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A FLASH PHOTOLYTIC STUDY OF THE PHOTO-OXIDATION OF SOME INORGANIC ANIONS BY THE URANYL ION

H. D. BURROWS and J. D. PEDROSA DE JESUS*

The Chemical Laboratory, University of Coimbra, Coimbra (Portugal)
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Summary

Transient species produced on photolysis of aqueous solutions of UO_2^{2+} and some inorganic anions have been studied by flash photolysis. With I^-, CNS^- and Br^- absorptions are observed which are assigned to the X_2^- radical anions formed by one-electron photo-oxidation by uranyl followed by reaction with the corresponding anion. Both intra- and inter-molecular mechanisms are suggested for this photo-oxidation. Decay of the I_2^- radical anion is second-order in radical anion, but the observed rate constant also shows a dependence on uranyl ion concentration. It is suggested that I_2^- may complex with UO_2^{2+}. With $(CNS)_2^-$ and Br_2^- the kinetic decay is found to be first-order in radical anion and to show an apparent dependence on uranyl ion concentration. Thermodynamic analysis suggests that the apparent dependence in UO_2^{2+} concentration is actually a dependence in UO_2^+ (the reduction product of uranyl ion) and that the radical anion decays by oxidizing uranium (V) back to uranium (VI). The difference between these and iodide provides a ready explanation for why photolysis of UO_2^{2+} with Br^- or CNS^- shows no overall reaction, whereas the uranyl–iodide system leads to formation of stable photoproducts. Flash photolysis of an aqueous solution of uranyl perchlorate and sodium bicarbonate yields a broad absorption assigned to CO_3^-, formed by one-electron oxidation of bicarbonate. However, the result was somewhat irreproducible, suggesting this system may be sensitive to the extent and type of complexation.

Introduction

Many systems involving the uranyl ion possess considerable photochemical reactivity. The most common reaction involves photo-

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*Present address: Universidade de Aveiro, Aveiro (Portugal).

oxidation of a substrate, often accompanied by a corresponding [1 - 3] photoreduction of the UO_2^{2+} species to uranium (V) or uranium (IV). Two general types of mechanism can be distinguished, those involving excitation of uranyl ion—ligand complexes, and those involving reaction between an electronically excited UO_2^{2+} species and the substrate [1, 2]. Photosensitivity has been observed for systems involving UO_2^{2+} and iodide ions [3 - 5] and halide ions have also been found to quench uranyl luminescence whilst giving no overall photoreaction [3, 5]. In the studies of Matsushima and coworkers [5] an intermolecular electron tranfer mechanism was proposed for the quenching of uranyl ion luminescence by halide ions from the correlation between the logarithm of the quenching efficiency and the standard oxidation potential of the quencher. At the quencher concentrations employed in this study (typically less than 10^{-5} mol/dm^3) complexation with UO_2^{2+} is not expected to be important.

In the present study we have had two main objectives. First, we wished to obtain information on the nature of any reactive intermediates formed. Secondly, we were interested in the decay reactions of any transient intermediates and, in particular, in the reasons why the uranyl—iodide system shows an overall photochemical reaction, whilst the photolysis of UO_2^{2+} and other halide or pseudo-halide ions does not.

Experimental

Reagents were of the purest grade commercially available, and were normally used without further purification. Uranyl perchlorate was prepared by reacting uranium trioxide with perchloric acid. Solutions of uranyl ion (as sulphate, nitrate or perchlorate) and iodide, bromide or thiocyanate (as potassium salts), or sodium bicarbonate were prepared in singly distilled water. With the halides and thiocyanate, the pH of the solution was normally between 1 and 2.

Flash photolysis experiments were carried out on solutions in 10 or 20 cm quartz cells using an Applied Photophysics GD-20 μs apparatus with photoelectric detection. Experiments were carried out with both aerated solutions, and with solutions degassed by three freeze—pump—thaw cycles under high vacuum. Both the photophysical processes of uranyl ion [6], and the reaction of dihalide radical anions [7] (the expected reaction intermediates) are unaffected by the presence of dissolved oxygen at its normal equilibrium concentration. When aqueous solutions of UO_2^{2+} and iodide ion were being frozen for degassing, a violet colour sometimes appeared on the surface of the ice and in the liquid phase. This disappeared on warning, normally leaving a brown colour in the aqueous phase. This interesting reaction was not pursued further, and flash photolysis experiments were only carried out on solutions which did not give this behaviour.
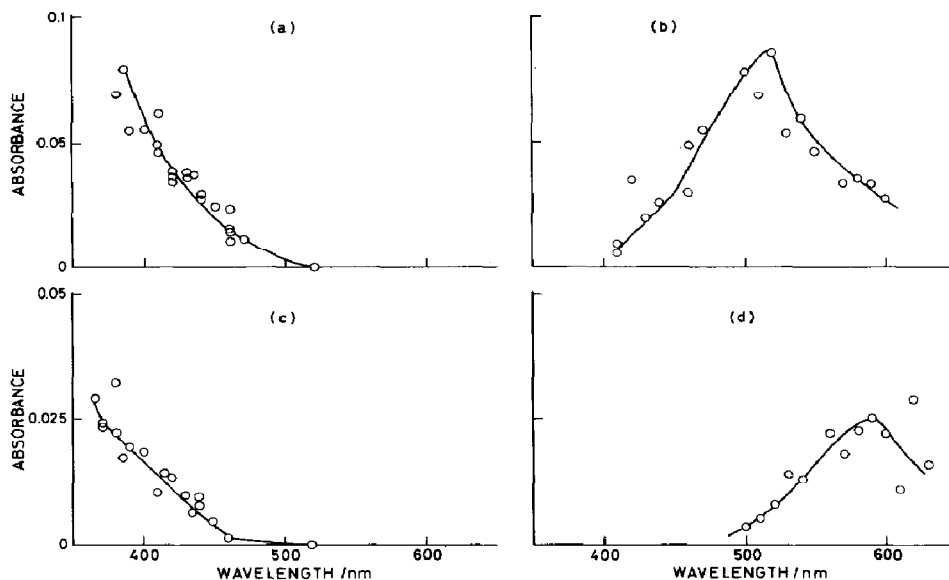
Fig. 1. End of μs flash spectra following flash photolysis of aqueous solutions of:
(a) uranyl sulphate (2×10^{-3} mol/dm^3) and potassium iodide (2×10^{-3} mol/dm^3);
(b) uranyl perchlorate (2×10^{-3} mol/dm^3) and potassium thiocyanate (2×10^{-3} mol/
dm^3); (c) uranyl perchlorate (2×10^{-3} mol/dm^3 and potassium bromide (2×10^{-3}
mol/dm^3); (d) uranyl perchlorate (2×10^{-3} mol/dm^3) and sodium bicarbonate
(10^{-2} mol/dm^3).

Results

Uranyl–iodide system

Following flash photolysis of aqueous solutions of uranyl perchlorate (2×10^{-3} mol/dm^3) and potassium iodide (2×10^{-3} - 2×10^{-2} mol/dm^3), a broad absorption was observed starting at 500 nm, and increasing in intensity at shorter wavelengths. It was not possible to locate the absorption maximum due to ground state absorptions by the uranyl–iodide system. The absorption was identical both in shape and intensity if uranyl perchlorate was replaced by uranyl sulphate, or if light only of wavelength longer than 300 nm was used for photolysis indicating that the transient species does not come purely from photolysis of the iodide ion, and must result from uranyl ion photo-oxidation. Degassing the solution had no effect on the observed behaviour. The absorption is assigned to the species I_2^- on the basis of the known behaviour of iodide ion on oxidation, and the similarity of the absorption of the transient to the literature spectrum of this species [8 - 10, 27]. The spectrum of the transient observed immediately (~ 50 μs) after flash photolysis is given in Fig. 1 (a).

Two possible mechanisms exist for the photo-oxidation. Either a photo-excited uranyl ion can oxidize iodide in an intermolecular reaction [5], or photo-oxidation proceeds by excitation of uranyl iodide complexes
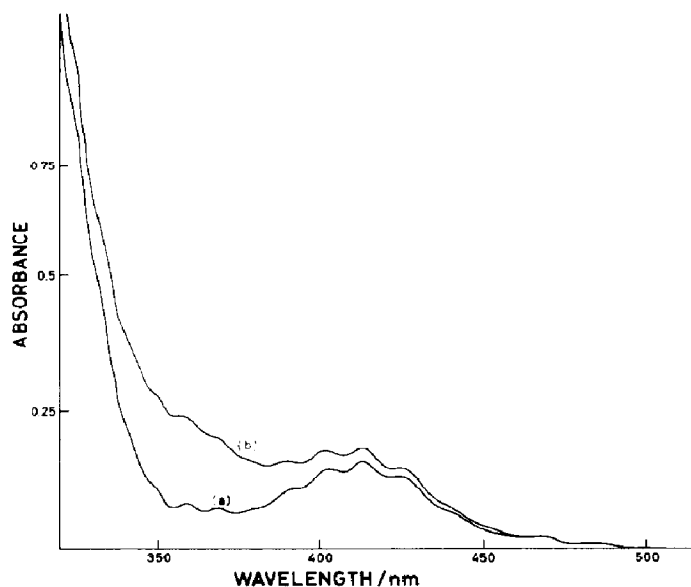
Fig. 2. Electronic spectra (1 cm cells) of aqueous solutions of: (a) uranyl nitrate $(1.9 \times 10^{-2} \text{ mol/dm}^3)$; (b) uranyl nitrate $(1.9 \times 10^{-2} \text{ mol/dm}^3)$ and potassium iodide $(1.9 \times 10^{-2} \text{ mol/dm}^3)$.

via a charge-transfer-to-metal (CTTM) transition. Uranyl iodide complexes are known to possess CTTM bands between 350 and 530 nm, the actual position of the bands depending upon the extent of complexation [11]. We have determined the absorption spectrum of an aqueous solution of UO_2^{2+} $(1.88 \times 10^{-2} \text{ mol/dm}^3)$ and I^- $(1.87 \times 10^{-2} \text{ mol/dm}^3)$, and find that, in addition to the transitions within the UO_2^{2+} group, there is a new broad absorption starting at ~ 480 nm and increasing in intensity at shorter wavelengths (Fig. 2). A similar, but somewhat weaker new band is present at lower uranyl concentrations. If we assume that the formation constant for uranyl iodide complexes is equal to or less than that of uranyl bromide complexes [12], then under these conditions less than 1% of the uranyl ion is present as the complex UO_2I^+. However, from Fig. 2 it would seem that the extinction coefficient of this species in the visible and near ultra-violet is equal to or greater than that of the uranyl ion. Under the conditions of our experiments it seems probable that photo-oxidation is going *via* both intermolecular (1, 2) and intramolecular (3) mechanisms:

$$UO_2^{2+} + h\nu \quad \rightarrow (UO_2^{2+})^* \tag{1}$$

$$(UO_2^{2+})^* + I^- \quad \rightarrow UO_2^+ + I^{\cdot} \tag{2}$$

$$UO_2I^+ + h\nu \quad \rightarrow UO_2^+ + I^{\cdot} \tag{3}$$

The iodine atom subsequently reacts very rapidly with iodide ion to give the dihalide anion [8]:

$$I^{\cdot} + I^- \quad \rightarrow I_2^- \tag{4}$$

TABLE 1

Kinetic decay of transient species produced on flash photolysis of aqueous solutions of uranyl ion with various inorganic anions

Probable transient species	UO_2^{2+} (mol/dm^3)	$k_{obs.}$
$I_2^{.-}$	2.5×10^{-4}	$2.05^a (\pm 0.11) \times 10^9$ dm^3 mol^{-1} s^{-1}
	8×10^{-4}	$0.90^a (\pm 0.08) \times 10^9$ dm^3 mol^{-1} s^{-1}
	1×10^{-3}	$0.80^a (\pm 0.32) \times 10^9$ dm^3 mol^{-1} s^{-1}
$Br_2^{.-}$	2×10^{-3}	$0.33^b \times 10^3$ s^{-1}
$CO_3^{.-}$	2×10^{-3}	$0.3^b \times 10^3$ s^{-1}

[a]Second-order rate constant, with standard deviation, calculated using extinction coefficient for $I_2^{.-}$ from ref. 15.
[b]Pseudo first-order rate constants.

The kinetics of decay of the di-iodide radical anion were studied. Normally this species decays in a bimolecular reaction [8] to give the stable species I_3^- and iodide ion:

$$2I_2^{.-} \rightarrow I_3^- + I^- \tag{5}$$

Under the conditions of our experiments the transient absorption at ~400 nm did indeed decay by a second order process, leaving a permanent absorption (possibly I_3^-) in the same region. However, the rate constant decrease with increasing uranyl ion concentration (Table 1). The iodide ion concentration was kept constant (10^{-3} mol/dm^3) as it is known that the di-iodide decay rate decreases with increasing iodide concentration [8]. The variation in rate constant with change in uranyl concentration cannot be due to a salt effect, as a reaction between two negatively charged species is expected to go faster at higher ionic strengths [13]. It is possible that, in spite of the good kinetic plots observed, the kinetics are not pure second-order. However, if there was any first-order component in the decay, possibly resulting from reaction of UO_2^{2+} with $I_2^{.-}$, then the observed rate would be expected to increase with increasing uranyl concentration. A third possibility which must be seriously considered is that $I_2^{.-}$ forms a complex with uranyl ion which either has a slower bimolecular decay, or a different extinction coefficient from $I_2^{.-}$.

$$UO_2^{2+} + I_2^{.-} \rightleftharpoons UO_2I_2^{.+} \tag{6}$$

Some support for the presence of such a species comes from the work of Laurence and Thornton [14] who have observed complex formation between dihalide radical anions and manganese (II). In their system, this is followed by intramolecular electron transfer from manganese to the dihalide group. In our system this cannot happen, and it is likely that electron-transfer from dihalide to uranyl is also thermodynamically unfavourable.
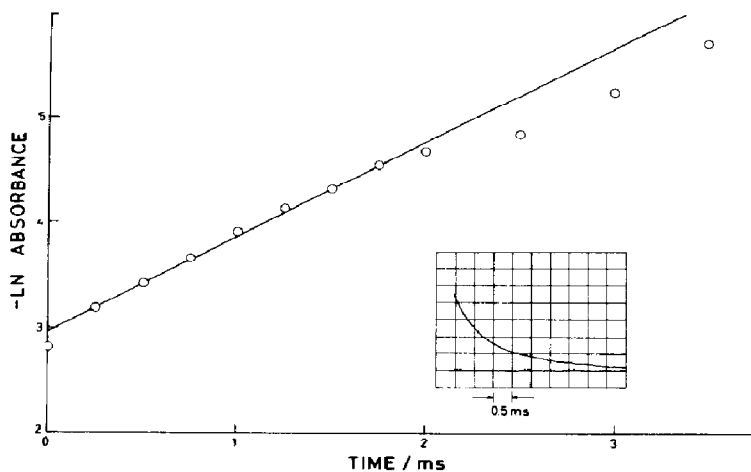
Fig. 3. First-order plot for decay of absorption at 530 nm following flash photolysis of an aqueous solution (pH 1) of uranyl perchlorate (2×10^{-3} mol/dm^3) and potassium thiocyanate (2×10^{-3} mol/dm^3). Inset shows oscilloscope trace for decay.

Uranyl–thiocyanate system

Flash photolysis of an aqueous solution (pH 1.0) of uranyl perchlorate (2×10^{-3} M) and potassium thiocyanate (2×10^{-3} M) yielded a broad transient absorption λ_{max} 515 ($\pm$20) nm, which was identical to that previously reported [10, 16, 17] for the $(CNS)_2^{\cdot-}$ radical anion (Fig. 1(b) . An identical spectrum was observed if the solution was photolyzed only with light of wavelength longer than 300 nm. The spectrum had the same shape at different uranyl and thiocyanate concentrations. The fact that the photo-oxidation could be induced with long wavelength light ($\lambda > 300$ nm) indicates that we are observing photo-oxidation of thiocyanate by UO_2^{2+}, and, as with the iodide, both inter- and intra-molecular routes are thought to be involved.

The kinetics of decay of the $(CNS)_2^{\cdot-}$ radical were studied as a function of uranyl ion concentration. In the absence of metal ions, the decay of this radical anion is known to be second-order [16, 17]:

$$2(CNS)_2^{\cdot-} \rightarrow (CNS)_2 + 2CNS^- \tag{7}$$
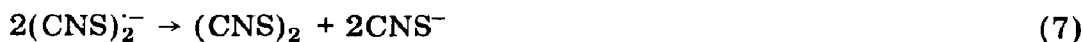
However, under the conditions of our experiments the decay of the transient followed good first-order kinetics. A typical decay is given in Fig. 3. Further, the rate of decay of the transient was found to depend on the uranyl ion concentration (Table 2 and Fig. 4, circles). When solutions were photolyzed using flashes of the same energy, the decay appeared to be first-order in uranyl ion. However, when similar concentrations of uranyl ion (2 and 2.5×10^{-3} mol/dm^3) were photolyzed with different energy flashes, the decay no longer appeared to be first-order in uranyl. A possible explanation of the observed behaviour comes from a consideration of the chemistry of the system. If uranyl ion were to react with the dithiocyanate radical anion, then the most likely reaction would be

TABLE 2

Kinetics of decay of dithiocyanate radical anion as a function of uranyl and uranium (V) concentrations

$[UO_2^{2+}] \times 10^3$ (mol/dm^3)	$[UO_2^+]$ [a] $\times 10^7$ (mol/dm^3)	$k_{obs.} \times 10^{-3}$ (s^{-1})
1	1.2	0.22
2	4.4	0.79 ($\pm$0.09)
2.5	0.9	0.13 ($\pm$0.01)
5	2.7	0.34 ($\pm$0.02)
8	3.4	0.43

[a]Approximate concentration immediately after photolysis estimated from initial optical density of $(SCN)_2^{\cdot-}$ absorption assuming extinction coefficient of this species from ref. 16.
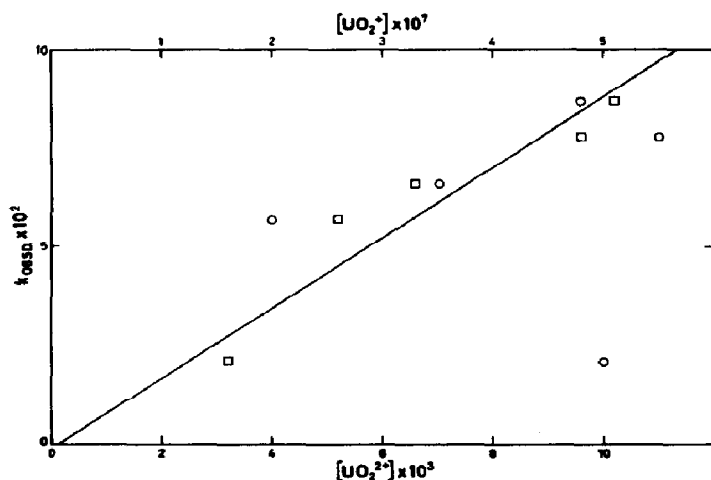

Fig. 4. Pseudo first-order rate constants for $(SCN)_2^{\cdot-}$ decay as functions of uranyl concentration ($\bigcirc$) and UO_2^+ concentration ($\square$). The line is the least-squares slope for the plot of $k_{obs.}$ vs. UO_2^+ concentration.

oxidation of $(CNS)_2^{\cdot-}$ in the process:

$$(CNS)_2^{\cdot-} + UO_2^{2+} \rightarrow (CNS)_2 + UO_2^+ \tag{8}$$

Uranyl ion has been found to oxidize diphenylketyl radical in a similar process [18]. However, no overall photoreaction is observed between uranyl ion and thiocyanate [5], so that if this reaction is occurring, it must be followed by oxidation of uranium (V) or uranium (IV) (formed by disproportionation of uranium (V) [19]) by $(CNS)_2$. Consideration of the standard reduction potentials [20] for the couples $(CNS)_2 \mid 2CNS^-$ (E^o + 0.77 V), $UO_2^{2+} \mid UO_2^+$ (E^o + 0.062 V) and $UO_2^{2+} \mid U^{4+}$ (E^o + 0.334 V) shows that such an oxidation by $(CNS)_2$ is favoured thermodynamically. If, however, this oxidation proceeds via a one electron process, it will involve the intermediacy of the $(CNS)_2^{\cdot-}$ radical anion, which is somewhat unlikely. We favour an alternative explanation. Varying the uranyl ion

concentration is expected to alter the extent of photoreaction, and consequently of uranium (V) production. Further, varying the intensity of light used in the photolysis by altering the flash energy is also expected to change the UO_2^+ concentration. If we assume that the uranium (V) concentration equals the $(CNS)_2^{\cdot-}$ concentration immediately after photolysis, then we can estimate this from the initial optical density of the dithiocyanate radical anion, and its known extinction coefficient [16]. Estimated values are presented in Table 2. A plot of pseudo first-order rate constant for $(CNS)_2^{\cdot-}$ decay against uranium (V) concentration shows a reasonable linear relationship (Fig. 4, squares), suggesting a rate law for the radical anion decay:

$$\text{rate} = k \mid UO_2^+ \mid \mid (CNS)_2^{\cdot-} \mid$$

where $k = 1.46 \ (\pm 0.34) \times 10^9 \ dm^3 \ mol^{-1} \ s^{-1}$. The most probable reaction here is:

$$UO_2^+ + (CNS)_2^{\cdot-} \rightarrow UO_2^{2+} + 2CNS^- \tag{9}$$

Whilst there is no information on the $(CNS)_2^{\cdot-} \mid 2CNS^-$ couple, we will see later that the corresponding reaction with Br_2^- is highly favoured thermodynamically. Similar oxidations by dihalide radical anions have been observed with titanium (III) [21], manganese (II) [14], cobalt (II) [7], iron (II) [22], vanadium (II) and chromium (II) [23].

There is a problem in our system, as if flash photolysis generates equal concentrations of UO_2^+ and $(CNS)_2^{\cdot-}$, then reaction (9) should strictly be second-order. However, the reaction will occur in parallel with reaction (7), the second-order decay of the radical anion, so that whilst the initial decay will be second-order, as the radical anion concentration becomes less than the UO_2^+ concentration, the reaction becomes pseudo first-order. The time resolution of our apparatus does not allow us to observe the first part of the decay to see if it is indeed second order.

Uranyl–bromide system

Flash photolysis of aqueous solutions (pH 1.7) of uranyl perchlorate $(2 \times 10^{-3} \ M)$ and potassium bromide $(2 \times 10^{-3} \ M)$ yielded a broad absorption starting at 460 nm, with absorption increasing at shorter wavelengths (Fig. 1(c)). As with the uranyl–iodide system, it was not possible to observe the maximum due to reagent absorptions. The spectrum is assigned to the Br_2^- radical anion on the basis of the behaviour expected on oxidation of bromide, and the known absorption of this species [8 - 10].

The kinetics of decay of this transient were studied. In the absence of metal ions, dibromide radical anion is known to decay by a bimolecular process [8]:

$$2Br_2^- \rightarrow 2Br^- + Br_2 \tag{10}$$

However, as with the $(CNS)_2^-$ species, the decay in our case followed pseudo first-order kinetics (Table 1). As with the thiocyanate system, the decay reaction is thought to involve the reoxidation of uranium (V) to uranium (VI):

$$UO_2^+ + Br_2^- \rightarrow UO_2^{2+} + 2Br^- \tag{11}$$

Evidence that this reaction is favoured thermodynamically comes from a consideration of the standard reduction potentials of the couples $Br_2 \mid Br_2^-$ ($E^o + 0.41$ V) [7], $Br_2^- \mid 2Br^-$ ($E^o + 1.8$ V) [7] and $UO_2^{2+} \mid UO_2^+$ ($E^o + 0.062$ V) [20].

Uranyl–bicarbonate system

Flash photolysis of an aqueous solution of uranyl perchlorate (2×10^{-3} M) and sodium bicarbonate (10^{-2} M) at the natural pH yielded a broad absorption, λ_{max} 580 nm (Fig. 1(d)). This spectrum corresponds to that reported in the literature [24] for the CO_3^- radical anion, suggesting that uranyl ion can also photo-oxidize the carbonate–bicarbonate system in the reaction:

$$UO_2^{2+} + HCO_3^- + h\nu \rightarrow UO_2^+ + CO_3^- + H^+ \tag{12}$$
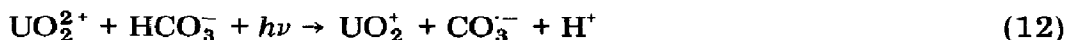
Under these conditions the absorption at 580 nm decayed by first-order kinetics (Table 1). The flash photolysis experiments on the uranyl–bicarbonate system were, however, somewhat irreproducible, and were not pursued further. It is known that UO_2^{2+} and carbonate ion form a variety of complexes in aqueous solution [25, 26] and it is possible that the photochemistry of this system is very sensitive to the type of species present, and possibly to the extent of protonation.

Discussion

The objectives of this study have been to obtain information on both the nature and reactivity of any intermediates formed on photolysis of solutions of uranyl ion with inorganic anions. The predominant photo-reaction with uranyl systems involves oxidation of suitable substrates, and reduction of the uranium to uranium (V) [1 - 3]. Transient absorptions were observed with iodide, thiocyanate, bromide and biocarbonate which were all assigned to the one electron oxidation products of the anions, formed in the overall electron-transfer reaction:

$$UO_2^{2+} + X^- + h\nu \rightarrow UO_2^+ + X^\cdot \tag{13}$$

Both intramolecular processes, involving excitation of CTTM bands in complexes, and intermolecular mechanisms, involving bimolecular reaction between excited uranyl ion and substrate, have been suggested for uranyl photo-oxidations [1, 2]. The predominant mechanism will depend on a number of factors, including the extent of complexation in solution. With

the uranyl–halide ion system, Matsushima and coworkers [5] have demonstrated that an intermolecular mechanism is responsible for the quenching of uranyl luminescence. Under the conditions of our experiments involving rather higher substrate concentrations a new absorption is observed in the uranyl–iodide system, and it seems probable that both intra- and inter-molecular processes are involved in the primary photo-chemical act.

Previous studies on photolysis of uranyl–halide systems [3 - 5] have shown that whilst the uranyl–iodide system gives an overall photochemical reaction, photolysis of systems involving uranyl and the other halide ions gives no overall reaction. In the present study it is seen that the di-iodide radical anion decays by a second-order process, possibly disproportionation, whilst the decay of $(CNS)_2^{\cdot-}$ and $Br_2^{\cdot-}$ is first-order in radical anion and apparently dependent on the concentration of uranium (VI). We believe that the apparent dependence on uranium (VI) concentration is in fact a first-order dependence in uranium (V), its photolysis product, and that with $Br_2^{\cdot-}$ and $(CNS)_2^{\cdot-}$ the decay reaction involves back electron-transfer from the uranium (V) to the dihalide radical anion. This provides a ready explanation for the lack of overall photochemical reaction in this case. With the $I_2^{\cdot-}$ radical anion, the observed second-order decay also varies with change in uranyl concentration. One possibility is that $I_2^{\cdot-}$ complexes with UO_2^{2+}. Such complexation may stabilize the $I_2^{\cdot-}$ to reduction by uranium (V), and so, in contrast to the other halides, favour formation of permanent products.

Acknowledgement

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