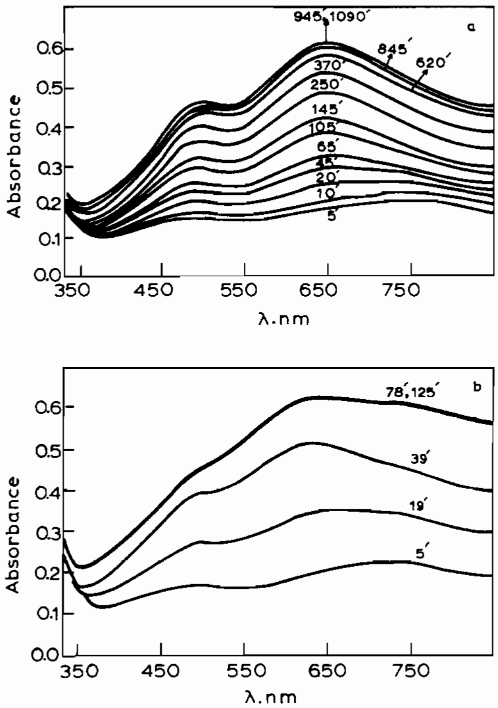

Fig. 1. Gradual formation of reduced HPC by photolysis of deaerated solutions in the presence of organic cpds. (a) PW_{12}^{3-}, 1×10^{-4} *M*; C_2H_5OH, 2 *M* in 0.1 *M* $HClO_4$; photolysis with high pressure Hg lamp with pyrex filter. (b) SiW_{12}^{4-}, 1×10^{-4} *M*; isopropyl alcohol 2 *M* in 0.1 *M* $HClO_4$; 150 W Xe lamp with pyrex filter.

Photosensitivity is a function of HPC used, and the nature and concentration of the organic reagent. Table I shows the quantum yield of the one-electron reduction product of PW_{12}^{3-} in the presence of various organic reagents with 254 nm light. Table II compares the quantum yields of the various HPC used.

It can be seen that photoreduction follows the order $PW_{12}^{3-} > SiW_{12}^{4-} > FeW_{12}^{5-} > H_2W_{12}^{6-}$ which is the same order as the increasing negative redox potential [11].

Generally photosensitivity, with minor exceptions, increases with concentration of HPC up to the point where there is 'complete' absorption of the incident light by HPC. Photosensitivity is also a function of the nature and concentration of the organic reagent.

The relative photoreducing ability of organic reagents toward PW_{12}^{3-} follows the order: primary and secondary alcohols > methanol, diols > hydroxy acids, tertiary alcohols > aminoacids, mono and dicarboxylic acids; Table I. A similar overall order is followed with $P_2Mo_{18}O_{62}^{6-}$ [6]. Photosensitivity increases with concentration of the organic compounds. However, the maximum concentration at which saturation of photosensitivity is obtained varies with the HPC used. For instance, for PW_{12}^{3-},

TABLE I. Quantum Yield of Formation of the 1-Electron Reduction Product of PW_{12}^{3-}, at 254 nm, in the Presence of Various Organic Compounds in $HClO_4$, 0.1 *M*.

Organic additive	*M*	PW_{12}^{3-}, *M*	$\Phi(PW_{12}^{4-})$
CH_3OH	1	5×10^{-4}	0.11
C_2H_5OH	1	5×10^{-4}	0.15
$CH_3CH_2CH_2OH$	1	5×10^{-4}	0.15
$(CH_3)CHOH$	1	5×10^{-4}	0.13
$(CH_3)COH$	1	5×10^{-4}	0.08
CH_2OHCH_2OH	0.5	5×10^{-4}	0.02
$CH_2OHCOOH$	1	1×10^{-3}	0.10
$CH_3CHOHCOOH$	1	5×10^{-4}	0.07
CH_3COOH	0.01	5×10^{-4}	0.03
$(COOH)_2$	0.5	1×10^{-3}	0.02
$CH_2(COOH)_2$	0.01	5×10^{-4}	0.02
$(CH_2)_3(COOH)_2$	1	1×10^{-3}	>0.01
$(CH_2OHCH_2)_3N$[a]	0.1	1.5×10^{-4}	0.05
$CH_2(NH_2)COOH$	1	1×10^{-3}	<0.01
$CH_3CH(NH_2)COOH$	0.5	5×10^{-4}	0.01

[a]$HClO_4$, 0.26 *M*. A white precipitate is formed at PW_{12}^{3-} concentrations larger than 2×10^{-4} *M*.

TABLE II. Comparative Photoreduction of Various HPC 5×10^{-4} *M*, in the Presence of Various Concentrations of Isopropyl Alcohol at 254 nm.

Isopropyl alcohol *M*	Φ of 1-electron reduction products			
	PW_{12}^{4-}	SiW_{12}^{5-}	FeW_{12}^{6-}	$H_2W_{12}^{7-}$
0.1	0.12	a	a	a
1.0	0.13	0.05	a	a
5.0	0.12	0.09	0.02	a
10.0		0.10	0.03	a

[a]Values less than 0.01. This is mainly due to thermal reoxidation by H^+ resulting in evolution of H_2; see text.

maximum photosensitivity is obtained with ~1 *M* organic reagent, whereas, for the other HPC maximum photosensitivity is obtained around 10 *M*. However, some abnormalities exist. For instance, in the presence of ethylene glycol, acetic acid and malonic acid, photosensitivity drops with higher concentrations. Similar results have also been obtained elsewhere [12].

The large concentrations (~10 *M*) required to quench the excited state indicate its short life-time. Attempts to obtain light emission from PW_{12}^{3-} and $P_2Mo_{18}^{6-}$, in the presence and absence of isopropyl alcohol upon excitation with <400 nm, were not successful. Again, no emission was observed from frozen solutions obtained from PW_{12}^{3-} and $P_2Mo_{18}^{6-}$ dissolved in EPA (5 parts ether, 5 parts 2-methyl butane and 2 parts ethyl alcohol). An order of magnitude of the life time of the excited HPC is obtained from $\tau = 10^{-4}/\epsilon_{max}$ [4], where ϵ_{max} is the extinction coefficient of the maximum absorption. For 1:12 tungstates ϵ_{max} is around 10^5 M^{-1} cm^{-1} (at 265 mm), which makes $\tau \sim 10^{-9}$ sec.

The maximum number of electrons added photochemically is a function of the HPC used, the organic reagent, and the intensity of the incident light. Table III shows the maximum number of electrons added on PW_{12}^{3-} in the presence of various organic reagents, under certain conditions. Addition of electrons drives the redox potentials to more negative values. Photolysis proceeds until the redox potential is negative enough to reduce H^+. Back reoxidation with concomitant hydrogen evolution then competes with photoreduction and a steady state is produced. Thus the maximum number of electrons obtained under identical conditions, follows the order $PW_{12}^{3-} > SiW_{12}^{4-} > FeW_{12}^{5-} > H_2W_{12}^{6-}$.

HPB, although absorbing strongly around 700 nm, are not photosensitive in visible light. This suggests that the metal to metal (M^{5+}–O–M^{6+}, where M = Mo or W) charge transfer bands, and d–d transitions of the d^1 metal ions, do not contribute to the photosensitivity [10, 13, 14]. Photosensitivity involves only the oxygen to metal charge transfer bands. This is shown in Fig. 2, where the quantum yield of the one-electron reduction product of PW_{12}^{3-} appears to be independent of wave length of irradiation in the oxygen to metal charge transfer bands.

TABLE III. Maximum Number of Electrons Added Photochemically on PW_{12}^{3-} in the Presence of Organic Reagents. PW_{12}^{3-}, 1×10^{-4} *M*, in 0.1 *M* $HClO_4$. Solutions deaerated with Ar and photolysed with high-pressure Hg lamp with pyrex filter.

Organic reagent	*M*	Number of added electrons
CH_3OH	2	2.13
CH_3CH_2OH	2	2.58
$CH_3CH_2CH_2OH$	2	2.06
$CH_3CHOHCH_3$	2	2.79
$(CH_3)_3COH$	2	1.2
CH_2OHCH_2OH	2	2.13
$CH_3CHOHCOOH$	2	1.59
CH_3COOH	0.5	0.85
$(COOH)_2$	0.5	0.61
$CH_2(COOH)_2$	0.5	0.85
$(CH_2OHCH_2)_3N$[a]	0.1	1.21
$CH_3CH(NH_2)COOH$	0.5	1.04
CH_3COCH_3	0.02	1.09

[a]In $HClO_4$, 0.26 *M*.

Tests to show formation of aggregates have been inconclusive. Several methods were used, including NMR Raman, UV and V spectra. Results have shown solvation by roughly 1 to 2 organic molecules per HPC. Minor association of HPC with organic species has also been reported [16]. A literature method [12], based on not necessarily valid assumptions,

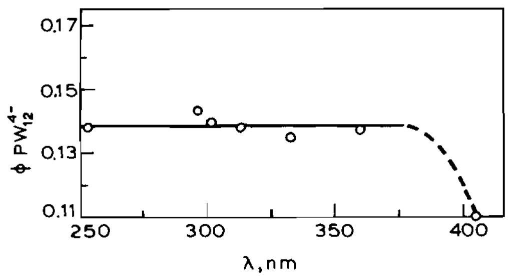

Fig. 2. Variation of $\Phi(PW_{12}^{4-})$ with wave length PW_{12}^{3-}, 4×10^{-3} *M*; isopropyl alcohol 1 *M* in 0.1 *M* $HClO_4$.

also gave similar results. Precipitation of $P_2Mo_{18}^{6-}$ in pure isopropyl alcohol showed 0.8 molecules of isopropyl alcohol per HPC. Generally, the intensity of shoulders of the oxygen to metal charge transfer bands, of HPC in presence of organic compounds, increases slightly but no significant shift of the peak of the absorption bands is observed [8, 15].

It has been stated earlier that excitation involves the oxygen to metal charge transfer band which renders the excited state a better oxidizing reagent than the ground state (tungsten atoms in the nonreduced species are in +6 oxidation state and therefore only reduction of HPC can take place). Excitation then results in reduction of HPC with concomitant oxidation of the organic species.

Photoreduction seems to be a hydrogen transfer process rather than electron transfer. For instance, photosensitivity in the presence of tertiary butyl alcohol, which is known not to render H atoms easily, is minor, whereas in the presence of Fe^{2+} no reaction takes place either thermally or photochemically. $P_2Mo_{18}^{6-}$ in the presence of excess Fe^{2+} turns blue thermally

$$P_2Mo_{18}^{6-} + 2Fe^{2+} \longrightarrow P_2Mo_{18}^{8-} + 2Fe^{3+}$$

The standard free energy calculated from the concentrations of the species involved in solution, and also from thermodynamic data, is of the order of 15 to 30 kj. However upon shining light the reaction did not proceed toward the products, but rather the reverse reaction took place by ~15%. In the dark, again, the forward reaction took place. This process was repeated many times with no loss in reactivity. Unfortunately photolysis drives the reaction toward the exoergonic direction. What is to be noted is that no forward reaction takes place with light, suggesting the necessity of H atoms. It should be noted, however, that inorganic reducing reagents such as Cr^{2+}, V^{2+} and Eu^{2+}, as well as organic reducing reagents, are known to thermally reduce heteropoly compounds to a certain extent. These compounds are also easily reduced electrochemically [17]. Although the mechanism of the thermal reduction by inorganic reducing reagents has not been studied, it is very likely to be by electron transfer.

Using, for instance, FeW_{12}^{5-} and ethanol the mechanism of the photoreduction can be presented as follows:

$$FeW_{12}^{5-} \xrightarrow{h\nu} FeW_{12}^{5-*} \quad (1)$$

$$FeW_{12}^{5-*} + CH_3CH_2OH \longrightarrow HFeW_{12}^{5-} + CH_3\dot{C}HOH \quad (2)$$

$$HFeW_{12}^{5-} \longrightarrow H^+ + FeW_{12}^{6-} \quad (3)$$

$$FeW_{12}^{5-} \text{ or } FeW_{12}^{6-} + CH_3\dot{C}HOH \longrightarrow FeW_{12}^{6-}, FeW_{12}^{7-} + CH_3CHO + H^+ \quad (4)$$

$$FeW_{12}^{7-} + FeW_{12}^{5-} \longrightarrow 2FeW_{12}^{6-}$$

The process is continued to higher reduction steps until hydrogen is evolved. FeW_{12}^{6-} is known to be deprotonated [17a], so that formation of $HFeW_{12}^{5-}$ is immediately followed by reaction 3. The overall mechanism proceeds through a radical (most probably $CH_3\dot{C}HOH$) which is capable of further reducing the HPC in solution [18].

Acknowledgments

We thank M. Z. Hoffman and D. Katakis for useful discussions and comments. We also thank A. Maliaris for help with the emission experiments. Financial support from NATO is gratefully acknowledged.

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