REDUCTION OF THE U(VI) ION. A FAST CONDUCTIMETRY STUDY

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Abstract—The reduction of U(VI) by e_{aq}^- was followed by means of fast conductimetry in acid and conductimetry and spectrophotometry in alkaline solutions. In alkaline solutions, the biomolecular rate constant of reaction between UO_4^{2-} and e_{aq}^- was determined as $k_4 = 4.50 \times 10^9 \, M^{-1} \, s^{-1}$. In acid solutions it has been observed that the analogous rate is within a range $1.7 \times 10^{10} < k_9 < 7.4 \times 10^{10} \, M^{-1} \, s^{-1}$ for the reaction between UO_2^{2+} and e_{aq}^-. Analytical methods applied in this work were too fast to follow the slow disproportionation of produced U(V)-ion, but it has been observed that in alkaline solutions it probably goes via a dimeric ion $[U(V)]_2$, which protonates with a rate $k_7 = 1.30 \times 10^5 \, s^{-1}$.

INTRODUCTION

Radiation chemistry of uranium compounds has been limited as yet to steady-state oxidation of U(IV) to U(VI) (Bhattacharyya and Saini, 1979) and to the back reduction (Guha et al. 1987) or to the determination of rate constants of e_{aq}^-, OH and H with various UO_2^{2+} or U(IV) species (Buxton et al. 1988), though much earlier it had been found already that producing U(V) ions with help of ionizing radiation enabled observation of disproportionation of that ion (Sobkowski and Zalkind, 1965).

There is virtually no radiation chemistry evidence on mechanism and kinetics of these, very complicated, processes which include not only charge transfer but also irreversible reactions changing the structure of the uranium ion.

Radiation chemistry methods are a very useful tool in studies on redox reactions in aqueous solutions and this marked omission is, probably, because all uranium species involved have extinction coefficients $< 50 \, M^{-1} \, cm^{-1}$. Such small values precluded in fact application of pulse radiolysis with spectrophotometric detection—the most common fast technique of radiation chemistry.

It seemed to us that, as the redox processes of the U(IV)–U(VI) pair include the formation of H^+ or OH^-, fast conductimetric detection offered a reasonable alternative, the more so as the U(V) intermediate is relatively stable.

Though the identity of the uranyl species at a given concentration and pH is still in dispute a general agreement† has been reached to that: (a) UO_2^{2+} exists in its hydrated form $UO_2(H_2O)_6^{2+}$ only at very low concentration and in strongly acidic solutions; (b) it

readily hydrolyses and di- or polymerizes with release of a corresponding number of H^+ ions; (c) the above characterizes also the U(IV) and to an extent U(V) ion as well (Selbin and Ortega 1969).

EXPERIMENTAL

Conductivity changes following irradiation by a pulse of electrons (3.5 MeV, 4–100 ns), produced by a Van de Graaff accelerator, were monitored using a.c. cell excitation and a balanced detection method which rejects artifacts due to electron pulse charge deposition in the cell. For slow work ($> 1 \, \mu s$) low volume pyrex conductivity cell was employed (cell constant $= 0.20 \, cm^{-1}$) while for fast work a combined optical and conductivity cell was used (cell constant $= 0.27 \, cm^{-1}$, optical path length $= 2.0 \, cm$) similar to that used in previous work (Vojnovic, 1983; Vojnovic et al., 1986). The cell current was monitored by using a transformer bridge circuit which could be coupled to a reference, unirradiated cell so that only changes in cell current are detected. The cell was excited with a 5–40 V sine wave at frequencies of 1–4 kHz synchronized to the electron pulse so that the pulse is fired at the peak of the wave. Phase sensitive detection (time resolution $= 250 \, \mu s$) of the resulting cell current was employed for very slow transients (5 ms–10 s) while for fast work (10 ns–10 ms), a demodulation method which can extract amplitude information during the a.c. cycle was used. The time resolution was $< 7 \, ns$. Solutions were prepared using $UO_2(CH_3COO)_2 \cdot 2H_2O$ and other compounds of analytical grade and water purified by a Milli-Q system ($\sigma = 0.06 \, \mu S \, cm^{-1}$) and were deoxygenated by ca. 20 min bubbling with oxygen-free N_2·pH was, in each case, adjusted by addition of a $HClO_4$ or NaOH solution. Samples were introduced into the cell using a fill-empty type

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†Details on chemistry of the U^{n+} ($n = 3, 4, 5, 6$) in aqueous solution are described in an extensive literature, the most recent summary being by Ahrland (1984).

of flow system and typically data from several samples was averaged (2–10 samples), the data being acquired on a Tektronix 7612D digitiser interfaced to a software analysis package. The pulse charge (i.e. dose) was monitored using an inductive monitor (Vojnovic, 1985) calibrated against degassed water or 10 mM thiocyanate solution.

RESULTS AND DISCUSSION

Considering that at concentrations *ca* 0.1 mM UO_2^{2+} the solution should be free from a significant amount of dimeric ions, the monomeric ones to be accounted for are UO_2^{2+}, UO_2OH^+ and UO_4^{2-}, the first of them being a predominant form at low pH, second in the range *ca* 5 < pH < *ca* 8 and the latter at the high pH level. To avoid difficulties in interpretation of the results, the irradiations were done at pH *ca* 9.6, where virtually all U(VI) ions will be in the UO_4^{2-} form, and at pH *ca* 2.9, where forms other than UO_2^{2+} may be neglected.

Radiolytic decomposition of water may be described by a general equation

$$H_2O \longrightarrow e_{aq}^-, H_3O^+, OH^-, H, OH, H_2, H_2O_2. \quad (1)$$
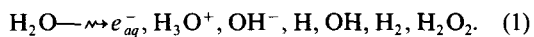
As H_2O_2 does not react with U(VI) and only very slowly with U(V) and U(IV) (Baker and Newton, 1961), the molecular products are excluded from further consideration. To avoid the interference of OH, solutions included 0.02 M tert. butanol, which considerably reduced reduction of U(VI) by H as well. At the chosen pH values the micromolar amounts of H_3O^+ and OH^- produced within duration of the electron pulse are too small to affect the behaviour of U(VI), hence it is assumed that they react only with the counter-ion. A similar assumption has been made in respect to other species present like Na^+, ClO_4^-, CH_3COO^- and N_2. The tert. butoxy radical, produced in the reaction of OH or H with tert. butanol has been shown not to react with U(VI), U(V) or U(IV) (Guha *et al.* 1987).

Eventually, the only species produced in the pulse and of importance in later reactions, is e_{aq}^-. Together with H_3O^+ and OH^- the hydrated electron is observed in the conductometric measurements and may be individually recorded optically; apart from U(VI) and H_3O^+ it does not react with any other substance present. The reaction

$$U(VI) + e_{aq}^- \rightarrow U(V) \quad (2)$$
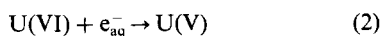
has been studied for a number of uranium compounds and at various pHs. Its rate constant, k_2, is high. Baxendale *et al.* (1965) observed $7.4 \times 10^{10} \, M^{-1} s^{-1}$ at an unspecified pH. Sullivan *et al.* (1976) determined 1.7×10^{10} at pH = 5.3 and $1.3 \times 10^{10} \, M^{-1} s^{-1}$ at 6.8, considering that at the lower pH the composition of U(VI) ions in the solution is $0.76 \, UO_2^{2+}$–$0.24 \, UO_2OH^+$ and at the higher $0.91 \, UO_2OH^+$–$0.09 \, UO_2^{2+}$ (Nash *et al.* 1981). The lack of the ligand effect on k_2 suggested to the
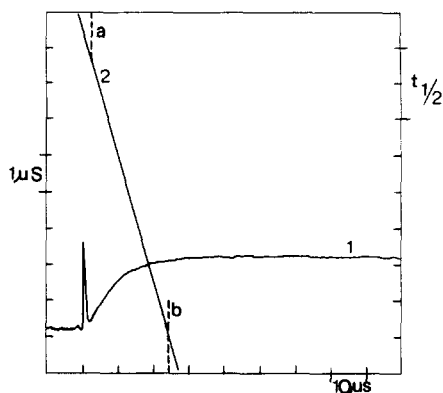

Fig. 1. Curve (1), changes in conductance (μS) upon pulse radiolysis of 1.21×10^{-4} M $UO_2(CH_3COO)_2$, 0.02 M tert. butanol, N_2-saturated solution, pH = 9.80, D = 12.55 Gy, cell constant = 0.20 cm^{-1}. Curve (2), test for kinetics of curve (1) between a–b ($t_{1/2}$).

same authors that (2) follows in fact the tunneling mechanism.

In this work we recorded the conductance change in the pulse-irradiated alkaline U(VI) solutions over the time range from ns to *ca* 8 s after the pulse and simultaneously the optical absorption of e_{aq}^- (at 600 nm) up to *ca* 10 μs. A typical conductance trace is shown in Fig. 1 (curve 1). The initial peak is followed by a fast decrease, below the background conductance level, and a subsequent, slower, increase to a permanent (up to 8 s) conductance value, higher than the initial one. The slow increase to the permanent value follows first-order kinetics over *ca* 4 half-life-times, as shown in Fig. 1 (curve 2), with $k = (1.30 \pm 0.30) \times 10^5 \, s^{-1}$.

The initial decays of conductance and optical absorption have been checked simultaneously (Fig. 2) and they proceed according to a different pattern. Whereas the absorption [Fig. 2 (curve 2)] decays to zero within *ca* 6 μs, the conductance decays very fast in the first *ca* 125 ns and then much slower, over *ca* 4 μs, to increase again subsequently. The rate of the
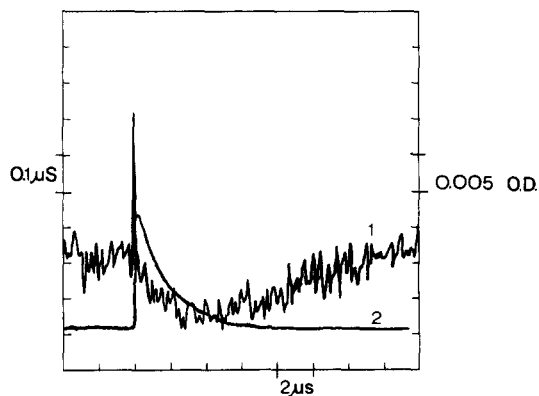

Fig. 2. Change in the pulse irradiated 1.10×10^{-4} M $UO_2(CH_3COO)_2$, 0.02 M tert. butanol, N_2-saturated solution, pH = 9.30, D = 3.243 Gy. Curve (1), conductance (μS), cell constant = 0.27 cm^{-1}; curve (2), optical absorption (O.D.) 600 nm, 2 cm cell path length.

Table 1. Relation between measured and calculated (see text) conductivity in alkaline solution of uranyl acetate

[U(VI)] $\times 10^4$ (M)	pH	D (Gy)	Permanent conductivity (μS cm^{-1})		B/A
			Measured A	Calculated B	
1.21	9.80	12.55	0.420	0.346	0.82
1.21	9.80	12.49	0.370	0.375	1.01
1.21	9.80	12.45	0.320	0.375	1.17
1.10	9.30	3.243	0.100	0.098	0.98
1.10	9.30	3.121	0.100	0.094	0.94
				Mean	0.98 ± 0.18

fast decrease of conductance has been estimated as *ca* 10^7 s^{-1} and most probably is connected with neutralization of the H_3O^+ produced in the pulse

$$H_3O^+ + OH^- \rightarrow H_2O. \tag{3}$$
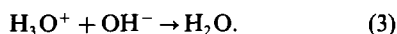
The hydrated electron, as recorded optically, decayed with a first-order rate constant $(5.00 \pm 0.20) \times 10^5$ s^{-1}. Slow decrease of conductance followed first-order kinetics as well with rate constant $(4.80 \pm 0.20) \times 10^5$ s^{-1}. Considering that both these processes are connected with the reaction

$$UO_4^{2-} + e_{aq}^- \rightarrow UO_4^{3-} \tag{4}$$
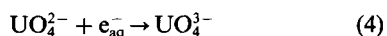
the bimolecular rate constant, $k_4 = (4.50 \pm 0.20) \times 10^9$ M^{-1} s^{-1}, has been calculated for the optical measurements; k_4 for conductometric observation is less dependable, though very close, as affected by two other processes. The values obtained by us are much lower than those mentioned earlier and observed in acidic solutions. We can not offer a plausible explanation of this discrepancy. Though the literature values tend to be larger at lower pH no systematic study of that problem has been done as yet and this tendency may be superficial.

The slow increase in conductance, but not in the optical absorption, is less easy to explain. The obvious interpretation would be that it is due to disproportionation of U(V) in a reaction

$$2UO_4^{3-} + 2H_2O \rightarrow UO_4^{2-} + UO_2 + {}^4OH^-. \tag{5}$$
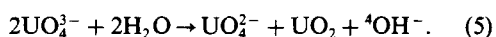
This mechanism has, however, to be rejected as (5) would follow the second order kinetics, whereas the observed change in conductance was a first-order one [Fig. 1 (curve 2)]. Moreover, it would suggest that the permanent increase of conductance over that of the background should be an effect of the increase in $[OH^-]$ equal to $[e_{aq}^-]$ produced in the pulse, which was not the case. The increase in the permanent conductance was calculated using following equivalent conductivities (λ): $H_3O^+ = 331$, $e_{aq}^- = 202$ and $OH^- = 188$ S cm^2 mol^{-1} (at 18°C corrected for proper temperature by $\Delta\lambda = 1.6\%$ per °C) (Landolt-Bornstein, 1960, Beck, 1969) and their respective radiation-chemical yields 0.371, 0.299 and 0.082 μM J^{-1} (Anderson *et al.* 1985) (1 μM J^{-1} $G = 9.65$). It was considered that $\lambda_{1/3UO_4^{3-}} = \lambda_{1/2UO_2^{2+}} = 32$ S cm mol^{-1} (Landolt-Bornstein, 1960) and, anyway, mobility of UO_2^{2+} is small. Results have been

collected in Table 1 and were obtained on assumption that $[OH^-] = 1/2[e_{aq}^-]$, which has been, eventually supported by the obtained mean 0.98. This stochiometry does not agree with that expected if the process in question were that of disproportionation.

Though disproportionation of U(V)-ions is a reaction proved by many investigators (Sobkowski and Zalkind, 1965; Selbin and Ortega, 1969; Ahrland, 1984) its mechanisms is not quite clear. Baker and Newton (1961) and Ekstrom (1974), analysing the likely mechanisms, suggested as most probable the following two reactions:

$$2U(V) \rightarrow [U(V)]_2 \tag{6}$$

$$[U(V)]_2 + H^+ \rightarrow products. \tag{7}$$
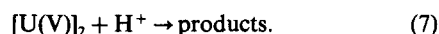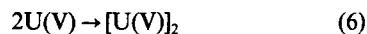
Our results are in agreement with this mechanism, reaction (7) including, probably, dissociation of H_2O and production of the free OH^-. $[U(V)]_2$ seems to escape both conductometric and optical recording. Though its optical properties remain unknown it is unlikely to have an extinction coefficient much larger than 28 M^{-1} cm^{-1} the value obtained for $U(V) \cdot U(VI)$ dimer (Ekstrom, 1974) and the equivalent conductivity can not be far apart from that of UO_2^{2+} either.

Reactions in acidic solutions of $UO_2(CH_3COO)_2$ are simpler, as illustrated by Fig. 3. The initial, fast, decrease is followed by a permanent (up to 8 s) conductance. On assumptions similar to those above
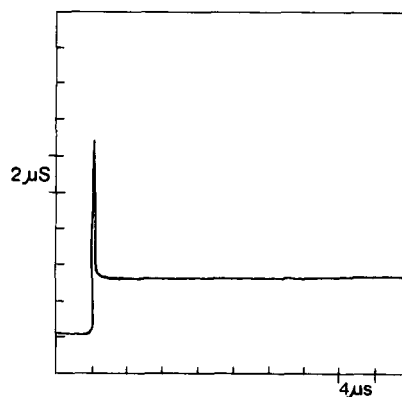

Fig. 3. Change in conductance (μS) in pulse irradiated 1.06×10^{-4} M $UO_2(CH_3COO)_2$, 0.02 M tert. butanol, N$_2$-saturated solution, pH = 2.90, D = 8.93 Gy, cell constant = 0.20 cm^{-1}.

Table 2. Relation between measured and calculated (see text) conductivities in acidic solution of uranyl acetate

[U(VI)] $\times 10^4$ (M)	pH	D (Gy)	Permanent conductivity (μS cm^{-1})			
			Measured	Calculated A	B	C
1.45	3.35	10.040	0.249	0.0632	0.236	1.023
1.06	2.90	9.103	0.585	0.0158	0.0530	0.256
1.50	2.90	2.243	0.0750	0.0059	0.0222	0.0961
0.986	2.70	3.188	0.0830	0.0032	0.0118	0.0505
1.76	2.70	3.158	0.0810	0.0056	0.0209	0.0902

we analyse the experimental results in terms of competition for e_{aq}^- between H_3O^+ and UO_2^{2+}

$$H_3O^+ + e_{aq}^- \rightarrow H + H_2O \tag{8}$$

$$UO_2^{2+} + e_a^- q \rightarrow UO_2^+ \tag{9}$$
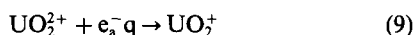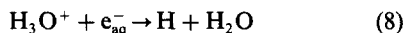
OH^- and e_{aq}^- produced in the pulse react in (3), (8) and (9), whereas H_3O^+ remains unreactive. Denoting their concentrations as $[e_{aq}^-]_a$, $[OH^-]_b$ and $[H_3O^+]_{a+b}$ it may be concluded that (3) and (8) do not affect the final conductance, as the amount of H_3O^+ removed from the solution by $[OH^-]_b$ is introduced to it by $[H_3O^+]_{a+b}$. The same source replenishes the loss of H_3O^+ in (8) and the fraction of the initial $[H_3O^+]_{a+b}$ which remains in the solution corresponds to $[e_{aq}^-]$ entering (9). Conductivities measured and calculated are collected in Table 2. In calculations the difference between $\lambda_{UO_2^+}$ and $\lambda_{1/2\,UO_2^{2+}}$ was neglected and the following rate constants were taken into account: $k_8 = 2.4 \times 10^{10}\,M^{-1}\,s^{-1}$ (Buxton, et al. 1985), (A) = $k_9 = 4.50 \times 10^9$ (this work, alkaline solution), (B) = 1.7×10^{10} (Sullivan et al., 1976; pH = 5.3) and (C) = 7.4×10^{10} (Baxendale et al., 1965; pH = ?).

Considering that H_3O^+ was known with precision to ca 0.05 pH the results in Table 2 show a satisfactory agreement between the measured and calculated conductivities in case (B) at pH = 3.35 and (C) at higher acidities. The lowest k_9 value applied (A) was that obtained at pH = 9.8 in this work and failed to explain the course of reaction at low pHs. The highest k_9 was obtained by Baxendale et al. (1965) probably at a low pH, as those authors used solutions at the natural pH, which in ca 0.1 mM UO_2^{2+} is about 4, i.e. much lower than 5.3, at which $k_g = 1.7 \times 10^{10}\,M^{-1}\,s^{-1}$ was determined by Sullivan et al. (1976). It may be therefore concluded that in acidic solutions $1.7 \times 10^{10} < k_9 < 7.4 \times 10^{10}\,M^{-1}\,s^{-1}$.

Finally, it should be mentioned that the permanent conductivities observed by us showed in fact a very small decay, of ca 5% over 8 s. If this decay is connected with disproportionation of U(V) the time involved does not disagree with values reported by Sobkowski and Zalkind (1965) and Ekstrom (1974).

CONCLUSIONS

Fast conductimetry has proved itself useful in direct studies of formation and reactions of U(V) transient ion. Contrary to other metal ions with unusual valency levels, decaying within a few ms

(Broszkiewicz, 1976), U(V) is quite stable, which confirms a stabilizing effect of oxygen ligands. The U(VI) structures at low or high pH, UO_2^{2+} and UO_4^{2-}, differ in behaviour. The rate constant for reaction with e_{aq}^- is much larger for the cationic than for the anionic form. In the latter case production of the dimer $[U(V)]_2$ is very likely, though our results do not disprove the existence of such an ion in acidic solutions.

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