

Deactivation processes of the lowest excited state of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ in aqueous solution †

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A detailed analysis of the photophysical behaviour of uranyl ion in aqueous solutions at room temperature is given using literature data, together with results of new experimental and theoretical studies to see whether the decay mechanism of the lowest excited state involves physical deactivation by energy transfer or a chemical process through hydrogen atom abstraction. Comparison of the radiative lifetimes determined from quantum yield and lifetime data with that obtained from the Einstein relationship strongly suggests that the emitting state is identical to that observed in the lowest energy absorption band. From study of the experimental rate and that calculated theoretically, from deuterium isotope effects and the activation energy for decay support is given to a deactivation mechanism of hydrogen abstraction involving water clusters to give uranium(v) and hydroxyl radicals. Support for hydroxyl radical formation comes from electron spin resonance spectra observed in the presence of the spin traps 5,5-dimethyl-1-pyrroline *N*-oxide and *tert*-butyl-*N*-phenylnitron and from literature results on photoinduced uranyl oxygen exchange and photoconductivity. It has previously been suggested that the uranyl emission above pH 1.5 may involve an exciplex between excited uranyl ion and uranium(v). Evidence against this mechanism is given on the basis of quenching of uranyl luminescence by uranium(v), together with other kinetic reasoning. No overall photochemical reaction is observed on excitation of aqueous uranyl solutions, and it is suggested that this is mainly due to reoxidation of UO_2^+ by hydroxyl radicals in a radical pair. An alternative process involving oxidation by molecular oxygen is analysed experimentally and theoretically, and is suggested to be too slow to be a major reoxidation pathway.

Introduction

The dioxouranium(vi) (uranyl) ion, UO_2^{2+} , possesses a rich and varied photochemistry. The first photochemical process involving reaction between this species and organic substrates was reported about 200 years ago,¹ and a vast literature exists on its photochemistry and photophysics, which has been extensively reviewed.^{2–11} A fairly detailed mechanistic understanding of the photoreactivity of uranyl ion now exists, with reactions generally involving photooxidation of substrates, occurring either by excitation of complexes or bimolecular reactions between excited uranyl ion and substrates.³ Excited uranyl ion is a strong oxidant ($E^\circ = 2.6$ V),^{5,6,12,13} and shows many similarities in its reactivity to the benzophenone triplet state. Its reactions include hydrogen atom abstraction, electron transfer and energy transfer.^{4,5,8}

The uranyl ion has played an important part in the development of photochemistry. Its luminescence in glasses was first reported by Brewster,¹⁴ and the study of this by Stokes led him to the general idea of the Stokes shift, whereby emission occurs at longer wavelengths than absorption.¹⁵ The first time-resolved investigations on luminescence, and indeed one of the earliest kinetic measurements, were made by E. Becquerel on the decay of uranium luminescence using the phosphoroscope.¹⁶ It was

during studies on this luminescence that his son, H. Becquerel noticed darkening of photographic plates by uranyl salts in the absence of light, which led him to the discovery of radioactivity.¹⁷ The nature of uranyl luminescence, whether it was fluorescence or phosphorescence, was the subject of considerable controversy in the early part of the 20th century, since it possesses a long lifetime (*ca.* 1 ms in the solid state), typical of phosphorescence, and yet shows the overlap of the long wavelength part of the absorption band with the emission spectrum, more commonly associated with fluorescence.¹⁸ To some scientists at that time,¹⁹ phosphorescence was only observed from solids, whereas photoluminescence was observed from both solid samples and solutions of uranyl salts, suggesting that the emission must be due to fluorescence. Many well known names in the development of photochemistry, including F. Perrin,²⁰ Vavilov and Levshin,²¹ and Pringsheim and Gaviola²² were involved in the discussions on the origin of uranyl luminescence, and it is only relatively recently that detailed understanding of the nature of the emitting species responsible has been achieved.

In fact, assignment of the electronic structure and excited states of uranyl ion has had a rather long and confusing history. In studies on absorption spectra of this species, Jørgensen²³ initially suggested that the lowest excited state results from charge transfer from oxygen to a vacant *f* orbital on uranium. Subsequently, McGlynn and Smith²⁴ used a methodology more appropriate to organic photophysics, and suggested that the

† Dedicated to the memory of Nobel Laureate, Lord George Porter FRSC FRS OM.

lowest energy absorption arises from a symmetry allowed, spin forbidden transition to three spin orbit components of the lowest triplet state. The lowest energy band in the absorption spectrum shows vibronic structure, associated with the O=U=O symmetric stretching vibration of the lowest excited state ($\nu_1 = 705 \text{ cm}^{-1}$). Associated with this absorption, there is a structured luminescence starting around 490 nm and extending above 600 nm. Bell and Biggers²⁵ expanded upon the description of McGlynn and Smith, and mathematically resolved the absorption spectra into a series of 24 Gaussian bands in 7 groups suggested to belong to components of the triplet state. However, indications were starting to appear that this may be better treated as a symmetry forbidden transition. Particularly valuable results came from Görller-Walrand and coworkers,²⁶ who have shown from analysis of intensities of a large number of spectra that transitions are inherently parity forbidden. Uranyl complexes are characterised by a linear (or near linear) UO_2^{2+} group O=U=O bonded to three, four, five or six ligands in the equatorial plane. These workers also showed significant dependence of intensities of the bands in the absorption spectra on the symmetry of complexes. Brint and McCaffery²⁷ have shown from magnetic circular dichroism that lowest energy transition is parity forbidden and involves two close lying triplet states. Jørgensen and Reisfeld²⁸ have argued that the lowest excited levels in uranyl ion have no well defined S or Λ because of the large spin-orbit coupling. However, the fact that the lowest excited state has some triplet character is strongly suggested by the observation of magnetic field effects in photochemical processes involving this species.²⁹ The most detailed and reliable picture of uranyl excited states probably comes from the work of the group of Denning.⁹ In this description, the lowest energy transition involves excitation of electron from σ_u HOMO to ϕ_u LUMO. For cylindrical symmetry this corresponds to a Σ_g^+ ($\Omega = 0$) to Π_g transition. Using two-photon spectroscopy (which has different selection rules from those in one-photon processes) Denning's group have also succeeded in determining the energies of the lowest nine close lying electronic excited states of $\text{CsUO}_2(\text{NO}_3)_3$.³⁰ In addition to its absorption and emission spectra, the uranyl ion also possesses a relatively intense excited state absorption around 570 nm.³¹⁻³⁵ In studies on single crystals of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ using polarised light, Denning and Morrison have shown that this excited state absorption is completely polarised along the O=U=O axis.³⁶

Although we now have a reasonable understanding of the basic photochemistry and electronic structure of the excited states of the uranyl ion, one aspect of its photochemistry still remains to be resolved: why the lifetime of its lowest excited state in aqueous solution is so short. Both physical deactivation, involving energy transfer to vibrational modes of water molecules³⁷⁻³⁹ and chemical quenching mechanisms involving fast, reversible electron-transfer⁴⁰ or hydrogen atom abstraction^{4,41-47} have been suggested. To attempt to resolve this outstanding problem, we describe a detailed analysis of the photophysics of uranyl ion in dilute acidic solution, using both a review of the existing literature and new experimental and theoretical data.

Experimental

Materials

All reagents were of the purest grade commercially available, and were used without further purification. Uranyl perchlorate solutions were prepared by dissolving uranium trioxide in perchloric acid, and then adjusting the pH using potassium or sodium hydroxide. Uranium(V) solutions are stable at low concentrations in the pH range 2–3 and solutions of this species were prepared either by electrochemical reduction^{48,49} or photolysis of uranyl salt solutions in the presence of isopropanol.⁵⁰ Solutions of uranyl salts were prepared using either

doubly distilled water or Millipore MilliQ water. No differences were observed in the photophysical behaviour of uranyl ion in these two solvents.

Apparatus and procedure

Absorption and luminescence spectra were run on Shimadzu UV-2100 and Jobin-Ivon SPEX Fluorolog 3–22 spectrometers, respectively. Flash photolysis experiments were performed in Coimbra and Clermont-Ferrand with Applied Photophysics LKS.60 Laser Flash Photolysis Spectrometers attached to a Hewlett-Packard Infinum oscilloscope, using the third-harmonic (355 nm) of the pulse from a Spectra-Physics Quanta Ray GCR-130 ND/YAG laser for excitation. Further details have been reported previously.⁵¹⁻⁵³ Electron spin resonance (ESR) spectra were recorded on a Bruker ER 200D spectrometer at 9.30 GHz with a modulation field of 100 kHz (Clermont Ferrand) and a RADIOPAN SE/X 2547 (Poland) spectrometer (Moscow). Solutions were degassed either on a high vacuum line or by bubbling with nitrogen. Light from a filtered Xe–Hg lamp ($\lambda > 335 \text{ nm}$) was used to irradiate samples directly in the ESR spectrometer cavity.

Results and discussion

Luminescence yields and lifetimes

A variety of experimental techniques have shown⁵⁴⁻⁵⁷ that at low pH and in the absence of complexing ligands, the dominant species present in aqueous solutions of uranyl salts is the pentaquo complex $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$. The X-ray crystal structure of this complex ion has been determined in uranyl perchlorate heptahydrate,⁵⁸ and reveals two short uranium–oxygen distances of ca. 1.75 Å due to the U=O bonds, and five longer U–O distances of ca. 2.45 Å due to the bonds between uranium and the oxygen atoms of the water molecules. Studies using XAFS indicate that the same structure is present in aqueous solutions.⁵⁶ The absorption spectrum of aqueous acidic solutions (pH \approx 1) of uranyl nitrate and perchlorate ($5\text{--}20 \times 10^{-3} \text{ M}$) were run, and showed identical spectra over the wavelength region studied, with the typical relatively weak structured absorption of the uranyl ion between 370 and 490 nm, together with more intense absorption at shorter wavelengths.^{25,35} A maximum molar absorption coefficient of the first band of $\epsilon_{419 \text{ nm}} = 11.9 \text{ M}^{-1} \text{ cm}^{-1}$ was determined, in excellent agreement with literature values.^{3,4,25,59} The luminescence spectrum was recorded of these solutions; this showed the typical structured uranyl ion emission, and was found to be independent of concentration, the counter ion or excitation wavelength. The luminescence spectrum of a solution of uranyl nitrate ($1 \times 10^{-2} \text{ M}$, pH 0.93) is shown in Fig. 1. Previous studies of the quantum yield of this species have used fluorescein as reference, since its emission spectrum closely overlaps that of the uranyl ion.⁶⁰ In fact, the trivial name for this dye, uranine, stems from the similarities between its spectrum and that of the uranyl ion. However, fluorescein shows some weaknesses as fluorescent standard, both due to its instability in solution and the marked dependence of its emission spectrum on pH.⁶⁰ We have, therefore, redetermined the luminescence quantum yield for this solution of uranyl nitrate using two separate references, quinine sulfate in 1 M sulfuric acid ($\phi_r = 0.546$)⁶¹ and quinizarin in ethanol ($\phi_r = 0.11$)⁶² with excitation wavelength 365 nm. Corrections were made for changes in refractive index of the medium as described elsewhere.⁶¹ Luminescence quantum yields of 3.4×10^{-3} (quinine sulfate standard) and 4.1×10^{-3} (quinizarin standard) were obtained. From these, and previous values under similar conditions,⁶⁰ we feel that the most reliable value of the luminescence quantum yield for $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ in aqueous acidic solutions is 3.8×10^{-3} , with an estimated uncertainty of ca. 15%.

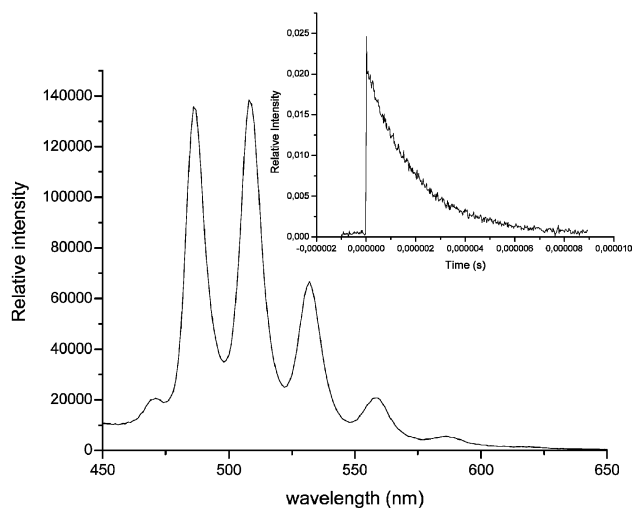


Fig. 1 The luminescence spectrum of a solution of uranyl nitrate (1×10^{-2} M, pH 0.93) at room temperature (20 ± 2 °C). The luminescence decay is shown in the inset.

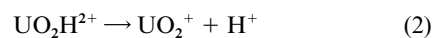
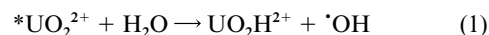
The decay of this emission was studied following excitation at 355 nm with the third harmonic of a Nd-YAG laser. Identical decays were observed at all wavelengths in the emission spectrum. A typical decay is shown as inset in Fig. 1. The decay fitted good first order kinetics, from which a luminescence lifetime $\tau = 1.9 \mu\text{s}$ was determined. This is in good agreement with previous literature values using both emission decay and decay of the excited state absorption.^{8,10,13,34,39,41-43,47,53,63-67} This is about an order of magnitude faster than the value calculated for hydrogen abstraction from a single water molecule, but is compatible with abstraction from a cluster of water molecules⁴⁴ or from one of the water molecules in the hydration sphere of the complex ion. In contrast, it is over two orders of magnitude faster than the lifetime calculated if decay involves energy transfer to vibrational modes of surrounding water molecules.⁴⁴ We, therefore, feel that a chemical mechanism is most appropriate for the excited uranyl decay. The unusual salt effects observed with the luminescence decay³⁹ may be associated with a mechanism involving hydrogen abstraction from water clusters. Support for a chemical rather than physical deactivation mechanism for excited uranyl ion in dilute solutions close to room temperature comes from observations both of an activation energy for the decay of 47.4 kJ mol^{-1} ,^{45,47} and a moderate deuterium isotope effect when the luminescence was studied in D_2O solutions.^{47,60} If the decay involved energy transfer to vibrational modes of water molecules, a much bigger isotope effect would be expected.⁴⁴

From the luminescence quantum yield and lifetime, the radiative decay constant (k_{rad}) of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ in aqueous solution was determined:

$$k_{\text{rad}} = \phi_f/\tau = 2.0 \times 10^3 \text{ s}^{-1}$$

This is in reasonable agreement with the value $1.4 \times 10^3 \text{ s}^{-1}$,⁶ calculated using the Einstein formula and the measured oscillator strength for the lowest energy absorption in anhydrous crystals of uranyl salts. This strongly suggests that the emitting state is identical to that observed in the lowest energy absorption band, that is the transition involves a ground state which is essentially a spin singlet and an excited state with considerable triplet character. This transition must be favoured by the strong spin-orbit coupling in this species.⁶ Attempts to observe formation of the lowest energy excited state in aqueous uranyl solutions using flash photolysis with ps time resolution showed that it was fully formed within the response time of the system (30 ps).⁶⁷ Considering our relatively poor understanding of spin-orbit coupling, it may be of interest to extend these flash photolysis studies to femtosecond timescales.

Although we believe that the above evidence shows that the lowest excited state of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ decays in aqueous solution by a hydrogen atom abstraction from water:



two weaknesses still exist with this mechanism: firstly, there is no evidence for formation of either uranium(v) or the hydroxyl radical, and secondly no overall photochemical decomposition of the uranyl solution is observed, such that any reduced uranium species must be oxidised back to uranium(vi). In the following sections we will address these points.

Spin trapping studies and other evidence for formation of reduced uranium species

Some support for the hydrogen atom abstraction reaction (1) comes from studies of the photolysis in the cavity of an ESR spectrometer of deoxygenated aqueous solutions of uranyl nitrate (10^{-2} – 10^{-1} M) in the presence of the spin traps 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) or *tert*-butyl-*N*-phenylnitron (PBN) at concentrations of *ca.* 0.1 M led to the appearance within a few seconds of ESR spectra (Fig. 2), which are identical to those of the hydroxyl radical adducts. For example, the PBN spin adduct in Fig. 2(b), formed in reaction (3):

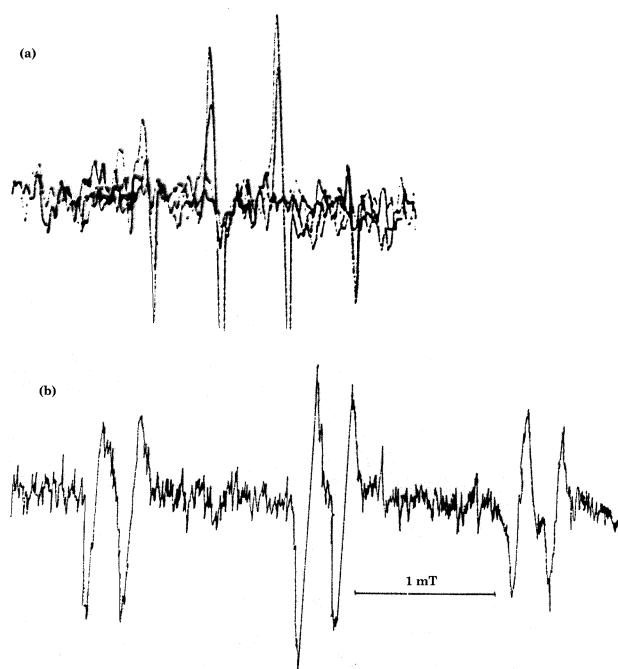
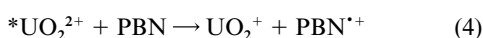


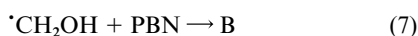
Fig. 2 ESR spectra observed upon photolysis of deoxygenated aqueous solutions of uranyl nitrate (0.01–0.1 M) in the presence of the spin traps: (a) 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO); (b) *tert*-butyl-*N*-phenylnitron (PBN) at room temperature (20 ± 2 °C) and *ca.* 0.1 M spin trap concentration.

has $g = 2.0059$, $a_{\text{N}} = 15.43$, $a_{\beta\text{-H}} = 2.71$, which can be compared with literature for the hydroxyl radical adduct of this species of $g = 2.0057$, $a_{\text{N}} = 15.30$, $a_{\beta\text{-H}} = 2.75$.^{68,69} The presence of air has little effect on the intensity of the spectra, and only shows the expected increase in linewidth due to paramagnetic broadening. This is in agreement with the lack of effect of oxygen on the excited state behaviour of uranyl ion.^{70,71} The removal of the hydroxyl radical in reaction (3) would be expected to lead to accumulation of uranium(v). Attempts were made to observe

uranium(v) formation spectroscopically following photolysis ($\lambda > 350$ nm) of aqueous solutions of uranyl nitrate (0.01 M) and PBN (0.01–0.1 M). Detection of uranium(v) was thwarted by formation of a yellow precipitate. However, although it has not been possible to characterise the precipitate, the fact that there is a reaction is consistent with the above mechanism. Spin trapping of hydroxyl radicals has previously been reported on photolysis of aqueous uranyl solutions in the presence of polymolybdate(vi) systems.⁷² We should note that the observation of the ESR spectra of the radicals from spin adducts is not conclusive evidence for reaction (1) since quenching of excited uranyl ion by the spin traps may produce radical cations, which can themselves produce hydroxyl radicals⁷³ through the reactions (for the case of PBN):

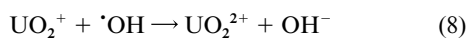


In addition, quenching of excited uranyl ion has been observed with nitroxyl free radicals.⁷⁴ However, we believe that the above results still favour the chemical quenching mechanism (1), because in competitive studies on photolysis of solutions of uranyl nitrate with PBN and methanol, in addition to the spectrum in Fig. 2(b), the spectrum of the $\cdot CH_2OH$ adduct, formed^{4,41,75} by the reaction sequence:



was observed, in addition to an as yet unidentified free radical. Reactions (3) and (7) are characterised by rate constants $k_3 = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_7 = 4.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$,⁶⁹ and the effect of varying methanol concentration on the relative intensities of these signals is consistent with competition between these processes, and, hence, formation of the hydroxyl radical in reaction (1). Whilst the parallel formation of $\cdot CH_2OH$ via hydrogen abstraction from methanol by oxidised PBN species cannot be ruled out, we do not have any kinetic data on this. Further, this will only affect the quantitative description and does not detract from the basic idea of competing hydrogen abstraction from water and methanol by excited uranyl ion.

Further support for reaction (1) has come from previous observations of photoinduced uranyl oxygen exchange. Studies on ligand exchange show that the rate of exchange of the uranyl oxygen atoms is slow ($k < 10^{-8} \text{ s}^{-1}$),⁷⁶ whereas the rate of exchange of the coordinated water molecules is fast ($k = 7.8 \times 10^5 \text{ s}^{-1}$).^{77,78} In contrast, the uranyl oxygen atoms exchange rapidly upon irradiation with ultraviolet or visible light.^{79–81} This can be readily explained by reactions (1) and (2) leading to the intermediate formation of uranium(v), in which there is rapid substitution of the coordinated oxygen atoms,^{77,79–82} followed by the back reaction (8):



Support for reactions (1) and (2) have also come from the observation of a transient increase in photoconductivity on photolysis of aqueous uranyl ions, attributed to formation of protons.⁸³

Against an exciplex mechanism for excited uranyl decay

Above *ca.* pH 1.5 uranyl luminescence spectrum loses structure and decay is no longer monoexponential. Explanations for nonexponential decay have included:

- Hydrolysis of uranyl solutions^{3,59,65,67,71,84}
- Reversible crossing between two electronic states^{60,63}

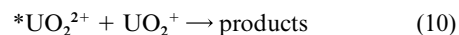
- Formation of a luminescent exciplex between excited uranyl ion and U(v)^{13,42,43,46}

For reasons which are discussed elsewhere⁶⁷ we now believe the reversible crossing model is not tenable. If, however, the chemical quenching mechanism is applicable, we have to provide evidence against the exciplex model of Marcantonatos. The uranyl ion and UO_2^+ are known to form a complex in aqueous solution,⁸⁵ whose structure is expected to be close to that of Marcantonatos' exciplex. However, this complex shows an absorption band at 737 nm,⁸⁵ which is not observed with the exciplex. Further, from kinetic studies on related systems⁸⁶ the rate of association of UO_2^{2+} and uranium(v) in aqueous solutions is likely to be considerably slower than the rate constant for excited uranyl decay. For example, for the reaction:



a second order rate constant $k \approx 3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ has been suggested.⁸⁶ Assuming a steady state concentration of excited uranyl ion on 1 μM , the lifetime for exciplex formation would be about 30s!

Final evidence against the exciplex mechanism comes from the study of uranyl fluorescence in the presence of uranium(v) prepared by controlled potential electroreduction. A solution of uranyl nitrate (0.1 M, pH 2.5), degassed by bubbling with nitrogen was electrolysed at a controlled potential of -0.364 V (relative to a saturated calomel reference electrode) and UV/visible absorption and emission spectra registered at various times. After about 5 min the solution turned green, and a new absorption band, attributed to uranium(v) was observed at 738 nm, in agreement with literature data.⁴⁸ At the same time, there was a marked decrease in the intensity of uranyl emission in the region 480–600 nm. On further electroreduction the band at 738 nm grew and the intensity of the luminescence continued to decrease. At the pH used, the solution was relatively stable, and there was no sign of either uranium(iv) formation or precipitation of uranium hydroxides. The concentration of uranium(v) was determined from the absorption spectrum using $\epsilon_{738 \text{ nm}} = 12 \text{ M}^{-1} \text{ cm}^{-1}$.⁴⁸ From this and the measured change in uranyl luminescence intensity a Stern–Volmer quenching constant $K_{sv} = 6400 \text{ M}^{-1}$ was obtained for the quenching reaction:



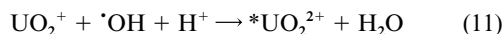
Using an average lifetime at this pH for excited uranyl ion of $\tau \approx 1.5 \mu\text{s}$ from data in references 60 and 63 gives a quenching rate constant for the above reaction $k_q \approx 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Similar quenching of uranyl luminescence by uranium(v), but produced by chemical reduction with europium(II), has previously been reported.⁸⁷ In that case, a very similar bimolecular quenching rate constant $k_q \approx 5\text{--}6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was reported.

The fact that uranium(v) quenches uranyl luminescence strongly rules against the exciplex mechanism, and in favour of the multiexponential decay of uranyl luminescence in aqueous solutions above pH 1.5 is due to hydrolysis, probably both in the ground and excited state.^{3,59,65,67,71} In fact, quite detailed speciation diagrams have been presented for all the emitting species.⁶⁵

Oxidation of uranium(v)

The remaining fact to be explained is how uranium(v) is oxidised back to uranyl ion. In reaction (8) we have suggested the hydroxyl radical as a good candidate for oxidant. Reaction may proceed either through an initially formed UO_2^+ /hydroxyl radical pair or through the separated species in solution. On thermodynamic grounds this is very feasible since the standard electrode potential for the $\cdot OH/OH^-$ couple (1.90 V)⁸⁸ is much greater than that for UO_2^{2+}/UO_2^+ (0.12 V).⁸⁹ Attempts to study the reaction of uranium(v) with hydroxyl radical using pulse

radiolysis have so far proved unsuccessful.⁹⁰ However, in studies on the electron transfer quenching of excited uranyl ion⁶⁴ a lifetime of ≈ 20 ns was estimated for the UO_2^{2+} /hydroxyl radical pair, such that the dissociation into free uranium(v) ions and hydroxyl radicals only has a very low probability. We note that in acidic solutions the couple H^+ , $\text{OH}/\text{H}_2\text{O}$ has a reduction potential 2.72 V⁸⁸ which is above the energy of the lowest excited state of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ ($20\,450\text{ cm}^{-1}$, 2.54 eV).⁶⁷ Chemiluminescence, leading to uranyl ion emission, has frequently been observed on oxidation of lower oxidation state of uranium.⁹¹ The energetically feasible reaction:



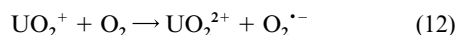
may well be an important step in the chemiluminescence reaction.

A further mechanism for oxidation of any free uranium(v) to UO_2^{2+} under aerated conditions that we have considered is reaction with molecular oxygen. Although the standard reduction potential in acid solution for H^+ , $\text{O}_2/\text{HO}_2^{\cdot}$ (0.12 V)^{88,89} is close to that of the uranium(vi)/(v) couple, under normal reaction conditions formation of UO_2^{2+} is possible by this route. We have carried out a theoretical and experimental study of the process. Uranium(v) was produced by the quantitative photochemical reduction of nitrogen saturated aqueous solutions of uranyl nitrate (0.5–1 mM, pH 2.20) with 2-propanol (0.25 M), as described by Howes, Bakac and Espenson.⁵⁰ The solutions were then equilibrated with air, and the reaction monitored by the decay of the uranium(v) absorption at 255 nm. For 0.5 mM uranium(v), the kinetics appear to follow mixed second- and first-order kinetics, which is reasonable since under these conditions the oxygen concentration (obtained by fitting of oxygen solubility as a function of temperature⁹² to a polynomial) is close to that of uranium(v). For 1 mM uranium(v), where $[\text{UO}_2^+] > [\text{O}_2]$, the decay follows pseudo-first-order kinetics, in agreement with the previously reported rate law:⁵⁰

$$\text{Rate} = k_2[\text{UO}_2^+][\text{O}_2]$$

Pseudo-first-order rate constants were obtained using Guggenheim's method,⁹³ and from these and the uranium(v) concentration an overall second-order rate constant $k_2 = 0.18 \pm 0.01\text{ M}^{-1}\text{ s}^{-1}$ was obtained at 20.5 °C. This can be compared with the value $31.4\text{ M}^{-1}\text{ s}^{-1}$ reported by Bakac and Espenson⁹⁴ at an unspecified temperature. The reasons for this difference are not clear, although the kinetics appear to show a marked dependence on the presence of any UO_2^{2+} . However, both sets of results show that oxidation of uranium(v) by molecular oxygen is a relatively slow way of regenerating UO_2^{2+} , and probably only of minor importance in the decay pathways of excited uranyl ion. The effect of temperature on this rate was studied over the temperature range 20.5–40.5 °C. A reasonable linear Arrhenius plot was observed, from which the activation energy $E_a = 6.0\text{ kJ mol}^{-1}$ was determined.

The simplest mechanism for reaction of uranium(v) with molecular oxygen is the outer-sphere electron transfer (ET) reaction:



The area of outer-sphere electron transfer has been treated extensively theoretically, notably with the Marcus Theory.^{95,96} However, whilst this has had considerable success in many areas, a number of anomalous cases have been presented,⁹⁷ which cannot be treated within this formalism. These have been shown to be more amenable to the alternative intersecting-state model (ISM).^{97–99} We have applied this model to the above reaction. From the calculations, the rate constant is $k = 3 \times 10^{-2}\text{ M}^{-1}\text{ s}^{-1}$, about 6 times lower than our experimental rate for oxidation of uranium(v). However, the calculated energy

barrier is about 10 times higher than the observed activation energy. These results strongly suggest that the oxidation of uranium(v) by molecular oxygen does not simply involve outer sphere electron transfer. Full details of these calculations will be presented elsewhere.¹⁰⁰

Conclusions

Strong evidence is presented based on both previous literature and new experiments that the decay of the lowest excited state of the complex ion $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ in dilute aqueous solutions at room temperature involves hydrogen atom abstraction to produce uranium(v) and the hydroxyl radical. Evidence for this comes from kinetic studies, theoretical calculations, spin trapping experiments, and photoinduced oxygen exchange. In view of certain similarities in photochemical behaviour of excited uranyl ion and benzophenone triplet state, it is of historical relevance that the initial suggestion for such a mechanism⁴ was stimulated by the observation by Ledger and Porter¹⁰¹ that the benzophenone triplet state also abstracts hydrogen atoms from water. The lack of overall photodegradation of solutions of uranyl ion in water is suggested to be due to a fast back reaction involving oxidation of uranium(v) by hydroxyl radicals. It should be noted, however, that the mechanism of deactivation of excited uranyl ion at low temperatures or in concentrated acid solutions may be different, and that physical deactivation mechanisms, notably energy transfer, may well be more important.^{37,39,44,47}

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