Quantum Yields and Reaction Rates in the Photo-oxidation of Hydrazine by Uranyl Ion

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Quantitative aspects of the photo-oxidation of hydrazine in HNO_3 and $HClO_4$ media by uranyl ion have been investigated in detail as a possible photochemical approach to the reprocessing of nuclear fuel, relying on the photo-production of U^{IV} which acts as a reductant for Pu^{IV} (to give solvent-separable Pu^{III} + U^{VI}). $\Phi(U^{IV})$, which is independent of irradiation wavelength, increases with hydrazine concentration in perchlorate media; a plot of $\Phi(U^{IV})^{-1}$ *versus* $[N_2H_5^+]^{-1}$ is linear with an intercept of 3.89, *i.e.* the limiting value of $\Phi(U^{IV})$ is 0.26. After relatively long irradiation times, when *ca.* 20—40% of U^{VI} is reduced, the stoicheiometry is approximately $N_2H_4 : U^{IV} : NH_3 = 2:1:2$ in both $HClO_4$ and HNO_3, but at much shorter times (when the few percent loss of N_2H_4 cannot be determined accurately) the $U^{IV} : NH_3$ ratio is approximately 1 : 1.25. N_2H_4 quenches the luminescence intensity of $[UO_2^{2+}]^*$ by a dynamic process, and τ for $[UO_2^{2+}]^*$ is systematically reduced on addition of N_2H_4. The quenching rate is affected somewhat by acidity and variation of ionic strength. A mechanism is proposed which accounts quantitatively for the variations both in quantum yield and lifetime. While the system has considerable interest as regards the efficient production of U^{IV}, its overall potential in the reprocessing of nuclear fuel is limited by the stoicheiometric product of ammonia, resulting, from the waste management viewpoint, in the build-up of unacceptable levels of ammonium nitrate, and attempts to circumvent the *partial* oxidation ($N_2H_4 \longrightarrow e^- + \frac{1}{2}N_2 + NH_4^+$), by addition of catalysts such as Cu^{II}, have failed. Alternative related reductants have been considered, but neither hydroxylamine nor its methylated analogues quenches $[UO_2^{2+}]^*$.

A key feature in the Purex process as applied by British Nuclear Fuels Ltd. (Sellafield), in the existing Magnox plant and the proposed Thermal Oxide Reprocessing plant for the reprocessing of spent nuclear fuel, is the separation of plutonium and uranium.[1] Currently the spent metal is dissolved in moderately strong HNO_3 solution to give U^{VI} and Pu^{IV}, which are separated from fission products by solvent extraction; iron(II) sulphamate is then used in a selective backwash to reduce Pu^{IV} to Pu^{III}, which is far less soluble than U^{VI} or Pu^{IV} in the organic phase. The presence of iron causes problems in waste management, however, and a highly desirable development would be that of a reductant for Pu^{IV} yielding no additional metallic salt to contend with in the active waste. The obvious candidate is U^{IV}, which would need to be generated from U^{VI} *via* reduction with a second reductant yielding only gaseous or innocuous end-products, such as N_2, H_2O, or CO_2. As U^{VI} is an established photo-oxidant of considerable power, the range of candidate reductants can be greatly extended by adopting a photochemical procedure, and specific attention along these lines has been devoted to such small inorganic molecules as tri-n-butyl-phosphite [2] and -phosphate [3] and ethanol,[4,5c] while hydrazine has also been suggested,[5] particularly if it could be oxidised completely to N_2. (Its ready oxidation by such thermal one-equivalent oxidants as Mn^{III} [6a] and Ce^{IV} [6b] is already well established.) There are considerable academic as well as technological interests associated with such a detailed study of the interaction of excited dioxouranium(VI) or uranyl ion with N_2H_4; most studies of this remarkable photo-oxidant have centred on organic systems or simple aquated metal ions and very few quantitative studies, either in terms of kinetics or product yields, have been carried out on non-metallic inorganic systems.[7] The photophysical properties of $[UO_2^{2+}]^*$ include a vivid green room-temperature luminescence in aqueous solution ($\lambda_{max.}$ = 509.3 nm) [8] with a relatively long lifetime (1.70 μs) in dilute $HClO_4$[9] and a high reduction potential $E^\ominus$ (*ca.* 2.60 V).[10] $[UO_2^{2+}]^*$ shows quite exceptional diversity in its interaction with electron-rich systems.[7] In addition to the expected processes of electron transfer [11] and hydrogen-atom abstraction,[12] it also engages in excimer [13] and exciplex formation, the latter with inorganic ions,[14] alkenes,[15] aromatic compounds,[16] and halogenoalkanes.[15] This paper describes in detail the kinetics, quantum efficiency, and product yields of the oxidation of N_2H_4 in aqueous acid (HNO_3 and $HClO_4$) by $[UO_2^{2+}]^*$. A brief comment is made on the interaction of $[UO_2^{2+}]^*$ with hydroxylamine and various of its methylated derivatives.

Experimental

The laser flash photolysis equipment, which delivers 40-ns pulses of 347 nm radiation of *ca.* 100 mJ energy, has been described before,[17] except that we have introduced a pulse-energy monitor which simply involves splitting the output of the triggering photodiode between the detection oscilloscope and a second storage oscilloscope (Iwatsu model DMS-510) which displays the relative height and form of each 694 nm pulse. Data analysis and computer fitting procedures are as given previously.[17] Luminescence spectra were recorded on Perkin-Elmer MPF-3 and LS-5 model instruments. Ferrioxalate actinometry [18] was performed using the optical bench described before, although the uranyl oxalate actinometer [19] was used occasionally for special purposes. Quantum yields were measured by observing the development of U^{IV} at its wavelength maximum of 648 nm, with $\varepsilon_{max.} = 49.5 \pm 0.2$ dm^3 mol^{-1} cm^{-1} for perchlorate medium (*cf.* lit.,[20] $\varepsilon_{max.} = 50$ dm^3 mol^{-1} cm^{-1}) but with $\varepsilon_{max.}$ varying in nitrate medium as indicated in Table 1. This shows that ε falls by up to 30% as the nitrate ion concentration is increased, in line with the observations of Ermolaev and Krot [21] on U^{IV} in nitric acid at various concentrations. Typical 'growth' plots for U^{IV} are illustrated in Figure 1.

Materials.—Water was distilled four times altogether, with the third distillation from alkaline $KMnO_4$. Materials were of AnalaR grade. Solutions of uranyl perchlorate were made by dissolving pure UO_3 in concentrated $HClO_4$. Hydrazine was used as the hydrate throughout.

Table 1. Variation of absorption coefficient of U^{IV} in nitrate media

(*a*) Variation with $[NO_3^-]([HNO_3] = 0.30$ mol dm^{-3})

$[NO_3^-]$/mol dm^{-3}	ε/dm^3 mol^{-1} cm^{-1}
0.30	44.7
0.60	38.5
0.90	36.4
1.50	35.0
2.10	33.2_5
3.00	30.9

(*b*) Variation with $[HNO_3]([NO_3^-] = 3.00$ mol dm^{-3})

$[HNO_3]$/mol dm^{-3}	ε/dm^3 mol^{-1} cm^{-1}
0.30	30.9
0.90	30.7_5
1.50	30.1_5
2.10	29.7_5
2.70	29.2_5

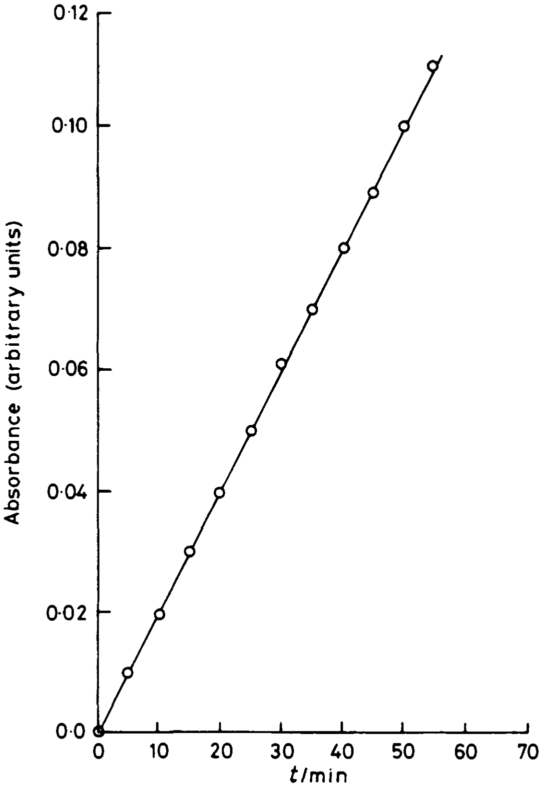

Figure 1. Development of absorbance of U^{IV} at 652 nm (5-cm pathlength cell) during the 401 nm photolysis of $N_2H_5ClO_4$ (0.104 mol dm^{-3}) and uranyl ion (0.05 mol dm^{-3}) in aqueous $HClO_4$ (0.30 mol dm^{-3})-$NaClO_4$ (2.72 mol dm^{-3}) medium after bubbling for 15 min with N_2 or argon

Table 2. Quantum yields (Φ) of U^{IV} in the photo-oxidation of N_2H_4 by excited uranyl ion *

(*a*) Variation with acidity: $[UO_2(NO_3)_2] = 0.05$, $[N_2H_5ClO_4] = 0.10$, $[ClO_4^-] = 3.00$ mol dm^{-3}

$[HClO_4]$/mol dm^{-3}	$\Phi(U^{IV})$
0.30	0.210
0.60	0.195
0.90	0.211
1.20	0.198
1.50	0.193
2.11	0.206
2.75	0.200

(*b*) Variation with ionic strength: $[UO_2(NO_3)_2] = 0.05$, $[N_2H_5ClO_4] = 0.10$, $[HClO_4] = 0.30$ mol dm^{-3}

$[ClO_4^-]$/mol dm^{-3}	$\Phi(U^{IV})$
0.40	0.138
1.00	0.147
1.60	0.145
2.10	0.164
2.50	0.173
3.00	0.207

* Perchlorate ion medium; irradiation wavelength 401 nm, $T = 293 \pm 2$ K.

Analytical Procedures.—Both hydrazine and ammonia were determined using established spectrophotometric techniques adapted by J. R. Embleton and P. D. Wilson of British Nuclear Fuels Ltd. (Sellafield). Ehrlich's reagent (*p*-dimethylaminobenzaldehyde) was used to analyse for hydrazine,[22] being sensitive over a hydrazine concentration range of 1×10^{-6} to 1×10^{-4} mol dm^{-3}. Ammonia was determined using the phenol-hypochlorite method,[23] which is sensitive over an ammonia concentration range of 6×10^{-6} to 2×10^{-5} mol dm^{-3}. (Test solutions were suitably diluted to achieve a figure in these ranges.)

Results

Quantum Yields.—These are expressed as $\Phi(U^{IV})$, the variation of which with acidity and ionic strength was determined in both perchlorate [Table 2(*a*) and (*b*)] and nitrate ion [Table 3(*a*) and (*b*)] media for irradiation at 401 nm. In the nitrate media it was critically important to use the absorption coefficient of U^{IV} appropriate to the nitrate ion concentration (from Table 1). It was observed that at $[N_2H_5^+]$ as low as 0.10 mol dm^{-3}, $\Phi(U^{IV})$ depended on $[HNO_3]$, but as $[N_2H_5^+]$ increased to 0.25 mol dm^{-3}, this effect disappeared. The limiting value of $\Phi(U^{IV})$ was 0.18 in nitrate media compared with 0.21 in perchlorate media. Changing the energy of the exciting photon over a wide range (313—449 nm) left $\Phi(U^{IV})$ unchanged (Table 4). Reducing the hydrazine concentration much below 0.10 mol dm^{-3} resulted in a gradual reduction of $\Phi(U^{IV})$, see Table 5. The typical 'scavenger plot' of Φ^{-1} *versus* $[N_2H_5^+]^{-1}$ (Figure 2) was linear with a slope of 0.303 ± 0.008 mol dm^{-3} and an intercept of 3.89 ± 0.16.

Product Yields.—In perchlorate media the *relative* yields of U^{IV} and NH_3, and of loss of N_2H_4, approximated to the 'theoretical' values expected from the simplest reaction scheme (see Discussion section) provided the irradiation time exceeded *ca.* 20 h [Table 6(*a*)]. At shorter irradiation times the yields could not be determined as accurately, and the 'hydrazine loss' not at all, but the ratio $[NH_3]/[U^{IV}]$ approximated to 0.8 rather than the expected 2.0 [Table 6(*b*)].

The same general results were obtained in nitrate media (Table 7), *i.e.* the ratio $[NH_3]/[U^{IV}]$ approximated to the 'ideal' figure of 2.0 at long irradiation times ($\geqslant$ 16 h) but fell to values considerably less than 1.0 at short times ($<$4 h). At the longer times, when loss of N_2H_4 could be determined accurately, the ratios $[U^{IV}]/[N_2H_4]$ and $[NH_3]/[N_2H_4]$ also approximated to the theoretical values of 0.50 and 1.0 respectively.

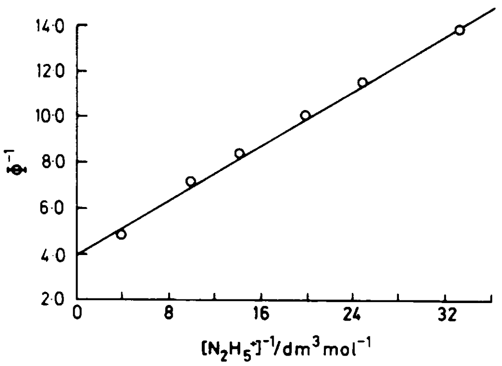

Figure 2. Hydrazine concentration dependence of $\Phi(U^{IV})$: $[UO_2(NO_3)_2]$ = 0.05, $[HClO_4]$ = 0.30, $[ClO_4^-]$ = 0.60 mol dm^{-3}; λ(irradiation) = 401 nm

Table 3. Quantum yields (Φ) of U^{IV} in the photo-oxidation of N_2H_4 by excited uranyl ion *

(*a*) Variation with acidity: $[NO_3^-]$ = 3.00 mol dm^{-3}

	$\Phi(U^{IV})$	
$[HNO_3]$/mol dm^{-3}	$[N_2H_5^+]$ = 0.10 mol dm^{-3}	$[N_2H_5^+]$ = 0.25 mol dm^{-3}
0.30	0.178	0.178
0.60	0.171	—
0.90	0.180	0.180
1.50	0.141	0.182
2.10	0.145	—
2.40	0.122	0.181
2.70	0.105	0.185

(*b*) Variation with ionic strength: $[HNO_3]$ = 0.30, $[N_2H_5NO_3]$ = 0.10 mol dm^{-3}

$[NO_3^-]$/mol dm^{-3}	$\Phi(U^{IV})$
0.4	0.130
1.5	0.160
3.0	0.178

* Nitrate ion medium; irradiation wavelength 401 nm, T = 293 ± 2 K, $[UO_2(NO_3)_2]$ = 0.05 mol dm^{-3}.

Table 4. Quantum yields (Φ) of U^{IV} in the photo-oxidation of N_2H_4 by excited uranyl ion at different irradiation wavelengths *

λ(irradiation)/nm	313	364	401	449
$\Phi(U^{IV})$	0.218	0.188	0.206	0.216

* $[UO_2(NO_3)_2]$ = 0.05, $[HClO_4]$ = 2.0, $[ClO_4^-]$ = 3.0, $[N_2H_5ClO_4]$ = 1.0 mol dm^{-3}.

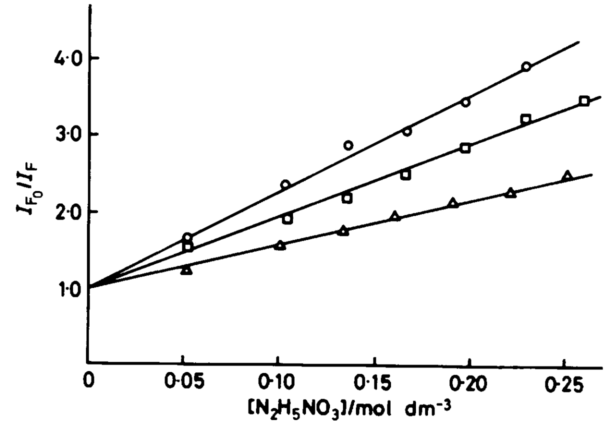

Figure 3. Stern–Volmer plots for the quenching of uranyl ion luminescence intensity (I_F) by added hydrazine: $[UO_2(NO_3)_2]$ = 0.05 mol dm^{-3}; $[HNO_3]$ = 0.594 (○), 1.49 (□), and 2.97 mol dm^{-3} (△); $[NO_3^-]$ = 3.20 mol dm^{-3}, λ(excitation) = 410 nm, λ(emission) = 510 nm

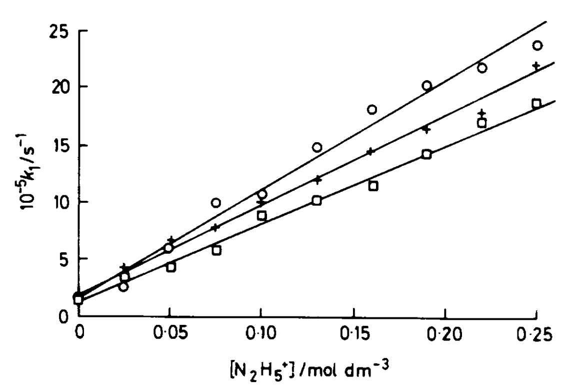

Figure 4. Dependence of reciprocal luminescence lifetime ($k_1 = \tau^{-1}$) of uranyl ion upon hydrazine concentration: $[UO_2(NO_3)_2]$ = 0.20; $[ClO_4^-]$ = 3.00 mol dm^{-3}; $[HClO_4]$ = 0.60 (○), 1.50 (+), and 3.00 mol dm^{-3} (□)

Table 5. Quantum yields (Φ) of U^{IV} in the photo-oxidation of N_2H_4 by excited uranyl ion at different N_2H_4 concentrations *

$[N_2H_5^+]$/mol dm^{-3}	$\Phi(U^{IV})$
0.030	0.072
0.040	0.087
0.050	0.100
0.070	0.116
0.100	0.140
0.200	0.206

* Irradiation wavelength 401 nm; $[UO_2(NO_3)_2]$ = 0.05, $[HClO_4]$ = 0.30, $[ClO_4^-]$ = 0.60 mol dm^{-3}.

Kinetic Measurements.—The kinetics of interaction between $[UO_2^{2+}]^*$ and hydrazine were investigated in two ways: (*i*) luminescence *yields* of uranyl solutions in the presence and absence of hydrazine, to give conventional Stern–Volmer plots with slopes $K^{SV} = k_2\tau_0$ (k_2 = quenching rate constant, τ_0 = lifetime of $[UO_2^{2+}]^*$ under reaction conditions in absence of N_2H_4) and (*ii*) luminescence *lifetimes* of uranyl solutions in the presence and absence of hydrazine, to give absolute rate constants k_2 for the quenching process. It was found that luminescence quenching of $[UO_2^{2+}]^*$ by N_2H_4 was ' ideal ' (Figure 3) in that the Stern–Volmer plots were linear, no spectral shift in the emission spectrum of $[UO_2^{2+}]^*$ resulted from addition of N_2H_4 and the quenching rate k_2 obtained on insertion of the value of τ_0 obtained under the acidity, ionic strength, and temperature quoted was in excellent agreement with that obtained by direct kinetic measurements. Thus at acidities (nitric acid) of 1.50 and 2.97 mol dm^{-3}, K^{SV} was 9.66 and 6.20 dm^3 mol^{-1} respectively. Insertion of lifetimes at these acidities for $[UO_2^{2+}]^*$ of 1.29 and 1.28 μs yielded k_2 values of 7.50 × 10^6 and 4.85 × 10^6 dm^3 mol^{-1} s^{-1} respectively. These compare with values of 7.60 × 10^6 and 4.80 × 10^6 dm^3 mol^{-1} s^{-1} obtained from lifetime quenching by hydrazine. Accordingly, the latter procedure was used throughout the remainder of this study.

The effect of added hydrazine upon the emission lifetime of

Table 6. Product yields and ratios in the photo-oxidation of N_2H_4 by $[UO_2^{2+}]^{\bullet}$ in perchlorate media [a]

$[HClO_4]$/mol dm^{-3}	Irradiation wavelength λ/nm	Irradiation time $10^{-2}t$/min	$10^{-20}\Delta n(U^{IV})$ [b]	$10^{-20}\Delta n(N_2H_4)$ [b]	$10^{-20}\Delta n(NH_3)$ [b]	$\frac{\Delta n(U^{IV})}{\Delta n(N_2H_4)}$	$\frac{\Delta n(NH_3)}{\Delta n(U^{IV})}$	$\frac{\Delta n(NH_3)}{\Delta n(N_2H_4)}$
(*a*) Long irradiation times								
0.30	401	12.00	1.34	2.95	2.48	0.45	1.86	0.84
0.30	439	10.20	1.18	2.29	2.49	0.51	2.11	1.09
1.50	439	13.20	2.42	5.25	4.71	0.46	1.945	0.90
3.00	439	9.90	2.31	4.35	4.07	0.53	1.77	0.94
3.00	439	38.70	4.15	7.78	7.47	0.53	1.80	0.96
1.50	401	25.20	2.19	4.81	4.49	0.46	2.05	0.935
(*b*) Short irradiation times								
0.30	401	0.95	0.104		0.0882		0.85	
0.30	401	1.10	0.115		0.0900		0.78	
1.50	401	1.15	0.135		0.115		0.85	
2.40	401	1.05	0.128		0.093		0.73	
2.70	401	1.35	0.165		0.138		0.84	
2.70	401	9.60	0.921		0.670		0.73	

[a] Initial concentrations: $[UO_2^{2+}]$ = 0.05, $[N_2H_5ClO_4]$ = 0.20, $[ClO_4^-]$ = 3.00 mol dm^{-3}. [b] Δn = Number of molecules.

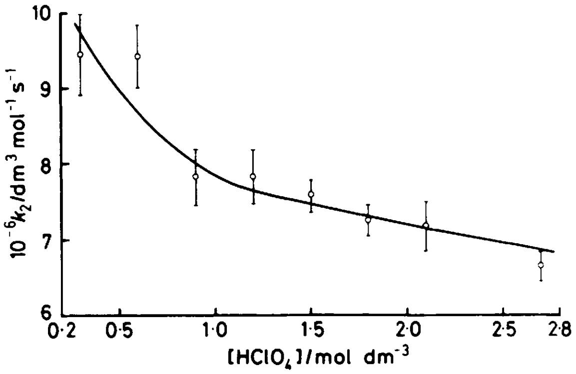

Figure 5. Acidity dependence of k_2 (perchlorate medium) at constant ionic strength (I = 3.0 mol dm^{-3}); $[UO_2(NO_3)_2]$ = 0.20 mol dm^{-3}

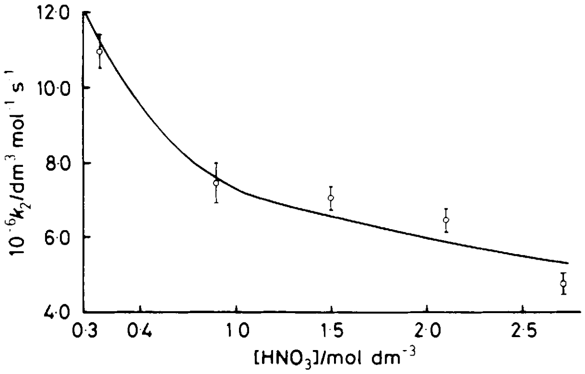

Figure 7. Acidity dependence of k_2 (nitrate medium) at constant ionic strength (I = 3.2 mol dm^{-3}); $[UO_2(NO_3)_2]$ = 0.20 mol dm^{-3}

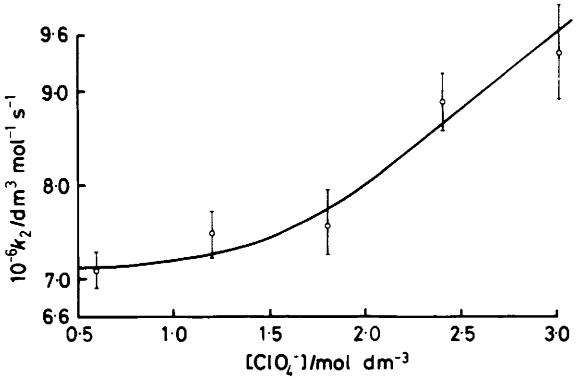

Figure 6. Ionic strength dependence of k_2 (perchlorate medium) at constant acidity ($[H_3O^+]$ = 0.3 mol dm^{-3}); $[UO_2(NO_3)]$ = 0.20 mol dm^{-3}

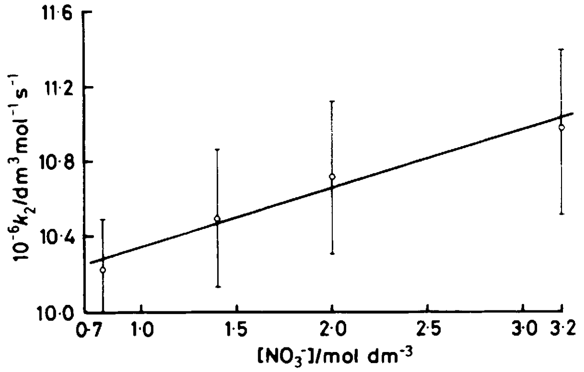

Figure 8. Ionic strength dependence of k_2 (nitrate medium) at constant acidity ($[H_3O^+]$ = 0.30 mol dm^{-3}); $[UO_2(NO_3)_2]$ = 0.20 mol dm^{-3}

$[UO_2^{2+}]^*$ at 510 nm was determined in both perchlorate and nitrate media. In all cases the kinetics of luminescence decay were strictly first order for 3—4 half-lives, and the values of k_1 so derived depended on the concentration of hydrazine according to the simple relation $k_1 = k_0 + k_2[N_2H_4]$, a typical example of which is illustrated in Figure 4.

The dependences of k_2 upon acidity (at constant ionic strength) and ionic strength (at constant acidity) were determined for both media and the results are summarised in Figures 5 and 6 (for perchlorate media) and Figures 7 and 8 (for nitrate media).

Table 7. Product yields and ratios in the photo-oxidation of N_2H_4 by $[UO_2^{2+}]^*$ in nitrate media [a]

$[HNO_3]$/mol dm^{-3}	Irradiation wavelength λ/nm	Irradiation time $10^{-2}t$/min	$10^{-20}\Delta n(U^{IV})$ [b]	$10^{-20}\Delta n(N_2H_4)$ [b]	$10^{-20}\Delta n(NH_3)$ [b]	$\frac{\Delta n(U^{IV})}{\Delta n(N_2H_4)}$	$\frac{\Delta n(NH_3)}{\Delta n(U^{IV})}$	$\frac{\Delta n(NH_3)}{\Delta n(N_2H_4)}$
(*a*) Long irradiation times								
0.30	439	13.50	2.60	6.87	6.03	0.38	2.32	0.88
0.30	439	12.00	2.43	4.58	3.37	0.53	1.39	0.74
1.50	439	11.40	2.69	5.38	5.28	0.50	1.96	0.98
2.70	439	13.20	2.93	5.26	6.23	0.56	2.12	1.18
2.70	439	38.40	4.49	8.70	8.85	0.52	1.97	1.02
2.70	401	11.40	10.95	2.29	2.02	0.48	1.84	0.88
(*b*) Short irradiation times								
0.30	401	2.30	0.241		0.154		0.64	
0.30	401	9.60	0.948		1.81		1.91	
2.70	401	2.30	0.200		0.189		0.93	
2.70	401	9.70	0.768		1.34		1.74	

[a] Initial concentrations: $[UO_2^{2+}] = 0.05$, $[N_2H_5NO_3] = 0.20$, $[NO_3^-] = 3.00$ mol dm^{-3}. [b] Δn = Number of molecules.

Hydroxylamine and its O- and N-*Methyl Derivatives*.—In view of the known high reactivity of NH_2OH towards such one-equivalent oxidants as Mn^{III},[24] Ce^{IV},[25] and $OH\cdot$,[26] a brief investigation was conducted of the interaction of $[UO_2^{2+}]^*$ with NH_2OH, especially as UO_2^{2+} oxidises NH_2OH thermally in the presence of Cu^{2+} in aqueous HF medium [27] (although in this case Cu^{2+} is the active oxidant). Surprisingly, addition of NH_2OH (as the sulphate salt, and *not* the chloride since Cl^- itself strongly quenches $[UO_2^{2+}]^*$,[11b] even at concentrations of 0.2 mol dm^{-3}) has *no* effect on the emission lifetime of UO_2^{2+}, nor is any U^{IV} produced on prolonged irradiation (48 h) of the solution with a bare-arc (200-W Xe/Hg) source.

Discussion

The results are interpreted in terms of the well established patterns both for the one equivalent oxidation of N_2H_4 [28] and for uranyl photochemistry:[8] equations (1)—(9).

$$UO_2^{2+} \xrightarrow{h\nu} [UO_2^{2+}]^* \quad (1)$$

$$[UO_2^{2+}]^* \xrightarrow{k_2} UO_2^{2+} + h\nu \quad (2)$$

$$[UO_2^{2+}]^* \xrightarrow{k_3} UO_2^{2+} \quad (3)$$

$$[UO_2^{2+}]^* + N_2H_4 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [UO_2^{2+}\cdot N_2H_4]^* \quad (4)$$

$$[UO_2^{2+}\cdot N_2H_4]^* \xrightarrow{k_5} UO_2^{2+} + N_2H_4 \quad (5)$$

$$[UO_2^{2+}\cdot N_2H_4]^* \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} UO_2^{+} + N_2H_4^{\cdot +} \quad (6)$$

$$2UO_2^{+} \xrightarrow{k_7} UO_2^{2+} + U^{IV} \quad (7)$$

$$2N_2H_4^{\cdot +} \xrightarrow{k_8} N_4H_8^{2+} \quad (8)$$

$$N_4H_8^{2+} \xrightarrow{k_9} N_2 + 2NH_4^{+} \quad (9)$$

Steps (1)—(9) lead to a stoicheiometry: $U^{VI} \equiv U^{IV} \equiv N_2 \equiv 2NH_3 \equiv 2N_2H_4$. The steady-state approximation can be applied to the scheme (1)—(9), assuming steps (7)—(9) to be very fast, to yield equation (10) for $\Phi(U^{IV})$. If k_{-6} can be neglected,

$$\Phi(U^{IV}) = \frac{0.5k_6}{(k_5 + k_6 + k_{-6})} \cdot \frac{k_4[N_2H_4]}{(k_4[N_2H_4] + k_{-4}[N_2H_4] + k_2 + k_3)} \quad (10)$$

then equation (10) can be simplified and rearranged to give equation (11).

$$1/\Phi(U^{IV}) = (2 + 2k_5/k_6)\{1 + (k_{-4}[N_2H_4] + k_2 + k_3)/(k_4[N_2H_4])\} \quad (11)$$

If, as seems very probable, we can also neglect k_{-4} in favour of k_5 as the principal mode of physical deactivation of the exciplex, then equation (12) is obtained. This implies that a

$$1/\Phi(U^{IV}) = (2 + 2k_5/k_6)\{1 + (k_2 + k_3)/k_4[N_2H_4]\} \quad (12)$$

plot of $[\Phi(U^{IV})]^{-1}$ *versus* $[N_2H_4]^{-1}$ should be linear with an intercept of $(2 + 2k_5/k_6)$ and a slope of $2(k_2 + k_3)(1 + k_5/k_6)/k_4$. This is tested successfully in Figure 2 with an intercept of 3.89 ± 0.16 and a slope of 0.303 ± 0.008 mol dm^{-3} indicating $k_5/k_6 = 0.945 \pm 0.08$. Now the lifetime (τ) of the excited uranyl ion, which is equal to $(k_2 + k_3)^{-1}$, fluctuates sharply with the purity of the aqueous solvent, as well as showing a systematic change with acidity. Taking τ as 3.0 ± 0.5 μs at $[HClO_4] = 0.3$ mol dm^{-3} and $[ClO_4^-] = 0.6$ mol dm^{-3}, $k_4 = (4.4 \pm 0.8) \times 10^6$ dm^3 mol^{-1} s^{-1}. This is in approximate agreement with the absolute quenching rate of $[UO_2^{2+}]^*$ by N_2H_4 at this acidity and ionic strength of $(7.1 \pm 0.2) \times 10^6$ dm^3 mol^{-1} s^{-1}. A simplified scheme involves no exciplex [step (4) and its reverse], and replaces steps (5) and (6) by (13) and (14). This yields equation (15). Thus the gradient

$$[UO_2^{2+}]^* + N_2H_4 \xrightarrow{k_{13}} UO_2^{2+} + N_2H_4 \quad (13)$$

$$[UO_2^{2+}]^* + N_2H_4 \xrightarrow{k_{14}} UO_2^{+} + N_2H_4^{\cdot +} \quad (14)$$

$$1/\Phi(U^{IV}) = 2 + 2(k_{13}/k_{14}) + 2(k_2 + k_3)/k_{14}[N_2H_4] \quad (15)$$

of the plot of $[\Phi(U^{IV})]^{-1}$ *versus* $[N_2H_4]^{-1}$ yields a slope of $2/k_{14}\tau$; *i.e.*, with $\tau = 3.0 \pm 0.5$ μs, $k_{14} = (2.27 \pm 0.45) \times 10^6$ dm^3 mol^{-1} s^{-1}. Now the intercept of 3.89 indicates k_{13}/k_{14} =

0.945 and $k_{13} = (2.15 \pm 0.43) \times 10^6$ dm^3 mol^{-1} s^{-1}; thus $(k_{13} + k_{14}) = (4.4 \pm 0.8) \times 10^6$ dm^3 mol^{-1} s^{-1}, *i.e.* the quantum yield data do not allow discrimination between the alternative mechanisms (4)—(6) and (13)—(14). The intercept in Figure 4 of 3.89 implies a maximum quantum yield of U^{IV} of 0.26 which compares with a theoretical maximum figure of 0.5, *i.e.* a 'deficiency' of 0.24 is devoted to the physical quenching steps (5) or (13) induced by N_2H_4. This is an acceptably high figure from the point of view of U^{IV} formation for reducing Pu^{IV} in nuclear fuel reprocessing, but it is less acceptable than the corresponding figure for ethanol of 0.5—0.6 [4a,13] in which case physical quenching is barely perceptible. By contrast with alkanols, aromatic aldehydes yield values for k_5/k_6 covering a very wide range (0.25—11.5).[29]

What makes the quite efficient photochemical reduction of U^{VI} by N_2H_4 less attractive with respect to nuclear fuel reprocessing is the pattern of products. From Tables 6 and 7 it is clear that the stoicheiometry closely follows $U^{IV} \equiv 2N_2H_4 \equiv 2NH_3 \equiv N_2$, *i.e.* the oxidation of hydrazine is inextricably associated with production of an equivalent of NH_3 and the build up, in the strong nitric acid medium utilised, of unacceptable levels of ammonium nitrate.

Attempts we have made to circumvent this by introducing Cu^{II} into the medium (to oxidise $N_2H_4^{\cdot +}$ radicals) have been unsuccessful: the presence of 5×10^{-3} mol dm^{-3} Cu^{II} (as the perchlorate) led to almost complete suppression of formation of the desired U^{IV}, probably because of oxidation of U^V by Cu^{II}.[13]

A short investigation of hydroxylamine and its derivatives, NH_2OMe and NHMeOMe, revealed that these are entirely without effect on either the lifetime or luminescence intensity of excited $[UO_2^{2+}]^*$, and no U^{IV} is produced on prolonged irradiation at 401 nm. The inertia of hydroxylamine is unexpected in view of its ready oxidation by one-equivalent reagents such as Ce^{IV},[25] Mn^{III},[24] and $OH\cdot$[26] in acidic media when the active species is NH_3OH^+.

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