Kinetics and Mechanism of Single Electron Oxidations of the Tervalent Uranium Ion, U^{3+}(aq), by Free Radicals in Aqueous Solutions†

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The specific rates of oxidation of U^{3+}(aq) by $OH^\bullet$, $Cl_2^{\bullet -}$, $Br_2^{\bullet -}$, $I_2^{\bullet -}$, $(NCS)_2^{\bullet -}$, $^\bullet CH_2CO_2H$, $^\bullet CH(CH_3)CO_2H$, $^\bullet CH_2C(CH_3)_2OH$, and $^\bullet CH_3$ are reported. The results are interpreted as indicating that all these reactions occur *via* an inner-sphere mechanism with an increase in co-ordination number. This conclusion contradicts earlier suggestions that oxidations of aqua complexes by $OH^\bullet$ radicals proceed *via* hydrogen-atom abstraction from one of the aqua ligands. The specific rate of the reaction $U^{3+}(aq) + H_2O_2$ is estimated to be 2×10^5 dm^3 mol^{-1} s^{-1}.

The kinetics of oxidation of many transition-metal complexes by hydroxyl radicals and other free radicals have been studied (the specific rates of these reactions are summed up in tables published by the National Bureau of Standards[1]). The mechanisms of these reactions have not been fully elucidated although they have been discussed in detail for many specific systems.[2] Thus for the reactions of hydroxyl radicals and in principle for other free radicals, $R^\bullet$, four different mechanisms, (*a*)—(*d*), have been proposed for the oxidation of aqua complexes.

(*a*) An outer-sphere electron transfer, probably through the formation of a contact pair, is shown by equation (1). This

$$[M(H_2O)_n]^{k+} + R^\bullet \xrightarrow{k_1} [M(H_2O)_n]^{(k+1)+} + R^- \quad (1)$$

mechanism was ruled out for R = OH as the specific rates of reaction (k_1) observed disagreed with expectations according to Marcus theory.[3] This observation is probably due to the fact that the self-exchange reaction [equation (2)] is expected to be

$$OH^\bullet + {}^*OH^-(aq) \longrightarrow OH^-(aq) + {}^*OH^\bullet \quad (2)$$

very slow due to the very large rearrangement energy of the reaction.[4] Similar arguments also probably apply for oxidations by other free radicals, *e.g.* $^\bullet CH_3$, $^\bullet CH_2CO_2H$, *etc.*[4,5]

(*b*) An inner-sphere electron-transfer mechanism is shown by equation (3). This mechanism was ruled out for many systems

$$[M(H_2O)_n]^{k+} + R^\bullet \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} (H_2O)_{n-1}M^{k+}(R) \longrightarrow$$
$$(H_2O)_{n-1}M^{(k+1)+}(R^-) \longrightarrow [M(H_2O)_n]^{(k+1)+} + R^- \quad (3)$$

as the overall rate of reaction was often faster than the rate of inner-sphere ligand exchange of M^{k+}.[3]

(*c*) After ruling out the outer- and inner-sphere mechanisms for the oxidation of aqua complexes by hydroxyl radicals, Berdnikov[3] proposed that the reaction mechanism involves an hydrogen-atom abstraction, equation (4). This mechanism was

$$[M(H_2O)_n]^{k+} + {}^*OH^\bullet \longrightarrow (H_2O)_{n-1}M^{k+}(OH) + H_2{}^*O \longrightarrow$$
$$(H_2O)_{n-1}M^{(k+1)+}(OH^-) \xrightarrow{H} [M(H_2O)_n]^{(k+1)+} \quad (4)$$

also suggested recently as a plausible mechanism for the oxidation of $[V(H_2O)_6]^{2+}$ [ref. 6(*a*)] and $[Eu(H_2O)_9]^{2+}$ [ref. 6(*b*)] by aliphatic free radicals, *e.g.* $^\bullet C(CH_3)_2OH$ and $^\bullet CH(CH_3)OC_2H_5$.

(*d*) Alternatively it was proposed[4,6] that oxidations by hydroxyl and aliphatic free radicals occur *via* an inner-sphere mechanism with a transition state or short-lived transient product, with an increased co-ordination number, *i.e.* equation (5), where the equilibrium step includes the redox process.

$$[M(H_2O)_n]^{k+} + R^\bullet \underset{k_{-51}}{\overset{k_{51}}{\rightleftharpoons}} [(H_2O)_nM{-}R]^{k+} \xrightarrow{k_{52}}$$
$$[M(H_2O)_n]^{(k+1)+} + R^- \quad (5)$$

We decided to measure the specific rates of oxidation of one aqua complex by an extended series of free radicals with the hope that from the relative rates of reaction we would be able to conclude which of the latter two mechanisms occurs. $[U(H_2O)_n]^{3+}$ ‡ was chosen as the aqua complex because: (*i*) it is a strong reducing agent, $E^\circ\{[U(H_2O)_n]^{3+}/[U(H_2O)_n]^{4+}\} = -0.63$ V,[8] and is therefore expected to be oxidized at a reasonable rate by many free radicals, and (*ii*) it has a strong absorption band in the near u.v. and thus the oxidation reactions can be followed spectrophotometrically even for free radicals which have no absorption bands in the region accessible to the pulse-radiolysis technique.

Experimental

Materials.—Solutions of tervalent uranium were prepared by reducing uranyl perchlorate with zinc amalgam in 0.5 mol dm^{-3} $HClO_4$ under an argon atmosphere. The concentration of $[U(H_2O)_n]^{3+}$ was determined spectrophotometrically at 352 nm (ε = 1 620 dm^3 mol^{-1} cm^{-1}).[9] All other materials were of AnalaR grade and were used without further treatment. All solutions were prepared with water purified by a Millipore set up, resistivity $\geqslant 10^6$ Ω cm^{-1}.

Kinetic Measurements.—The pulse-radiolysis apparatus at the Hebrew University of Jerusalem was employed. Short pulses, 0.1—1.5 μs from the linear electron accelerator, 5 meV, 200 mA, were used to produce $(0.1—3) \times 10^{-5}$ mol dm^{-3} free radicals. The experimental procedure has been described in detail elsewhere.[10] The kinetics were followed by observing the bleaching of the absorption due to the free radicals and/or the $[U(H_2O)_n]^{3+}$.

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

‡ The exact co-ordination number of U^{3+} and U^{4+} in aqueous solutions is not known. However, recent results seem to indicate a co-ordination number of eight or seven and even 12.[7] In this paper all the equations are written with an unkown equilibrium co-ordination number of *n*. The arguments do not depend on the knowledge of *n*.

Production of the Free Radicals.—The radiolysis of aqueous solutions can be summarised by equation (6),[11] the yields of

$$H_2O \xrightarrow{\gamma,e^-} e^-(aq), OH, H, H_2, H_2O_2, [H_3O]^+ \quad (6)$$

the primary products being $G[e^-(aq)] = G(OH) = 2.65$, $G(H) = 0.60$, $G(H_2O_2) = 0.75$, and $G(H_2) = 0.45$ (where G represents the number of molecules of product formed on absorption of 100 eV by the system). In acidic solutions the hydrated electrons are transformed into hydrogen atoms *via* reaction (7).[11]

$$e^-(aq) + H_3O^+ \longrightarrow H \quad (7)$$

The free radicals $X_2^{\bullet -}$ (X = Cl, Br, I, or NCS) are produced by irradiating 0.1 mol dm^{-3} solutions of NaX. Under these conditions reactions (8) and (9) occur.[12] In acidic solutions

$$OH^\bullet + X^- \longrightarrow X^\bullet + OH^- \quad (8)$$

$$X^- + X^\bullet \rightleftharpoons X_2^{\bullet -} \quad (9)$$

reactions (8) and (9) are diffusion controlled for all the halides and NCS$^-$,[1] as the specific rate of the disproportionation reaction, equation (10),[12] is about an order of magnitude slower than that of the reactions (11)[13] and (12);[14] about 10 μs after

$$2X_2^{\bullet -} \longrightarrow X_3^- + X^- \quad (10)$$

$$2H^\bullet \longrightarrow H_2 \quad (11)$$

$$H^\bullet + X^\bullet \longrightarrow H^+ + X^- \quad (12)$$

the pulse over 90% of the free radicals present in the solution are $X_2^{\bullet -}$.

The aliphatic free radicals $^\bullet CH_2CO_2H$, $^\bullet CH(CH_3)CO_2H$, $^\bullet CH_2OH$, $^\bullet CH(CH_3)OH$, $^\bullet C(CH_3)_2OH$, and $^\bullet CH_2C(CH_3)_2OH$ are formed in 0.1—1.0 mol dm^{-3} of the corresponding solute by reaction (13).[1,15]

As reaction (14) is slow [$k = 8 \times 10^4$ dm^3 mol^{-1} s^{-1} (ref.

$$OH^\bullet/H^\bullet + RH \longrightarrow R^\bullet + H_2O/H_2 \quad (13)$$

$$H^\bullet + C(CH_3)_3OH \longrightarrow {}^\bullet CH_2C(CH_3)_2OH + H_2 \quad (14)$$

16)] most of the hydrogen atoms in 0.1 mol dm^{-3} $C(CH_3)_3OH$ react *via* reaction (11) and not *via* reaction (14).

The methyl radicals, $^\bullet CH_3$, are formed in the reaction sequence[17] given by (15) and (15a).

$$OH^\bullet + (CH_3)_2SO \longrightarrow (CH_3)_2SO(OH); \quad k = 7.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (15)$$

$$(CH_3)_2SO(OH) \longrightarrow {}^\bullet CH_3 + CH_3SO_2H; \quad k = 1.5 \times 10^7 \text{ s}^{-1} \quad (15a)$$

Results and Discussion

When $[U(H_2O)_n]^{3+}$ is added to acidic solutions (0.5 mol dm^{-3} $HClO_4$) containing 0.1 mol dm^{-3} NaX (X = Cl, Br, I, or NCS) the rate of disappearance of $X_2^{\bullet -}$ is accelerated. From the dependence of the observed rate on $[U(H_2O)_n{}^{3+}]$ the specific rates of reaction (16) were calculated; the results are given in the

$$[U(H_2O)_n]^{3+} + X_2^{\bullet -} \longrightarrow [U(H_2O)_nX]^{3+} + X^- \quad (16)$$

Table. In all the systems a further reaction, causing a small increase in the light transmission in the near u.v., was observed. In the NaCl solution this reaction is well separated in time from the first reaction and has a rate of (3.4 ± 0.6) × 10^4 s^{-1}. We attribute this process to the ligand loss reaction (17).

$$[U(H_2O)_nX]^{3+} \longrightarrow [U(H_2O)_n]^{4+} + X^- \quad (17)$$

Table. Specific rates of oxidation of tervalent uranium, U^{3+}(aq), by free radicals in aqueous solutions[a]

Oxidant (Ox)	k[Ox + U^{3+}(aq)]/ dm^3 mol^{-1} s^{-1} [b]	E°/V [c]
$OH^\bullet$	4.1 × 10^8	2.8
$Cl_2^{\bullet -}$	4.2 × 10^9	2.29[d]
$Br_2^{\bullet -}$	3.4 × 10^9	1.77[e]
$I_2^{\bullet -}$	1.2 × 10^9	1.00[d]
$(NCS)_2^{\bullet -}$	1.4 × 10^9	1.49[f]
$^\bullet CH_3$	1.5 × 10^9	2.2[g]
$^\bullet CH_2CO_2H$	1.2 × 10^8	−0.4[h]
$^\bullet CH(CH_3)CO_2H$	2.1 × 10^7	
$^\bullet CH_2OH$	<2 × 10^7	−0.9[h]
$^\bullet C(CH_3)_2OH$	<1 × 10^7	
$^\bullet CH_2C(CH_3)_2OH$	<5 × 10^6	

[a] Measured in 0.5 mol dm^{-3} $HClO_4$, helium-saturated solutions. [b] Accuracy ±15%. [c] *Versus* standard hydrogen electrode. [d] Ref. 12(*e*). [e] Ref. 12(*b*). [f] J. Lati, Ph.D. Thesis, The Weizman Institute of Science, Rehovoth, Israel, 1978. [g] A. Toffel and A. Henglein, *Faraday Discuss. Chem. Soc.*, 1977, **63**, 124. [h] Polarographic half-wave potentials (see footnote *g*). Due to very large overpotentials (footnote *g*) the actual oxidation potentials are considerably more positive.

We identify the transient as $[U(H_2O)_nX]^{3+}$ and not as $[U(H_2O)_{n-1}X]^{3+}$, as the ligand-exchange rate of $[U(H_2O)_n]^{3+}$ is *ca.* 3 × 10^6 dm^3 mol^{-1} s^{-1}.[18] Thus clearly an inner-sphere mechanism with $k > 10^9$ dm^3 mol^{-1} s^{-1}, which has to be assumed as reaction (17) is observed, has to involve a transition state, or an intermediate, with an extended co-ordination sphere. It is however plausible that the intermediate observed is $[U(H_2O)_{n-1}X]^{3+}$, formed by fast loss of an aqua ligand from the transition state. Reaction (17) cannot be attributed to any acid–base reaction of the type $[U(H_2O)_{n-1}(OH)]^{3+} + H_3O^+ \rightleftharpoons [U(H_2O)_n]^{4+}$ as the forward reaction is expected to have a rate of *ca.* 10^{10} dm^3 mol^{-1} s^{-1}, as do all proton-transfer reactions of this type. Also, as the first pK_a of $[U(H_2O)_n]^{4+}$ is 1.7 the back reaction (proton loss) will be much faster than the observed process. Furthermore, this process was not observed following the oxidations by $^\bullet CH_3$ and $^\bullet OH$ although it would have been expected from the relative rates.

We have checked the possibility that the oxidation reaction observed is that shown by equation (18), followed by a fast

$$(H_2O)_{n-1}U^{III}(X^-)^{2+} + X_2^{\bullet -} \longrightarrow (H_2O)_{n-1}U^{III}(X^\bullet)^{3+} + 2X \quad (18)$$

metal-to-ligand electron transfer, by changing the concentration of X^- for X = Br. The rate of reaction does not change in the concentration range 1 × 10^{-3}—0.1 mol dm^{-3}, thus this reaction has to be ruled out.

The specific rate of reaction of $OH^\bullet$ with $[U(H_2O)_n]^{3+}$ was measured by following the bleaching of the absorption due to $[U(H_2O)_n]^{3+}$ caused by the pulse in solutions containing (0.3—2.4) × 10^{-4} mol dm^{-3} $[U(H_2O)_n]^{3+}$ and 0.5 mol dm^{-3} $HClO_4$, Figure (*a*). As hydrogen atoms are also present under these conditions the reaction observed could be due to the reaction of H atoms or $OH^\bullet$ radicals or both. In order to check these possibilities 0.9 mol dm^{-3} Bu^{t}OH was added to the solutions. Under these conditions the fast reaction which causes the bleaching is not observed [see Figure (*b*)]. As the Bu^{t}OH

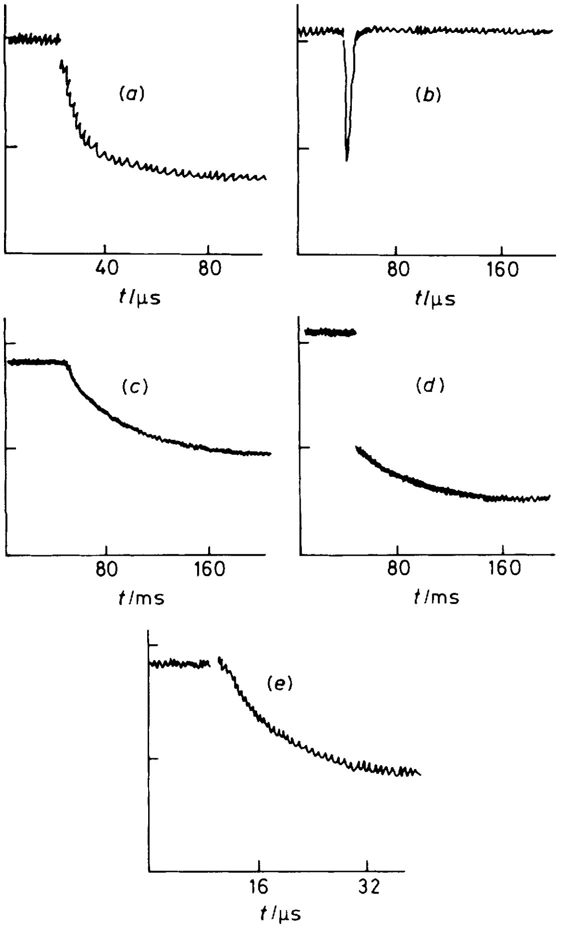

Figure. Kinetic traces of: (*a*), (*d*) 3.4 × 10^{-5} mol dm^{-3} U^{3+}(aq) in 0.5 mol dm^{-3} $HClO_4$ (helium-saturated solutions measured at 350 nm); (*b*), (*c*) 4.0 × 10^{-5} mol dm^{-3} U^{3+}(aq) in 0.5 mol dm^{-3} $HClO_4$ and 0.88 mol dm^{-3} Bu^{t}OH (helium-saturated solutions measured at 355 nm); and (*e*) 4 × 10^{-5} mol dm^{-3} U^{3+}(aq) in 0.5 mol dm^{-3} $HClO_4$ and 0.1 mol dm^{-3} $(CH_3)_2SO$ (helium-saturated solutions measured at 355 nm). The vertical axes represent the light intensity in arbitrary units

scavenges all the $OH^{\bullet}$ radicals but reacts slowly, reaction (14), with H atoms it is concluded that the reaction observed in the absence of Bu^{t}OH is the oxidation of $[U(H_2O)_n]^{3+}$ by $OH^{\bullet}$ radicals. The results also indicate that $k\{^{\bullet}CH_2C(CH_3)_2OH + [U(H_2O)_n]^{3+}\} \leqslant 5 \times 10^6$ dm^3 mol^{-1} s^{-1}.

Both in the presence and absence of Bu^{t}OH another process which causes a bleaching of the $[U(H_2O)_n]^{3+}$ absorption is observed, see Figure (*c*) and (*d*). This process is clearly too slow to be attributed to a reaction of any of the free radicals formed by the pulse as their lifetime is considerably shorter. We attribute this process to reaction (19), where the H_2O_2 is formed by the pulse [reaction (6)]. From the kinetic results, including

$$[U(H_2O)_n]^{3+} + H_2O_2 \xrightarrow{H^+} [U(H_2O)_n]^{4+} + OH^{\bullet} + H_2O \quad (19)$$

the dependence of the rate on $[U^{3+}]$ and the degree of bleaching on the pulse intensity which changes the H_2O_2 yield, $k\{[U(H_2O)_n]^{3+} + H_2O_2\} = (2 \pm 1) \times 10^5$ dm^3 mol^{-1} s^{-1} is calculated.

The specific rates of reaction of the $^{\bullet}CH_3$, $^{\bullet}CH_2CO_2H$, $^{\bullet}CH(CH_3)CO_2H$, $^{\bullet}CH_2OH$, and $^{\bullet}C(CH_3)_2OH$ radicals with $[U(H_2O)_n]^{3+}$ were measured in solutions containing 0.1—1.0 mol dm^{-3} of the corresponding organic solute and 0.5 mol dm^{-3} $HClO_4$ (see above). The results obtained are given in the Table and a typical result for $^{\bullet}CH_3$ is shown in the Figure (*e*). The reactions of $^{\bullet}CH_3$, $^{\bullet}CH_2CO_2H$, and $^{\bullet}CH(CH_3)CO_2H$ are clearly too fast to occur *via* the inner-sphere mechanism according to mechanism (*b*), reaction (3). Similar arguments to those raised for $OH^{\bullet}$ also exclude the possibility that these reactions follow the outer-sphere mechanism.[4,5]

Thus the two mechanisms which have to be considered for both the aliphatic and the $OH^{\bullet}$ radicals are mechanisms (*c*), reaction (4), and (*d*), reaction (5). It is difficult to envisage that the specific rate of hydrogen abstraction from a co-ordinated water molecule, reaction (4), by an aliphatic radical will be faster or only slightly slower than that by $OH^{\bullet}$ radicals as the C–H bond formed is considerably weaker than the O–H bond formed, or broken.[19] It is also difficult to explain why the rate of hydrogen abstraction should be so much slower for $^{\bullet}CH_2C(CH_3)_2OH$ and $^{\bullet}CH_2OH$ than for $^{\bullet}CH_3$ or $^{\bullet}CH_2CO_2H$. On the other hand if mechanism (*d*), reaction (5), describes the mechanism of reaction then steric effects are expected to considerably affect k_{51}. Furthermore it is known that in several systems the rate of the homolytic decomposition k_{-51} is considerably faster for $R^{\bullet} = {}^{\bullet}CR^1R^2OH$ than for $R^{\bullet} = {}^{\bullet}CR^1R^2H$ and $^{\bullet}CR^1R^2CO_2H$.[20] The combination of these two factors seems to explain well the order of reactivity $^{\bullet}CH_3 > {}^{\bullet}CH_2CO_2H > {}^{\bullet}CH(CH_3)CO_2H > {}^{\bullet}CH_2C(CH_3)_2OH$, $^{\bullet}CH_2OH$, $^{\bullet}C(CH_3)_2OH$.

It is somewhat surprising that $k\{[U(H_2O)_n]^{3+} + {}^{\bullet}CH_3\} > k\{[U(H_2O)_n]^{3+} + OH^{\bullet}\}$. This might be due to some specific interaction between the $OH^{\bullet}$ and the hydration sphere of the tervalent uranium which slows down k_{51}.

Conclusions

The results indicate that the mechanism of oxidation of $[U(H_2O)_n]^{3+}$ by a series of free radicals occurs *via* an inner-sphere mechanism with an increase in the co-ordination number. It is plausible that this mechanism also describes other oxidations of aqua transition-metal complexes by hydroxyl and aliphatic radicals.

Acknowledgements

This work was supported in part by a grant from the Israel–U.S. Binational Science Foundation, Jerusalem, Israel. We also thank Mr. D. Carmi for technical assistance.

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Received 15*th March* 1984; *Paper* 4/417