Catalytic Photo-oxidation of Cyclohexene by Aqueous Uranyl–Polymolybdate(VI) Systems

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The mechanism of catalytic photo-oxidation of organic substrates by the aqueous uranyl–polymolybdate system has been studied. The photoactive species is the excited uranyl ion, the reactivity of which towards organic solutes is enhanced by the presence of polycondensed molybdate ions. The role of the mixed valence blue polymolybdates in the catalytic cycle of alkene oxidation has been elucidated; the formation of a long-lived exciplex $[Mo_mO_y{}^{p-}, UO_2{}^{2+}]^*$ species in the primary steps of the mechanistic scheme is suggested.

Although the oxidation of alkenes or aromatic compounds by the uranyl ion $UO_2{}^{2+}$ was not observed in earlier experiments,[1–3] these types of molecule strongly quench uranyl fluorescence: however this is a physical quenching phenomenon,[1] taking place *via* a uranyl–substrate π-complex.[3]

Uranyl has an oxido-reduction potential a little higher than that of cyclohexene (Table 1), but in this case the kinetic phenomenon is of greater importance. Oxidation of olefins in pyridine has been reported.[4] Recently[5] it was shown that irradiation with visible light of an acidic uranyl–polymolybdate solution containing cyclohexene led to reduced polymolybdate species[6,7] in their blue form. We now report a study of the mechanism of photo-oxidation, and establish the condition for genuine catalysis.

Materials and Methods

Uranyl nitrate hexahydrate (Labosi) and sodium molybdate dihydrate (Merck) were reagent grade and were used as received. Propan-2-ol, cyclohexene, and benzene were Fluka puriss grade and were used as received. Toluene (Prolabo Normapur) was distilled from sodium metal before use. Water was triply distilled or highly purified by use of a Millipore Milli-Q filtration system. Argon U was used for degassing. All other chemicals and solvents were reagent grade or better and were used as received.

U.v.–visible spectroscopic measurements were carried out with a Perkin-Elmer Lambda 5 instrument.

Continuous Photolysis.—A typical photolysis experiment with dilute solutions was carried out as follows. From a stock solution of $UO_2{}^{2+}$ (10^{-2}M; pH 1) and a stock solution of Na_2MoO_4 (4×10^{-2}M; pH 1) was prepared a sample solution (50 µl) with $[UO_2{}^{2+}]$ (4—8) $\times 10^{-3}$M, $[Mo^{VI}]$ (8—16) $\times 10^{-3}$M, and pH 1.0. All pH adjustments were made with sulphuric acid or NaOH and a pH meter (Tacussel TS 70/N). Dilute solutions of cyclohexene were prepared by addition of small amounts (5—10 µl) of a stock solution (1—2mM) with a microlitre syringe. After thorough mixing, a sample of solution (3 ml) was transferred to a 1-cm-square Pyrex cell equipped with a magnetic stirrer, and the cell was capped. Irradiations were then performed at room temperature with a Schoeffel 1 000 W mercury-xenon arc lamp equipped with a 20-cm-thick aqueous $CuSO_4$ filter in a Pyrex vessel, which transmitted visible light in the range 330—700 nm. When it was desirable to perform irradiations under anaerobic conditions rather than the normal aerobic conditions, argon gas was vigorously bubbled through the solution with stirring for at least 20 min, in a special cell equipped with a septum cap, and an argon blanket was maintained over the solution during the photolysis. Cyclohexene lost by evaporation was replenished by adding 2—3 µl to the cell with a microlitre syringe. U.v.–visible spectra were taken before and after irradiation.

Table 1. Approximate values of $E_{ox/red}$ (V *vs.* hydrogen electrode)[22]

Compound	$E_{ox/red}$
Cyclohexene	2.5
Cyclohexa-1,3-diene	2
Naphthalene	2
Benzene	2.5

When the reaction was carried out under a stream of pure oxygen, CO_2 was characterized by i.r. (ν 2 350 cm^{-1}) and by formation of a white crystalline precipitate of $BaCO_3$ when the gas was passed through a solution of $Ba(OH)_2$. The whole CH_2Cl_2 extract of the reaction mixture gave i.r. bands at 3 700, 3 500, and 1 720 cm^{-1}, corresponding to an organic acidic function. Adipic acid was identified (M^+ 146; m.p. 152—153 °C). When tetramethylethylene was used instead of cyclohexene, and the gas was passed through a solution of phenylhydrazine hydrochloride, yellow crystalline acetone phenylhydrazone was obtained, m.p. 122—124 °C (M^+ 238).

Fluorimetry.—Very dilute solutions of $UO_2{}^{2+}$ were used, to avoid spectrum distortion by an inner filter effect: the optical densities of the solutions were less than or equal to 0.05 for a cell of optical pathlength 1 cm.

The excitation wavelength was 420 nm, and the fluorescence spectra were recorded with a Perkin-Elmer λ S spectrofluorimeter.

A N_2 laser VSQN 337 fluorimeter was used for the time-resolved experiments. In this case, the excitation wavelength was 337 nm and the pulse duration was 3 ns. The quenching data obtained with cyclohexene as quencher substrate were expressed in the form of Stern–Volmer plots.

E.s.r.—The e.s.r. equipment and the products have been described previously.[8]

Laser Flash Photolysis.—The laser system used has been previously described.[9] The Nd-YAG Laser system frequency was tripled (λ 355 nm) in order to excite the $UO_2{}^{2+}$ species. The decay of the absorption of the $UO_2{}^{2+}$ excited state at 570 nm and the formation of the blue, mixed-valence polymolybdate(V/VI) complex absorbing at 810 nm (limited by detector response) were measured by time-resolved absorption spectroscopy. A Mo^{VI} concentration of 0.25M was required to produce a sufficient signal: the pH was maintained between 0.5 and 1.0 by using H_2SO_4, NaOH, and a pH meter. All experiments were conducted in optical cells of dimensions 1 × 10 or 2 × 10 mm. The analysing beam was perpendicular to the laser beam, and its optical pathlength was 10 mm. The cells had long necks to facilitate deoxygenation. This was accomplished when desired by bubbling argon through the solution for at least 30 min, and then maintaining an argon blanket over the solution during the experiment. Both propan-2-ol and cyclohexene were degassed separately before being introduced into the cell by microlitre syringe.

I.r. Spectroscopy.—I.r. spectra were measured with a Perkin-Elmer 782 spectrophotometer (range 4 000—400 cm^{-1}). The pellets were made with dried KBr. When necessary $CHCl_3$ was used as solvent.

Electrochemical Measurements.—The $E_{\frac{1}{2}}$ values were measured with a Tacussel PR 65 polarograph with EP4E recorder. The solvent was aqueous 0.05M-H_2SO_4/0.1M-Na_2SO_4. The reference electrode was saturated calomel (s.c.e.).

Results

Acidification of normal molybdate solutions leads to the formation of several polycondensed varieties: the best known are the heptamolybdate $[Mo_7O_{24}]^{6-}$ (3 < pH < 5) and the octamolybdate $[Mo_8O_{26}]^{4-}$ (pH < 3). Other polymerized and protonated species have been reported but their nature is controversial.[6,7,10]

Most of the isopolymolybdates turn blue on chemical, electrochemical, or photochemical reduction,[11] giving mixed-valence compounds[6,7] having acquired one or more additional electrons per molecule. The electrons can be reversibly or irreversibly restored to the medium.[6] This property was used in our experiments.

In concentrated medium, some cations induce the formation of discrete or infinite (chain-like, two- or three-dimensional network) polymolybdates which are formed extensively owing to their insolubility.[7] This probably occurs with the uranyl cation, which gives an amorphous yellow precipitate in an insufficiently acidified and highly concentrated medium ($[UO_2^{2+}] \geqslant 10^{-1}$M).[7] This precipitate has been identified by analysis and *X*-ray diffraction: it corresponds to an iriginite ($UO_2[MoO_4]_2 2H^+ \cdot 2H_2O$).[12] Its exact nature is discussed in the next section.

To avoid the formation of the precipitate and in view of the electrochemical properties of the solutions[13] we controlled the experimental conditions (pH $\leqslant$ 1) by addition of 0.5M-H_2SO_4, with $[UO_2^{2+}] \leqslant 10^{-2}$M.

The solutions of molybdate alone, acidified to pH 1, can be reduced to Mo^{V} (by $Na_2S_2O_4$ or Zn granules). The absorption of the reduced Mo^{V} species shows a maximum at 750 nm with a shoulder at 620 nm; its reduction potential is −0.1 V (*vs.* s.c.e.) or +0.144 V (*vs.* hydrogen). Permanganate titrations of reduced polymolybdate solutions of known optical density give $\varepsilon = 2 \times 10^3$ dm^3 mol^{-1} cm^{-1} for λ 800 nm.

U.v.–Visible Spectroscopy.—The u.v. and visible absorption spectra of solutions of Mo or UO_2^{2+} under our experimental conditions are the same as those reported in the literature.[1,6] The polymolybdate species (pH 1, [Mo] 0.001M) possess a very broad transfer band at about 250 nm (ε 3 000 dm^3 mol^{-1} cm^{-1} at 250 nm) with a tail extending to 350 nm (ε 500 dm^3 mol^{-1} cm^{-1} at 300 nm). Absorption spectra of mixtures of Mo^{VI} and UO_2^{2+} at various concentrations (to 0.1M in U^{VI}) and Mo/UO_2^{2+} ratio do not show the existence of any mixed U^{VI}Mo^{VI} complex.

Continuous Photolysis.—Irradiation of dilute solutions of molybdate alone or mixtures of UO_2^{2+} and Mo^{VI} (10^{-3}M-UO_2^{2+}; 10^{-2}M-Mo^{VI}) at pH 1 produced virtually no spectrophotochemical change during 3 h in the absence of any organic substrate. Addition of cyclohexene or cyclohexa-1,3-diene, or any compound that typically reacts with UO_2^{2+} alone (*i.e.* propan-2-ol, acetone, acetaldehyde, *etc.*) caused a blue coloration to appear within a few minutes of the start of irradiation in aerated or anaerobic solution. However, irradiation of concentrated acidic solutions of Mo^{VI} (10^{-1}M; ε 500 dm^3 mol^{-1} cm^{-1} at 300 nm) or mixtures with UO_2^{2+} (10^{-1}M) produced a weak blue coloration without addition of organic substrate. This is due to weak oxidation of water. The aqueous mixture of Mo^{VI} and U^{VI} oxidizes the alkenes at pH 1 and affords the blue mixed-valence molybdate. It was confirmed that this blue species is the same as that formed in presence of alcohol. In the concentrated uranyl–molybdate medium the blue species (5×10^{-3}M < $[UO_2^{2+}]$ < 10^{-2}M; Mo $\geqslant 10^{-2}$M) appears immediately after initiation of photolysis, with initial $\lambda_{max.}$ 810 nm. The absorption continues to grow in the dark and for the more concentrated solutions ($[UO_2^{2+}]$ 10^{-1}M) $\lambda_{max.}$ shifts to longer wavelength, finally ending at 830 ± 20 nm after about 100 min. At this point, in aerated solutions, the absorption slowly begins to decrease. In cases where photolysis has proceeded to some extent, the blue species reversibly disappears in the dark in the presence of oxygen to restore the original mixture. We detected the presence of U^{IV} (λ 650 nm) only when propan-2-ol was the solute and for low concentrations of molybdenum (10^{-3}M). In none of the reactions with alkene or aromatic systems was any U^{IV} detected.

The measurements of the oxidation rate of cyclohexene were carried out with a constant concentration of U^{VI} (0.01M) and variable concentration of Mo.

A supplementary filter in the range 370—700 nm was used to avoid the absorption of the isopolymolybdate. After 10 min photolysis the optical density of the blue solution was measured at 810 nm.

For all the cyclohexene-saturated solutions, after 1 h irradiation, the optical density of the blue polymolybdate reached a plateau. For various Mo/UO_2^{2+} ratios, the percentages of oxidation reaction, calculated from the Mo^{VI} optical density at the plateau, are given in Table 2.

The results show that the reaction is close to first-order during the first few minutes of the experiments, and during this time the visible absorption maximum is always 810 nm.

Laser Flash Photolysis.—Nanosecond time-resolved photolysis of solutions of $UO_2^{2+}(NO_3)_2$ (0.25M; pH 1) yielded an intense long-lived transient absorption with maximum at 580 nm, similar to that previously found by Hill *et al.*,[2a] which disappeared with first-order kinetics [k (1.6—0.5) × 10^5 s^{-1}].

Measurements of the uranyl excited-state lifetime at λ 570 nm gave a value (6.3 ± 0.2 μs) five times greater than that found by Hill[2a] (1.25 μs) in water.

Flash photolysis of acidic solutions of uranyl ion alone or uranyl ion with polymolybdate produced the excited $(UO_2^{2+})^*$ state as a transient. In order to follow the photochemical

Table 2. Oxidation of cyclohexene at various Mo/UO_2^{2+} ratios

Mo/UO_2^{2+}	% Oxidation of cyclohexene
1:1	11.7
2:1	37
4:1	48.1

Table 3. Laser flash photolysis: mechanism of formation of blue polymolybdates; data for pseudo-first-order kinetics; treatment of the two successive reactions ([Mo] = 0.25M, [UO_2^{2+}] = 0.06 or 0.12M, pH 0.8).

[UO_2^{2+}]/Mo	First reaction	Second reaction
0.06	$k_1 = (0.63 \pm 0.02) \times 10^3\ s^{-1}$ $t_1 = (1.6 \pm 0.1) \times 10^{-3}$ s	$k_2 = (0.032 \pm 0.02) \times 10^3\ s^{-1}$ $t_2 = (33.3 \pm 6) \times 10^{-3}$ s
0.12	$k_1 = (1.55 \pm 0.2) \times 10^3\ s^{-1}$ $t_1 = (0.64 \pm 0.1) \times 10^{-3}$ s	$k_2 = (0.018 \pm 0.02) \times 10^3\ s^{-1}$ $t_2 = (55 \pm 6) \times 10^{-3}$ s

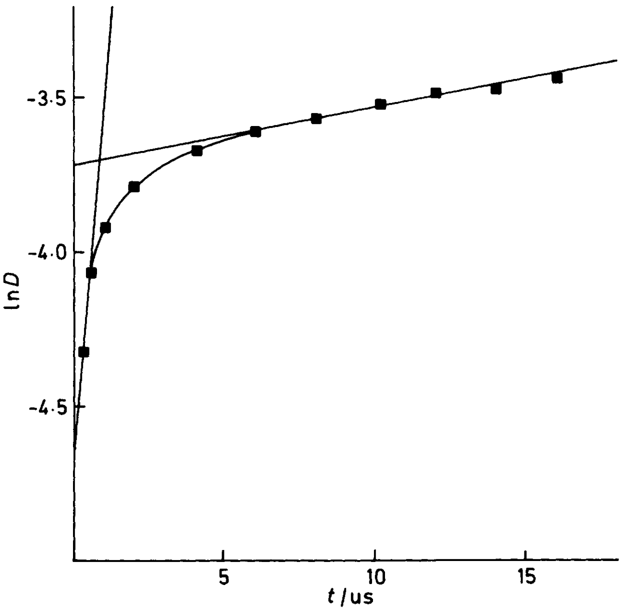


Figure 1. Laser flash photolysis: formation of the blue polymolybdate. Pseudo-first-order kinetic treatment of the two successive reactions; [Mo] = 0.25M, [UO_2^{2+}] = 0.12M. Plot of ln D (optical density at 810 nm) as a function of time

formation of the blue species, we chose propan-2-ol as organic substrate because of its known high reactivity towards (UO_2^{2+})*,[2,3] the known behaviour of its radical,[14] and its solubility in water. In UO_2^{2+}–polymolybdate(VI) solutions, flash photolysis of samples containing propan-2-ol led to the increasing disappearance of the (UO_2^{2+})* absorption band, with increasing propan-2-ol concentration, and to the appearance of an absorption at 810 nm (separable into a rapid formation in less than 10^{-3} s, and a second, much slower formation lasting more than 40 × 10^{-3} s).

The plots are in agreement with two successive reactions, supporting a pseudo-first-order kinetic treatment. In neither case were the formation kinetics altered by the presence of oxygen.

Pseudo-first-order kinetic treatment of (UO_2^{2+})* decay at 570 nm gave a rate constant for disappearance of (UO_2^{2+})* with propan-2-ol equal to (2.3 ± 0.1) × 10^7 dm^{-3} mol^{-1} s^{-1}.

We obtained similar results with saturated solutions of cyclohexene. The absorption of the blue species was measured at 810 nm (Figure 1 and Table 3).

No chemical intermediates corresponding to either U^V [15,16] or U^{IV} [2b,17] were seen in the UO_2^{2+} or UO_2^{2+}–polymolybdate(VI) solutions with propanol concentrations up to 2 × 10^{-1}M. This is not surprising, since transient U^V has only been observed once,[15] and both U^V and U^{IV} have relatively weak molar extinction coefficients. Thus their presence or absence cannot be demonstrated by this method.

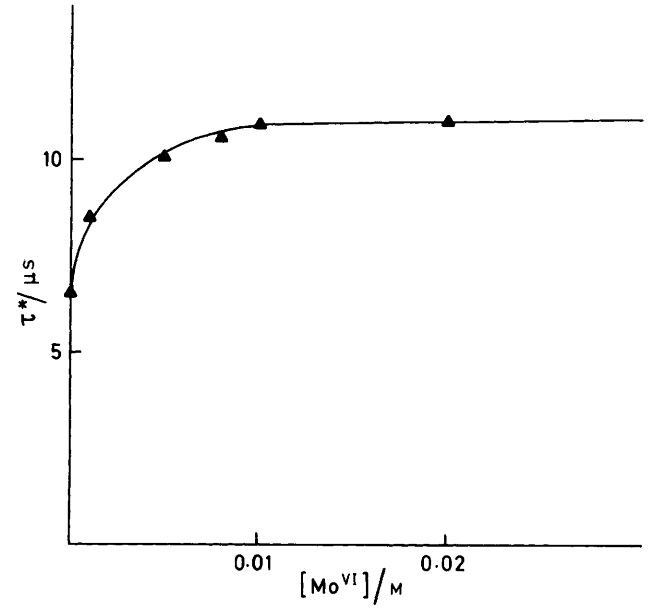


Figure 2. Plot of τ* (lifetime of the excited uranyl species without cyclohexene) as a function of [Mo]

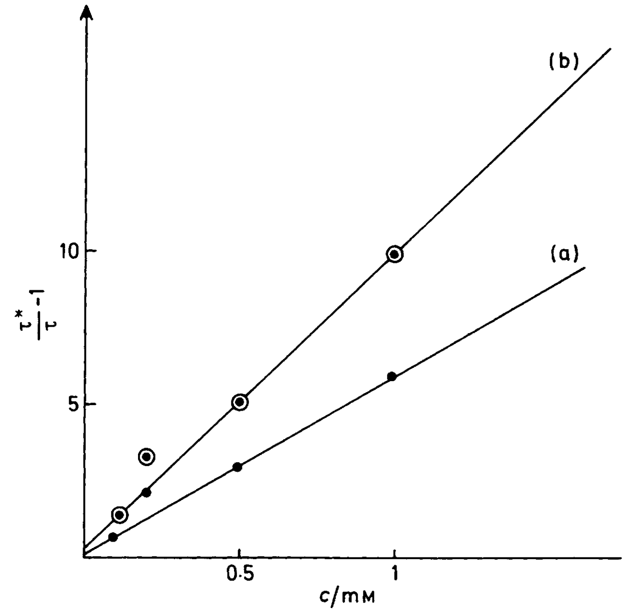
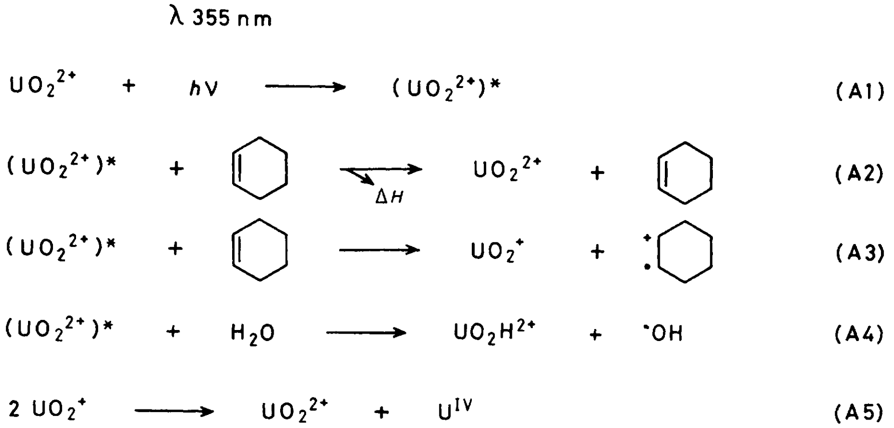


Figure 3. Stern–Volmer plots of τ*/τ − 1 against cyclohexene concentration (c) (τ = lifetime of the excited uranyl species): (a) [UO_2^{2+}] = 0.01M, [Mo] = 0; (b) [UO_2^{2+}] = 0.01M, [Mo] = 0.01M; slope = K_{SV}

Furthermore, these solutions cannot be analysed because the deep colour obtained after several laser flashes prevents the analysing beam from being transmitted.

Fluorescence Data.—The fluorescence spectrum of (UO_2^{2+})* remains unchanged in the presence of the polymolybdate species for molybdate concentrations up to 0.005M. In more concentrated molybdate solutions ($\geqslant$0.01M), a slight shift (5 nm) to low frequency is observed.

Furthermore, the time-resolved fluorimetric experiments performed using a pulsed nitrogen laser (3 ns; $\lambda_{exc.}$ 337 nm) show that the lifetime of the transient species depends on the molybdate concentration (Figure 2). Values of 6.3 and 11 μs, respectively, were found for the (UO_2^{2+})* species in the absence



Scheme 1. Mechanism A

and in the presence of molybdate (0.01M) in the 480—560 nm wavelength range.

The plot of $\tau^* = f[\text{Mo}]$ (Figure 1) reaches a limiting value for $[\text{Mo}] \geqslant 0.01\text{M}$, giving the experimental values for the subsequent determination of the Stern–Volmer plots for the two sets of solutions (Figure 3) as follows: $[UO_2^{2+}] = 0.01\text{M}$, $[\text{Mo}] = 0$; $[UO_2^{2+}] = 0.01\text{M}$, $[\text{Mo}] = 0.01\text{M}$. We used the two corresponding lifetime values (τ^*) to establish these plots. The Stern–Volmer constants (K_{SV}), calculated from the slopes of the curves, were 9.1 ± 0.5 and $(6.0 \pm 0.51) \times 10^3$ dm^3 mol^{-1} in the presence and in the absence of Mo.

All these results lead us to suggest the existence of a $[UO_2^{2+}, Mo_mO_y^{p-}]^*$-type exciplex in concentrated Mo solutions. The quenching rate constant values (k_q) calculated from K_{SV} and the lifetime values indicate that the quenching of the UO_2^{2+} excited state by cyclohexene is as efficient in the presence of Mo as in its absence. Indeed, k_q is, respectively, 8.3×10^8 and 9.5×10^8 dm^3 mol^{-1} in the absence and in the presence of Mo. These values are higher than those found for propan-2-ol and show that cyclohexene is about three times more efficient than propan-2-ol in the UO_2^{2+} excited-state quenching process. This leads us to suggest that the long-lived $[UO_2^{2+}, Mo_mO_y^{p-}]^*$-type exciplex favours alkene oxidation.

The fact that the lifetime of the exciplex reached a plateau for Mo concentrations above 0.01M strongly argues for the participation of a unique reactive Mo polycondensed species in the exciplex formation.

E.s.r. Study.—Visible light irradiation ($\lambda > 350$ nm) of aerated or anaerobic solutions of the uranyl–polymolybdate(VI) system at pH 1 in the presence of spin traps resulted in the observation of nitroxide radicals. Spin traps above pH 1 gave no spin adduct; under short or continuous photolysis (10—15 min) spin adducts appeared in the UO_2^{2+}–Mo^{VI} solutions. 2,2-Dimethyl-3,4-dihydropyrrole 1-oxide (DMPO) showed a characteristic quartet (1:2:2:1) due to the spin adduct with OH˙ radical, from oxidized water. This result is in agreement with the continuous photolysis data.[11] The coupling parameters are $a_H = a_N = 14.0 \pm 0.2$ G; $g_{iso} = 2.0055 \pm 0.0001$. With α-(1-oxido-4-pyridinio)-*N*-t-butylnitrone (4-POBN) the parameters are a_N 15.02, $a_H = 1.66 \pm 0.2$ G; $g_{iso} = 2.0069 \pm 0.0001$. These signals are comparable with the spectrum attributed to the hydroxyl radical spin adduct with DMPO or 4-POBN.[11,18–20] When an organic compound was added to this mixture, one could see in addition a spin adduct corresponding to an organic free radical. For example, with cyclohexene, $a_N = 15.15$, $a_H = 20.5 \pm 0.2$ G; $g_{iso} = 2.0054 \pm 0.0003$; with propan-2-ol $a_N = 15.1$, $a_H = 23.8 \pm 0.2$ G; $g_{iso} = 2.0054 \pm 0.2$.

Direct analysis of the blue solution at room temperature (293 K) or at low temperature (120 K) gave an isotropic e.s.r. spectrum corresponding to Mo^V.[21] The spectrum is better resolved at low temperature. Mixtures containing cyclohexene or propan-2-ol give similar e.s.r. spectra: $g_1 = 1.9258 \pm 0.0003$, $g_2 = 1.8948 \pm 0.0003$ (aqueous solution saturated with cyclohexene), $g_1 = 1.9564$, $g_2 = 1.9026 \pm 0.0003$ (aqueous solution containing 30% of propan-2-ol).

At low and at higher field, it is possible to distinguish six weak satellite lines due to ^{95}Mo and ^{97}Mo ($I = 5/2$; natural abundance 25%). The medium ratio of the hyperfine splitting constant is 52.5 ± 0.34 G.

Discussion

On the basis of the spectroscopic and photolytic data obtained with the various techniques, the roles of the uranyl ion and polymolybdates in the various systems studied will be discussed.

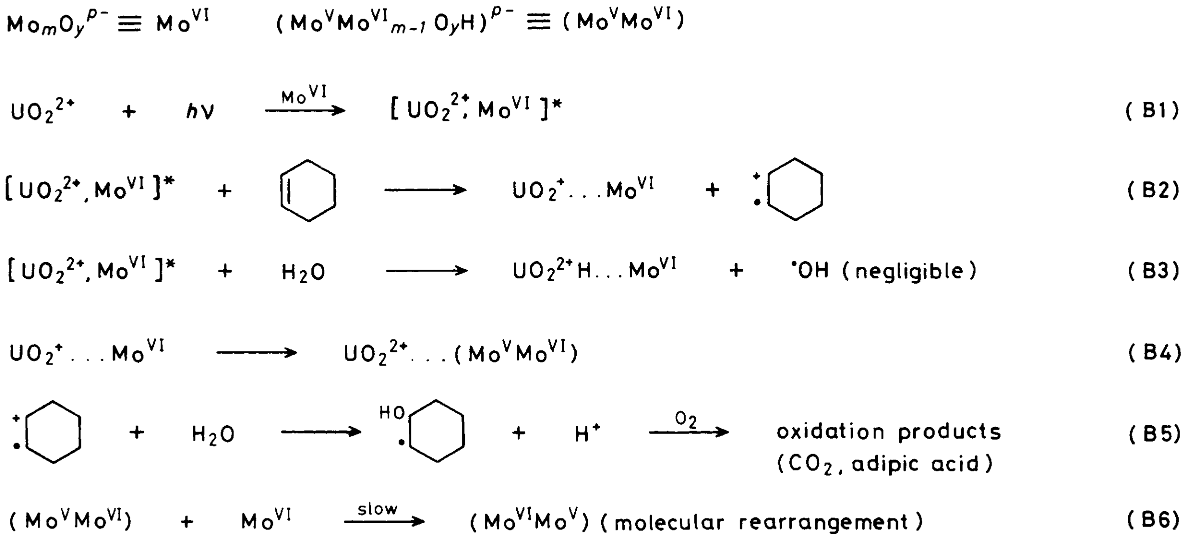
The reactions occurring on irradiation of the aqueous UO_2^{2+}–cyclohexene system can be explained by mechanism A (Scheme 1). In this mechanism, only the reactions (A1) and (A2) are important. Reaction (A2) represents the dynamic quenching of excited uranyl by cyclohexene. The data obtained by the various techniques show that (A3) and (A4) can be neglected: neither the e.s.r. nor the photolysis results gave any evidence of the formation of hydroxyl or cyclohexenyl radicals or U^{IV} species. In fact the absorption band at 650 nm, characteristic of U^{IV}, is not observed in the cyclohexene–uranyl mixture.

The polymolybdates alone can be slightly reduced by H_2O and cyclohexene during u.v. irradiation, but under our experimental conditions ($\lambda > 330$ nm) these reactions can be neglected.

In contrast, the acid mixture of UO_2^{2+} and polymolybdate(VI) rapidly turned an intense blue colour on irradiation in the visible range in the presence of cyclohexene.

In this case, our e.s.r. experiments gave evidence for the formation of Mo^V, alkyl radical species, and small quantities of OH˙ radicals, probably arising from the weak oxidation of water.[23] The CO_2 evolved was characterized and i.r. spectroscopy gave evidence of oxidation products (acetone and adipic acid).

The fact that the reactivity of $(UO_2^{2+})^*$ towards the organic solutes is greatly enhanced in these media leads us to suppose that the polymolybdate species might play an important role in the process. Hitherto, to our knowledge, no observation of any mixed complexes in aqueous solution has been reported, and we did not observe such species (see Experimental section). However, we have suggested the formation of a transient-long lived $[UO_2^{2+}, Mo_mO_y^{p-}]^*$ exciplex-type species which not only favours alkene oxidation but also favours the reduction



Scheme 2. Mechanism B

of the polymolybdate species to a mixed valence species $(\mathrm{Mo^{V}Mo^{VI}}_{m-1}\,\mathrm{O}_y\mathrm{H})^{p-}$ owing to the proximity of the ions.

As previously mentioned, the kinetics of formation of the polymeric blue species can be explained in terms of two successive pseudo-first-order reactions relative to Mo. The first reaction is very fast and depends on the $\mathrm{UO_2}^{2+}$ concentration (Table 2). We therefore identify it as the charge-transfer reaction between $\mathrm{UO_2}^{+}$ and Mo$^{\mathrm{VI}}$, giving rise to the $(\mathrm{Mo^{V}Mo^{VI}})$ species.[23,24] The second reaction, which is slower (*t ca.* 40 ms), could be a structural modification such as in the mechanism suggested for the reduction of heptamolybdate.[5,16]

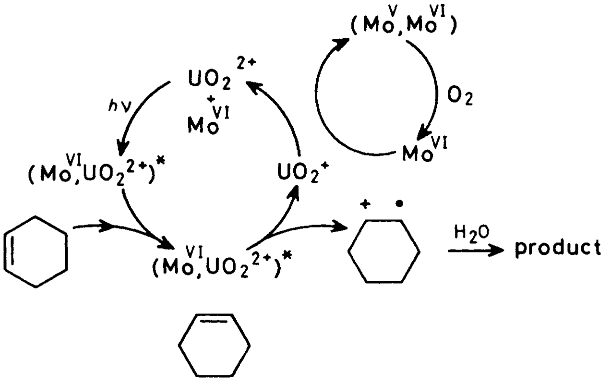
In the light of these results, we propose mechanism B (Scheme 2) for alkene oxidation in the aqueous $\mathrm{UO_2}^{2+}$–polymolybdate(VI) system.

Our e.s.r. study is in agreement with the existence of several polycondensed molybdates. Furthermore, i.r. spectra have been recorded for the blue precipitate obtained by irradiation of concentration solutions ($[\mathrm{UO_2}^{2+}] = 0.1\mathrm{M}$, $[\mathrm{Mo}] = 0.1\mathrm{M}$) and for the yellow iriginite precipitate. The same i.r. absorption bands (980, 908, 850, and 350 cm^{-1}) have been found for both species. These bands have been observed for polymerized octamolybdate $[(\mathrm{NH_4})_6\mathrm{Mo_8O_{27}}\cdot 4\mathrm{H_2O}]_\infty$.

In spite of a slight difference in composition, we suggest that the polyoctamolybdate anion is among the most active and reductive polymolybdates in our system.

The products characterized by physical methods and by chemical analysis allow us to infer that the photo-oxidation of an alkene by our system is a direct oxidation and not an abstraction of an allylic hydrogen atom, by analogy with the reactions with alcohols.[2,3] The quenching of uranyl fluorescence by unsaturated compounds depends upon the π-donor capacity and ionization potential of the substrate, and not upon the ease of hydrogen-atom abstraction.[2,3] Moreover, reactions between alkenes and strongly oxidizing hard acid ions such as Co$^{\mathrm{III}}$ and Mn$^{\mathrm{III}}$ also proceed by direct oxidation of the olefin or of the solvent.[26]

The uranyl–polymolybdate system is able to oxidize other unsaturated compounds such as benzene ($E_{\mathrm{ox/red}}$ 2.5 V *vs.* hydrogen electrode[22]). We observed this behaviour in some preliminary experiments. The appearance of small amounts of the blue polymolybdate(V/VI) on brief irradiation of the concentrated $\mathrm{UO_2}^{2+}$–polymolybdate solutions and the detection of hydroxyl radicals by e.s.r. during the photo-oxidation experiments suggest that this system is also capable of oxidizing water, as has been proposed before.[1,4,23] Nevertheless, this should make a relatively small contribution to the overall system.



Scheme 3. Catalytic cycle; for simplification $\mathrm{Mo^{VI}} \equiv (\mathrm{Mo}_m\mathrm{O}_y)^{p-}$; $(\mathrm{Mo^{V}Mo^{VI}}) \equiv (\mathrm{Mo^{V}Mo}^{\mathrm{VI}}_{m-1}\mathrm{O}_y\mathrm{H})^{p-}$

Under the conditions in the foregoing paragraph (brief irradiation), the triplet ground-state oxygen reoxidizes the blue species. This allows the cycle to be catalytic. In view of the foregoing conclusions, we present a schematic catalytic cycle scheme (Scheme 3).

As in the photocatalytic dehydrogenation of alcohols, the polymolybdates(VI) have a two-fold role: (1) they favour the electron-transfer reaction between $\mathrm{UO_2}^{+}$ and polymolybdate by increasing the lifetime of the excited $(\mathrm{UO_2}^{2+})^*$ species; and (2) they permit the system to work photocatalytically by reoxidizing U$^{\mathrm{V}}$ to U$^{\mathrm{VI}}$.

In conclusion, the aqueous acidic mixture of $\mathrm{UO_2}^{2+}$ and polymolybdate(VI) constitutes an especially efficient system for the oxidation of alkenes, owing to the oxidizing power of the excited uranyl cation and the electronic reactivity of the isopolymolybdates. The polymolybdate increases the oxidizing power of the excited uranyl species and acts as an electron acceptor in aqueous acidic solutions. Thus, polymolybdates inhibit the disproportionation of U$^{\mathrm{V}}$ to U$^{\mathrm{VI}}$ and U$^{\mathrm{IV}}$ by fast oxidation of U$^{\mathrm{V}}$ to U$^{\mathrm{VI}}$. Since it is possible to recover the original mixture in the presence of oxygen the system constitutes a good catalyst for the oxidation of alkenes.

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