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# Aerobic photocatalytic oxidation of adamantane with heteropolyoxometalates $[X^{n+}W_{12}O_{40}]^{8-n}$ where $X = Si, Co^{2+}, Co^{3+}$

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## Abstract

Photolysis ( $\lambda > 260$  nm) of dioxygen saturated acetonitrile–water (98/2) solution of 1:12 heteropolytungstates  $[X^{n+}W_{12}O_{40}]^{8-n}$  where  $X = Si$  (1),  $Co^{2+}$  (2),  $Co^{3+}$  (3) and adamantane give a mixture of adamantanol-1, adamantanol-2 and adamantanone in 4:1:3 ratio. The quantum yields of this photooxidation reaction catalyzed by 1–3 are  $5.5 \cdot 10^{-3}$ ,  $4.5 \cdot 10^{-3}$  and  $0.8 \cdot 10^{-3}$ , respectively. The suggested mechanism envisages the hydroperoxides formation in the solvent cage followed by their photodecomposition to alcohols and ketone.

*Keywords:* Photolysis; Dioxygen; Heteropolytungstates; Adamantane; Quantum yield; Hydroperoxide; Autooxidation

## 1. Introduction

Heteropolyanions (HPA) of tungsten can be reduced to give the well known heteropoly blue compounds [1–3]. Photocatalytic oxidation with tungstic acid, its salts and heteropolyacids such as 12-tungstophosphoric acid has been reported to be sensitive to UV light in the presence of a suitable reducing agent [4]. These heteropolyanions can be photoreduced in the presence of alcohols [5–9] and a variety of organic substrates [10,11]. This reduction has also been achieved by radiolysis through a variety of short-living organic radicals [12].

The particularly interesting characteristic properties of these compounds are that they are able to accept a certain number of electrons in

separate reduction steps without noticeable decomposition and the process can be reversible since they can give back the electrons with concomitant reoxidation to the original form [6]. Under excess of dioxygen, catalytic photooxidation of secondary alcohols initiated by irradiation at charge transfer bands of heteropolytungstophosphates has been investigated [13–16]. The reoxidation of the reduced heteropolytungsten compounds is very easy with dioxygen and this reaction is the basis for the photocatalytic action of these compounds [17]. Such reoxidation can be also performed under anaerobic conditions by catalytic  $H_2$  evolution from alcohols in the presence of co-catalysts [7,13,14,18,19]. There has been an extensive study of the photochemical oxidation of saturated C–H bonds with dodecatungstophosphate [20–23]. Catalysts with  $Si, Co^{2+}, Co^{3+}$  het-

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eroatoms have been studied in the photooxidation of several alcohols but the photoreactivity with saturated C–H bonds has been found to be negligible [9].

## 2. Results and discussion

In the present paper we have examined the photoreactivity of 1:12 heteropolytungstates such as  $K_4SiW_{12}O_{40}$  (1),  $HK_5Co^{2+}W_{12}O_{40}$  (2) and  $K_5Co^{3+}W_{12}O_{40}$  (3), in the presence of dioxygen and under irradiation of UV light  $\lambda > 260$  nm (Corex filter), by using adamantane as a substrate.

UV-visible spectra of these catalysts show  $\lambda_{max}$  at 263 nm. In the case of heteropolytungstate with  $Co^{2+}$  and  $Co^{3+}$  ions, there is a supplementary band at 625 and 388 nm, respectively (Table 1).

By excitation of compounds 1–2 in the charge transfer band at  $\lambda > 263$  nm in the presence of adamantane we have obtained a moderate yield of oxydation products (around 25%) after 80 h of irradiation (Fig. 1). In the presence of 3 the oxidation rate of adamantane is considerably slower. The behaviour of this latter reaction is a more complicated process because there were a colour change (yellow to blue) and a solid phase separation during the irradiation period. UV-visible spectroscopic analysis of this precipitate showed that the band at 388 nm, characteristic for  $K_5Co^{3+}W_{12}O_{40}$ , disappeared and a new band at 625 nm, corresponding to  $HK_5Co^{2+}W_{12}O_{40}$ , was present. The formation of  $HK_5Co^{2+}W_{12}O_{40}$  in a saturated solution of  $K_5Co^{3+}W_{12}O_{40}$  can explain the apparition of

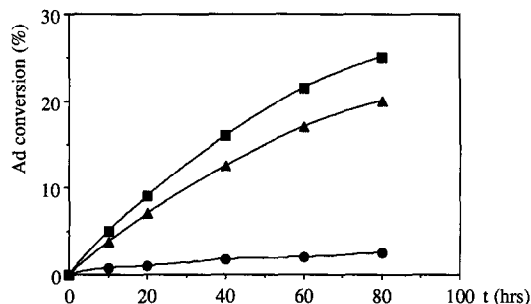
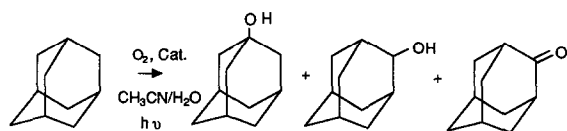


Fig. 1. Photochemical oxidation of adamantane catalyzed by dodecatungstates: 1 ■; 2 ▲; 3 ●.

solid phase. Probably, light scattering and aggregation lead to the decreasing of adamantane oxidation rate.

The photooxidation of adamantane in the presence of  $K_4SiW_{12}O_{40}$  at  $\lambda > 260$  nm gave adamantanol-1, adamantanol-2 and adamantanone in 4:1:3 ratio and after a long period of irradiation (80 h) a small amount (1%) of polyoxygenated compounds was observed.



Iodometric titration and GC analysis confirm that during the course of the reaction the hydroperoxides were not present. In order to check the possibility of hydroperoxides formation as intermediates, this reaction has been performed with a medium pressure Hg lamp and a Pyrex cut off  $\lambda > 280$  nm filter (under such conditions the hydroperoxides are known to be stable). The ratio adamantanol-1:adamantanone was changed to 2:1:1 (the adamantane hydroperoxides have been obtained and analysed by GC after their reduction to corresponding alcohols by phosphite method). Photolysis at  $\lambda > 260$  nm of the reaction mixture (obtained by irradiation at  $\lambda > 280$  nm) under anaerobic conditions resulted in the hydroperoxides decomposition and the same ratio reached the value already mentioned above

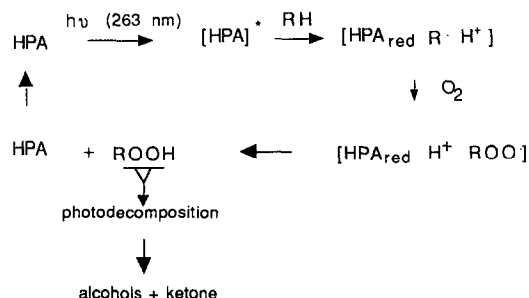
Table 1  
UV spectral data for dodecatungstates 1–3

Catalyst	Solvent	$\lambda_{max}$ (nm) ( $\epsilon$ ( $M^{-1} cm^{-1}$ ))
$K_4SiW_{12}O_{40}$	$CH_3CN/H_2O$	262
$HK_5Co^{2+}W_{12}O_{40}$	$H_2O$	262, 625 (230)
$K_5Co^{3+}W_{12}O_{40}$	$H_2O$	262, 388 (1150)

(4:1:3). So, under the latter wavelength range irradiation, the hydroperoxides were transformed into corresponding alcohols and ketone [24]. The hydroperoxides photodecomposition rate was equal or faster than the rate of their formation since the iodometric test is negative during the oxidation of adamantane. Hydroperoxides photolysis at  $\lambda > 260$  nm in the absence of catalyst under anaerobic condition led to the same (4:1:3) products distribution but hydroperoxides photodecomposition rate increased in four–five times. It has been demonstrated that in adamantane photooxidation at  $\lambda > 280$  nm in the presence of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  (this catalyst gave the selective formation of the hydroperoxides as primary products [25]) this ratio was 35:20:1.

So, in accordance with the type of the products formed in this reaction and their ratio we suggest that adamantane oxidation in the presence of the dodecatungstates was occurring by the formation of hydroperoxides in the solvent cage followed by their photodecomposition giving alcohols and ketone (Scheme 1).

The irradiation of HPA (1–3) at the band with  $\lambda_{\text{max}}$  263 nm leads probably to an intramolecular  $\text{O}(2p) \rightarrow \text{W}(5d)$  charge transfer forming the excited species  $\text{HPA}^*$  which abstract hydrogen from RH to produce a radical  $\text{R}^\cdot$  and one electron reduced HPA. The radical  $\text{R}^\cdot$  reacts immediately with dioxygen to build an alkyl peroxy radical. The latter can reoxidize the catalyst inside the solvent cage to give hydroperoxides, their photodecomposition leads to the formation of alkoxy and hydroperoxy free radicals which give alcohols and ketone. These



Scheme 1.

Table 2

Quantum yields for the photocatalysed oxidation of adamantane in the presence of dodecatungstates 1–3

Catalyst	Quantum yield $\Phi$ ( $10^3$ )
$\text{K}_4\text{SiW}_{12}\text{O}_{40}$	5.5
$\text{HK}_5\text{Co}^{2+}\text{W}_{12}\text{O}_{40}$	4.5
$\text{K}_5\text{Co}^{3+}\text{W}_{12}\text{O}_{40}$	0.8

alkoxy and hydroxy free radicals can participate to an oxidative chain process. The behaviour of this overall reaction is similar to the one recently observed for carbonylation and vinylation of C–H bond by Hill et al. [26,27]. So, such overall process is a superposition of three simultaneous types of reaction:

(i) alkane photocatalytic oxidation in the presence of HPA (1–3) with the formation of hydroperoxides,

(ii) photodecomposition of these hydroperoxides giving alkoxy and hydroperoxy free radicals which initiate a chain process,

(iii) reactivity of formed free radicals with alkane and solvent to give alcohol and ketones (propagation and termination chain reaction).

The quantum yield for the photooxidation of adamantane in the mixture acetonitrile–water 98/2 in the presence of the dodecatungstates was defined here as the number of moles of oxidized alkane divided by the einsteins of photons which were absorbed by the photolyte. The quantum yields, presented in Table 2, demonstrate the activity of the dodecatungstates in the adamantane oxidation. For comparison, the quantum yield for this reaction in the presence of  $\text{Na}_4\text{W}_{10}\text{O}_{32}$  is 0.11 [25].

### 3. Experimental

#### 3.1. Materials

Acetonitrile (SDS, analytical grade) was used as purchased. Adamantane (Aldrich, reagent grade) was purified by recrystallization from heptane. The dodecatungstates  $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ ,

$\text{HK}_5\text{Co}^{2+} \text{W}_{12}\text{O}_{40}$  and  $\text{K}_5\text{Co}^{3+} \text{W}_{12}\text{O}_{40}$  have been prepared following established methods [28,29]. All the heterododecatungstates were crystallized three times from water and checked for purity by UV-visible spectroscopy and gave good elemental analysis.

### 3.2. Methods

The samples were prepared by dissolving the alkane (0.18 mmol) and the dodecatungstate catalyst ( $5.5 \cdot 10^{-3}$  mmol) in the solvent (RCN:H<sub>2</sub>O = 98:2, 10 ml), saturated with dioxygen for 15 min and then transferred into a photochemical reactor for irradiation. A cylindrical quartz reactor equipped with a Corex tube  $\lambda > 260$  nm and a deep-in quartz cold water cut-off filter (reactor optical path length 1 cm) and preheated Rayonet apparatus equipped with four U-shaped 10 W Hg low pressure lamps, were used for photochemical reactions at  $\lambda > 260$  nm. The reaction solutions were kept under a constant slight overpressure of pure dioxygen. For the irradiations at  $\lambda > 280$  nm a cylindrical Pyrex reactor with a bottom porosity 4 sintered glass filter disc (as a dioxygen inlet) equipped with a deep-in Pyrex cold water cut-off filter (reactor optical path length 1 cm) and a preheated 125 W medium-pressure Hg arc lamp (HPK) were used.

The iodometric determination of hydroperoxides was performed by a standard method, modified for organic media [30,31].

The quantitative GC analysis were performed on a Varian 3400 instrument, equipped with a DB-WAX fused silica capillary column (25 m  $\times$  0.25 mm i.d.), flame ionisation detector and a Varian 4400 electronic integrator. Nitrogen was the carrier gas. The 1.0 ml aliquots of the photolyte were treated with 0.2 ml of trimethyl phosphite [32] before GC-analysis to reduce the hydroperoxides to the corresponding alcohols and to prevent the hydroperoxides decomposition in the injector. Cyclododecane was added as standard and the samples were analysed with the programming of the temperature. GC-MS

analyses were performed on a INCOS 50 instrument.

The quantum yields were determined at 260 nm using the potassium ferrioxalate actinometry developed by Parker and Hatchard [33] in 1.0 cm quartz cell using the standard solutions. The light source was a Rayonet apparatus (Corex filter) described above.

UV spectra were taken on a Perkin-Elmer Lambda 5 spectrometer.

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