

Photogalvanic Cells using Heteropoly Electrolytes

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Heteropoly compounds upon irradiation with near visible and ultra violet light, in the presence of organic reagents, undergo reduction with concomitant oxidation of the organic species which is consumed during the reaction. The potential difference developed between the photoreduced 'light' half-cell and a similar 'dark' half-cell is the basis for the photogalvanic cell studied. Connection between the two half-cells, both with Pt-electrodes, produces a current until equilibrium is established. The dark cell is air oxidized to the original non-reduced form, whereas light regenerates the reduced 'light' half-cell. With $\{PW_{12}O_{40}\}^{3-}$, 1×10^{-4} M, isopropyl alcohol ~ 0.8 M in 0.1 M $HClO_4$, maximum photopotentials of ~ 600 mV were recorded. The cycle was repeated more than 20 times with no loss in activity other than consumption of the organic reagent. Other combinations of heteropoly compounds and organic reagents can be used to optimize the results.

Introduction

Heteropoly compounds (HPC) of molybdenum and tungsten are capable of multi-electron reduction in distinct reduction steps. The reduction is reversible in that the compounds can be re-oxidized to the original species without decomposition [2]. HPC are also photoreduced in the presence of a variety of organic compounds producing the same reduction products [3].

The potential difference created between the various oxidation states, *i.e.*, between the light and dark electrode is the basis for photogalvanic action.

Whereas photogalvanic cells can be easily constructed with many chemicals that undergo photo-redox reaction, regenerative photogalvanic cells with the aim of solar energy storage capabilities limit the use of chemicals [4].

We have made use of the ease of reoxidation of some reduced HPC by oxygen and report here a regenerative photogalvanic cell using heteropoly tungstates and molybdates with various organic reagents which are consumed during the process (sacrificial

reagents). Other photogalvanic cells using molybdenum compounds, but not HPC, have been reported [5, 6].

Experimental

HPC were prepared with standard methods [7]. No dioxane was used since it interferes with the experiments. All chemicals used were analytical grade.

Photolysis was performed with a 150 watt Xenon illuminator using filters, and a 254 nm low pressure Hg resonance immersion lamp. The lamp intensity was monitored with a selenium photocell that was calibrated with potassium iron (III) oxalate. The photopotential was measured with a Beckman Model 3500 pH meter, whose impedance was much greater than $20M\Omega$, connected with a recorder.

The 'light' half-cell had a suprasil window for illumination and a Pt electrode. The dark half-cell was similar. Connection between the two electrodes was made through an agar-agar KCl bridge. In all experiments the starting solution in both electrodes was identical. Both solutions were made oxygen-free by bubbling through Ar scrubbed with V^{2+} .

Results and Discussion

When HPC are subject to illumination with near visible and UV light in the presence of a great variety of organic reagents (sacrificial reagents), they produce the known heteropoly blue products (HPB) with concomitant oxidation of the organic compound [3].

The extent of reduction depends on the HPC used, namely molybdates or tungstates, which apparently relate to the ease with which they accept electrons, and the organic reagent used. Thus, it has been shown that $\{P_2Mo_{18}O_{62}\}^{6-}$ ($P_2MO_{18}^{6-}$) in presence of isopropyl alcohol can accept 6-electrons whereas $\{PW_{12}O_{40}\}^{3-}$ (PW_{12}^{3-}) accepts 2-electrons [8].

The ease of re-oxidation of reduced HPC by oxygen is the basis for the regenerative photogalvanic action reported here.

Figure 1 shows a typical photopotential response of PW_{12}^{3-} , 1×10^{-4} M in presence of isopropyl alcohol, 0.8 M in 0.1 M $HClO_4$. The dark electrolyte was an identical solution. Care was taken to avoid any temperature difference between the two half-cells.

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[‡]See ref. [1].

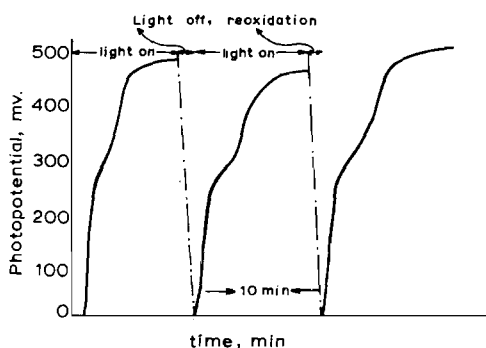


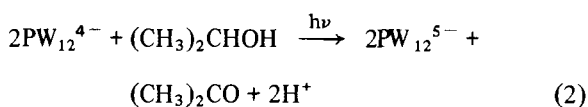
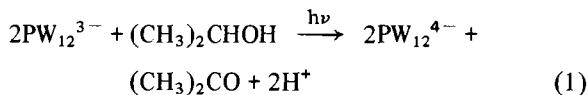
Fig. 1. Photopotential cycles between 'light' and 'dark' electrodes composed of: PW_{12}^{3-} , $1 \times 10^{-4} M$; isopropyl alcohol, $0.8 M$ in $0.1 M \text{HClO}_4$ deaerated with Ar. Light source, 150 W Xe-lamp; reoxidation by atmospheric oxygen.

Upon illumination with near visible and UV light the solution becomes bright blue, whereas that of the dark electrolyte remains colourless. The photopotential developed between the two electrodes produced, initially, $\sim 150 \mu\text{A}$ current, dropping eventually to zero. At the same time the dark electrode turns blue indicating flow of electrons (reduction) to the dark half-cell. Leaving the dark electrode open to the air brings about re-oxidation to the colorless PW_{12}^{3-} form, thereby re-establishing the dark electrode to its original form. Further illumination restores the photopotential and the cycle is repeated. The cycles could be repeated 20–30 times with no loss in activity of PW_{12}^{3-} except that alcohol had to be replenished.

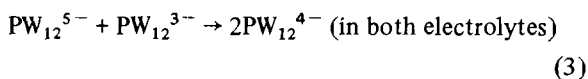
The photopotential develops in two steps, corresponding to stepwise addition of two electrons as shown in Fig. 1. This is to be expected, for it is in reality a photoredox titration similar to one obtained with reducing reagents, for example Cr^{2+} or polarography [9].

The oxidation states in the light and dark electrolytes could be followed by the characteristic spectra of the reduced (HPB) [3]. For instance, the photochemical and electrochemical reactions for PW_{12}^{3-} and isopropyl alcohol are as follows:

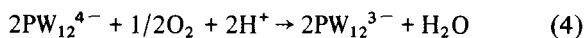
Light electrode, photochemical reactions:



Overall electrochemical reaction

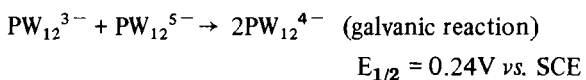


Dark electrode:



Reaction (4) restores the 'dark' electrode to its original form whereas light drives the 'light' electrode to its PW_{12}^{5-} oxidation state (reaction 2).

The half-wave potentials of the polarographically reversible reduction steps are indicated below [9]. As is well known, the latter correspond to standard redox potential unless there is a marked difference between the diffusion coefficient of the oxidized and reduced form.



Thus in principle the standard free energy corresponding to the above galvanic reaction is -23.6 kJ .

It is understood that other combinations of HPC and organic reagents can be used to optimize the energetics involved.

A rough estimate for the photogalvanic cell described shows that the yield in electric current produced relative to the light absorbed by the system is of the order of 1–3 electrons per 100 photons. This result was obtained by allowing the photopotential to reach $\sim 500 \text{ mV}$ then shutting off the light and measuring the current produced by the galvanic cell. This is the same order of magnitude with the quantum yield of ~ 7 and $\sim 0.7\%$ (under these conditions) [10] for addition of one and two electrons respectively.

Acknowledgement

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