

Aerobic photocatalysed oxidation of alkanes in the presence of decatungstates: products and effects of solvent and counter-ion of the catalyst¹



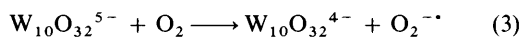
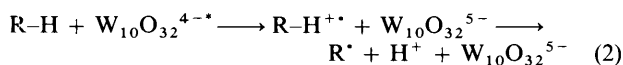
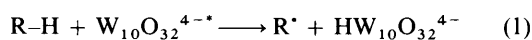
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The aerobic photocatalysed oxidation of alkanes in the presence of decatungstates $Q_4W_{10}O_{32}$ ($Q = Na, Me_4N, Pr_4N, Bu_4N, Hex_4N$) leads to hydroperoxides as primary products. Nitrile solvents and organic counter-ions of the catalyst compete in this photooxidation with alkane substrate. The influence of this competition on quantum yield, rate and selectivity for the oxidation of adamantane is quantitatively evaluated. A catalytic cycle, describing the formation of primary and secondary oxidation products, is proposed.

Introduction

During the last ten years, photocatalysed oxidation and functionalization of unactivated C–H bonds in the presence of polyoxometallates (POM) has attracted considerable attention due to its potential application in petrochemistry, environmental and material sciences, energetics, as well as for organic synthesis.² Despite the fact that the reaction has been studied in detail for several POM–substrate couples under both aerobic and anaerobic conditions, our knowledge of the mechanism of photooxidation is still incomplete. The following sequence of reactions (1)–(4) gives an insight into the mechanism of aerobic



alkane oxidation in the presence of decatungstate $Q_4W_{10}O_{32}$ ($Q = \text{metal or tetraalkylammonium cation}$) quoted in the literature.

Irradiation of $W_{10}O_{32}^{4-}$ (λ_{\max} 323 nm) with UV light $\lambda > 280$ nm leads to an intramolecular O(2p)→W(5d) charge transfer forming the excited species $W_{10}O_{32}^{4-*}$ which abstracts a hydrogen from the alkane R–H to produce a radical R^{\cdot} and a one-electron reduced POM $HW_{10}O_{32}^{4-}$ or $W_{10}O_{32}^{5-}$. The two mechanisms proposed for this step—hydrogen atom transfer [AT, reaction (1)]⁴ and non-adiabatic electron transfer (ET) followed by proton transfer [reaction (2)]⁵—have not been supported by a great deal of experimental evidence, and both can probably be operative depending on the POM–substrate couple. Under aerobic conditions, the radical R^{\cdot} reacts with dioxygen, and a large variety of oxidation products—hydroperoxides, alcohols, carbonyl compounds, acids, *etc.*—have been reported for this reaction. In order to explain their formation, the classical autooxidation mechanism has been proposed by some authors,^{6,7} but considered to be inconsistent with observations made by others.^{4a} Reoxidation of a one-electron reduced catalyst $HW_{10}O_{32}^{4-}$ (or $W_{10}O_{32}^{5-}$) is supposed to proceed in a separate step by dioxygen [reactions (3) and (4)].^{6a,8}

The discrepancy between the observed products and the proposed mechanism prompted us to reinvestigate the aerobic

photocatalysed oxidation of alkanes in the presence of decatungstates. The quantitative evaluation of the influence of solvents and organic counter-ions of the catalyst has also been studied.

Experimental

Materials

Acetonitrile (SDS, analytical grade) was used as purchased. Propionitrile and isobutyronitrile (Fluka, reagent grades) were purified by filtration through a column with activity I basic aluminium oxide followed by fractionation. After a GC check for purity, the middle cuts of *ca.* 50% of the batches were used for the whole series of experiments. Adamantane (Aldrich, reagent grade), was purified by recrystallization from heptane. Cyclododecane (Fluka, reagent grade), trimethyl phosphite and triethyl phosphite (Aldrich) were used without further purification. The decatungstates $Na_4W_{10}O_{32}^{4-}$ ^{4a} and $(Bu_4N)_4W_{10}O_{32}^{4-}$ ⁹ were prepared according to literature methods. The decatungstates $Q_4W_{10}O_{32}$ ($Q = Me_4N, Pr_4N, Hex_4N$) were synthesized by an analogous procedure to that used for $(Bu_4N)_4W_{10}O_{32}$. All the decatungstates were crystallized three times from acetonitrile and checked for purity by UV–VIS spectroscopy and microanalysis. $(Me_4N)_4W_{10}O_{32}$ (Found: C, 6.98; H, 1.81; N, 2.04; W, 69.20. $C_{16}H_{48}N_4O_{32}W_{10}$ requires: C, 7.26; H, 1.83; N, 2.12; W, 69.45%); $\lambda_{\max}(\text{CH}_3\text{CN})/\text{nm}$ 323 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 13 900). $(Pr_4N)_4W_{10}O_{32}$ (Found: C, 18.27; H, 3.27; N, 1.62; W, 58.90. $C_{48}H_{112}N_4O_{32}W_{10}$ requires C, 18.62; H, 3.65; N, 1.81; W, 59.38%); $\lambda_{\max}(\text{CH}_3\text{CN})/\text{nm}$ 323 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 13 800). $(Hex_4N)_4W_{10}O_{32}$ (Found: C, 30.58; H, 5.11; N, 1.49; W, 47.50. $C_{96}H_{208}N_4O_{32}W_{10}$ requires C, 30.59; H, 5.56; N, 1.49; W, 48.18%); $\lambda_{\max}(\text{CH}_3\text{CN})/\text{nm}$ 323 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 13 800).

Methods

The samples were prepared by dissolving the alkane (1.8×10^{-3} mol) and the decatungstate catalyst (5.5×10^{-5} mol) in the chosen solvent (RCN:H₂O = 98:2, 100 ml), which was then saturated with dioxygen for 15 min and quickly transferred into a photochemical reactor for irradiation. A cylindrical Pyrex reactor with a bottom porosity four sintered glass filter disc (as a dioxygen inlet), equipped with a deep-in Pyrex cold water cut-off filter ($\lambda > 280$ nm; reactor optical path length 1 cm) and a preheated 125 W medium-pressure Hg arc lamp (HPK), was used for photochemical reactions. The reactor geometry and catalysts' concentration ensure the absorption of at least 99.9% of the incident light. Aliquots of the photolyte were removed for

analysis at appropriate time intervals using a syringe through a side-arm Teflon stopcock.

CAUTION! Prolonged irradiation of the nitriles under aerobic conditions in the presence of photooxidation catalysts may produce HCN!

The iodometric determination of hydroperoxides was performed by using a standard method, modified for organic media.¹⁰

The quantitative GC analyses were performed on a Varian 3400 instrument, equipped with a DB-WAX fused silica capillary column (25 m × 0.25 mm i.d.), flame ionization detector and a Varian 4400 electronic integrator. Nitrogen was the carrier gas. The 1.0 ml aliquots of the photolytes were treated with 0.2 ml of an appropriate trialkyl phosphite.¹¹ Cyclododecane was then added as standard and the samples were analysed at a temperature of 50 °C (2 min), which was then increased to 200 °C at a rate of 10 °C min⁻¹. The hydroperoxides of alkanes were decomposed during the GC analysis giving a mixture of the corresponding alcohols and ketones. In the case of hydroperoxycyclododecane the mixture of cyclododecanol and cyclododecanone (*ca.* 1:1) was formed during the direct GC analysis of the sample while the only detectable product (after its reduction with trimethyl phosphite) was cyclododecanol. Control experiments showed that (MeO)₃P did not reduce cyclododecanone to cyclododecanol. The GC-MS analyses were performed on a Finnigan 4000 instrument.

The quantum yields were determined at 320 nm (interference filter) by Aberchrome 540 actinometry¹² in a 1.0 cm quartz cell, using the standard solutions. The light source was a 150 W medium-pressure Hg arc lamp.

The ¹H and ¹³C NMR spectra were recorded on a Bruker AC-200 spectrometer,† the IR spectra were recorded on a Nicolet FT-IR 205 instrument, the UV spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer and the CI-MS spectra were recorded on an AEI MS-9 instrument with methane, isobutane or NH₃ as the reactant gases. Microanalyses were performed by the Laboratory of Microanalysis (ICSN-CNRS).

The isolation of the hydroperoxides was performed using medium-pressure liquid chromatography (MPLC) on Michel-Miller chromatography columns, home-filled with silica gel 60 (0.040–0.063 mm, Merck), operating with a Waters Model 510 pump, a Waters R401 differential refractometer and a BBS SE 120 chart recorder.

Preparation of hydroperoxides

Hydroperoxycyclododecane. A solution of cyclododecane (303 mg, 1.8 × 10⁻³ mol) and Na₄W₁₀O₃₂ (134 mg, 5.5 × 10⁻⁵ mol) in 100 ml of CH₃CN-H₂O (98:2) was irradiated for 30 min under dioxygen. The solvent was evaporated, the residue was extracted with ethyl acetate, filtered, concentrated and purified by MPLC. Elution with ethyl acetate-heptane (3:7) yielded hydroperoxycyclododecane (90 mg, 25%) as a colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3398, 2933, 2864, 1470, 1446, 843; $\delta_{\text{H}}(200 \text{ MHz}; \text{CD}_3\text{CN})$ 9.14 (1 H, s, OOH), 5.47 (1 H, m, CH), 1.2–1.6 (22 H, m, CH₂); $\delta_{\text{C}}(50 \text{ MHz}; \text{CD}_3\text{CN})$ 83.20, 40.66, 28.17, 25.32, 25.26, 25.00, 24.94, 24.47, 24.05, 23.96, 23.01, 21.75; CI-MS (isobutane) *m/z* 201 (M + H)⁺, 183 (M + H - H₂O)⁺, 167 (M + H - H₂O₂)⁺, 165. Iodometric titration—97% purity.

Hydroperoxyacetonitrile. A solution of Na₄W₁₀O₃₂ (134 mg, 5.5 × 10⁻⁵ mol) in 100 ml of CH₃CN-H₂O (98:2) was irradiated for 4 h under dioxygen. Work-up and isolation as described above for hydroperoxycyclododecane afforded hydroperoxyacetonitrile (145 mg) as a volatile oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3346, 2270, 1414, 1383, 1345, 1046, 903, 822;

$\delta_{\text{H}}(200 \text{ MHz}; \text{CD}_3\text{CN})$ 10.65 (1 H, s, OOH), 4.66 (2 H, s, CH₂); $\delta_{\text{C}}(50 \text{ MHz}; \text{CD}_3\text{OD})$ 116.7 (CN), 62.6 (CH₂). Iodometric titration—97% purity.

2-Hydroperoxypropionitrile. The same procedure as described above, was followed except that acetonitrile was replaced by propionitrile, to afford 2-hydroperoxypropionitrile (174 mg) as an oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3348, 2260, 1414, 1379, 1336, 1146, 1095, 1042, 854; $\delta_{\text{H}}(200 \text{ MHz}; \text{CD}_3\text{CN})$ 10.50 (1 H, s, OOH), 4.80 (1 H, q, *J* 6.9, CH), 1.49 (3 H, d, *J* 6.9, CH₃); $\delta_{\text{C}}(50 \text{ MHz}; \text{CD}_3\text{OD})$ 119.4 (CN), 70.5 (CH), 16.9 (CH₃). Iodometric titration—96% purity.

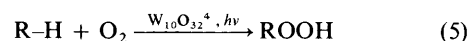
2-Hydroperoxy-2-methylpropionitrile. The same procedure as described above, except that acetonitrile was replaced by isobutyronitrile, afforded 2-hydroperoxy-2-methylpropionitrile (240 mg) as an oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3358, 2251, 1385, 1369, 1336, 1218, 1203, 1172, 849; $\delta_{\text{H}}(200 \text{ MHz}; \text{CD}_3\text{CN})$ 10.24 (1 H, s, OOH), 1.57 (6 H, s, 2 CH₃); $\delta_{\text{C}}(50 \text{ MHz}; \text{CD}_3\text{OD})$ 117.8 (CN), 77.1 (quart. C), 24.5 (CH₃). Iodometric titration—98% purity.

Results

Alkane

In order to study the selectivity and at the same time to avoid multiple product formation, adamantane was chosen in this study as the main alkane substrate for photocatalysed oxidation. Limited data on the oxidation of cyclododecane is also given when appropriate.

Irradiation of adamantane in acetonitrile in the presence of Na₄W₁₀O₃₂ with UV light $\lambda > 280 \text{ nm}$ in an atmosphere of dioxygen led to the accumulation of peroxides as can be followed by iodometric titration. Experiments in a closed system with the simultaneous control of gas volume, iodometric titration of peroxides and a quantitative GC analysis of the photolytes, demonstrated that the quantities of consumed dioxygen and the formed peroxides were approximately equal when the conversion of adamantane was kept at less than 10%. As the chromatographic separation of the adamantane peroxides proved difficult, we investigated the oxidation of cyclododecane. This gives a major product which was isolated and identified as hydroperoxycyclododecane. These results reveal the overall stoichiometry of reaction (5) and rule out the



possibility that an independent step [reactions (3) or (4)] is needed for reoxidation of the catalyst, which requires additional dioxygen.

The hydroperoxides of alkanes which were tested (adamantane, cyclododecane, cyclooctane, cyclohexane and some alkylbenzenes) proved to be thermally unstable and were decomposed during the GC analysis¹³ giving a mixture of alcohols and ketones. The reduction of hydroperoxides with trimethyl phosphite before the GC analysis led to alcohols which were detected. The photocatalytic oxidation of adamantane in acetonitrile in the presence of Na₄W₁₀O₃₂ was studied using the quantitative reduction of hydroperoxides to the corresponding alcohols followed by GC analysis. This is found to be a highly selective process leading to hydroperoxides as the primary reaction products. As can be seen from Fig. 1, the hydroperoxides are practically the only products when the conversion of adamantane was less than 25%. Adamantanone and poly-oxygenated products appeared in significant quantity later on during the oxidation run. So, after 70% conversion of adamantane, 71% of hydroperoxides, 9% of adamantanone and 20% of poly-oxygenated products were obtained. The selectivity for attack at the tertiary *vs.* secondary position was found to be 5:1 (after correction for the number of equivalent hydrogen atoms in the adamantane molecule). A variety of

† *J* Values are given in Hz.

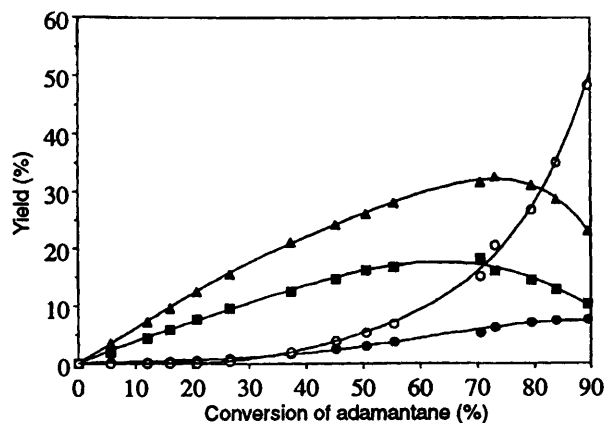


Fig. 1 Aerobic photocatalysed oxidation of adamantane in CH_3CN in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$. Plot of product yield against conversion of adamantane. Determined by quantitative GC analysis after reduction of the hydroperoxides to the corresponding alcohols with trimethyl phosphite; other conditions are described in the Experimental section. Adamantan-1-ol (\blacktriangle); adamantan-2-ol (\blacksquare); adamantanone (\bullet); polyoxygenated products (\circ).

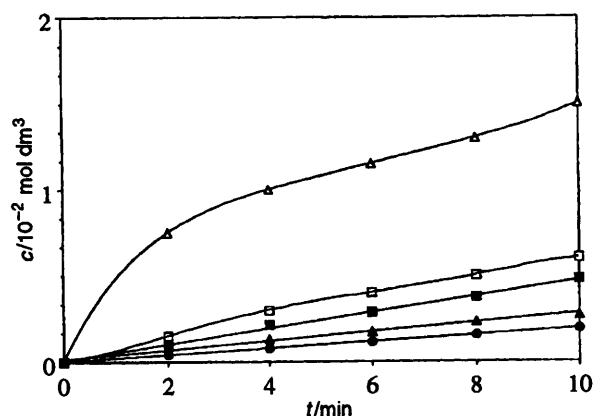


Fig. 2 Accumulation of the adamantane hydroperoxides (filled symbols) and total hydroperoxides (open symbols) in aerobic photocatalysed oxidation of adamantane in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ in CH_3CN (\blacksquare , \square), $\text{CH}_3\text{CH}_2\text{CN}$ (\blacktriangle , \triangle) and $(\text{CH}_3)_2\text{CHCN}$ (\bullet , \circ). Hydroperoxides of adamantane were determined as the corresponding alcohols by quantitative GC analysis after the reduction of photolytes with trimethyl phosphite. Total hydroperoxides were determined by iodometric titration of the photolytes.

dihydroperoxy-, hydroperoxyoxo- and dioxo-adamantanes was also identified (as their corresponding hydroxy derivatives, after reduction with trimethyl phosphite) by GC-MS among the products in the prolonged oxidation.

Solvent

Monitoring of the photocatalysed oxidation of adamantane in acetonitrile in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ by GC and iodometric titration has demonstrated that the total quantity of hydroperoxides in the photolyte (determined by iodometric titration) systematically exceeded that of adamantane hydroperoxides (determined by GC as adamantanols after reduction of photolytes with trimethyl phosphite) when the hydroperoxides were practically the only products of this reaction (Fig. 2). This result could be explained only by taking into consideration the oxidation of the solvent.

Therefore, the irradiation of acetonitrile in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ was carried out, the accumulation of a hydroperoxide was followed by the iodometry, and the previously unknown hydroperoxyacetonitrile, HOCH_2CN , was isolated as a colourless, moderately volatile liquid with acrid smell. It possesses stronger oxidizing properties compared with $\text{Bu}'\text{OOH}$ (as indicated by a comparison of their rates of

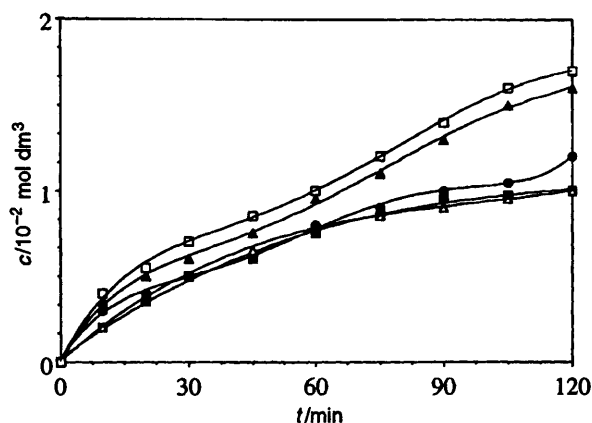


Fig. 3 Accumulation of hydroperoxides (by iodometric titration) during the irradiation of the acetonitrile solutions of decatungstates $\text{Q}_4\text{W}_{10}\text{O}_{32}$ under O_2 . Q: Na (\blacksquare); Me_4N (\triangle); Pr_4N (\bullet); Bu_4N (\blacktriangle); Hex_4N (\square)

reaction with KI). When the same experiments were performed with propionitrile and isobutyronitrile, the homologous α -hydroperoxyalkanenitriles were obtained. All new compounds were characterized using IR, ^1H and ^{13}C NMR spectra and molecular weight determination by iodometric titration. Upon longer irradiation times, α -hydroperoxyalkanenitriles could probably undergo further oxidation into acyl cyanides followed by their hydrolysis to produce HCN.

In order to study the influence of solvent reactivity on the oxidation of alkanes, the photocatalytic oxidation of adamantane in homologous nitrile solvents in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ was undertaken. No specific effects of solvent on the selectivity of oxidation of adamantane were detected. The net effect of solvent oxidation on the reaction consisted in a decrease of the adamantane consumption rate due to solvent competition for the photoactivated catalyst, as was judged by GC and iodometry (Fig. 2). Thus, after 10 min of irradiation the conversions of adamantane in these solvents were approximately 27% for acetonitrile, 15% for propionitrile and 11% for isobutyronitrile. The proportion of hydroperoxides of adamantane to the solvent hydroperoxides was 80:20 in acetonitrile and 18:82 in propionitrile. The oxidation of isobutyronitrile was so rapid that the correct determination of the total amount of hydroperoxides formed was not possible—the reaction mixture soon turned blue and became turbid due to the formation of a fine white precipitate (probably a solvent-hydroperoxyde-catalyst complex).

Effect of counter-ion

In order to evaluate the reactivity of the counter-ions, the irradiation of the series of catalysts $\text{Q}_4\text{W}_{10}\text{O}_{32}$ (Q = Na, Me_4N , Pr_4N , Bu_4N , Hex_4N) in acetonitrile was followed by iodometric titration. A comparison of these results has demonstrated that the rate of hydroperoxide accumulation increased in the order $\text{Me}_4\text{N} < \text{Pr}_4\text{N} < \text{Bu}_4\text{N} < \text{Hex}_4\text{N}$ in proportion to the amount of oxidizable C-H bonds in the organic counter-ions (Fig. 3). It should be noted that $(\text{Me}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, which was not expected to be oxidizable, showed a hydroperoxide accumulation profile identical to that which had been found upon irradiation of acetonitrile in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$. After prolonged photolysis catalysed by $(\text{Hex}_4\text{N})_4\text{W}_{10}\text{O}_{32}$, the quantity of the hydroperoxide groups due to counter-ions oxidation could reach up to 1 equiv. per alkyl group. The catalyst from this reaction was recovered significantly modified, as a waxy semi-solid, possessing a strong O-H (ν_{max} 3380 cm^{-1}) and a carbonyl (ν_{max} 1717 cm^{-1}) absorption band in its IR spectrum. Unfortunately, no valuable information was obtained from the ^1H and ^{13}C NMR spectra due to problems of solubility and non-homogeneity of this material.

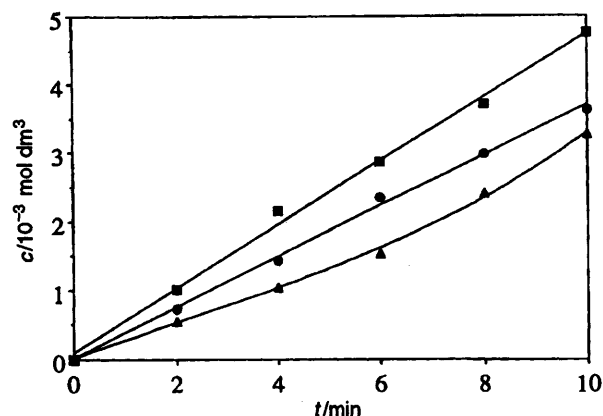


Fig. 4 Effect of counter-ion reactivity on the rate of photocatalysed oxidation of adamantane in CH_3CN in the presence of decatungstates: $\text{Na}_4\text{W}_{10}\text{O}_{32}$ (■); $(\text{Hex}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ (▲); $\text{Na}_4\text{W}_{10}\text{O}_{32}$ + 4 equiv. Hex_4NBr (●). Accumulation of adamantane oxidation products was followed by quantitative GC analysis of photolytes after reduction of the hydroperoxides to the corresponding alcohols with trimethyl phosphite.

Table 1 Quantum yields in aerobic photocatalysed oxidation of adamantane

Reaction system	Quantum yield, Φ (± 0.01)
AdH- $\text{Na}_4\text{W}_{10}\text{O}_{32}$ - CH_3CN	0.11
AdH- $(\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ - CH_3CN	0.09
AdH- $(\text{Hex}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ - CH_3CN	0.08
AdH- $\text{Na}_4\text{W}_{10}\text{O}_{32}$ - $\text{CH}_3\text{CH}_2\text{CN}$	0.06
AdH- $\text{Na}_4\text{W}_{10}\text{O}_{32}$ - $(\text{CH}_3)_2\text{CHCN}$	0.04

It was found that the influence of increased counter-ion reactivity on the photooxidation of the alkane was a decrease of the conversion of the latter. Thus, in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ the rate of oxidation of adamantane exceeded that obtained in the presence of $(\text{Hex}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ (Fig. 4). In addition, in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ + 4 equiv. Hex_4NBr the photooxidation gave an intermediate result between those obtained with $\text{Na}_4\text{W}_{10}\text{O}_{32}$ and $(\text{Hex}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ as the catalysts (Fig. 4). This high reactivity of organic cations is probably due to an association phenomenon.

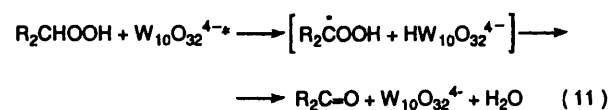
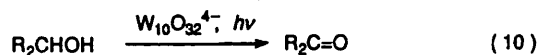
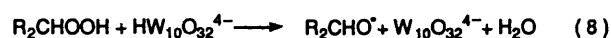
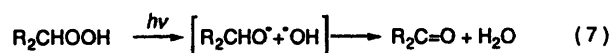
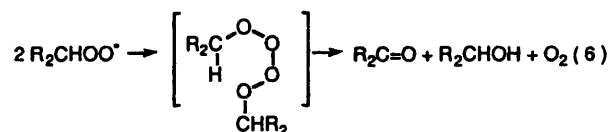
Quantum yields

The quantum yield was defined in this study as the number of moles of oxidized alkane divided by the number of moles of photons which were absorbed by the photolyte. Quantum yields are given in Table 1 for the adamantane oxidation in the nitrile solvents in the presence of representative tetraalkylammonium decatungstates. These results provided the quantitative data on the competitive effects of the alkane substrate, solvent and organic counter-ions of catalyst for the photoactivated decatungstate cluster in this reaction.

Discussion

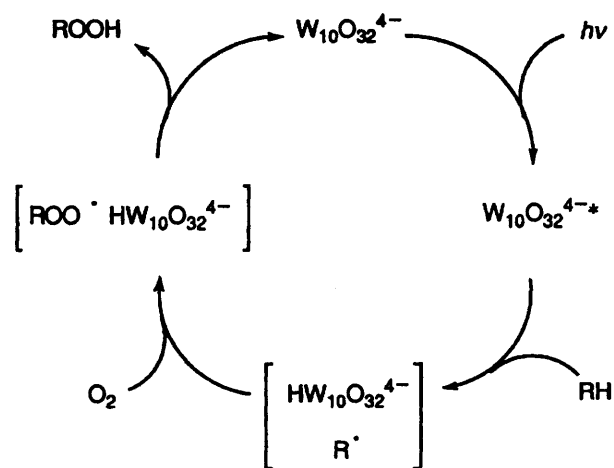
Simultaneous control of the reactions by GC and iodometric titration methods has demonstrated that all the components of the catalytic system possessing C-H bonds (alkane substrate, nitrile solvent, organic counter-ion of a catalyst and primary oxidation products thereof) are liable to photocatalytic oxidation. The hydroperoxides formed as the main products in this reaction are stable under the reaction conditions. The origin of a minor product in the oxidation of adamantane—adamantanone—was considered to be of special importance for understanding the mechanism of this reaction. Four possible origins for adamantanone could be considered: (i) recombin-

ation of freely diffusing 2-adamantyl peroxide radicals [reaction (6)];¹⁴ (ii) photolysis of 2-adamantyl hydroperoxide [reaction (7)];¹⁵ (iii) reduction of 2-adamantyl hydroperoxide with reduced catalyst $\text{HW}_{10}\text{O}_{32}^{4-}$ to adamantan-2-ol [reactions (8) and (9)]¹⁶ followed by its photooxidation [reaction (10)];^{8d,17} (iv) direct photocatalysed oxidation of adamantyl 2-hydroperoxide [reaction (11)].



Pathway (i) [reaction (6)] was ruled out on account of the high inherent hydroperoxide-producing selectivity of the reaction as can be seen from Fig. 1. Pathway (ii) [reaction (7)] does not take place as was shown in a control experiment, by the irradiation of Bu^tOOH in acetonitrile in the presence of $\text{Na}_4\text{W}_{10}\text{O}_{32}$ under anaerobic conditions. The photochemical stability of the hydroperoxy group can be explained by its very low absorption at $\lambda > 300 \text{ nm}$ ^{7,15} and by the powerful light shielding effect of the catalyst ($\epsilon 13 900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $\lambda 323 \text{ nm}$). Pathway (iii) [reactions (8) and (9)] could only be operative within a radical chain mechanism that is inconsistent with the quantum yield in this reaction (see Table 1), the stoichiometry of dioxygen consumption as well as a number of other observations.^{4a}

We therefore consider adamantanone to be a product of the consecutive oxidation (iv) [reaction (11)] of 2-adamantyl hydroperoxide that is consistent with the dynamics of the ratio 2-adamantyl hydroperoxide:adamantanone during photooxidation. The observations above support a catalytic cycle for the aerobic oxidation of alkanes as follows (Scheme 1).



Scheme 1

The alkyl radical R, produced from R-H by AT or ET mechanisms, reacts with dioxygen at a near diffusion-controlled rate ($k > 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)^{14,18} to give an alkyl peroxide radical ROO \cdot . The latter reoxidizes $\text{HW}_{10}\text{O}_{32}^{4-}$ inside the solvent cage to give hydroperoxide as a primary oxidation product and $\text{W}_{10}\text{O}_{32}^{4-}$ thus closing the catalytic cycle. In the case of secondary alkyl hydroperoxides, further oxidation (anaerobic by its nature) can proceed *via* α -hydrogen atom abstraction by the photoactivated catalyst to give α -hydroperoxyalkyl radicals. The latter are known to undergo fast fragmentation to give ketones.¹⁹ An electron transfer mechanism can also be operative for this second oxidation.²⁰

The photocatalysed oxidation of acetonitrile under anaerobic (giving succinonitrile)^{4a,21,22} and aerobic (giving unidentified product)^{6a} conditions have been reported in the literature. However its reactivity has been considered negligible and has thus far not been taken into account, even in kinetic studies. Identification of the hydroperoxides as the primary products in oxidation of both alkane and solvent has made possible a further comparison of their reactivity towards the photoactivated catalyst.

The solvent oxidation rates increase with a decrease of the C-H bond strength in their molecules [$\text{H}-\text{CH}_2\text{CN}$ $389 \pm 10.5 \text{ kJ mol}^{-1}$, $\text{H}-\text{CH}(\text{CH}_3)\text{CN}$ $376.1 \pm 9.6 \text{ kJ mol}^{-1}$, $\text{H}-\text{C}(\text{CH}_3)_2\text{CN}$ $361.9 \pm 8.4 \text{ kJ mol}^{-1}$]²³ as can be expected for a hydrogen-atom transfer mechanism. However, taking into account that the solvent concentration is three orders of magnitude higher than that of the alkane, and the high bond energy values for adamantane (*tert*-C-H 412 kJ mol^{-1} , *sec*-C-H 402 kJ mol^{-1}),²⁴ the surprisingly low oxidizability of acetonitrile is difficult to reconcile with the interpretation of the radical generation step as an AT process. An AT mechanism cannot be completely ruled out since the failure to conform to a simple linear free energy relationship in the atom-transfer reactions is quite a common observation for heterogeneous sets of substrates. Treatment of the activation energy for the hydrogen-atom transfer by the extended Evans-Polanyi relationship with inclusion of polar effects,²⁵ known to be operative in a transition state of AT reaction,²⁶ would probably provide more insight into the mechanism of photocatalysed oxidation. On the other hand, recent calculations have shown that generation of the more stable radical (an argument often used to support the AT mechanism for photocatalysed oxidation) can be explained perfectly well by the free energy change in the deprotonation of the radical cation within the ET mechanism.²⁷ It has been suggested that the distinction between the AT and ET mechanisms could be made by time-resolved spectroscopy data following laser flash photolysis of the decatungstate solutions.†

Conclusions

Extensive studies on the photocatalysed aerobic oxidation of alkanes in the presence of decatungstates lead us to conclude: (i) the aerobic photocatalysed oxidation of alkanes in the presence of decatungstates follows the mechanism of Scheme 1 with its essential feature of recombination of the radical pair inside the solvent cage, and leads to the hydroperoxides as the primary products. (ii) All components of the reaction mixture—alkane substrate, nitrile solvent, organic counter-ions of the catalyst, and primary oxidation products thereof—are susceptible to photocatalytic oxidation. (iii) Oxidation of the alkyl hydroperoxides (secondary and primary) by the photoactivated decatungstate is anaerobic in nature and leads to carbonyl compounds. (iv) The net effect of solvents and organic counter-ions of the catalyst on the oxidation of alkanes consists in their competition for the photoactivated decatung-

state cluster that results in the retardation of the main reaction without affecting its selectivity. (v) The rates of the solvent and/or the quaternary ammonium ions oxidation should not be ignored, especially in kinetic studies.

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† Ongoing studies in this laboratory.

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