Photochemical behavior of Keggin ions and related compounds

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Abstract

The photochemical behavior of Keggin heteropolytungstates is reinvestigated using a useful thin layer electrochemical cell. This new device allows to measure the molar fraction of the polycompound as oxidized and reduced form at the same time. Some previous results can be confirmed but new aspects of the redox behavior of excited HPC have been evidenced. It has been proved that the photoprocess occurs via the charge transfer reaction between terminal oxygen atoms and tungsten atoms. The limiting rate for the primary electron exchange is depending on the free enthalpy of the first reduction step of the HPC in its fundamental state and not depending on the nature of alcohol. The chromophore involved in the excitation process as well as the oscillator strength can be defined and the quantum yields measured. The rate constant appears to be independent of pH and temperature. An unexpected catalytic effect of the reaction products is evidenced and explained by an interconversion transfer between excited HPC and carbonyl compound.

Keywords: Heteropolytungstates; Photochemistry; Thin layer electrochemical cell; Alcohol oxidation; Catalytic effect of carbonyl compounds; Kinetic measurements; Rate of electron exchange

Homogeneous catalysis by polyoxometalates is now intensively investigated, partly as a consequence of their unusual versatility. Many reviews reported some aspects of polyoxometalates. The most recent, which includes more than 200 references, is from Hill and Prosser-McCartha [1]. Some others reported more precisely photochemistry and photocatalytic behavior of heteropolycompounds (HPC) [2–4], and more particularly [4]. In addition, there are several reviews involving heterogeneous and homogeneous catalysis [5]. Structural considerations about HPC are now well known and the classical reviews from Pope are always very

useful [6]. In photochemical applications of HPC, the most reported results were related to the blue color of the reduced compounds (analytical determinations, electrochromism, photography ...). More recently, the works are focused on the catalytic properties of HPC in the photodecomposition of water [7] or photooxydation of alcohols [2,7,8]. The redox properties of HPC are characterized by their ability to accept and release some number of electrons in distinct redox steps without decomposition. This redox chemistry has been reported in now well known articles or reviews [8–10]. Non-reduced HPC are characterized by oxygen–metal charge transfer absorptions in the near-UV area.

Now, it is well known that, for a redox reagent, the excited state is a better oxidant than

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the ground state. Thus, for heteropolytungstate under UV light a powerful oxidizing behavior is expected, even for oxidizing a weak reducing substrate. The organic compounds investigated include alcohols, amines and carboxylic acids. Many studies claim that the quantum yield is related to the redox potential of the HPC, the nature of the organic reagent and the pH [11]. By a different way, a generally accepted mechanism implies a H-transfer step in which the hydroxyalkyl radicals are the effective reducing reagents [12,13]. Unfortunately, most of the experiments were conducted in a classical photochemical cell and followed by absorbance measurements or hydrogen evolution measurements. If we remember that many reduced HPC have very similar absorption spectra, especially in the 600–900 nm area (broad bands) [14], it seems difficult to be sure of the true mechanism of the photochemical reaction. On the other hand, only few results about the photophysical parameters of Keggin ions are reported. For these reasons we attempt to do some fine measurements about photooxidation of alcohols using a new thin layer electrochemical cell which allows us to determine precisely the molar fraction of each reduced stage of HPC with respect to the time.

1. Experimental part

1.1. Materials

All usual compounds were purchased from a chemical company as purissimum grade and used without further purification. The HPC was synthesized and recrystallized according to now well-known procedures [15].

The experiments were generally conducted with a solution of 10^{-4} M HPA and 0.5 M HCl. The temperature was monitored to 20°C.

1.2. Thin layer cell

The thin layer cell was a home-made apparatus; the electrochemical cell is a three electrode system with a classical calomel electrode as the reference electrode and a platinum wire (1 mm diameter) as the counter electrode. The original part of the cell concerns the working electrode which is made of a small glassy carbon (Carbon Lorraine V25) crucible (12.5 mm height, 12.5 mm diameter and 2 mm thickness). The crucible is sealed with an epoxy resin (Buehler) into a Pyrex tube. Then the carbon electrode is mechanically polished successively with abrasive discs (Mecaprex-Presi 400-600-1200) and finally optically polished successively with 6 and 3 μm diamond paste (Lamplan-diamand Hyprez) with the help of felts (Lamplan 415 and 432). When the electrode is correctly polished, it is washed with ethanol (95%) to eliminate the residual diamond paste and then washed with distilled water.

The electrode can then be loaded with mercury (about 500 g). The mercury pool ensures a good electrical junction between the carbon crucible and a platinum wire.

The thin layer is built itself by the pressure of the working electrode onto an optically polished quartz disc (infrasil, 42 mm diameter, 2 mm thickness) covered by a polymer wedge (Nafion 125 kindly supplied by Dupont de Nemours: resistivity 2 Ω cm^{-2}; 133 $\pm$ 4 μm thickness). The Nafion film is pierced with a circular hole (10 $\pm$ 1 mm diameter) leading to a mean volume of $V = 10 \pm 1$ mm^3 for the resulting layer (estimate from 10 determinations).

A view of this very useful cell is shown in Fig. 1a and b.

1.3. Lighting apparatus

The thin layer solution can be illuminated through the quartz window with monochromatic radiation. A very powerful light beam is produced from a high pressure arc light (Xenon 450 W OSRAM XBO) connected to a stabilized power supply (Spotlight DC 150/1000R E-type 25A-18V). In conventional operation the lamp emits a continuous spectrum which is similar to a black-body emission at 6000 K. The light is

(a)

12.5 mm

12.5 mm

Pt wire

Hg pool

pyrex tube

epoxy resin

(b)
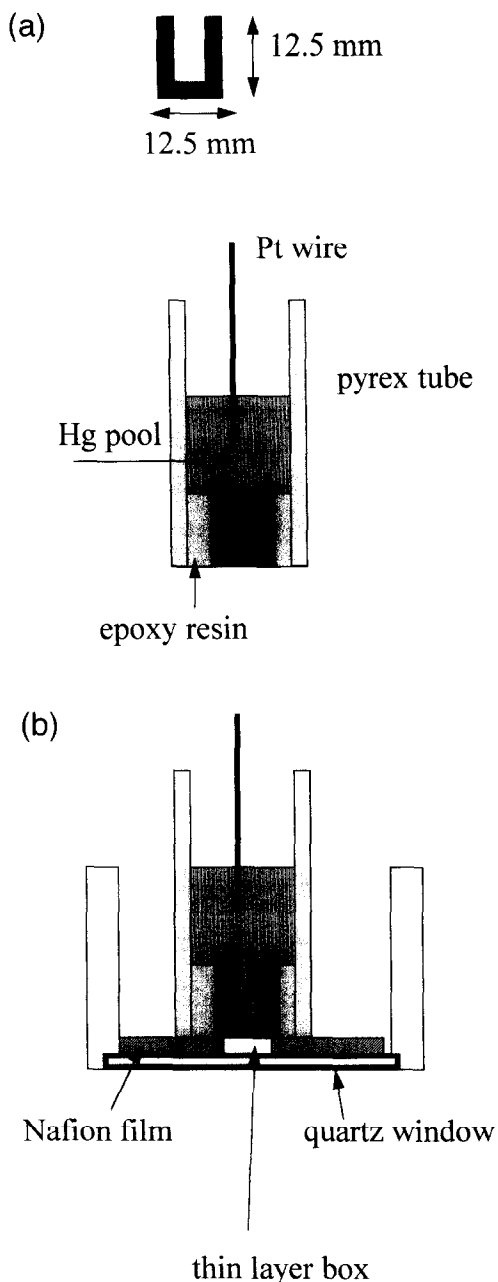
Nafion film

quartz window

thin layer box

Fig. 1. A view of: (a) glassy carbon crucible and of carbon working electrode. (b) The thin layer cell made from the pressure of the working electrode on a quartz window. The window allows the irradiation of the thin layer solution.

then filtered to eliminate infra-red radiation, using a caloric filter equipped with quartz infrasil windows. The resulting light is then admitted inside a symmetrical monochromator (Kratos GM 252) using a 1180 line diffraction grating. The disposable wavelength field is then 180–800 nm with a dispersing power of 3.3 nm cm^{-1}. In usual utilization, the lamp current supply was monitored by a 24 A intensity: the monochromator slits have a 6.5 mm height and a 4 mm width producing a band of about 13 nm under a power of 48 μW. The flux is measured either by ferrioxalate actinometer or by a selenium photodiode supplied by a numerical photometer (Macam photometrics PR 30 10)

1.4. Thin layer working criteria

Three conditions for a good thin layer measurement are required: first it is necessary to avoid any diffusion process between the layer and the outside solution during time measurement. Secondly, the potential scanning has to be adjusted in order to avoid a diffusion inside the layer. Third, the thin layer thickness has to be smaller than the thickness of the diffusion layer. For HPC these conditions can be easily verified if the time of measurement remains lower than 4 h (criterion 1), if the scanning time is about 0.5 mV s^{-1} (criterion 2), and if the time of measurement exceeds 13 s (criterion 3)

1.5. Thin layer calibration

The calibration was made using $SiMoW_{11}O_{40}^{4-}$ as standard HPC (10^{-4} M in HCl 0.5 M solution). This compound has reasonable stability in a large pH range (0–4) and two quite distinct monoelectronic waves ($E^{o}_{1} = +0.315$ V and $E^{o}_{2} = -0.380$ V versus E.C.S.).

If Q_{ox} and Q_{red} are the quantities of electricity exchanged to oxidize HPC_{red} and to reduce HPC_{ox}, the HPC_{ox}/HPC_{red} ratio can be determine by two successive reverse scans. Thus, if the system is reversible the equilibrium potential is in accord with Nernst's law:

$$E_{eq} = E^{o} + RT/nF \ln Q_{red}/Q_{ox} \qquad (1)$$

where E_{eq} and E^{o} are, respectively, the equilibrium potential of the carbon electrode and the
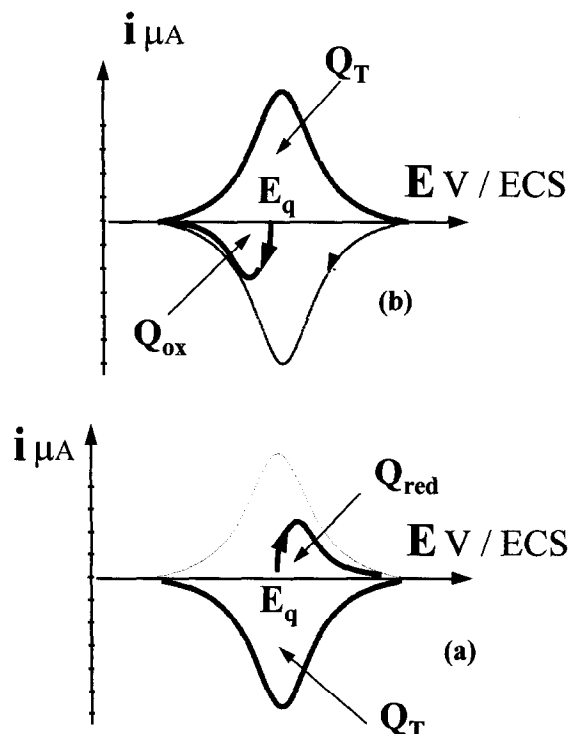
Fig. 2. Principle of microcoulometric determination from the thin layer solution equilibrium. (a) Cathodic scanning followed by anodic oxidation; (b) anodic scanning followed by cathodic reduction.

standard apparent potential of the couple $SiMoW_{11}O_{40}^{4-}/SiMoW_{11}O_{40}^{5-}$.

The potential measurement coupled with the coulometric determination then facilitates confirmation of the reversibility of the process, the number of electrons exchanged and the precise apparent standard potential of the exchange. A typical example of coulometric determination is shown Fig. 2.

With the compound $SiMoW_{11}O_{40}^{4-}$ the mean values (10 determinations) are $Q_{red} = 9.5 \times 10^{-10}$ F and $Q_{ox} = 8.5 \times 10^{-10}$ F (expected value from the thin layer volume: $Q = 10 \times 10^{-10}$ F, where F is the symbol of the molar amount of electricity). Q remains proportional to the volume of the layer if $V < 15$ mm^3. In the same way the dependence of Q with the HPC concentration is linear in a 10^{-4}–10^{-3} M range. This is good proof that our cell is an
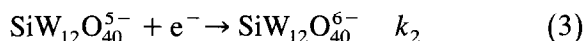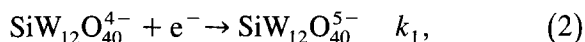
effective tool for the determination of the kinetic characteristics of HPA under illumination.

2. Results

2.1. Photoreduction of $SiW_{12}O_{40}^{4-}$ in ethanol–HCl media

A 10^{-4} M $SiW_{12}O_{40}^{4-}$ in EtOH 3.4 M (20% v.v)–HCl 0.5 M solution is illuminated at 280 nm.

The light power is 100 μW. The reduction of the HPA appears decomposable into two first order steps and the coulometry allows to identify the two successive reversible monoelectronic exchanges

$$SiW_{12}O_{40}^{4-} + e^- \rightarrow SiW_{12}O_{40}^{5-} \quad k_1, \qquad (2)$$

$$SiW_{12}O_{40}^{5-} + e^- \rightarrow SiW_{12}O_{40}^{6-} \quad k_2 \qquad (3)$$

where k_1 and k_2 are the rate constants of the electronic exchanges.

The mean values from 10 determinations are:

$$k_1 = 6 \times 10^{-3} \text{ s}^{-1} \text{ and } k_2 = 2 \times 10^{-5} \text{ s}^{-1}.$$

A good verification of the separation of the two steps can be obtained by an initial in-situ electroreduction of the oxidized HPA to one-electron reduced compound, and then illuminating the reduced compound; the value obtained in this second experiment is very close to the previous one: $k_2' = 1.8 \times 10^{-5} \text{ s}^{-1}$.

The first step of the photoreduction is a first order law with respect to ethanol as it can be shown by plotting the normalized rate constant (k_1/ϕ) versus alcohol concentration (Fig. 3). The dependence is $1.3 \times 10^{-5} \mu W^{-1} M^{-1} s^{-1}$.

2.1.1. Influence of the flux of photons

The photoreaction is conducted under the same conditions (HPA 10^{-4} M, EtOH 3.4 M, HCl 0.5 M). The flux can be adjusted by varying the lamp intensity, the slit height or the slit width. Then, in every case, the dependence of the rate constant of the first step reaction, k_1,
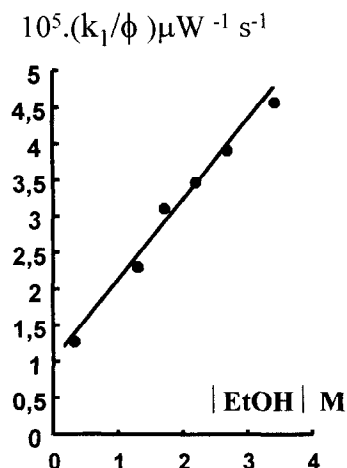
$10^5.(k_1/\phi)\mu W^{-1} s^{-1}$

Fig. 3. Linear dependence of the normalized rate, for the first reduction step, on the ethanol concentration.

versus the light flux is about 4.5×10^{-5} μW^{-1} s^{-1}. That shows that the first step reaction is a first order rate law with respect to the light, i.e. the primary process is a photochemical activation of the HPA. That can be easily verified by measuring the normalized rate constant at different wavelengths. It is apparent that the constant tracks the absorption spectrum of the $SiW_{12}O_{40}^{4-}$ ion (Fig. 4). Thus the efficiency of the photoreduction process is very closely linked to the band gap of the HPC; and that the primary process is the charge transfer between the oxo ligand and the tungsten atom.

2.1.2. Dependence of k_1 with the pH and with the ionic strength

Without buffer the photoreaction produces protons as is readily observed when the HPA(sodium salt)/EtOH solution is lighted: the pH decreases from 5.7 to 4.5.

When a solution of 10^{-4} M $SiW_{12}O_{40}^{4-}$/EtOH 3.7 M is irradiated at 280 nm in a constant ionic strength medium (0.5 M) but at variable protons concentration, the normalized rate constant (k_1/ϕ) remains constant $(5 \times 10^{-5}$ μW^{-1} $s^{-1})$. This zero order law with respect to H^+ can be understood if we remember that the first reduction step is not pH dependent when the alcohol concentration is lower than 8.5 M (50% v/v).

That can be verified by measuring the half-wave potential in polarography (Hg cathode).

In the same way at constant acidity (0.3 M) the ionic strength has no effect on the normalized constant; that seems to indicate that the primary electronic exchange may be an ion–molecule reaction or an ion pair evolution.

2.1.3. Effect of the temperature

As expected for a purely photonic activation followed by a very fast electronic exchange, the formation of $SiW_{12}O_{40}^{5-}$ appears to be independent of temperature.

2.2. Photooxidation of propanol-2

The experimental conditions are the same as for the photooxidation of ethanol. Remember that 20% of isopropanol means a concentration of 2.56 M.

The phenomena are very similar. The first step reaction (formation of $SiW_{12}O_{40}^{5-}$) is a first order law with respect to HPC $(k_1'/\phi = 4 \times 10^{-5}$ μW^{-1} s^{-1}; mean value of 10 measurements). The reaction is also of first order versus isopropanol with an alcohol dependence very close to that of ethanol dependence $(k_{app}/\phi = 1.5 \times 10^{-5}$ μW^{-1} M^{-1} $s^{-1})$ and independent of pH $(k_1'/\phi = 4 \times 10^{-5}$ μW^{-1} $s^{-1})$. Surpris-
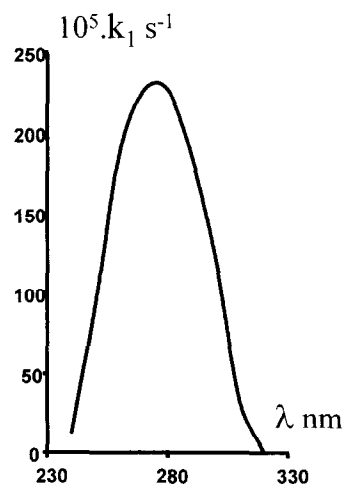
$10^5.k_1$ s^{-1}

Fig. 4. Wavelength effect on the rate constant of the first reduction step. HPC 10^{-4} M, HCl 0.5 M, EtOH 3.4 M. $\phi = 35$ μW.

ingly, the normalized constant exhibits a slight dependence upon ionic strength.

2.2.1. Effect of the photooxidation product

The photoproduct formed from isopropanol oxidation is acetone. When the photoreaction is performed with acetone in the medium (0.065 M) the reaction becomes clearly faster. The curve giving the photopotential versus the time is similar to a classical potentiometric curve showing the successive formations of the $SiW_{12}O_{40}^{5-}$ and $HSiW_{12}O_{40}^{5-}$ ions (noted I^{5-} and $H(II)^{5-}$ to recall the one-electron reduced compound and the protonated two-electron reduced compound). The limiting photopotential was observed at -0.700 V/E.C.S.

A microcoulometry at different steps of the reaction confirms the apparition of I^{5-} and $H(II)^{5-}$ but reveals a mixture of $H(II)^{5-}$ and $H_8SiW_{12}O_{40}^{4-}$ (8 electrons reduced HPA noted $VIII'$) [16].

This shows the similar behavior of the photoreduction and the electroreduction processes. The electron donor is the alcohol instead of polarized metal. As noticed in electroreduction, no hydrogen production was apparent in this photoreaction even if the final potential allows it. This data is consistent with the point that the
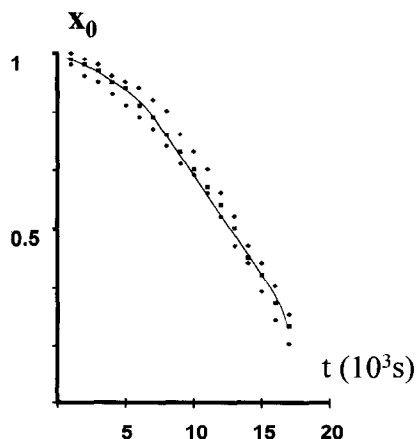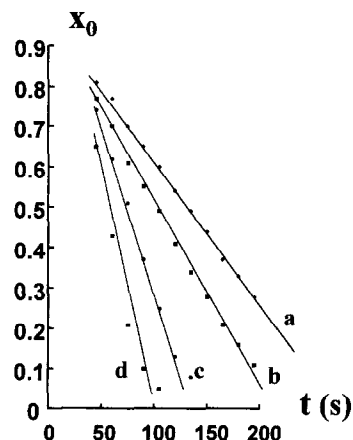
Fig. 6. Effect of acetone concentration on the molar fraction of $SiW_{12}O_{40}^{4-}$ with respect to time. (a) 0.013 M, (b) 0.026 M, (c) 0.065 M, (d) 0.13 M.

reduced HPA is not directly involved in the photoproduction of H_2 from water.

The photoreaction in HCl 0.5 M–acetone mixture but without isopropanol shows that the first step is not a first order rate law with respect to HPA but seems independent of acetone concentration (Fig. 5). The reaction is very slow and the initial reaction rate gives an approximate value of the rate constant $k_0'' = 1.6 \times 10^{-5}$ s^{-1}. This value is very close to that of the second step (Eq. (3)) when the reaction is performed with alcohol alone.

The aspect of the molar fraction of $SiW_{12}O_{40}^{4-}$ (O^{4-}) evolution reveals an autocatalysed reaction. As acetone exhibits only a very weak absorption near 280 nm ($\varepsilon = 15$ mol^{-1} · L · cm^{-1}) compared to that of HPC ($\varepsilon \approx 30{,}000$ mol^{-1} · L · cm^{-1}) the percentage of the incident light absorbed by acetone is only 30% versus the light absorbed by the polyoxometalate. However, the fact that without electron-donor the rate does not depend on the acetone concentration suggests that the main light absorption is due to the HPC photochemical behavior.

When the photoreaction is performed in HCl 0.5 M–20% v/v isopropanol–acetone medium, and if the acetone concentration is lower than 0.5 M, the formation of I^{5-} and $H(II)^{5-}$ seems to be zero order versus HPA (Fig. 6). Thus, the
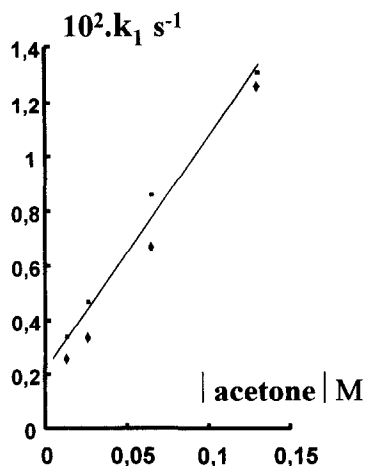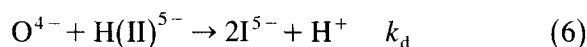
Fig. 5. Evolution of the molar fraction of $SiW_{12}O_{40}^{4-}$ with time for different concentrations of acetone: (● 0.13 M, ■ 1.3 M, ◆ 0.65 M.

Fig. 7. Effect of acetone concentration on the rate of the two successive reduction steps. ■ k_1, ♦ k_2.

respective molar fractions x_i (estimated from the potential curve) can be expressed as $x_0 = 1 - k_1 t$ and $x_1 = 1 - k_2 t$.

For example, with 0.13 M acetone (1%), $k_1 = 1.3 \times 10^{-3}$ s^{-1} and $k_2 = 1.2 \times 10^{-3}$ s^{-1} with a same linear dependence versus acetone concentration (8×10^{-2} M^{-1} s^{-1}; Fig. 7).

A possible mechanism, when the electron donor is in excess, could be simply:

$$O^{4-} \rightarrow I^{5-} \quad k_1, \tag{4}$$

$$I^{5-} \rightarrow H(II)^{5-} \quad k_2, \tag{5}$$

$$O^{4-} + H(II)^{5-} \rightarrow 2I^{5-} + H^+ \quad k_d \tag{6}$$

where k_d is the disproportionation constant of the two-electron reduced compound.

In a good reversible system the dismutation process is generally a fast reaction as it can be evidenced by polarographic measurements [10] and the stationary state can be applied to $H(II)^{5-}$. Then the molar fraction for O^{4-} can be expressed as:

$$x_0 = [1/(k_2 - k_1)][k_2 - k_1 \exp(k_2 - k_1)t]. \tag{7}$$

If the alcohol concentration is sufficient (no electron exchange limiting reaction) $k_2 \# k_1$ and $x_0 \rightarrow (1 - k_1 t)$ (zero order).

When the concentration of acetone is fixed to 0.13 M and if the concentration of isopropanol varies, the evolution of the molar fraction x_0 is very similar to the one observed with only acetone and seems independent of isopropanol concentration. Thus the acetone seems to act as a catalyst in the photoreaction.

With ethanol the phenomenon is similar but more pronounced. If we express the rate of reaction $v = -k_1 \exp(k_2 - k_1)t$, then $\ln v = f(t)$ is expected as a straight line with a slope of $(k_2 - k_1)$ and an origin ordinate of $\ln(-k_1)$. When the reaction is performed with 3.4 M EtOH and 0.65 M acetone we get $k_1 = 2.4 \times 10^{-3}$ s^{-1} and $k_2 = 26 \times 10^{-3}$ s^{-1}, respectively. As the rate of the primary process (photochemical excitation) without acetone is the same for ethanol and isopropanol we could conclude that the catalytic process arises in a second step in which the alcohol is involved. That may be occurring from a charge transfer between radicals produced in the primary step and acetone.

2.3. Photooxidation of other alcohols

Some others substrates have been examined. In every case, the first step is always a first order reaction with similar rate constants. These results are reported in Table 1. From this, we can conclude that ethanol, propanol-1 and propanol-2 have the same reactivity. Methanol and glycerol are half as reactive and ethylene glycol is one fifth as reactive. These observations do not agree with the old scheme proposed for the hydrogen evolution from the reduced HPC and water [8].

Table 1
Normalized rate constant of the first electron exchange for different alcohols

Alcohol	k_1/ϕ (10^{-5} μW^{-1} M^{-1} s^{-1})
Methanol	0.7
Ethanol	1.3
Propanol-1	1.5
Propanol-2	1.5
Glycerol	0.65
Ethyleneglycol	0.3

When the methanol is used as electron donor the effect of the formaldehyde is checked in order to verify a possible catalytic process. No effect is observed. The reason may be the presence of formaldehyde as its hydrate, $CH_2(OH)_2$, in aqueous medium. If we consider that ethylene glycol has a very weak effect this can be the same way for the acetal.

## 2.4. Photooxidation of isopropanol with other heteropolycompounds.

Numerous heteropolytungstates exhibit analogous charge transfer process [17]. We can dispose of many 'photosensitiseur' of close optical properties but with different electrical charges and very different potentials. It is also possible to replace one tungsten atom by another transition metal. Removing the tungsten atom generates a vacancy. In the later case the redox potentials are very strongly perturbed. On the other hand, it can be possible to use HPC (for example Dawson compounds) with redox properties very close to those of $SiW_{12}O_{40}^{4-}$ but with different charge transfer capabilities.

Illuminated in standard conditions (10^{-4} M HPC, isopropanol 10%, HCl 0.5 M or acetic buffer) most of these compounds exhibit a photoreactivity. In every case, even when no reaction is observed, acetone speeds up the rate of reaction. These results are summarized in Table 2 for the first step.

3. Discussion

From these results it seems clear that, without catalyst, the primary step of the photoreaction can be considered as a first order rate law with respect to reagents (photons, alcohol, HPC). In this case, the second step is always slower than the first one. However, when acetone is present the rate of the two steps increases and the rate law is zero order with respect to alcohol and first order versus acetone. That can be explained by Hill's mechanism [13] but has to be modified to take into account the energy transfer of excited HPC to excited states (S_1, T_1 or T_2) of acetone. It is well known [18] that the T_1 state can react with a protic substrate giving two radicals. In the case of isopropanol these two radicals are the same.

$$(CH_3)_2CO^* + (CH_3)_2CHOH \rightarrow 2(CH_3)_2C^\circ OH. \tag{8}$$
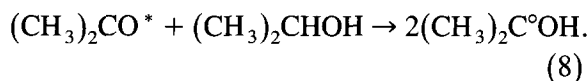
Another way is the conversion of the T_2 state to a very reactive biradical state ($CH_3)C^\circ O$ and $(CH_3)^\circ$

Thus two competitive mechanisms can come from the photoexcited state of HPC.

First, a scheme where the alcohol is the main electron donor, i.e. neglecting the spontaneous desexcitation:
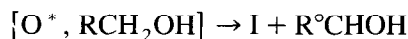
$$O + h\nu \rightarrow O^* \quad I_A, \tag{9}$$

$$O^* + RCH_2OH \rightarrow [O^*, RCH_2OH]$$
$$K|O*| \cdot |RCH_2OH|, \tag{10}$$

$$[O^*, RCH_2OH] \rightarrow I + R^\circ CHOH$$
$$k_1|O^*, RCH_2OH|, \tag{11}$$

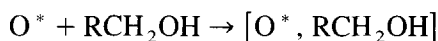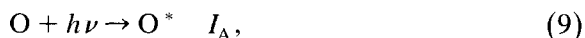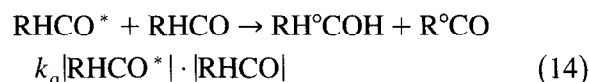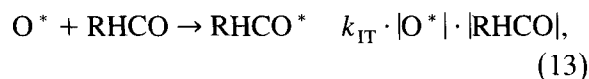$$R^\circ CHOH + O \rightarrow I + RHCO \quad k_1'|O| \cdot |R^\circ CHOH|. \tag{12}$$

Table 2
Normalized rate constant of the first electron exchange for different HPC

Ion	Buffer	k_1/ϕ (10^{-5} μW^{-1} M^{-1} s^{-1})
α-$PW_{12}O_{40}^{3-}$	HCl 0.5 M	10.8
α-$SiW_{12}O_{40}^{4-}$	HCl 0.5 M	1.5
	AcH 1 M/ Ac$^-$ 1 M	4
α-$BW_{12}O_{40}^{5-}$	AcH 1 M/ Ac$^-$ 1 M	0.15
α-$H_2W_{12}O_{40}^{6-}$	HCl 0.5 M	0.008
β-$SiW_{12}O_{40}^{4-}$	HCl 0.5 M	0.8
α-$SiW_{11}CrO_{40}H_2^{5-}$	HCl 0.5 M	very slow
α-$SiW_{11}MoO_{40}^{4-}$	HCl 0.5 M	66
α-$SiW_{11}O_{39}^{8-}$	AcH 1 M/ Ac$^-$ 1 M	very slow
α-$H_2AsW_{18}O_{62}^{7-}$	HCl 0.5 M	0.3
α-$P_2W_{18}O_{62}^{6-}$	HCl 0.5 M	1.7

Second, a mechanism in which the donor is a radical issued from an energy transfer on to the carbonyl compound:

$$O^* + RHCO \rightarrow RHCO^* \quad k_{IT} \cdot |O^*| \cdot |RHCO|, \tag{13}$$

$$RHCO^* + RHCO \rightarrow RH°COH + R°CO$$
$$k_q |RHCO^*| \cdot |RHCO| \tag{14}$$

where I_A is the intensity of the absorbed light, k_1 and k_1' are the rate constants, K the equilibrium constant of the charge-transfer complex, k_{IT} the rate constant of the energy transfer and k_q the rate constant of quenching. According to usual notation in HPC electrochemistry [6], Roman numerals are used instead of HPC formulae particularly when the compounds are reduced anions without other chemical changes: O for $SiW_{12}O_{40}^{4-}$, I for $SiW_{12}O_{40}^{5-}$, II for $SiW_{12}O_{40}^{6-}$, and when the ions are protonated forms H(I) for $HSiW_{12}O_{40}^{4-}$, H(II) for $HSiW_{12}O_{40}^{5-}$ ... Formulae into square brackets mean the concentration of the corresponding compound, i.e. |O| concentration of $SiW_{12}O_{40}^{4-}$, $\cdot|RHCO|$ concentration of carbonyl compound....

If the radicals have sufficient reducing power, a chain reaction can be initiated leading to high reduction steps for HPC. As we can assume that the reactions of HPC and radicals are very fast, the stationary state for $RHCO^*$, $RH°COH$ and $R°CO$ allow us to write the rate of the reaction:

$$v = 2 k_{IT} |O^*| \cdot |RHCO| = 2 k_{IT} I_A |RHCO| \tag{15}$$

which is a first order rate law with respect to the carbonyl compound and a zero order rate law with respect to HPC.

We have now to estimate the quantum yield and to compare the rate of deexcitation to the rate of electronic exchange.

3.1. Quantum yield

At 280 nm a light power of 1 μW corresponds to 1.4×10^{12} photons s^{-1} or 2.3×10^{-12} einstein s^{-1}. If we remember that the thin layer

volume is 10 mm^3 it implies a light intensity received by the cell of $I_0 = 2.3 \times 10^{-7}$ E · L^{-1} · s^{-1} per 1 μW power exiting the monochromator slit. If the absorbance A of the cell is weak (130 nm thickness) then the light intensity absorbed can be approximated as $I_A = 2.3 A \cdot I_0$. The rate of the first step reaction can be expressed as:

$$k_1 = k_0 + k_1' |ROH| \cdot I_A \tag{16}$$

where k_0 is the rate constant in pure water. As we can verified (no photoreaction with pure water), $k_0 \ll k_1'$.
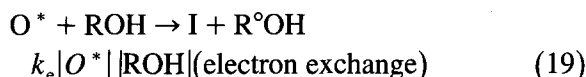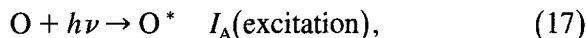
The absorbance measured as the area of the absorption band allows the calculation of the oscillator strength f^* [18]. For example, the two Keggin anions $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ have respectively $f^* = 1.18$ and $f^* = 1.11$, values in good agreement with the values of very intense transitions. So, the quantum yield, R, can be expressed as the ratio of the rate of $(I)^{5-}$ formation and the photons flux per time unit: $R = v/I_A = k_1 |SiW_{12}O_{40}^{4-}|$. These results are reported in Table 3. Except the $SiMoW_{11}O_{40}^{4-}$ ion, it appears that R is generally weak. The greater value is reached by the $PW_{12}O_{40}^{3-}$ ion. There is a good correlation between R and the free energy $\Delta G°$ of the first electronic exchange. Except $PW_{12}O_{40}^{3-}$ ion, these results agree with the previous reported ones for irradiation at 252 nm [2] but do not agree with its dependance on the alcohol or pH.

Table 3
Quantum yield, free energy of the first electron process and oscillator strength for different HPC

Ion	R	$\Delta G°$ (kJ · mol^{-1})	f^*
α-$PW_{12}O_{40}^{3-}$	0.47	-16.4	1.05
α-$SiW_{12}O_{40}^{4-}$	0.09	$+4.8$	1.16
	0.28	$+4.8$	1.16
α-$BW_{12}O_{40}^{5-}$	0.02	-4.3	1.15
α-$H_2W_{12}O_{40}^{6-}$	0.003	$+27$	1.13
β-$SiW_{12}O_{40}^{4-}$	0.04	-4.3	
α-$SiW_{11}MoO_{40}^{4-}$	3.2	-51.1	1.05
α-$H_2AsW_{18}O_{62}^{7-}$	0.005	$+3.4$	
α-$P_2W_{18}O_{62}^{6-}$	0.1	-19.3	

3.2. Electronic exchange and deexcitation process

The oscillator strengths are always very close to 1, meaning that the efficiency of the excitation process is very good. The great evolution of R with respect to different HPC can result from the differences between the rate constant of fluorescence and electronic exchange.

$$O + h\nu \rightarrow O^* \quad I_A(\text{excitation}), \tag{17}$$

$$O^* \rightarrow O \quad k_D|O^*|(\text{deexcitation}), \tag{18}$$

$$O^* + ROH \rightarrow I + R^\circ OH$$

$$k_e|O^*| \, |ROH|(\text{electron exchange}) \tag{19}$$

and if we assume a stationary state for O^*

$$v = k_e \cdot I_A|ROH| \cdot /(k_D - k_e|ROH|), \tag{20}$$

$$R = k_e \cdot |ROH/(k_D - k_e|ROH|) \tag{21}$$

where $k_e \cdot |ROH| = k_1$

$$R = k_1/(k_D - k_1) \tag{22}$$

k_D can be estimated from the oscillator strength (for $SiW_{12}O_{40}^{4-}$ $k_D = 1.16 \times 10^9$ s^{-1}, see Table 3).

These values are very close together for Keggin anion showing the good structural similarity of the compounds when considering molecular orbitals. The oscillator strength allows a rough evaluation of the oscillator length associated with the chromophore leading to a mean value of 0.16 nm which is very close to the tungsten–terminal oxygen bond length. This calculation is consistent with Klemperer's assumption which proposes to consider that HPC have carbonyl behavior.

Table 4
Quantum yield, oscillator strength, fluorescence rate and electron exchange rate for different HPC

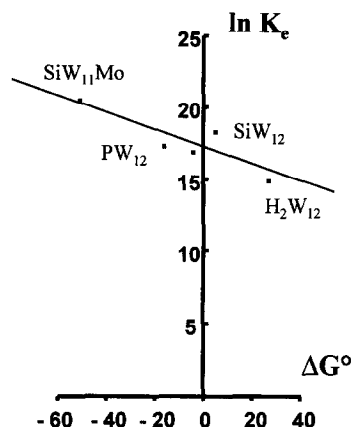| Ion	R	f^*	k_D ($\cdot 10^9$ s)	k_e ($\cdot 10^7$ s)
α-$PW_{12}O_{40}^{3-}$	0.47	1.05	1.04	3.3
α-$SiW_{12}O_{40}^{4-}$	0.09	1.16	1.16	9.5
α-$BW_{12}O_{40}^{5-}$	0.02	1.15	1.15	2.2
α-$H_2W_{12}O_{40}^{6-}$	0.003	1.13	1.13	0.3
α-$SiW_{11}MoO_{40}^{4-}$	3.2	1.05	1.05	80

Fig. 8. Relationship between the rate constant of electron exchange and the free energy of the first reduction step of HPC.

From the values of k_D and R we can calculate k_e (Table 4).

Then plotting $\ln k_e = f(\Delta G^\circ)$ a good linear dependance is observed (Fig. 8).

As expected, it implies that, for the primary step, the electron exchange is only governed by the HPC redox potential.

The very fast fluorescence process makes any measurement of redox properties of excited HPA very difficult, even if some work has reported a very weak light emission from excited HPC [17].

4. Conclusion

The use of an original thin layer cell facilitates the demonstration that the photooxidation of alcohols involves multi-monoelectronic steps for HPC. The reaction rate does not depend strongly on the alcohol but mainly on the standard redox potential of the first electronic exchange of the HPC. An unexpected catalytic effect from the photoproduct is observed. A surprising similarity between W–Ot bond and –C=O bond is shown. Perhaps this may explain the easy energy transfer between excited HPC and carbonyl compounds. The photooxidation of alcohol seems to occur via a radical process.

Studies of similar reactions using solid materials could provide very useful information about the oxidehydrogenation process in heterogeneous oxidation.

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