PHOTOCATALYTIC MULTIELECTRON PHOTOREDUCTION OF 18-TUNGSTODIPHOSPHATE IN THE PRESENCE OF ORGANIC COMPOUNDS — PRODUCTION OF HYDROGEN

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Summary

$[P_2W_{18}O_{62}]^{6-}$ ("W_{18}^{6-}") undergoes stepwise multielectron photoreduction with near-visible and UV light in the presence of a great variety of organic compounds. Photolysis with high intensity light at low pH produces a reduction by one, one, two, two and four electrons followed by decomposition, as is the case with chemical and electrochemical reactions. The reduction proceeds via steps to the extent that the reduction of hydrogen is thermodynamically allowed. This takes place both with and without a platinum catalyst. At a higher pH, *i.e.* as the reduction potential for hydrogen evolution becomes more negative, only the higher reduction products produce hydrogen. The rate constants for hydrogen evolution are a function of the reduction step and the pH and are of the order of 10^{-4} s^{-1}.

1. Introduction

Heteropoly compounds (HPCs) are known to undergo multielectron reduction by chemical and electrochemical means without decomposition [1]. HPCs are also photosensitive to both near-visible and UV light, undergoing multielectron photoreduction with a concomitant oxidation of the organic compounds [2, 3]. The extent of the reduction depends on the HPC used and on the nature of the reducing reagent. In HPCs photoreduction proceeds via reduction steps to the extent that the reduction of hydrogen is thermodynamically allowed. A steady state is produced at which the rate of photoreduction is matched by the rate of reoxidation, with a concomitant evolution of hydrogen [4].

Research on solar energy focuses on systems that are able to convert and store solar energy as chemical energy (fuel). Hydrogen has been the most popular fuel and has produced the best results in a number of systems [5 - 7].

[†] Part of Ph.D. Thesis.

This paper reports the photoreduction of $[P_2W_{18}O_{62}]^{6-}$ ("$W_{18}{}^{6-}$") in the presence of a variety of organic compounds and the subsequent evolution of hydrogen. It focuses on the reactivity of various reduced $W_{18}{}^{6-}$ species (obtained photochemically) towards hydrogen evolution at various pHs ($W_{18}{}^{6-}$ is resistant to hydrolytic degradation up to pH 6 [8, 9]) both in the presence and absence of a platinum catalyst. This compound has two isomers (α form and β form) which have slightly different redox potentials and spectra [8, 9]. When necessary, we have used a single isomer (specifically the α form) in order to improve the comparison between chemical and photochemical data.

2. Experimental details

$W_{18}{}^{6-}$ was prepared according to well-established literature methods and analysed from its spectra and polarography data [8, 9].

Aqueous solutions of the HPC containing organic compounds were deaerated with argon or N_2 which was scrubbed with V^{2+} or alkaline pyrogallol, and were photolysed with a high-pressure mercury arc and a 150 W xenon lamp using filters or a monochromator. The actinometry was monitored using a selenium photocell calibrated with iron(III) oxalate. The liberated hydrogen was analysed using a Perkin–Elmer gas chromatograph with nitrogen as the carrier gas and a 50 - 60 mesh molecular sieve (column 1.0 mm in diameter and 4 m long). Colloidal platinum was prepared by boiling H_2PtCl_6 with sodium citrate [10]. It can also be made *in situ* from K_2PtCl_4 by reduction with photochemically-reduced tungstates before the evolution of hydrogen. It should be noted that in this case also the efficiency of the platinum catalyst dropped to about 50% after the photolysis had been in progress for about 20 h [4].

The number of electrons added photochemically was calculated by referring to the known spectra of the reduced tungstates and by performing back titrations with $Cr_2O_7{}^{2-}$, or indirectly by adding an excess of Fe^{3+} and titrating the resulting Fe^{2+} potentiometrically with $Cr_2O_7{}^{2-}$. The latter method was standardized using known solutions as the end point of the titrations was not sharp.

3. Results and discussion

Like other HPCs, $W_{18}{}^{6-}$ is photoreduced in near-visible and UV light at the oxygen-to-metal charge transfer bands, in the presence of a great variety of organic reagents, producing the characteristic heteropoly blue products [2, 3, 11]. Table 1 shows the quantum yield for the one-electron reduction product ($W_{18}{}^{7-}$) with various organic reagents. The quantum yield is a function of the concentration of the organic compound and increases with concentration up to about 2 M.

TABLE 1

Quantum yield of formation of the one-electron reduction product of $W_{18}{}^{6-}$ in the presence of various organic compounds at 252 nm ($[W_{18}{}^{6-}] = 1 \times 10^{-4}$ M in 0.1 M $HClO_4$)

Organic reagent	Concentration (M)	$\Phi(W_{18}{}^{7-})$
CH_3OH	5	0.046
CH_3CH_2OH	5	0.062
$(CH_3)_2CHOH$	5	0.093
$(CH_3)_3COH$	5	0.027
CH_2OHCH_2OH	5	0.051
CH_3COCH_3	5	0
$CH_2OHCOOH$	5	0.097
CH_3COOH	5	0.006
$CH_2(COOH)_2$	2	0.010
CH_2NH_2COOH	2	0.046
$EDTA^a$	0.1	0.024
$N(CH_2CH_2OH)_3{}^a$	0.5	0.006
$N(CH_2CH_2OH)_3$	0.5	0.021

^{a}pH, 4.8.

Unlike $[P_2Mo_{18}O_{62}]^{6-}$ [2] the quantum yield of the one-electron reduction product was independent of pH for $[H^+]$ values of 0.5, 0.1, 10^{-2} and 10^{-3} M, suggesting that H^+ does not participate in the photoreduction, in agreement with the fact that the thermal reduction

$$W_{18}{}^{6-} + e^- \longrightarrow W_{18}{}^{7-}$$
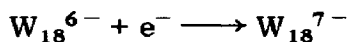
is independent of $[H^+]$, as has been shown polarographically [8].

Under high intensity radiation with UV and near-visible light a maximum number of 10 electrons could be added stepwise, this being followed by the decomposition of the highly-reduced tungstate.

The spectra of successively-reduced tungstates generally show small blue shifts on further reduction (Fig. 1). The tungstates could be recognized, at least the lower reduction products, by their characteristic wavelengths and absorbances [9]. The number of electrons added was also derived from back titrations with oxidizing reagents as has been explained above.

Table 2 shows the values of $E_{1/2}$ for the various reduction steps at various pHs obtained with a dropping mercury electrode (DME) [8]. It can be seen that the reduction of H^+ by the reduced products is thermodynamically allowed, as has been stated previously [4, 10, 12]. Indeed this occurs both with and without the platinum catalyst. Figure 1 shows the reoxidation of reduced tungstate by H^+ and the corresponding kinetic plot. The rate constants for reoxidation of reduced tungstates in 0.1 M $HClO_4$ and the concomitant hydrogen evolution in the presence and absence of the platinum catalyst are shown in Table 3. These were calculated after photochemically producing the corresponding reduction step on shutting off the lamp
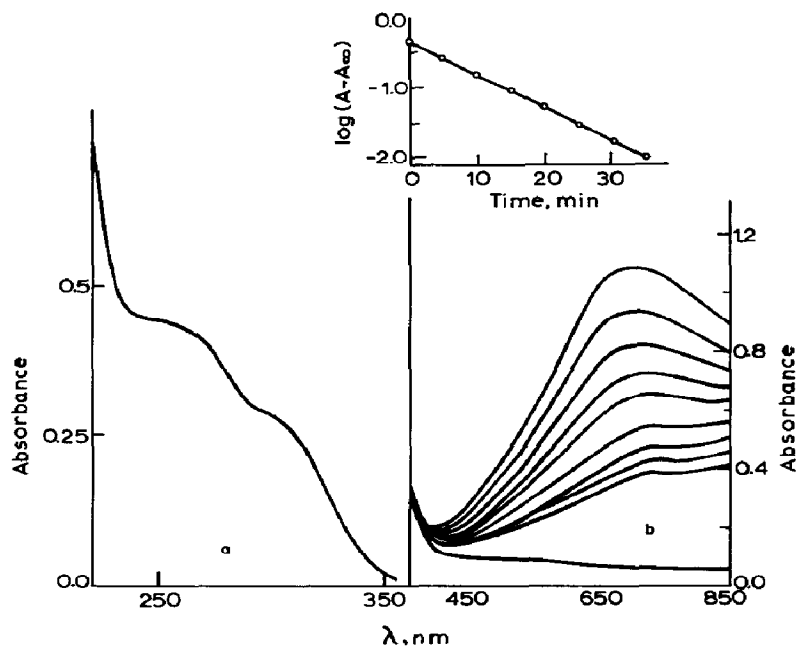
Fig. 1. Absorption spectra and kinetics of reoxidation of photoreduced W_{18}^{6-} with the concomitant evolution of hydrogen: curve a, $[W_{18}^{6-}] = 1 \times 10^{-5}$ M in 0.1 M $HClO_4$ showing the oxygen-to-metal charge transfer band responsible for the photosensitivity; curves b, spectra of photoreduced W_{18}^{6-} showing gradual reoxidation by H^+ after illumination had been shut off. ($[W_{18}^{6-}] = 1 \times 10^{-4}$ M; [isopropyl alcohol] = 1.1 M in 0.1 M $HClO_4$; photolyzed with a xenon lamp with a Pyrex filter.)

TABLE 2

$E_{1/2}$ of various reduction steps at various pHs of α-W_{18}^{6-} obtained with a DME [8]

pH	$E_{1/2}$ (V versus NHE) for reduction step			
	$1e^-$ [a]	$1e^-$ [b]	$1e^- \nwarrow \quad \overset{2e^-}{} \quad \nearrow 1e^-$	
1	0.306	0.084		-0.213
3	0.306	0.084		-0.304
5	0.306	0.084	-0.233	-0.430

NHE, normal hydrogen electrode.
[a]Refers to $W_{18}^{6-} + e^- \rightarrow W_{18}^{7-}$.
[b]Refers to $W_{18}^{7-} + e^- \rightarrow W_{18}^{8-}$.
[c]Below pH 3, refers to $W_{18}^{8-} + 2e^- + 2H^+ \rightarrow H_2W_{18}^{8-}$. Above pH 3, refers to $W_{18}^{8-} + e^- \rightarrow W_{18}^{9-}$ and $W_{18}^{9-} + e^- \rightarrow W_{18}^{10-}$.

and observing the reoxidation of the reduced tungstates by H^+. The reduction step was recognized from the wavelength and absorbance data. Overall the rate of reoxidation of W_{18}^{8-} measured spectrophotometrically was about 9.7×10^{-11} mol s^{-1} and this matched the rate of hydrogen evolution
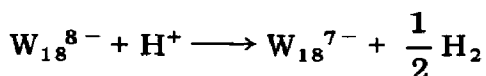
TABLE 3

Rate constants[a] for hydrogen evolution for reactions measured spectrophotometrically with and without the platinum catalyst ($[\alpha\text{-}W_{18}{}^{6-}] = (0.5 \cdot 1.0) \times 10^{-4}$ M, [isopropyl alcohol] = 1 - 2 M in 0.1 M $HClO_4$)

	$k \times 10^4$ s^{-1}	
	$W_{18}{}^{8-} + H^+ \rightarrow$ $W_{18}{}^{7-} + 1/2\ H_2$	$W_{18}{}^{10-} + 2H^+ \rightarrow$ $W_{18}{}^{8-} + H_2$ [b]
With platinum	6.1	17
Without platinum	4.0	0.73

[a]Calculated from pseudo-first-order rate plots; values are within 50%.
[b]It is known that $W_{16}{}^{10-}$ is protonated at low pH so that the species exists as $H_2W_{18}{}^{8-}$; see text.

at the steady state (about 4.2×10^{-11} mol s^{-1} with the platinum catalyst). The rate of hydrogen evolution was obtained by dividing the total hydrogen produced at the steady state by time. The rates are indeed within the stoichiometric requirements of the reaction

$$W_{18}{}^{8-} + H^+ \longrightarrow W_{18}{}^{7-} + \frac{1}{2}\,H_2$$

The thermodynamics suggest that the rate of reoxidation of $W_{18}{}^{10-}$ by H^+ should be faster than that of $W_{18}{}^{8-}$ (Table 2). This is indeed the case when platinum is used as the catalyst (Table 3). In the absence of platinum though, the reoxidation of $W_{18}{}^{10-}$ is slower than that of $W_{18}{}^{8-}$ contrary to their redox potentials. This tends to suggest that the addition of two more electrons and protons ($W_{18}{}^{10-}$ is known to be protonated, i.e. it exists as $H_2W_{18}{}^{8-}$ at low pH [8]) reduces the effectiveness of the HPC as a catalyst, apparently by distorting the structure of the anion.

Table 4 shows the rate constants of reoxidation (hydrogen evolution) of photoreduced one-, one- and two-electron products at various pHs measured spectrophotometrically. It can be seen that as the pH increases and the reduction potential of hydrogen evolution becomes more negative only the higher reduction products produce hydrogen. We have reported [4] that photoreduction proceeds until the rate of photoreduction is matched by the rate of reoxidation by H^+, at which point a steady state is produced. The steady state, i.e. the point at which the maximum number of electrons at which the rate of photoreduction matches the rate of reoxidation, is a function of the intensity of the radiation, as has been explained previously [4]. With $W_{18}{}^{6-}$ a steady state is obtained rather easily when photoreduction does not produce a more than two-electron product. Once the intensity of the radiation is increased, photoreduction continues stepwise up to the addition of 10 electrons and the eventual decomposition of the anion. Steady-state conditions are difficult to achieve with more than two electrons under

TABLE 4

Rate constants[a] for hydrogen evolution measured spectrophotometrically at various pHs adjusted with $HClO_4$, and various reduction stages

pH	E^0 versus NHE[b]	k for reduction step ($\times 10^{-4}$ s^{-1})				
		$1e^-$ c	$1e^-$ c	$1e^-$	$2e^-$ c	$1e^-$
1	−0.059	0	4.0		0.73	
3	−0.177	0	0		0.77	
5	−0.295	0	0	0[d] ←	0.77	→ 0[d]

[a]Values are within 50%.

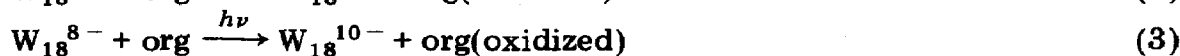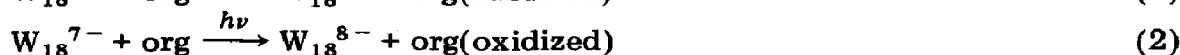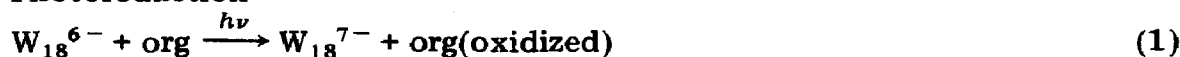[b]Refers to the reduction potential of $2H^+ + 2e^- \longrightarrow H_2$ at the corresponding pH.

[c]Numbers refer to electrons added photochemically.

[d]Hydrogen is only evolved in the presence of the platinum catalyst and the k values are 1.6×10^{-4} s^{-1} and 2.9×10^{-4} s^{-1} for the third and fourth electron respectively.
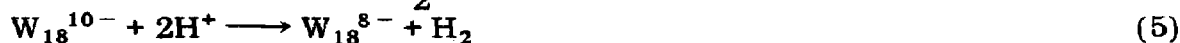
the experimental conditions used so far, and without using the platinum catalyst, unless the intensity of the radiation is carefully controlled.

The basic overall photochemical reactions for the initial reduction steps at low pH are as follows:

Photoreduction

$$W_{18}^{6-} + org \xrightarrow{h\nu} W_{18}^{7-} + org(oxidized) \qquad (1)$$

$$W_{18}^{7-} + org \xrightarrow{h\nu} W_{18}^{8-} + org(oxidized) \qquad (2)$$

$$W_{18}^{8-} + org \xrightarrow{h\nu} W_{18}^{10-} + org(oxidized) \qquad (3)$$

Hydrogen evolution

$$W_{18}^{8-} + H^+ \longrightarrow W_{18}^{7-} + \frac{1}{2} H_2 \qquad (4)$$

$$W_{18}^{10-} + 2H^+ \longrightarrow W_{18}^{8-} + H_2 \qquad (5)$$

where org is the organic compound. (It is very likely that reaction (3) proceeds via the addition of one electron followed by the disproportionation

$$2W_{18}^{9-} \longrightarrow W_{18}^{8-} + W_{18}^{10-}$$

by analogy with the corresponding molybdates [13]; however, this is of no significance in the overall scheme.) An analogous mechanism can be written for higher reduction steps.

W_{18}^{10-} is known to be protonated below pH 3, i.e. it exists as $H_2W_{18}^{8-}$. This species, as well as the deprotonated forms, produces hydrogen. It appears then that the catalytic properties of the HPC for hydrogen evolution might be attributed to H^+ "absorbed" in the HPC rather than to protonated hydrogen, as has also been suggested previously [7].

Acknowledgments

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