lowers the energy of ^1A_P to almost the same as at the equilibrium point at $\delta = 30°$ (point 2). Then, if θ is kept at 120° and the phosphine groups are turned 60° out of the CNiC plane, intersystem crossing takes place. When the Ni–C distance is decreased to 2.55 Å, the energy of the ^3B state is similar to the energy of the ^1A state (point 3). The next step is to increase δ to 90°. This value being kept constant, Ni–C is decreased to 2.50 Å and θ opened to 140° (point 4) and then to 160°, where the energy of the triplet reaches its minimum (point 5). The next point describes $\delta = 180°$, all other parameters being constant. (The value of the barrier to interconversion is $\approx$25 kcal/mol.) This is, of course, only a rough path and a more concerted motion might lower the barrier considerably. Although it is still quite large, we believe that this raises the possibility that an isomerization, perhaps solvent controlled, may take place, especially if steric effects are also taken into consideration. In fact, the experimental results[8] are not inconsistent with a possible interconversion between the planar and tetrahedral forms. Indeed, they show that cyclobutane, generated from square-planar forms, is the major product of thermal decomposition of various $(R_3P)_2NiC_4H_8$ complexes, in toluene, at 9 °C. However, it must be kept in mind that (i) the routes of decomposition vary with varying R (methyl, phenyl, cyclohexyl, or a chelating system), (ii) there is always a small amount (6–15%) of ethylene in the gaseous products, with the exception of the rigid planar compound where $(R_3P)_2$ is a bidentate system, (iii) the thermal decomposition is particularly susceptible to the nature of the solvent (6% ethylene in toluene, 16% in acetonitrile, and 72% in pyridine, for R = phenyl), and (iv) photochemical decomposition always yields an increased amount of ethylene.

More experimental data and calculations are necessary to clarify this aspect further. At a minimum, the result underlines the necessity, for this type of process, of including motions more complex than the simple "rigid" displacements that first come to mind.

Concluding Remarks

The orbital diagrams and, in fact, the energetics, resulting from our local density functional calculations, are to a large extent consistent with the EH analysis of ref 9. The sole point where we would propose a possible alternative has to do with the facility of interconversion of the square-planar and tetrahedral forms of $(PH_3)_2NiC_4H_8$. We believe it may be possible to find a pathway of lower energy than usually assumed, which does not involve breaking Ni–P bonds. This could then lead to the possibility of forming (some) ethylene, in addition to cyclobutane, without necessitating the decomposition of a tris(triphenylphosphine) complex. A more detailed computational verification, in a reasonable manner, will require the use of analytical gradient techniques, which are currently under development.[36]

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Electron Transfer from Halide Ions to UO_2^{2+} Excited-State Ions in Aqueous Solution: Formation and Decay of Dihalide Radical Anions

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The decay of the excited uranyl ion in water in the presence of Cl^-, Br^-, I^-, and SCN^- is studied by laser flash kinetic spectrophotometry. The four anions all quench $*UO_2^{2+}$ by a bimolecular process suggested to involve electron or charge transfer. Steady-state luminescence studies suggest that there is also some static contribution to the quenching. For Br^-, I^-, and SCN^-, radical anions, $X_2^{\bullet-}$, are observed. However, kinetic studies indicate that these are not formed directly from $*UO_2^{2+}$ but probably come by bimolecular reaction of an intermediate uranium(V)/radical pair with the corresponding halide ion. The extinction coefficient for the $*UO_2^{2+}$ absorption is reported, and by use of this and transient absorbance data radical-anion yields are obtained and found to depend linearly upon the halide anion concentration. The variation of the yield in the series I^-, SCN^-, and Br^- is interpreted in terms of the effect of overall free energy change on back-electron-transfer in the uranium(V)/radical pair. With the chloride system no significant yield of radical anion was observed. The decay of $X_2^{\bullet-}$ was found to be unaffected by the presence of uranyl ion, supporting the previously suggested mechanism for radical-anion decay in these systems.

The excited uranyl ion, $*UO_2^{2+}$, is a powerful oxidant, with an estimated standard electrode potential of $E° = +2.5–2.7$ V.[1-3] It has long been known[4-7] that the halide ions, with the exception of F^-, and other polarizable anions such as SCN^- are effective quenchers of the green luminescence of the uranyl ion, and this effect has found application in eliminating interferences from luminescence in Raman spectral studies on this species. A number of studies on the quenching process have been reported using both dynamic and steady-state luminescence quenching,[8-10] and the general consensus is that the dominant mechanism involves an electron-transfer reaction from the halide to excited uranyl ion.[6,8-10] However, only with the uranyl iodide system is any permanent change observed on photolysis.[11,12] In all of these systems, except

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the chloride, anion radicals, $X_2^{\bullet -}$, have been observed by flash photolysis.[10,13] and we have suggested that in the cases of the bromide and thiocyanate these are reduced back to the corresponding anions by electron transfer from uranium(V) in the overall sequence[13]

$$^*UO_2^{2+} \rightarrow UO_2^{2+} + h\nu + \Delta \qquad (1)$$

$$^*UO_2^{2+} + X^- \rightarrow UO_2^+ + X^\bullet \qquad (2)$$

$$X^\bullet + X^- \rightarrow X_2^{\bullet -} \qquad (3)$$

$$UO_2^+ + X_2^{\bullet -} \rightarrow UO_2^{2+} + 2X^- \qquad (4)$$

where reaction 1 includes both radiative and nonradiative decay of the excited uranyl ion. A recent pulse-radiolysis study[14] has shown that UO_2^+ reduces $Cl_2^{\bullet -}$, and the kinetics of oxidation of uranium(V) have been analysed by using the Marcus theory.[14,15] Various other examples testify to the ability of halide radical anions to oxidize metal ions.[16-19]

However, several details of these reactions are missing, in particular information on the reactions leading to $X_2^{\bullet -}$ formation. In this study, laser flash kinetic spectrophotometry has been employed to obtain such data.

Experimental Section

Reagents. All reagents were of the purest grade commercially available and were, in general, used without further purification. The potassium salts of the halides and thiocyanate were used. Uranyl nitrate was recrystallized twice from dilute nitric acid. Water, deionized by passing through a Millipore ion-exchange system, was employed, and solutions were freshly prepared before each experiment. This is particularly important with SCN^-, which is susceptible to hydrolysis in acidic solution.[20,21]

Apparatus and Methods. Most of the experiments reported here were carried out at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. Fluorescence and ground-state absorption spectra were measured by using respectively Perkin-Elmer LS-5 and Hewlett-Packard 8450 A spectrometers. Laser flash kinetic spectrophotometry studies used a Q-switched Nd:YAG laser, frequency tripled to give pulses of about 120 mJ at 355 nm with ca. 11-ns duration. Solutions were in 1-cm^2 quartz cells, and spectra and kinetics of generated transient species were monitored at right angles to the laser beam by using a conventional xenon lamp, monochromator, and photomultiplier system, and, where necessary, filters placed in front of the monochromator to cut out second-order bands. The details of this computer-controlled single-beam kinetic spectrophotometer and of the data acquisition and analysis system have been given elsewhere.[22,23] In kinetic studies, each rate constant is the average of five or ten decays. Solutions for fluorescence and laser flash kinetic spectrophotometry studies were not, normally, degassed, as oxygen has no significant effect on the uranyl excited state.[24] Pulse-radiolysis experiments were carried out with electron pulses of 100- or 200-ns duration delivered to nitrous oxide saturated solutions in quartz cells of 2.4-cm optical path length. Transient absorptions were measured by using a conventional kinetic spectrophotometer system and photomultiplier signals transferred by a Biomation 8100 transient recorder to an on-line PDP 11/70 computer. Details of the data acquisition and analysis system are described in ref 23. Uranyl sulfate was used in these studies, as NO_3^- is known to react with hydrogen atoms produced on water radiolysis.[25]

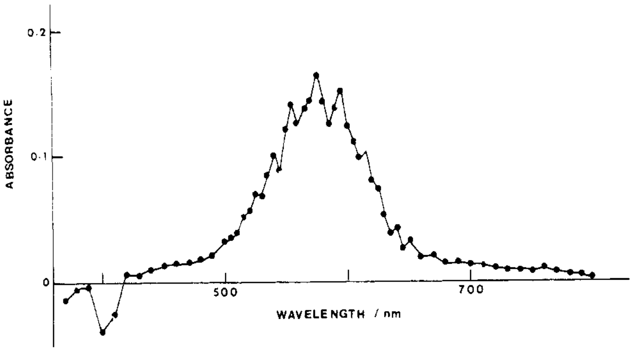

Figure 1. Transient absorption spectrum observed 120 ns after excitation of an aqueous solution of uranyl nitrate (0.1 M, pH 1.9) with a 355-nm laser pulse.

Analysis of radical-anion yields in these systems required knowledge of the extinction coefficient of the excited uranyl ion in water. As an accurate value of this was not found in the literature, it was determined by the relative actinometry method[26,27] using benzophenone triplet state ($^3BP^*$) absorption at 535 nm as a standard and assuming quantum yields of unity for $^3BP^*$ and $^*UO_2^{2+}$ formation. Because of its low solubility in water, most of the benzophenone experiments were carried out in degassed benzene solutions, with solute concentrations adjusted to give absorbance at the laser wavelength (355 nm) between 0 and 0.5. Over this range the initial $^3BP^*$ absorption at constant laser intensity was a linear function of the ground-state absorption at 355 nm. At higher concentrations, deviations from linearity were observed, probably due to excessive absorption of the exciting laser beam outside the region of the analyzing light. Various solute concentrations were studied, and excited-state concentrations were calculated with the recommended value of 7220 M^{-1} cm^{-1} for the $^3BP^*$ extinction coefficient in benzene. To minimize solvent problems, two concentrations of benzophenone were also studied in degassed aqueous solution, and an extinction coefficient of 5800 M^{-1} cm^{-1} was used for $^3BP^*$.[28] Within the accuracy of these measurements (±30%) good agreement was obtained from measurements in the two solvents. Least-squares analysis of the relationship between the benzophenone ground-state absorption at 355 nm and the calculated excited-state concentration showed a reasonable linear correlation (correlation coefficient 0.979). Various concentrations of uranyl nitrate and sulfate were studied, with ground-state absorption at 355 nm in the same range as the standard. No significant difference was observed between the initial excited-state absorption of the two salts. The extinction coefficient of $^*UO_2^{2+}$ in water at the absorption maximum (570 nm) was determined by least-squares analysis of data at various salt concentrations to be 4450 (±700) M^{-1} cm^{-1}. Chibisov and colleagues[29] have reported values for this extinction coefficient of 2500 M^{-1} cm^{-1} in 1 M phosphoric acid and 700 M^{-1} cm^{-1} in 1 M sulfuric acid. They used a kinetic method to determine initial excited-state concentrations, and it is possible that the lower values observed by these workers may reflect a more complex reaction scheme than that presented. Alternatively, the differences may be due to the presence of different complex species. At the pH and salt concentration used in the present study, literature data[30] indicate there is no significant formation of hydrolyzed uranyl species, and the excited state refers to that derived from $[UO_2(H_2O)_5]^{2+}$.[31] Studies of uranyl glasses[32,33] have given estimates of molecular absorption cross sections for $^*UO_2^{2+}$, from which molar extinction coefficients can be calculated.[34] Values calculated for uranyl in glasses at 570 nm vary between 3500 and

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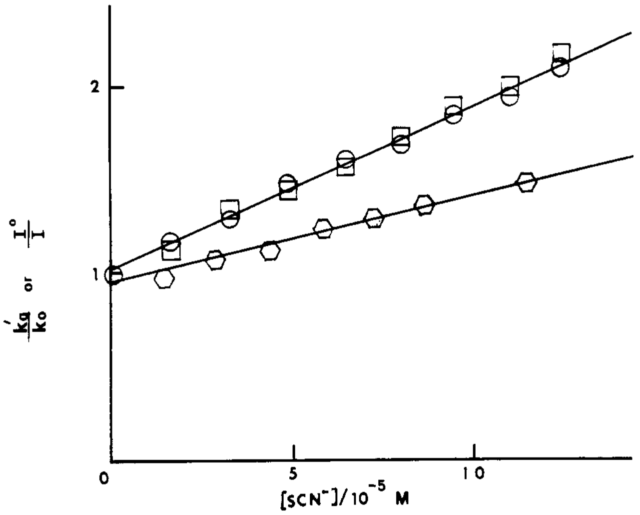

Figure 2. Stern–Volmer plots for the quenching of the uranyl ion excited state by potassium thiocyanate: hexagons, data for decay of $*UO_2^{2+}$ absorption at 590 nm; circles and squares; steady-state data for quenching of uranyl fluorescence at 490 nm with excitation wavelengths of 355 and 410 nm, respectively.

Table I. Bimolecular Rate Constants and Steady-State Stern–Volmer Constants for the Quenching of $*UO_2^{2+}$ by Halide Anions in Water (pH 1.9)

anion	$k_0{}^a/10^5$ s^{-1}	$k_q'{}^a/10^9$ M^{-1} s^{-1}	$K_{SV}{}^b/10^3$ M^{-1}	$(K_{SV}/\tau)^c/10^9$ M^{-1} s^{-1}
Cl^-	8.77	1.90	2.63	2.17
Br^-	7.66	5.69	8.26	6.83
I^-	8.19	7.77	10.92	9.02
SCN^-	7.60	4.41	8.54	7.06

[a] Values obtained by using linear regression of pseudo-first-order rate constants of $*UO_2^{2+}$ decay as functions of anion concentration. See text for significance of symbols. [b] Determined with λ_{ex} 355 nm and λ_{em} 490 nm. [c] Using an average lifetime (τ) of 1.21 μs determined for $*UO_2^{2+}$ under these conditions.

6500 M^{-1} cm^{-1}, while rather higher values are obtained for crystals of $Cs[UO_2(NO_3)_3]$ and $UO_2SO_4{\cdot}3H_2O$.[33] These differences may reflect the effect of complexing on the band shape. Similar changes in band structure and extinction coefficient are well documented in the absorption spectra of uranyl complexes in the ground state.[35]

Results and Discussion

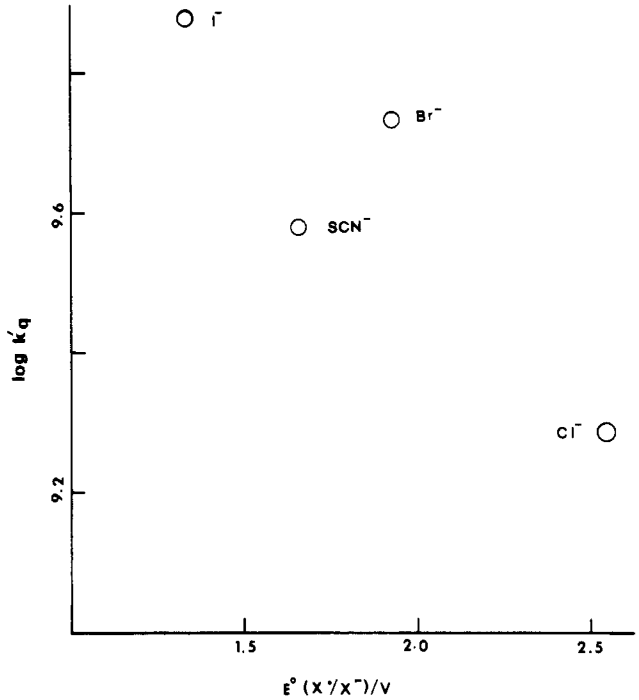

Figure 3. Plot of the logarithm of the rate constant for halide ion quenching of $*UO_2^{2+}$ as a function of the standard electrode potential of the $X^\bullet/X^-$ couple.

Quenching of the UO_2^{2+} Excited State. Following excitation of aqueous solutions of uranyl nitrate (0.1 M, pH 1.9) with a frequency-tripled Nd:YAG laser pulse, a structured transient absorption was observed around 570 nm, accompanied by depletion of the ground-state UO_2^{2+} absorption at 400 nm. The new band is assigned to the excited $*UO_2^{2+}$ species,[29,36] and the observed spectrum is presented in Figure 1, as a rather wider spectral range was studied than in any previous report. Although a rather large spectral band-pass was used in this work, analysis of the observed vibronic structure allows one to estimate an average vibrational spacing of 550 (±80) cm^{-1} in this spectrum, in good agreement with the previously reported value of $\simeq$580 cm^{-1}.[36] The decay of excited uranyl ion has been shown to be strongly dependent upon the medium, temperature, excitation intensity, etc. and under some conditions is biexponential.[37,38] However, at the relatively low-pH, high uranyl concentration and laser intensity used in this study the decay of $*UO_2^{2+}$ followed good first-order kinetics at all wavelengths. The decay was faster in the presence of Cl^-, Br^-, I^-, and SCN^- and obeyed the overall rate law

$$\frac{-d[*UO_2^{2+}]}{dt} = (k_0 + k_q'[X^-])[*UO_2^{2+}]$$

Good linear plots of pseudo-first-order rate constant as a function of X^- concentration were observed in all cases (correlation coefficient >0.99), from which values of k_0 and k_q' were obtained (Table I). A typical plot for SCN^- is shown in Figure 2. The values of k_0 are identical with the rate constant for decay in the absence of quencher, and the average value calculated from the data in the table (k_0 = 8.06 (±0.55) × 10^5 s^{-1}) is in excellent agreement with the value of 8.02 × 10^5 s^{-1} reported for the decay of excited uranyl ion under similar conditions.[36] The mechanism most commonly presented for the quenching process in this system involves electron transfer to the excited uranyl ion.[6,8–10] Both theoretical models and experimental observations suggest that, except for very exothermic reactions, a linear relation may exist for homogeneous families of reactions between the activation energy and the overall free energy change for such processes.[39–42] This is most commonly presented in the form of a correlation between the logarithm of the quenching constant and the change in standard electrode potential ($\Delta E°$). Results for the present study are shown in Figure 3, using $E°$ values for the $X^\bullet/X^-$ couples from ref 43 and 44. The rate constants for these reactions are close to those for diffusion-controlled processes and should strictly be corrected for this. However, this was not judged necessary, as too much uncertainty exists in the calculation of diffusion-controlled rate constants for reactions between charged species in solution to provide any useful correction for this case. The figure shows a rough correlation and supports suggestions from previous steady-state[8] and dynamic[10] luminescence quenching studies that an electron- or charge-transfer mechanism is involved.

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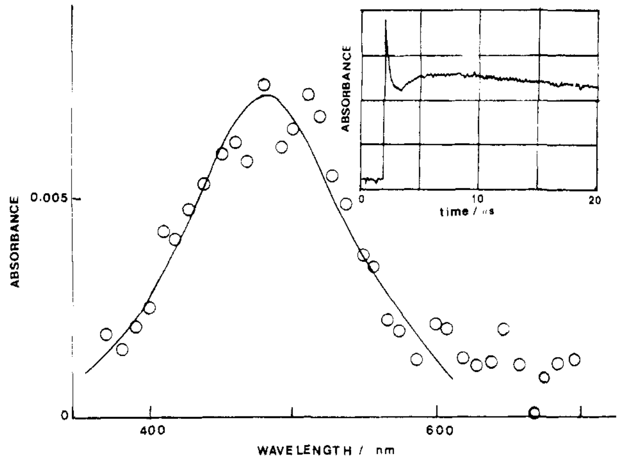

Figure 4. Circles: Transient absorption spectrum observed to grow in ≃ 5 μs after laser flash photolysis of an aqueous solution of uranyl nitrate (0.1 M) and KSCN (1×10^{-4} M). *Solid line: Literature spectrum of* $(SCN)_2^{\bullet-}$ from ref 52. Inset: Kinetic trace observed at 475 nm followed excitation of a solution of UO_2^{2+} (0.1 M) and SCN^- (1.8×10^{-4} M).

Further information on the quenching comes from steady-state luminescence measurements under identical conditions. Excitation of the above solutions with light of wavelengths 300–450 nm leads to the well-characterized uranyl luminescence. This is quenched by all four anions, and Stern–Volmer plots are linear up to millimolar concentrations. However, the slopes are, in general, higher than those of the corresponding graphs for excited-state decay data, as can be seen for SCN^- in Figure 2, and the Stern–Volmer quenching constants (K_{SV}) in Table I. The difference is most readily explained in terms of some static contribution to the quenching, associated with complexing in the ground state between UO_2^{2+} and halide ions. Support for this comes from UV/visible absorption spectra, where slight increases in absorbance are observed in the presence of these anions. The spectrum for the UO_2^{2+}/I^- system has been previously reported,[13] and in the present work similar results are observed with the other anions. However, all of the systems studied here only form weak complexes,[45] and from the reported stability constants[45,46] the concentration of inner-sphere uranyl halide complexes is very low under the conditions of these experiments.[47] The uranyl ion in water is present mainly as $[UO_2(H_2O)_5]^{2+}$,[31] and the observed spectral changes are most probably associated with contact charge-transfer transitions in $[UO_2(H_2O)_5]^{2+},X^-$ ion pairs, as observed in various related systems.[48,49] It should be noted that "second-sphere" electron-transfer processes may be induced upon excitation in these bands,[49-51] although the present results do not allow determination of the extent of such processes.

Halide Radical-Anion Formation and Decay. As previously observed in microsecond flash-photolysis experiments,[10,13] confirmation of the electron-transfer mechanism for the quenching comes from the observation of the $X_2^{\bullet-}$ radical anions for X = Br, I, and SCN following laser flash photolysis of the respective solutions. A typical spectrum observed for $(SCN)_2^{\bullet-}$ is shown in Figure 4 and compared with standard data.[52] Results for the long-lived absorption observed after the decay of $^*UO_2^{2+}$ in the bromide and iodide systems are in agreement with the literature band of the $X_2^{\bullet-}$ species in the 350–400-nm regions. For $I_2^{\bullet-}$, the weaker band[52] at 700–750 nm was also observed.

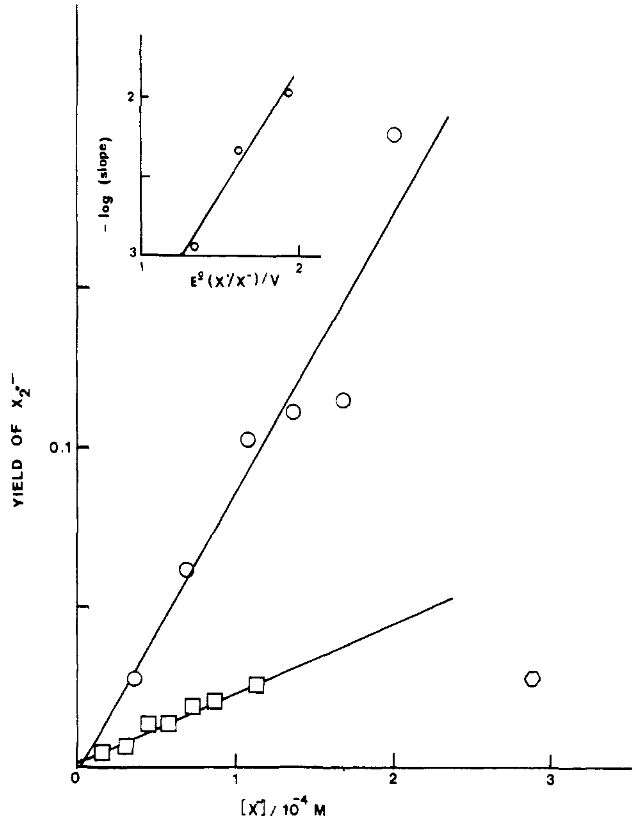

Figure 5. Effect of anion concentration upon the yields of formation of $I_2^{\bullet-}$ (circles), $(SCN)_2^{\bullet-}$ (squares), and $Br_2^{\bullet-}$ (hexagons) for the uranyl-/halide system. Inset: Logarithm of the reciprocal of the slope of these plots as a function of the standard electrode potential of the $X^{\bullet}/X^-$ couple.

The rates of formation of the radical anions are, however, slower than the rates of decay of excited uranyl absorption. This shows up most clearly in the kinetic traces observed at 475 nm following excitation of the UO_2^{2+}/SCN^- system (Figure 4 insert). Both $^*UO_2^{2+}$ and $(SCN)_2^{\bullet-}$ absorb at this wavelength, and an initial fast spike, corresponding to excited uranyl decay, is seen, followed by the grow-in of the $(SCN)_2^{\bullet-}$ absorption and its subsequent decay. Increasing the SCN^- concentration affected the rates of the first two steps and also the yield of $(SCN)_2^{\bullet-}$. Although analysis of the various consecutive kinetic processes was complicated, it was possible to obtain reasonable pseudo-first-order kinetics for the radical anion grow-in. The rate constant for this was a linear function of SCN^- concentration, and least-squares analysis of the data gave an overall second-order rate constant of $k = 3.82\ (\pm 0.61) \times 10^9\ M^{-1}\ s^{-1}$ for this reaction. This is considerably lower than the value of $9 \times 10^9\ M^{-1}\ s^{-1}$ reported[53] for the forward reaction in

$$SCN^{\bullet} + SCN^- \rightleftharpoons (SCN)_2^{\bullet-} \qquad (5)$$

which suggests that radical-anion formation in this case does not involve electron transfer in step 2 followed by reaction 5 but proceeds by a different route. Further, the amount of $(SCN)_2^{\bullet-}$ formed is considerably lower than the initial $^*UO_2^{2+}$ yield. To quantify this, the concentrations of the two species were calculated in each experiment from the measured absorbances, the recommended value[52] of 7600 $M^{-1}\ cm^{-1}$ for the extinction coefficient of $(SCN)_2^{\bullet-}$ at 475 nm, and the value determined here for the $^*UO_2^{2+}$ extinction coefficient. The yield of $(SCN)_2^{\bullet-}$, defined as the concentration ratio $[(SCN)_2^{\bullet-}]/[^*UO_2^{2+}]$, was found to be relatively low but was a linear function of the thiocyanate concentration over the range studied (Figure 5). This can readily be explained by including formation of a uranium(V)/SCN$^{\bullet}$ pair

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in the mechanism and its subsequent decay either by back-electron-transfer or by bimolecular reaction with SCN^-. For completeness, a physical quenching process (eq 6) is also included in

$$^*UO_2^{2+} + X^- \rightarrow UO_2^{2+} + X^- \qquad (6)$$

$$^*UO_2^{2+} + X^- \rightarrow (UO_2^+X^\bullet) \qquad (7)$$

$$(UO_2^+X^\bullet) \rightarrow UO_2^{2+} + X^- \qquad (8)$$

$$(UO_2^+X^\bullet) + X^- \rightarrow UO_2^+ + X_2^{\bullet-} \qquad (9)$$

the scheme. Formation of uranium(V) radical pairs with organic species has been confirmed by CIDNP.[54] Exciplexes have been proposed as intermediates in the electron-transfer quenching of excited uranyl ion by various organic substrates[29] and in the quenching of excited states of water-soluble anthroquinones,[55,56] benzophenones,[57] and iridium bipyridine complexes[58] by inorganic anions. Under the present conditions, the formation of such species is kinetically indistinguishable from radical-pair formation. However, it is worth noting that uranium(V) has a number of low-lying excited states,[59] such that if any exciplex was produced it would be expected to be very short-lived. Further, the aqueous medium used in these studies is expected to favor conversion of such exciplexes to radical pairs. It can also be noted that with the anthroquinone[55,56] and benzophenone[57] systems, anion-radical formation was only observed at high halide concentrations (above $\simeq$ 0.1 M), whereas in the present case there is evidence for $(SCN)_2^{\bullet-}$ formation even at 10^{-5} M thiocyanate. It, thus, seems likely that radical-pair formation is the dominant route here.

In their studies on the photochemical reactions of uranyl ions with organic molecules, Sergeeva et al.[29] showed that the relative importance of physical and chemical quenching pathways in uranyl systems is strongly dependent upon the nature of the substrate. Of the possible physical routes for quenching in this case, electronic energy transfer is ruled out by the lack of any low-lying electronic states in SCN^-, while heavy-atom perturbation, such as that invoked in the intraradical spin–orbit coupling model,[55] is rendered unlikely by the very high spin–orbit coupling constant ($\zeta_{U(VI)} \simeq$ 2000 cm^{-1})[60] of the uranyl ion itself. Indeed, because of this high ζ value, spin is probably not a good quantum number for UO_2^{2+}.[61] I, therefore, wish to suggest that in this system reaction 7 is more important than reaction 6 and that the major quenching route involves radical-pair formation.

For the system UO_2^{2+}/I^-, the rate of grow-in of the $I_2^{\bullet-}$ absorption at 390 or 700 nm was slower than that of the uranyl excited-state decay and was a linear function of I^- concentration over the range studied (up to 2×10^{-4} M). Least-squares analysis of the data provided an overall second-order rate constant k = 5.20 (±0.86) × 10^9 M^{-1} s^{-1} for $I_2^{\bullet-}$ formation. This is considerably lower than the value of 1.1×10^{10} M^{-1} s^{-1} reported for the ($I^\bullet$ + I^-) reaction[53] but is comparable to the rate of $(SCN)_2^{\bullet-}$ formation in reaction 9, suggesting that a similar mechanism is operating. As with thiocyanate, the relative yield of $I_2^{\bullet-}$ was determined by using the recommended extinction coefficient (9400 M^{-1} cm^{-1} at 390 nm),[52] and a plot of this against I^- concentration was linear over the range studied (Figure 5). There is considerable scatter in the data, as may be expected from the cumulative effect of errors in the various parameters and the fact that the laser intensity may not have been completely constant from one pulse to another. However, it is clear that the slope of the plot for the iodide case (880 ± 140 M^{-1}) is considerably higher than that for thiocyanate (220 ± 20 M^{-1}). With the UO_2^{2+}/Br^- system, it was not possible to observe the grow-in of $Br_2^{\bullet-}$, as there was considerable ground-state absorption in the region of the radical-anion maximum (360 nm)[52] and $^*UO_2^{2+}$ had a stronger absorption than this species at all other wavelengths. At the highest bromide concentration studied (2.9×10^{-4} M) it was possible to monitor the $Br_2^{\bullet-}$ absorption at 370 nm at the end of the excited uranyl decay and by using a value of 9400 M^{-1} cm^{-1} calculated for the radical-anion extinction coefficient at this wavelength from literature data,[52] estimate a yield of 0.027 for the radical anion under these conditions. For convenience, this point is also included in Figure 5. If one assumes, as with the other systems, that the yield of $Br_2^{\bullet-}$ is a linear function of bromide concentration, the slope for the corresponding plot in this case is 95 M^{-1}. If, as suggested, reaction 7 is the main route for quenching $^*UO_2^{2+}$, the yield of $X_2^{\bullet-}$ is given by

$$\text{yield of } X_2^{\bullet-} = \frac{k_9[X^-]}{k_8 + k_9[X^-]}$$

which, for low halide concentrations ($k_8 \gg k_9[X^-]$) reduces to

$$\text{yield of } X_2^{\bullet-} = \frac{k_9[X^-]}{k_8}$$

This provides a ready explanation for the behavior observed in Figure 5, and the slopes in this case correspond to k_9/k_8. The values for k_9 for SCN^- and I^- are presumed to be those reported here for formation of the respective anion radicals (3.82×10^9 and 5.20×10^9 M^{-1} s^{-1}) and do not depend significantly upon the anion. The rates for formation of these species by anion/radical combination are also virtually independent of the nature of the halide.[53] The variation in slope in Figure 5 must, therefore, reflect variations in k_8. Back-electron-transfer in radical pairs may depend upon both spin multiplicity[62] and overall free energy change.[63] For some metal complex/organic cation-radical pairs a bell-shaped dependence of the logarithm of the rate of this reaction upon $\Delta G°$ has been observed.[63] Although in the present study, detailed results are only available for thiocyanate and iodide systems, and for one concentration of bromide, the logarithm of the reciprocal of the slopes of Figure 5 (corresponding to k_8/k_9) increases linearly with the standard electrode potential for the $X^\bullet/X^-$ couple (Figure 5, insert), suggesting that the radical-pair back-electron-transfer in these cases occurs in a normal Marcus region. These results may help to resolve one of the dilemmas concerning uranyl ion excited-state decay in aqueous solution. It is suggested[37,64,65] that the relatively short lifetime of $^*UO_2^{2+}$ in this medium compared with the solid state is due to deactivation by a chemical process involving oxidation of a water molecule. However, no evidence has ever been obtained for formation of products of oxidation of H_2O. If one assumes that this chemical deactivation pathway involves formation of a hydroxy radical/uranium(V) radical pair by the reactions

$$^*UO_2^{2+} + H_2O \rightarrow (UO_2H^{2+}HO^\bullet) \rightleftharpoons (UO_2^+HO^\bullet) + H^+ \qquad (10)$$

a lifetime of this intermediate of $\tau \simeq$ 20 ns can be estimated from the above correlation by using a value of $E°$ = 1.9 V for the $OH^\bullet/OH^-$ couple[43] and a value of 4.5×10^9 M^{-1} s^{-1} for k_9. This lifetime is considerably shorter than the time scale for formation of this species, such that the normal steady-state concentration is expected to be too low for detection by conventional techniques.

Attempts to observe formation of $Cl_2^{\bullet-}$ were frustrated by the facts that the spectrum of this species (λ_{max} 340 nm)[52] is hidden under the more intense ground-state absorption of the UO_2^{2+}/Cl^- system and that the reaction is only marginally favored energetically. Following laser excitation of a solution of uranyl nitrate (0.1 M) in the presence of KCl (5×10^{-4} M), the recovery of ground-state absorption at 350 nm and the decay of $^*UO_2^{2+}$

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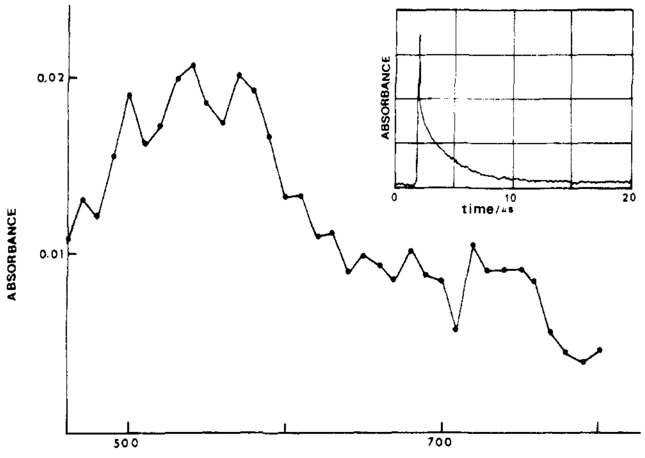

Figure 6. Transient absorption spectrum observed 100 ns after excitation of an aqueous solution of uranyl chloride (0.1 M, pH 2.55). Inset: Kinetic decay observed at 570 nm in this system.

absorption at 360 nm were monitored. At the end of these processes there was no evidence for any long-lived absorption that could be attributed to $Cl_2^{\bullet -}$. Evidence for formation of this species was sought following laser flash photolysis of aqueous solutions of uranyl chloride (0.1–0.25 M, pH 2.55). A transient absorbance was observed around 550 nm (Figure 6), which was much less intense (ca. 10%) and which differed somewhat in structure from that observed upon excitation of solutions of uranyl sulfate or nitrate. The transient absorbance was fully formed within the risetime of the detection system ($\simeq$2 ns) and decayed by an initial fast "spike" ($t_{1/2}$ = 7 ± 3 ns)[66] followed by a slower first-order process (k = 3.66 (±0.28) × 10^5 s^{-1}). The fast process is compatible with decay of uncomplexed $*[UO_2(H_2O)_5]^{2+}$ in the presence of Cl^-, while the longer lived absorption presumably corresponds to the excited state of some uranyl chloride complex(es). Following decay of this species, a very weak absorption was observed between 350 and 400 nm, which may be due to $Cl_2^{\bullet -}$. However, the low yields of this indicates that anion-radical formation is not a significant process in the uranyl chloride system.

The radical-anion absorptions for the iodide, bromide, and thiocyanate decayed over several hundred microseconds. The conditions used in these studies did not permit accurate evaluation of the decay kinetics, but studies on the initial rate in the thiocyanate case were consistent with an overall second-order decay with rate constant close to diffusion control. More information on the decay process has been previously presented,[13] and the method used by Sullivan and colleagues[14] would seem to provide an ideal way of studying reaction 4.

Table II. Second-Order Rate Constants for Decay of Dihalide Radical Anions in Aqueous Solution in the Absence and Presence of Uranyl Sulfate

	$2k^a/10^9$ M^{-1} s^{-1}	
radical anion	alone	with uranyl sulfate[b]
$I_2^{\bullet -}$	8.42	9.22
$Br_2^{\bullet -}$	4.20	4.33
$(SCN)_2^{\bullet -}$	2.17	2.46

[a] Calculated by using extinction coefficients from ref 52. [b] 5 × 10^{-3} M and pH 3.8.

In our previous report,[13] the possibilities of halide radical-anion decay involving reaction with uranium(V) or -(VI) were discussed, and it was concluded on thermodynamic grounds that reaction 4 is the most important decay route for $(SCN)_2^{\bullet -}$ and $Br_2^{\bullet -}$. To confirm that reactions between halide radical anions and UO_2^{2+} do not contribute significantly, nitrous oxide saturated aqueous solutions of KSCN, KBr, and KI (0.01 M) were studied by pulse radiolysis in the absence and presence of uranyl sulfate. Under these conditions, radiolysis is known to produce the halide radical anions through the sequence[67,68]

$$H_2O \rightsquigarrow e_{aq}^-, {}^\bullet H, {}^\bullet OH, H_2, H_2O_2, H^+ \tag{11}$$

$$e_{aq}^- + N_2O \rightarrow N_2 + O^\bullet \xrightarrow{H_2O} {}^\bullet OH + OH^- \tag{12}$$

$${}^\bullet OH + X^- \rightarrow HOX^{\bullet -} \rightarrow OH^- + X^\bullet \tag{13}$$

$$X^\bullet + X^- \rightleftharpoons X_2^{\bullet -} \tag{14}$$

The decay of the radical anion in all cases followed good second-order kinetics, with rate constants ($2k$) close to literature values.[16] Identical yields of radical anions were observed in the absence and presence of uranyl sulfate (5 × 10^{-3} M, pH 3.8). Within experimental error, the decays were unaffected by the presence of this compound (Table II), confirming that UO_2^{2+} does not react appreciably with $X_2^{\bullet -}$ and supporting the mechanism previously suggested for their decay in these systems.[13] The apparent decrease we reported for $I_2^{\bullet -}$ decay rate in the presence of the uranyl ion using microsecond flash photolysis was not observed here and may well have been an experimental artifact.

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