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Photochemistry of Heteropoly Electrolytes. The 18-Molybdodiphosphate

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Heteropoly and isopoly compounds are photosensitive in presence of various categories of organic compounds, forming blue products in analogy with classical reducing reagents. Solid heteropoly compounds precipitated out or dryed with alcohols or 1,4-dioxane also turn blue when they are exposed to light. Photoreduction of $\{P_2Mo_{18}O_{62}\}^{6-}$, *(*$Mo_{18}^{6-}$*), in presence of isopropyl alcohols proceeds to formation of 2, 4 and 6 electron blues. The blue reduction products, absorbing broadly at around 700 nm, are not photosensitive at this wavelength. The yield for the first two electron reduction step of* Mo_{18}^{6-} *is a function of heteropoly compound concentration and organic additive increasing with concentration of organic additive, in the case of isopropyl alcohol, up to at least 5–10 mol/dm*^{3}*. The photosensitivity is also a function of wavelength and for* Mo_{18}^{6-} *follows the absorbance of the non reduced species. It is also a function of pH as is the case of reduction,* i.e., $E_{1/2}$ *in polarography. Preliminary tests indicate that primary alcohols form aldehydes whereas secondary alcohols ketones. The results tend to suggest a kinetic encounter mechanism between the excited* Mo_{18}^{6-} *at the oxygen to metal charge transfer band and the organic additive. The species undergo interelectron or hydrogen transfer resulting in reduction of the heteropoly compound and oxidation of the organic additive.*

Introduction

Heteropoly (HPC) and isopoly compounds are known to be photosensitive in presence of reducing reagents. This property has been patented in several U.S. patents for possible use in photography; Mo^{3+} ions among others, can be used as photosensitizers in polymerization of vinyl compounds [1, 2].

The photosensitivity of HPC has been barely investigated in view of the confusion, in the literature, on the species in solution. Various Russian workers have investigated the photoreduction of Mo(VI) and W(VI) in acid media for analytical purposes [3]. In those cases various isopoly and heteropoly electrolytes had been formed depending on the experimental conditions and one is not sure as to the real nature of the reactants. There is now a much better understanding on the chemistry and structure of these compounds and this has prompted us to undertake a more systematic investigation on the subject.

This paper is concerned with the general characteristics with emphasis on the photochemistry of $\{P_2Mo_{18}O_{62}\}^{6-}$, ($Mo_{18}^{6-}$), which is a good representative of the heteropoly molybdates with Dawson's structure [4]. This compound was also selected because of its stability to hydrolytic degradation relative to other heteropoly molybdates.

Experimental

Literature methods were used for the preparation of heteropoly electrolytes [5]. No dioxane was used in recrystallizations since the adhered dioxane molecules [6] interfere with the experiments. All chemicals used were analytical grade.

Aqueous solutions of HPC with organic additives in 0.1 *M* $HClO_4$, deaerated with Ar, scrubbed with V^{2+}, were sealed and photolysed at time intervals. Spectra of the photoreduced heteropoly blues (HPB) were recorded on a Hilger-Watts and a Cary-14 spectrophotometers.

Photolysis was performed with a 254 nm low pressure Hg resonance immersion lamp, and a high pressure Hg arc lamp using either filters or a high intensity Bausch and Lomb monochromator.

Actinometry was performed with potassium iron(III) oxalate. $\{Co(NH_3)_5Cl\}^{2+}$ was also used for the 254 nm Hg immersion lamp for which (Co^{2+}) ≅

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TABLE I. Comparative Photoreduction of Aqueous Solutions of Mo$_{18}^{6-}$, 1 × 10^{-4} mol/dm^3, in Presence of Various Organic Additives 5.0 mol/dm^3 in 0.1 mol/dm^3 $HClO_4$. Solutions were Deaerated with Ar, Photolysed with High-Pressure Hg-lamp with Pyrex Filter.

Organic additive	Mo$_{18}^{8-}$ formation, Relative units
CH_3OH	1.81
C_2H_5OH	2.50
$(CH_3)_2CHOH$	1.96
$(CH_3)_3COH$	0.42
C_3H_7OH	2.44
$(CH_2OH)_2$	3.19
$CH_2OH{\bullet}COOH$	3.51
$CH_3CHOHCOOH$	5.48
$HCOOH$	0.79
CH_3COOH	0.1
$(COOH)_2$, 0.1 mol/dm^3	~0.0
$HOOCCH_2COOH$	6.45
$HOOC(CH_2)_2COOH$, 0.5 mol/dm^3	0.88
$HOOC(CH_2)_3COOH$, 1.0 mol/dm^3	1.00
NH_2CH_2COOH, 1.0 mol/dm^3	1.38
$CH_3CH(NH_2)COOH$, 1.0 mol/dm^3	1.26

0.17 [7]. Preliminary analysis for aldehydes and ketones was done with ammoniacal silver nitrate and with gas chromatography. NMR spectra were run with Varian XL 100 using Tiers salt as internal standard.

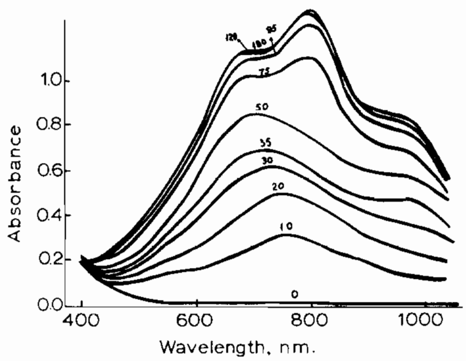

Fig. 1. Typical heteropoly blue spectra produced by photolysis of Mo$_{18}^{6-}$ with high pressure Hg-lamp with pyrex filter in presence of organic additives. This figure: Mo$_{18}^{6-}$, 5 × 10^{-5} *M*, isopropyl alcohol 5 *M* in 0.1 *M* $HClO_4$. Solution deaerated with Ar. Time (min) is indicated on spectra.

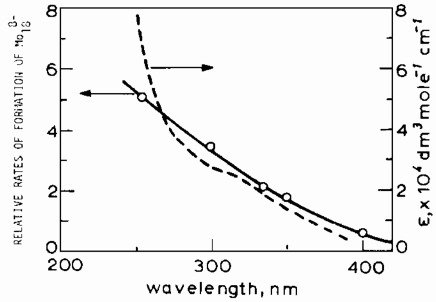

Fig. 2. Variation of the photosensitivity of Mo$_{18}^{6-}$, in presence of isopropyl alcohol, with wavelength (solid line); Mo$_{18}^{6-}$ = 1 × 10^{-4} M, isopropyl alcohol 5.0 *M*, in 0.1 *M* $HClO_4$. Absorbance of Mo$_{18}^{6-}$ (dashed line).

Results and Discussion

HPC in presence of a great variety of organic species, upon exposure to visible and ultra violet light turn blue producing the so called HPB products. Table I shows the results obtained with a pyrex filter to avoid excitation of the organic additives (Pyrex filter was used to secure higher intensities at the expense of monochromatic radiation).

The formation of HPB species follows zero order kinetics. The extent of reduction could be followed by the characteristic spectra of HPB [8]. Photoreduction of Mo$_{18}^{6-}$ proceeds by successive addition of 2, 4 and 6 electrons, as has been shown by spectra (Fig. 1) and back titration with $KMnO_4$ in the case of isopropyl alcohol (number of electrons found 5.7 ± 0.3 per Mo$_{18}^{6-}$, at the point at which no more HPB was formed with photolysis, Fig. 1). The spectra, although they have the overall characteristics of HPB they are not exactly the same in the case of 6_e^- blue. Photosensitivity is a matter of wavelength and for Mo$_{18}^{6-}$ occurs below ~550 nm (Fig. 2). The organic species are oxidized at least in the case of alcohols. Tests indicate that ethyl alcohol gives CH_3CHO whereas isopropyl alcohol ketone. Solid HPC precipitated out or dryed with alcohol or 1,4-dioxane also turn blue when they are exposed to light. Neither HPC in H_2O nor the organic additives (in particular alcohols) are photosensitive over 254 nm. Solutions of HPC in presence of organic additivex exposed to sun light do not turn blue with low concentrations of organic additives. If, however, air is excluded or when oxygen is consumed the solution turns blue. This is because the HPB formed photochemically are reoxidized by the dissolved oxygen. This property might be useful for the catalytic photooxidation of organic compounds in presence of HPC. Photoreduced Mo$_{18}^{6-}$ oxidized back with H_2O_2 gave the characteristic UV spectra of the non-reduced species.

The spectra of the non-reduced HPC of both molybdates and tungstates are characterized by oxygen to metal charge transfer bands at the near UV and UV region, and no absorption in the visible (all metal ions are Mo(VI) or W(VI) with d^0 confi-

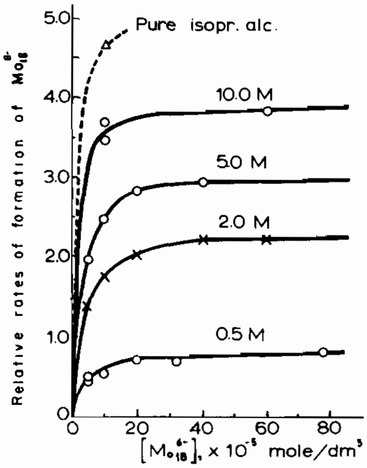

Fig. 3. Variation of the relative rates of formation of Mo_{18}^{8-} with concentration of Mo_{18}^{6-} for various concentrations of isopropyl alcohol, in 0.1 *M* $HClO_4$. High pressure Hg-lamp with pyrex filter (solution deaerated with Ar).

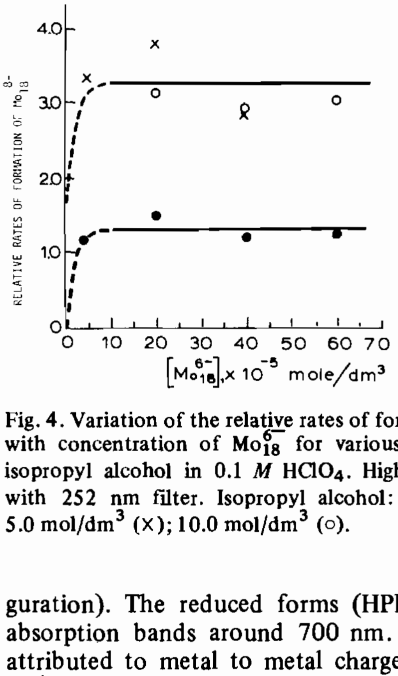

Fig. 4. Variation of the relative rates of formation of Mo_{18}^{8-} with concentration of Mo_{18}^{6-} for various concentrations of isopropyl alcohol in 0.1 *M* $HClO_4$. High pressure Hg-lamp with 252 nm filter. Isopropyl alcohol: 1.0 mol/dm^3 (●); 5.0 mol/dm^3 (X); 10.0 mol/dm^3 (○).

guration). The reduced forms (HPB) present broad absorption bands around 700 nm. These bands are attributed to metal to metal charge transfer ($M^{5+} \rightarrow M^{6+}$, M = Mo or W, and are responsible for the blue color of the compounds, and to d–d transitions of the d^1 metal ions [9–11].

The reduced heteropoly molybdate is not photosensitive over 550 nm in the presence of organic additives suggesting that the above mentioned bands of the HPB are not responsible for the photochemistry.

The relative rates of HPB formation (Mo_{18}^{8-}) is a function of HPC concentration and organic additive increasing with concentration of organic additive up to at least 5–10 mol/dm^3 (Fig. 3). Similar results have been obtained with monochromatic radiation (254 nm) (Fig. 4).

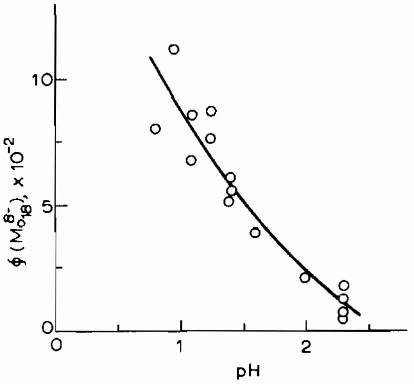

Fig. 5. Variation of $\Phi(Mo_{18}^{8-})$ with pH adjusted with $HClO_4$ at 254 nm. Mo_{18}^{6-}, 1 X 10^{-4} *M*, isopropyl alcohol 2 *M*. Solutions deaerated with Ar.

Photoreduction is pH dependent. Figure 5 shows the variation of $\Phi(Mo_{18}^{8-})$ with pH adjusted with $HClO_4$. This behaviour is reminescent of the variation of $E_{1/2}$ of the polarographic reduction with pH. It has been shown [12] that polarographic reduction involves addition of $2H^+$ per $2e^-$

$$\{P_2Mo_{18}O_{62}\}^{6-} + 2e^- + 2H^+ \rightarrow \{H_2P_2Mo_{18}O_{62}\}^{6-}$$

The variation of $\Phi(Mo_{18}^{8-})$ with pH indicates also that protonation accompanies photoreduction. This is quite reasonable since the overall photoreduction appears to be analogous to the reduction with classical reducing reagents and polarography producing Mo_{18}^{8-} [12].

Excitation seems to involve the oxygen to metal charge transfer bands of the HPC. UV spectra of the non-reduced forms of HPC show very minor change with addition of alcohols especially the tungstates. A minor overall increase is observed with no specific new bands, although the intensity of the shoulder at 241 nm of Mo_{18}^{6-} (an oxygen to metal charge transfer band) becomes slightly more pronounced. If there is an 'association' between the HPC and alcohols it must have a very low equilibrium constant. Pope and Barcza [13] have shown that HPC exhibit a very minor association with organic species. NMR studies of Mo_{18}^{6-} in presence of CH_3OH in D_2O acidified with D_2SO_4 showed no change in methyl chemical shift. The 1e$^-$ blue of the 18-tungstophosphate, $\{P_2W_{18}O_{62}\}^{7-}$, known to be paramagnetic [9], made by photolysis under above conditions showed again no change in methyl chemical shift.

Figure 3 shows that the relative rates of formation of Mo_{18}^{8-} become independent of the concentration of Mo_{18}^{6-} for concentrations greater than ≈3 X 10^{-4} *M*, no matter what the concentration of isopropyl alcohol is. In addition, experiments with monochromatic radiation (254 nm) showed that the photosensitivity is independent of the concentration of Mo_{18}^{6-}, for concentrations greater than ~5 × 10^{-5} *M, i.e.,* when the absorbance of Mo_{18}^{6-} gets to be greater than ~2.5 ($\epsilon_{254\,\mathrm{nm}} \cong 5 \times 10^4\ M^{-1}\ \mathrm{cm}^{-1}$). In other words when there is ~100% absorption of the impinging light from the HPC the photosensitivity is independent of the concentration of Mo_{18}^{6-}, no matter what the concentration of the alcohol is.

These observations, then, coupled with the fact that the photosensitivity is a function of the wavelength of absorption of Mo_{18}^{6-} (Fig. 2) is an indication that the photoactive species is Mo_{18}^{6-} at the oxygen to metal charge transfer band, rather than an associative inorganic-organic intermediate.

The photoexcited HPC reacts with the organic additives by inter-electron or hydrogen transfer resulting in the reduction of HPC and oxidation of organic additives

$$\mathrm{Mo}_{18}^{6-} \xrightarrow{h\nu} \mathrm{Mo}_{18}^{6-*}$$

$$\mathrm{Mo}_{18}^{6-*} + \mathrm{org} + 2\mathrm{H}^+ \rightarrow \mathrm{H}_2\mathrm{Mo}_{18}^{6-} + \mathrm{org(oxid.)}$$

Acknowledgements

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