Rate Constants for Reactions of Radiation-Produced Transients in Aqueous Solutions of Actinides

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Rate constants have been critically compiled for reactions of ions of the actinides Am, Cf, Cm, Np, Pu, Th, and U, as well as the element Tc, in different oxidation states with various chemical species in aqueous solution. The reactants include products of the radiolysis of water (hydrated electrons, hydrogen atoms, hydroxyl radicals, hydrogen peroxide) and transient species derived from other solutes (e.g., carbonate radical). The data are useful in the estimation of migration properties of actinides, which are relevant to waste management studies.

Key words: actinides; aqueous solution; critical data compilation; radiation chemistry; rate constants.

1. Introduction

Knowledge of the rate constants for reactions of transients produced in aqueous solutions containing actinides is essential for prediction of the oxidation states of the actinides in systems containing water. Such data are useful in estimating the migration properties of actinides, properties which are needed in studies related to nuclear waste management. It has only been with the advent of the powerful tools associated with pulse radiolysis that the scientific community has been able to describe the redox reactions involving various unstable oxidation states of the actinides. Pulse radiolyses of actinides in aqueous solutions are necessary extensions of the early investigations that were concerned with the changes of oxidation state of Pu ions in solution due to self-irradiation. The results of the self-irradiation studies provide data of limited scientific importance.

This is an attempt to provide a critical compilation of the kinetic data which have been reported in the literature for reactions of actinide ions with the fundamental species produced in aqueous solution by radiolysis, e_{aq}^-, $\cdot$H, $\cdot$OH, and H_2O_2. In addition to reactions with primary products of water radiolysis, the compilation includes reactions of secondary radicals produced by the reactions of the primary radicals with another solute, e.g. $(SCN)_2\cdot^-$, $CO_3\cdot^-$, as well as some of the reactions of unstable actinide valencies, e.g. Am(IV). For data on reactions of actinides in stable valency states the critical review by Newton[1] on redox reactions of actinides should be consulted. A recent book by Pikaev[2] contains a detailed survey of the radiolysis of the actinides.

In the present evaluation the following factors were considered: methods, effects of ionic strength, concentration, and hydrolysis of the actinide ions. The factors which should be considered by the user of this compilation are specifically noted in the comments in the Table. We have presented essentially all of the data available to us but have also noted apparent inconsistencies and suggested limitations on the accuracy of the given results.

2. Evaluation of the Data

2.1. Methods and Errors

Results of direct observation of decay kinetics (d.k.) or product buildup kinetics (p.b.k.) by optical absorption pulse radiolysis[3] (p.r.) techniques are more reliable than those obtained by competition kinetics (c.k.). The latter may be biased by secondary reactions such as complex formation. In a few cases flash photolysis (f.p.) with optical detection has been used to study the kinetics of the transients. Flow techniques (with esr or optical detection) have also been used for reactions which occur on a longer time scale ($k < 10^6$ L mol^{-1} s^{-1}).

Error estimates given by the authors have been in-

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cluded. It is noted that when the errors in the rate constants are determined by least squares procedures they are based on the internal consistencies in the data. It is not feasible to present estimates of absolute errors. Since these solutions are highly radioactive, there is some autoradiolysis changing the composition of the solution during the experiment. Therefore the actual error limits in the rate constants are higher than those quoted.

2.2. Hydrolysis

We have preferred to use the IUPAC notation (with Roman numerals representing the oxidation state) for the actinide ion when there is possible ambiguity in the composition of the reactant due to hydrolytic pre-equilibra or where the structure is unknown. In cases where the structure of the actinide complex ion is known it is listed, but associated water molecules are omitted.

2.3. Ionic Strength

We prefer to list the observed rate constant at the given ionic composition of the solution. The values calculated for extrapolation to infinite dilution (and the formalism used) are noted in the comments; if an extrapolated value is listed the observed values are given in the comments whenever possible.

2.4. Concentration

We also note in the comments the concentration range over which the study has been conducted. When the method involves decay kinetics based on the optical absorption of transient species, the most reliable values are obtained by following pseudo first order changes over a series of concentrations of reactant. The radioactive decay of the actinides should also be considered. The following data[4] are presented for background information to assist the reader in evaluating self-irradiation effects.

Element	Isotope	Major decay mode	Half-life (yr)
Am	243	α	7.4×10^3
Cf	249	α	352
Cm	248	α	3.4×10^5
Np	237	α	2.1×10^6
Pu	242	α	3.8×10^5
Tc	99	β^-	2.1×10^5
Th	232	α	1.4×10^{10}
U	238	α	4.5×10^9

3. Arrangement of the Table

The actinide ions are arranged in alphabetic order with separate entries for the various actinide species, in order of increasing oxidation number. The reactions are given in the first column; products are not shown if they have not been identified. The pH and the experimentally determined rate constants are given in the second and third columns. Ionic strength is listed if it was reported, or if sufficient details concerning the system were available for it to be calculated. The method, and other information relevant to evaluation of the data are included under Comments. References to the table are indicated by the serial number from the Radiation Chemistry Data Center Bibliographic Data Base; the first two characters of the reference number specify the year of publication.

4. Acknowledgments

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5. References to Text

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Table of rate constants

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
Americium(II) ion					
$Am(II) \xrightarrow{H_2O} Am(III)$	5.2	$(9.7 \pm 0.3) \times 10^4$ s^{-1}		p.r., D.k. at 312 nm in He-satd. soln. contg. 0.1 mol L^{-1} *tert*-BuOH and 2.6×10^{-2} mol L^{-1} ^{243}Am(III) perchlorate; Am(II) from e^-_{aq} + Am(III).	78A044
Americium(III) ion					
$e^-_{aq} + Am^{3+} \rightarrow Am(II)$	6	3×10^8		p.r.; P.b.k.; soln. contains 3×10^{-3} mol L^{-1} Am^{3+} and 0.1 mol L^{-1} *tert*-BuOH.	761232
	5.8	$(1.6 \pm 0.04) \times 10^8$	0.11	p.r.; D.k. at 650 nm in He-satd. soln contg. (0.079-1.24) $\times 10^{-3}$ mol L^{-1} Am^{3+}, 0.1 mol L^{-1} *tert*-BuOH and 0.11 mol L^{-1} $LiClO_4$. The error is based on a least squares plot and reflects only the internal consistency of the data.	78A044
$\cdot OH + Am^{3+} \rightarrow OH^- + Am(IV)$	5.1	$(4.1 \pm 0.4) \times 10^8$		p.r.; P.b.k. at 320 nm in N_2O–satd. soln. contg. 0.11 mol L^{-1} $LiClO_4$ and (0.733–8.22) $\times 10^{-3}$ mol L^{-1} Am^{3+}.	78A044
	4	3.0×10^8		p.r.; P.b.k. in N_2O–satd. soln. contg. 5 or 6.7×10^{-5} mol L^{-1} Am^{3+}; at pH 2, 1, 0, k = 3.4, 1.1 and 1.6×10^8, resp.	771130 77A243
Americium(IV) ion					
$Am(IV) + Am(IV) \rightarrow Am^{3+} + AmO_2^+$	5.1	$(5 \pm 1) \times 10^6$	0.11	p.r.; Calcd. from d.k. of abs. at 320 nm (12 determinations) and assumed concn. Am^{4+} = OH; $\epsilon = 750 \pm 75$ L mol^{-1} cm^{-1}; N_2O–satd. soln. contg. $LiClO_4$ and (1.03–8.22) $\times 10^{-3}$ mol L^{-1} Am^{3+}; rate constant is $2k$.	78A044
	2.0–4.3	5.4×10^6 (ave.)		p.r.; D.k. at 340 nm in N_2O–satd. soln. contg. (2.0–8.7) $\times 10^{-3}$ mol L^{-1} $Am(ClO_4)_3$; rate constant is $2k$; ϵ(340–360 nm) = 700–1200 L mol^{-1} cm^{-1} at pH 0–4.3.	771130 77A243
$HO_2\cdot + Am(IV) \rightarrow H^+ + Am^{3+} + O_2$	1 2 3.2 4.4	6.4×10^7 5.2×10^7 5.0×10^7 2.7×10^7		p.r.; D.k. in air-satd. soln.; k varies with pH due to different degrees of hydrolysis of Am(IV); calcd. from measurement at one concn. at each pH.	771130 77A243
$H_2O_2 + Am(IV) \rightarrow H^+ + Am^{3+} + HO_2\cdot$	~4	1.4×10^6		p.r.; D.k. in soln. contg. 6×10^{-3} mol L^{-1} Am(III) (satd. with nitrous oxide) and 1.27×10^{-3} mol L^{-1} H_2O_2 (10 determinations).	771130 77A243
Americium(V) ion					
$e^-_{aq} + AmO_2^+ \rightarrow Am(IV)$	5.2 6.0	$(2.8 \pm 0.1) \times 10^{10}$ $(3.2 \pm 0.01) \times 10^{10}$	0.11	p.r.; D.k. at 650 nm in He-satd. soln. contg. 0.1 mol L^{-1} *tert*-BuOH, (1.24–28.0) $\times 10^{-5}$ mol L^{-1} Am(V) and 0.11 mol L^{-1} $LiClO_4$. The error is based on a least squares plot and reflects only the internal consistency of the data.	78A044
Americium(VI) ion					
$e^-_{aq} + AmO_2^{2+} \rightarrow AmO_2^+$	5.3 6.0	$(3.1 \pm 0.1) \times 10^{10}$ $(3.9 \pm 0.9) \times 10^{10}$	0.11	p.r.; D.k. at 650 nm in He-satd. soln. contg. 0.1 mol L^{-1} *tert*-BuOH, (1.04–12.0) $\times 10^{-6}$ mol L^{-1} Am(VI) and 0.11 mol L^{-1} $LiClO_4$.	78A044
$H_2O_2 + AmO_2^{2+} \rightarrow AmO_2^+ + HO_2 + H^+$	~0	$(3.8 \pm 0.5) \times 10^4$	1.0	stopped–flow; D.k. at 350 nm over a range of concentrations.	74M401
Californium(II) ion					
$Cf(II) \xrightarrow{H_2O} Cf^{3+}$	5.3	$(7 \pm 1) \times 10^4$ s^{-1}		p.r., D.k. ($\epsilon/\approx 500$ L mol^{-1}cm^{-1} at 270 nm) in He–satd. soln. contg. 5×10^{-4} mol L^{-1} $Cf(ClO_4)_3$ and 0.1 mol L^{-1} *tert*–BuOH.	83A171
Californium(III) ion					
$e^-_{aq} + Cf^{3+} \rightarrow Cf(II)$	5.3	$> 3 \times 10^9$		p.r.; D.k. in soln. contg. 5×10^{-4} mol L^{-1} ^{249}Cf(III) and 0.1 mol L^{-1} *tert*–BuOH; counter ion ClO_4^-.	83A171

Table of rate constants — Continued

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
Curium(II) ion					
$Cm(II) \xrightarrow{H_2O} Cm(III)$	5.3–6.0	$\sim 6 \times 10^4$ s^{-1}		p.r.; D.k. at 240 nm in He–satd. soln. contg. $\sim 10^{-3}$ mol L^{-1} ^{248}Cm(III) perchlorate and 0.1 mol L^{-1} *tert*-BuOH; Cm(II) from e^-_{aq} + Cm(III).	761118
Curium(IV) ion					
$Cm(IV) \xrightarrow{H_2O}$	5.3–6.0	$\sim 3 \times 10^4$ s^{-1}		p.r.; D.k. at 260 nm in N_2O–satd. soln. contg. $\sim 10^{-3}$ mol L^{-1} ^{248}Cm(III) perchlorate; Cm(IV) from ·OH + Cm(III).	761118
Neptunium(IV)					
$\cdot OH + Np(IV) \rightarrow OH^- + NpO_2^+$	~0	$(3.2 \pm 0.4) \times 10^8$		p.r.; C.k.; 1.0 mol L^{-1} $HClO_4$, (1–5) $\times 10^{-2}$ mol L^{-1} Np(IV) and 5×10^{-3} mol L^{-1} KCNS; complicated due to $NpCNS^{3+}$ complex; rel. to $k(OH + SCN^-) = 1.1 \times 10^{10}$.	82A376 85A236
$NO_3\cdot + Np(IV) \rightarrow NO_3^- + NpO_2^+$	~0	$(5.4 \pm 3.0) \times 10^5$		γ–r.; Calcd. from assumed mechanism and obs. $G(NO_3)$ and $G(-Np^{IV})$ and $G(H_2)$ in 1–6 mol L^{-1} HNO_3 soln.	81G249
Pentacarbonatoneptunate(IV) ion					
$e^-_{aq} + Np(CO_3)_5^{6-} \rightarrow$		5×10^9	0.3	p.r.; D.k. in Ar–satd. soln. contg. 0.1 mol L^{-1} $HClO_4$ 0.025 mol L^{-1} H_2SO_4, and 0.1–4 mol L^{-1} K_2CO_3. Calcd. $k = 1.3 \times 10^8$ for $I \rightarrow 0$ [751177], uncertain.	741170
Bis(carbonato)dioxoneptunate(V) ion					
$e^-_{aq} + NpO_2(CO_3)_2^{3-} \rightarrow Np(CO_3)_5^{6-}$		2.5×10^9	0.4	p.r.; D.k. at 800 nm in soln. contg. 0.1–5 mol L^{-1} K_2CO_3 and 2×10^{-4} mol L^{-1} U(V). Calcd. $k = 4.5 \times 10^8$ for $I = 0$ [751177], uncertain.	741170
Tris(carbonato)dioxoneptunate(V) ion					
$CO_3\cdot^- + NpO_2(CO_3)_3^{5-} \rightarrow CO_3^{2-} + NpO_2(CO_3)_3^{4-}$		1.5×10^7		p.r.; D.k. at 600 nm in 0.05 mol L^{-1} sodium carbonate; Np(V) produced by hydrated electron reaction with Np(VI), $CO_3\cdot^-$ from ·OH + CO_3^{2-}.	84A155
Neptunium(V) ion					
$e^-_{aq} + Np(V) \rightarrow Np(IV)$	~ 14	$(5.0 \pm 0.6) \times 10^9$		p.r.; D.k. at 650 and 700 nm in soln. contg. 1.0 mol L^{-1} OH^- and (4.4–7.5) $\times 10^{-5}$ mol L^{-1} Np(V); k = 6.1, 6.6, and 3.2 $\times 10^9$ at 2.0, 5.0, and 7.5 mol L^{-1} OH^-, resp.	731123
$e^-_{aq} + NpO_2^+ \rightarrow NpO_2$	3	2.45×10^{10}	→0	p.r.; D.k. in soln. contg. 0.01 mol L^{-1} EtOH and (0.2–1.0) $\times 10^{-3}$ mol L^{-1} NpO_2ClO_4; assuming $k(e^-_{aq} + H^+) = 2.3 \times 10^{10}$; standard deviation 2%; for k_{obs} see graph. p$K(NpO_2^+)$ = 4.5, 8.75.	80A130
	5.3	$(2.0 \pm 0.04) \times 10^{10}$	10^{-3}	p.r.; D.k.; (0.21–2.1) $\times 10^{-4}$ mol L^{-1} U(V), counter ion ClO_4^-; at pH 5.8 and 6.1 k = (5.43 ± 0.18) $\times 10^{10}$ and (2.13 ± 0.03) $\times 10^{10}$, resp. The error is based on a least squares plot and reflects only the internal consistency of the data.	761084
$H\cdot + NpO_2^+ \rightarrow$	~0	$<5 \times 10^6$		p.r.; C.k. in soln. contg. 1 mol L^{-1} $HClO_4$, 5×10^{-4} mol L^{-1} BzOH, 0–10^{-2} mol L^{-1} Np(V) and 0.2 mol L^{-1} *tert*-BuOH.; rel. to $k(H + BzOH \rightarrow H\text{-}BzOH) = 1 \times 10^9$. Uncertain; complication in competition kinetics due to Np complex formn. with H–BzOH.	82A420 85A236
$\cdot OH + NpO_2^+ \rightarrow OH^- + NpO_2^{2+}$	< 4	$(4.3 \pm 0.1) \times 10^7$		p.r.; D.k. (condy.) in N_2O–satd. soln. contg. 5×10^{-4} mol L^{-1} NpO_2ClO_4.	83A071

Table of rate constants — Continued

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
	~0	$(4.3 \pm 0.5) \times 10^8$		p.r.; C.k.; 1.0 mol L^{-1} $HClO_4$, $(1\text{–}5) \times 10^{-2}$ mol L^{-1} Np(V) and 5×10^{-3} mol L^{-1} KCNS; at pH ~1 and 2.52–2.96 $k = (4.4 \pm 0.5) \times 10^8$ and $(5.7 \pm 0.6) \times 10^8$, resp.; rel. to $k(OH + SCN^-) = 1.1 \times 10^{10}$. Uncertainty in competition kinetics due to SCN^- complex formation with Np.	82A376 85A236
$NO_3\cdot + NpO_2^+ \rightarrow NpO_2^{2+} + NO_3^-$	~0	10^4		γ–r.; Calcd. from assumed mechanism and G values in 0.5–3 mol L^{-1} HNO_3 in Pu(VI)–Np(VI) soln.	82G267
Neptunium(VI) ion					
$e_{aq}^- + NpO_2^{2+} \rightarrow NpO_2^+$	2.5	1.0×10^{11}	→0	p.r.; Extrapolated from d.k. (condy.) in soln. contg. 1, 2 and 4×10^{-3} mol L^{-1} solute and 0.05 mol L^{-1} *tert*-BuOH; counter ion ClO_4^-; $k_{obs} = 6.8 \times 10^{10}$.	83A071
$e_{aq}^- + NpO_2OH^+ \rightarrow NpO_2OH$		$(2.9 \pm 0.8) \times 10^{10}$	→0	p.r.; Extrapolated from k detd. in soln. at pH 2.5 (condy.) and at $k_{obs} = 6.32 \times 10^{10}$ $(0.2\text{–}2) \times 10^{-4}$ mol L^{-1} Np(VI) at 5.3 and $k = 5.43 \times 10^{10}$ $(0.2\text{–}3) \times 10^{-4}$ mol L^{-1} Np(VI) at 5.8 [761084]; pK = 5.45.	83A071
$e_{aq}^- + Np(VI) \rightarrow Np(V)$	~ 13	$(2.3 \pm 0.6) \times 10^{10}$		p.r.; D.k. at 650 and 700 nm in soln. contg. $(1.5\text{–}5.3) \times 10^{-5}$ mol L^{-1} Np(VI) and 0.5 mol L^{-1} OH^-; k = 1.3, 1.3, 2.0, 1.1, 0.83, 0.68 x 10^{10} at 1.0, 2.0, 5.0, 7.5, 10.0, and 12.5 mol L^{-1} OH^-, resp.	731123 76G651
$H\cdot + NpO_2^{2+} \rightarrow H^+ + NpO_2^+$	~0	$(4.0 \pm 0.5) \times 10^8$		p.r.; C.k. in soln. contg. 1 mol L^{-1} $HClO_4$, 5×10^{-4} mol L^{-1} BzOH, $0\text{–}7.5 \times 10^{-4}$ mol L^{-1} Np(VI) and 0.2 mol L^{-1} *tert*-BuOH.; rel. to $k(H + BzOH \rightarrow H\text{–}BzOH) = 1 \times 10^9$. Uncertain; complication in competition kinetics due to Np complex formn. with H–BzOH.	82A420 85A236
	1-3	$<10^7$		p.r.; P.b.k. at 980 nm (as well as condy.) in He-satd. soln. contg. $HClO_4$; no reaction. Preferred value.	83A071
$O\cdot^- + Np(VI) \rightarrow OH^- + Np(VII)$	>12	8.0×10^7		p.r.; P.b.k. (Np^{VII}) at 412 and 620 nm in N_2O-satd. soln. contg. 0.033 mol L^{-1} LiOH and 4×10^{-3} mol L^{-1} Np(VI); higher concns. LiOH (to 2 mol L^{-1}) and Np(VI) $(4\text{–}10 \times 10^{-3}$ mol L^{-1}) also studied; $k = (6.1 \pm 1.2) \times 10^7$ in NaOH soln. (1.7–0.5 mol L^{-1}); in acid soln. Np(VII) is not formed.	78A463
$H_2O_2 + NpO_2^{2+} \rightarrow NpO_2^+ + H^+ + O_2$	5.0	$(5.9 \pm 0.05) \times 10^5$		p.r.; P.b.k. at 980 nm in soln. contg. 1.0×10^{-3} mol L^{-1} Np(VI) (~ 2×10^{-5} mol L^{-1} H_2O_2 produced by p.r.); stoichiometry is $2NpO_2^{2+}/H_2O_2$. The error is based on a least squares plot and reflects only the internal consistency of the data.	761084
Tris(carbonato)dioxoneptunate(VI) ion					
$e_{aq}^- + NpO_2(CO_3)_3^{4-} \rightarrow NpO_2(CO_3)_3^{5-}$		1.9×10^{10}	0.3	p.r.; D.k. in soln. contg. 0.05 mol L^{-1} Na_2CO_3 and 0.05 mol L^{-1} $NaHCO_3$ to 5 mol L^{-1} CO_3^{2-} and $(2.7\text{–}5.4) \times 10^{-5}$ mol L^{-1} Np(VI). Calcd. $k = 2.1 \times 10^9$ for $I = 0$ [751177], uncertain.	741170
		$(2.3 \pm 0.12) \times 10^{10}$		p.r.; D.k. at 600 nm in 0.05 mol L^{-1} sodium carbonate soln. contg. $(0.2\text{–}8.0) \times 10^{-4}$ mol L^{-1} Np(VI). The error is based on a least squares plot and reflects only the internal consistency of the data.	84A155

Table of rate constants — Continued

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
Neptunium(VII) ion					
$e_{aq}^- + \mathrm{Np(VII)} \rightarrow$	~ 13	$(2.9 \pm 0.3) \times 10^{10}$		p.r.; D.k. at 650 and 700 nm in soln. contg. (2–8)× 10^{-5} mol L^{-1} Np(VII) and 0.1 mol L^{-1} OH^-; $k = 3.2, 2.0, 2.1, 1.7, 1.3, 0.88$, and 0.6×10^{10} at 0.5, 1.0, 2.0, 5.0, 7.5, 10.0, 12.5 mol L^{-1} OH^-, resp.	731123
$\mathrm{Np(VII)} + \mathrm{Np(V)} \rightarrow$ 2 Np(VI)	> 12	$(2.3 \pm 0.9) \times 10^{7}$		p.r.; Calcd. from assumed mechanism and second order d.k. (620 and 412 nm) of Np(VII) in N_2O-satd. soln. contg. Np(VI) and 0.033–2.0 mol L^{-1} LiOH.	78A463
Plutonium(III) ion					
$\cdot OH + Pu^{3+} \rightarrow$ Pu(IV)	0	$(4.2 \pm 0.5) \times 10^{8}$		p.r.; C.k.; soln. contains 1.0 mol L^{-1} $HClO_4$ and (1–5)× 10^{-2} mol L^{-1} Pu(III) and 5×10^{-2} mol L^{-1} KCNS; rel. to $k(\cdot OH + SCN^-) = 1.1 \times 10^{10}$.	85A236
$NO_3\cdot + Pu^{3+} \rightarrow$ Pu(IV) + NO_3^-	~0	10^7		γ-r.; Calcd. from assumed mechanism and G values in 0.5–3 mol L^{-1} HNO_3 in Pu(VI)–Np(VI) soln.	82G267
Plutonium(IV) ion					
$NO_3\cdot$ + Pu(IV) $\rightarrow PuO_2^+ + NO_3^-$	~0	10^4		γ-r.; Calcd. from assumed mechanism and G values in 0.5–3 mol L^{-1} HNO_3 in Pu(VI)–Np(VI) soln.	82G267
Plutonium (V) ion					
$NO_3\cdot + PuO_2^+ \rightarrow PuO_2^{2+} + NO_3^-$	~0	10^7		γ-r.; Calcd. from assumed mechanism and G values in 0.5–3 mol L^{-1} HNO_3 in Pu(VI)–Np(VI) soln.	82G267
Tris(carbonato)dioxoplutonate(V) ion					
$CO_3\cdot^- + PuO_2(CO_3)_3^{5-} \rightarrow CO_3^{2-} + PuO_2(CO_3)_3^{4-}$		2.7×10^7		p.r.; D.k. at 600 nm in 0.05 mol L^{-1} sodium carbonate soln.; Pu(V) produced by hydrated electron reaction with Pu(VI); $CO_3\cdot^-$ from $\cdot OH + CO_3^{2-}$.	84A155
Plutonium(VI) ion					
$e_{aq}^- + PuO_2^{2+} \rightarrow PuO_2^+$	5.6	$(6.4 \pm 0.67) \times 10^{10}$	10^{-3}	p.r.; D.k.; (0.12–1.0) × 10^{-4} mol L^{-1} Pu(VI), counter ion ClO_4^-; at pH 6.1 $k = (5.76 \pm 0.27) \times 10^{10}$; p$K = 6.3 \pm 0.1$ [83A071]; $k = 1.4 \times 10^9$ on SiO_2 colloid [83Z122].	761084
$e_{aq}^- + \mathrm{Pu(VI)} \rightarrow$	~ 14	$(1.9 \pm 0.3) \times 10^{10}$		p.r.; D.k. at 650 and 700 nm soln. contg. (2.6–5.2) × 10^{-5} mol L^{-1} Pu(VI) in 2 mol L^{-1} OH^-; $k = 2.0$ and 0.66×10^{10} at 5.0 and 7.5 mol L^{-1} OH^-.	731123
Tris(carbonato)dioxoplutonate(VI) ion					
$e_{aq}^- + PuO_2(CO_3)_3^{4-} \rightarrow PuO_2(CO_3)_3^{5-}$		2.3×10^{10}	0.3	p.r.; D.k.; soln. cont. 0.1–5 mol L^{-1} CO_3^{2-} and (3.85–4.85) × 10^{-5} mol L^{-1} Pu(VI). Calcd. $k = 2.2 \times 10^9$ for $I \rightarrow 0$ [751177], uncertain.	741170
		$(2.3 \pm 0.11) \times 10^{10}$	0.2	p.r.; D.k. at 600 nm in 0.05 mol L^{-1} sodium carbonate soln. contg. (0.2–8.0) × 10^{-4} mol L^{-1} Pu(VI). The error is based on a least squares plot and reflects only the internal consistency of the data.	84A155
$H_2O_2 + PuO_2(CO_3)_3^{4-} \rightarrow$	8.3	$(6.9 \pm 0.8) \times 10^3$		stopped-flow; D.k. at 360 nm in soln. contg. 0.05 mol L^{-1} $NaHCO_3$, 3×10^{-3} mol L^{-1} H_2O_2 and 6×10^{-4} mol L^{-1} Pu(VI); doubling of H_2O_2 concn. gave $k = (7.2 \pm 0.7) \times 10^3$; peroxo complex forms and decays to Pu(V).	80A448

Table of rate constants — Continued

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
Plutonium(VII) ion					
$e_{aq}^- + Pu(VII) \rightarrow Pu(VI)$	14	$(3.5 \pm 0.6) \times 10^{10}$		p.r.; D.k. at 650 and 700 nm in soln. contg. (2–4)$\times 10^{-5}$ mol L^{-1} Pu(VII) and 1.0 mol OH$^-$; k = 4.2, 2.3, 2.0 $\times 10^{10}$ at 2.0, 5.0 and 7.5 mol L^{-1} OH$^-$.	731123
Technetate(VI) ion					
$\cdot OH + TcO_4^{2-}$ $\rightarrow OH^- + TcO_4^-$		$(2 \pm 1) \times 10^9$		p.r.; D.k. at 360 nm in soln. contg. 5 $\times 10^{-3}$ mol L^{-1} KTcO$_4$; Tc(VI) from $e_{aq}^- + TcO_4^-$. Slower d.k. (1.5 $\times 10^7$) attributed to Tc(VI) + $H_2O_2 \rightarrow$ Tc(VII) and 2 Tc(VI) $\rightarrow$ Tc(VII) + Tc(V)	77A245
Technetate(VII) ion					
$e_{aq}^- + TcO_4^- \rightarrow TcO_4^{2-}$	6.0–6.5	1.9×10^{10}		p.r.; D.k. at 580 nm in Ar-satd. soln. contg. *tert*-BuOH and K^{99}TcO$_4$.	81A173
	~7	$(1.3 \pm 0.2) \times 10^{10}$		p.r.; D.k. at 700 nm as well as p.b.k. at 360 nm in soln. contg. 5 $\times 10^{-2}$ mol L^{-1} *tert*-BuOH and (1–6) $\times 10^{-5}$ mol L^{-1} $^{99}TcO_4^-$.	77A245
	13	$(2.5 \pm 0.05) \times 10^{10}$		p.r.; D.k. in soln. contg. 0.10 mol L^{-1} NaOH and (1–6) $\times 10^{-5}$ mol L^{-1} $^{99}TcO_4^-$.	78A390
Thorium(IV)–hydroperoxy complex					
$HO_2\cdot/O_2\cdot^- + Th(IV)–HO_2$ $\rightarrow Th^{4+} + H_2O_2 + O_2$	1	$(8.0 \pm 2.0) \times 10^5$		Flow–esr method; radical from Ce(IV)–H$_2$O$_2$; 2 k(Th(IV)–HO$_2 \rightarrow$ Th(IV) + H$_2$O$_2$ + O$_2$) = (5 ± 2) $\times 10^2$.	739071
Thorium(IV) ion					
$e_{aq}^- + ThSO_4^{2+} \rightarrow ThSO_4^+$	3	$(1.0 \pm 0.5) \times 10^{10}$	→0	p.r.; D.k. at 650 nm in soln. contg. (0.1–1.5) $\times 10^{-2}$ mol L^{-1} Th(SO$_4$)$_2$ and *tert*-BuOH; soln. contains Th^{4+}, ThSO$_4^{2+}$ and Th(SO$_4$)$_2$.; k_{obs} (10^8–10^{10}) shown on graph	83A127
$e_{aq}^- + Th^{4+} \rightarrow$	3	$(1.9 \pm 0.2) \times 10^{10}$	→0	p.r.; D.k. at 650 nm in Ar-satd. soln. contg. (0.1–1.5) $\times 10^{-2}$ mol L^{-1} Th(ClO$_4$)$_4$; rel. to $k(e_{aq}^- + H^+) = 2.3 \times 10^{10}$; k_{obs} shown on graph.	82A416
$HO_2\cdot/O_2\cdot^- + Th^{4+} \rightarrow$ $Th(IV) - HO_2$	1	$(1.8 \pm 0.2) \times 10^6$		p.r.; P.b.k.; at 270 nm in soln. contg. 10^{-3} mol L^{-1} Th(SO$_4$)$_2$, 0.1 mol L^{-1} HClO$_4$ and 5 $\times 10^{-2}$ mol L^{-1} H$_2$O$_2$. $K_{eq} = (4 \pm 1) \times 10^4$ L mol^{-1}.	741107
	~1	$> 5 \times 10^6$		Flow–esr method; radical from Ce(IV)–H$_2$O$_2$.; $K_{eq} = (1.7 \pm 0.4) \times 10^5$ L mol^{-1}.	739071
Uranium(III) ion					
$\cdot OH + U^{3+} \rightarrow UOH^{3+}$	~1	$(4.1 \pm 0.6) \times 10^8$		p.r.; D.k. at 350 nm in He-satd. soln. contg. 0.5 mol L^{-1} HClO$_4$ contg. (0.3–2.4) $\times 10^{-4}$ mol L^{-1} U^{3+}; inner-sphere mechanism.	85A122
$Cl_2\cdot^- + U^{3+} \rightarrow UCl^{3+} + Cl^-$	~1	$(4.2 \pm 0.6) \times 10^9$		p.r.; D.k. in He-satd. soln. contg. 0.5 mol L^{-1} HClO$_4$ contg. 0.1 mol L^{-1} NaCl; inner-sphere mechanism; radical from ·OH + Cl$^-$.	85A122
$Br_2\cdot^- + U^{3+} \rightarrow UBr^{3+} + Br^-$	~1	$(3.4 \pm 0.5) \times 10^9$		p.r.; D.k. in He-satd. soln. contg. 0.5 mol L^{-1} HClO$_4$ contg. 0.1 mol L^{-1} NaBr; inner-sphere mechanism; radical from ·OH + Br$^-$.	85A122
$I_2\cdot^- + U^{3+} \rightarrow UI^{3+} + I^-$	~1	$(1.2 \pm 0.2) \times 10^9$		p.r.; D.k. in He-satd. soln. contg. 0.5 mol L^{-1} HClO$_4$ contg. 0.1 mol L^{-1} NaI; inner-sphere mechanism; radical from ·OH + I$^-$.	85A122
$(SCN)_2\cdot^- + U^{3+} \rightarrow$ $USCN^{3+} + SCN^-$	~1	$(1.4 \pm 0.2) \times 10^9$		p.r.; D.k. in He-satd. soln. contg. 0.5 mol L^{-1} HClO$_4$ contg. 0.1 mol L^{-1} NaSCN; inner-sphere mechanism; radical from ·OH + SCN$^-$.	85A122
$\cdot CH_3 + U^{3+} \rightarrow UCH_3^{3+}$	~1	$(1.5 \pm 0.2) \times 10^9$		p.r.; D.k. at 355 nm in He-satd. soln. contg. 0.5 mol L^{-1} HClO$_4$ contg. dimethyl sulfoxide; radical from ·OH + DMSO.	85A122

Table of rate constants — Continued

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
$\cdot CH_2CO_2H + U^{3+} \rightarrow UCH_2CO_2H^{3+}$	~1	$(1.2 \pm 0.2) \times 10^8$		p.r.; D.k. at 355 nm in He-satd. soln. contg. 0.5 mol L^{-1} $HClO_4$ contg. acetic acid; radical from $\cdot OH + CH_3CO_2H$.	85A122
$CH_3CHCO_2H + U^{3+} \rightarrow UCH(CH_3)CO_2H^{3+}$	~1	$(2.1 \pm 0.3) \times 10^7$		p.r.; D.k. at 355 nm in He-satd. soln. contg. 0.5 mol L^{-1} $HClO_4$ contg. propionic acid; radical from $\cdot OH + CH_3CH_2CO_2H$.	85A122
$\cdot CH_2OH + U^{3+} \rightarrow$	~1	$<2 \times 10^7$		p.r.; D.k. at 355 nm in He-satd. soln. contg. 0.5 mol L^{-1} $HClO_4$ contg. methanol; radical from $\cdot OH + CH_3OH$.	85A122
$(CH_3)_2COH + U^{3+} \rightarrow$	~1	$<1 \times 10^7$		p.r.; D.k. at 355 nm in He-satd. soln. contg. 0.5 mol L^{-1} $HClO_4$ and 2-propanol; radical from $\cdot OH$ + 2-PrOH.	85A122
$\cdot CH_2C(CH_3)_2OH + U^{3+} \rightarrow$	~1	$<5 \times 10^6$		p.r.; D.k. at 355 nm in He-satd. soln. contg. 0.5 mol L^{-1} $HClO_4$ and 0.88 mol L^{-1} *tert*-butyl alcohol and 4×10^{-5} mol L^{-1} U^{3+}; radical from $\cdot OH$+ *tert*-BuOH.	85A122
$H_2O_2 + U^{3+} \rightarrow U^{4+} + \cdot OH + H_2O$	~1	$(2 \pm 1) \times 10^5$		p.r.; D.k. at 355 nm in He-satd. soln. contg. 0.5 mol L^{-1} $HClO_4$ and 0.88 mol L^{-1} *tert*-BuOH; estd. from dependence on concn. of U^{3+} and pulse intensity $[H_2O_2]$.	85A122
Uranium(IV) ion					
$e^-_{aq} + U^{4+} \rightarrow U^{3+}$	~0	1.0×10^{11}		p.r.; C.k.; obs. absorption of U(III) in soln. contg. 0.01–0.1 mol L^{-1} U(IV) and 1 mol L^{-1} $HClO_4$; rel. to $k(e^-_{aq} + H^+) = 1.15 \times 10^{10}$.	81A410 85A236
$e^-_{aq} + UOH^{3+} \rightarrow UOH^{2+}$	~1	9.2×10^{10}	→0	p.r.; Calc. from measurements at 0.1 and 0.05 mol L^{-1} $HClO_4$ at 0.01–0.1 mol L^{-1} U(IV) where U(IV) contains 20% and 30% of UOH^{3+} and $k_{obs} = 6.5 \times 10^{10}$ and 6.8×10^{10}; rel. to $k(e^-_{aq} + H^+) = 2 \times 10^{10}$ and 1.5×10^{10}, resp.	81A410 85A236
$\cdot OH + U^{4+} \rightarrow OH^- + U^{5+}$	~0	$(8.6 \pm 0.5) \times 10^8$		p.r.; C.k.; 1.0 mol L^{-1} $HClO_4$, $(1–5) \times 10^{-2}$ mol L^{-1} U(IV) and 5×10^{-3} mol L^{-1} KCNS (4–16% bound as $UCNS^{3+}$); rel. to $k(OH + SCN^- = 1.1 \times 10^{10})$.	81A410 82A459 85A236
$\cdot OH + UOH^{3+} \rightarrow OH^- + UOH^{4+}$	~1	$(9.2 \pm 0.5) \times 10^8$		p.r.; C.k.; 0.1 mol L^{-1} $HClO_4$, $(1–5) \times 10^{-2}$ mol L^{-1} U(IV) and 5×10^{-3} mol L^{-1} KCNS (12–42% complexed as $UCNS^{3+}$); rel. to $k(OH + SCN^- = 1.1 \times 10^{10}$.	81A410 82A459 85A236
$UCl^{3+} \xrightarrow{H_2O} U^{4+} + Cl^-$		$(3.4 \pm 0.6) \times 10^4$ s^{-1}		p.r. Increase in light transmission following $Cl_2\cdot^- + U^{3+}$ reaction.	85A122
Uranyl(V) ion					
$UO_2^+ + UO_2^+ \rightarrow U^{4+} + UO_2^{2+}$		6.8×10^5		f.p.; D.k. at 580 nm (ϵ = 50 L mol^{-1} cm^{-1}), and p.b.k. at 656 nm U(IV) in soln. contg. 5 *N* H_2SO_4, 0.35 mol L^{-1} ethanol; U(V) from e^-_{aq} + U(VI).	72A023
	~1	$(3.5 \pm 0.08) \times 10^2$	2.50	stopped-flow; P.b.k. at 640 nm (ϵ = 40 L mol^{-1} cm^{-1}) in $HClO_4$ soln. contg. 1.3×10^{-2} mol L^{-1} U(V) (from U(VI) + Eu(II)), 0.75 mol L^{-1} H^+; k increases with $[H^+]$ 0.25–2 mol L^{-1} to 8×10^2 and with addn. of sulfate ion (2.8×10^{-2} mol L^{-1}) to $\sim 2 \times 10^3$.	749139
$(SCN)_2\cdot^- + UO_2^+ \rightarrow SCN^- + UO_2^{2+}$	1.0	$(1.46 \pm 0.34) \times 10^9$		f.p.; D.k. (first order) in KCNS–U(VI) perchlorate soln. (both 2×10^{-3} mol L^{-1}); radical from photooxidation of SCN^- by UO_2^{2+}; reaction probably reoxidation of U(V) to U(VI); assume $[(SCN)_2\cdot^-] = [UO_2^+]$. Similar pseudo first order decays obs. in U(VI) soln. contg. KBr or $NaHCO_3$ postulated to involve $Br_2\cdot^-$ or $CO_3\cdot^-$.	767279

Table of rate constants — Continued

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
Triscarbonatodioxouranate(V) ion					
$CO_3\cdot^- + UO_2(CO_3)_3^{5-} \rightarrow CO_3^{2-} + UO_2(CO_3)_3^{4-}$		4.9×10^8		p.r.; D.k. at 600 nm in 0.05 mol L^{-1} sodium carbonate soln.; U(V) produced by hydrated electron reaction; $CO_3\cdot^-$ from $\cdot OH + CO_3^{2-}$.	84A155
Uranium(VI)–hydroperoxy complex					
$HO_2\cdot/O_2\cdot^- + UO_2\text{–}HO_2^{2+} \rightarrow UO_2^{2+} + H_2O_2 + O_2$		$(5 \pm 1) \times 10^5$		p.r.; D.k. at 330 nm; $k(2\ UO_2^{2+}\text{–}HO_2 \rightarrow UO_2^{2+} + H_2O_2 + O_2) = (8 \pm 2) \times 10^4$.	741107
	~1	$(9.0 \pm 1.5) \times 10^5$		Flow–esr method; $k(2\ UO_2^{2+}\text{–}HO_2 \rightarrow UO_2^{2+} + H_2O_2 + O_2) = (4 \pm 1) \times 10^4$.	739071
Uranyl(VI) ion					
$e_{aq}^- + UO_2^{2+} \rightarrow UO_2^+$	5.3	$(1.7 \pm 0.01) \times 10^{10}$	10^{-3}	p.r.; D.k.; $(0.5\text{–}10) \times 10^{-4}$ mol L^{-1} U(VI), counter ion ClO_4^-; 24% $UO_2(H_2O)_5OH^+$ [81A148], pK_a = 5.2 [78G312]; k reduced by factor of 10 in sodium dodecylsulfate soln. [81N168]. The error is based on a least squares plot and reflects only the internal consistency of the data.	761084
$e_{aq}^- + UO_2OH^+ \rightarrow UO_2OH$	6.8	$(1.3 \pm 0.02) \times 10^{10}$	10^{-3}	p.r.; D.k.; $(0.1\text{–}1) \times 10^{-4}$ mol L^{-1} U(VI), counter ion ClO_4^-; 9% $UO_2(H_2O)_6^{2+}$ [81A148]. The error is based on a least squares plot and reflects only the internal consistency of the data.	761084
$H\cdot + UO_2^{2+} \rightarrow H^+ + UO_2^+$	~0	$(4.5 \pm 0.5) \times 10^7$		p.r.; C.k. in soln. contg. 1 mol L^{-1} $HClO_4$, 5×10^{-4} mol L^{-1} BzOH, 0–10^{-2} mol L^{-1} U(VI) and 0.2 mol L^{-1} *tert*-BuOH.; rel. to $k(H + BzOH) = 1 \times 10^9$.	82A420 85A236
$HO_2\cdot/O_2\cdot^- + UO_2^{2+} \rightarrow UO_2\text{–}HO_2^{2+}$	1	$(1.5 \pm 0.1) \times 10^5$		p.r.; P.b.k. at 320 nm in O_2–satd. soln. contg. 0.1 mol L^{-1} $HClO_4$, 0.1 mol L^{-1} H_2O_2 and $(0.1\text{–}1) \times 10^{-3}$ mol L^{-1} U(VI) sulfate; $K_{eq} = (1.7 \pm 0.3) \times 10^3$ L mol^{-1}.	741107
	~1	$> 1 \times 10^5$		Flow–esr method; radical from Ce(IV)–$H_2O_2\cdot$; $K_{eq} = (2.7 \pm 0.4) \times 10^3$ L mol^{-1}.	739071
$H_2O_2 + UO_2^{2+} \rightarrow UO_2^{2+}\text{–}H_2O_2$	5.2	1.4×10^4		p.r.; P.b.k. in soln. contg. 1.0×10^{-4} mol L^{-1} U(VI) (~ 2×10^{-5} mol L^{-1} H_2O_2 produced by p.r.).	761084
	5.2	$(5.9 \pm 0.05) \times 10^3$		stopped-flow; P.b.k. in soln. contg. $0.5\text{–}5 \times 10^{-4}$ mol L^{-1} U(VI) and $0.5\text{–}1 \times 10^{-3}$ mol L^{-1} H_2O_2; at 2.5×10^{-3} mol L^{-1} H_2O_2 $k = (1.31 \pm 0.16) \times 10^4$. The error is based on a least squares plot and reflects only the internal consistency of the data.	761084
Triscarbonatodioxouranate(VI) ion					
$e_{aq}^- + UO_2(CO_3)_3^{4-} \rightarrow UO_2(CO_3)_3^{5-}$	11.4	$(1.3 \pm 0.01) \times 10^{10}$		p.r.; D.k. in soln. contg. 0.1 mol L^{-1} *tert*-BuOH and 0.01 mol L^{-1} carbonate and $0.4\text{–}7 \times 10^{-4}$ mol L^{-1} U(VI); k increased in hexadecyltrimethylammonium bromide soln. to 1×10^{11} [81N168]. The error is based on a least squares plot and reflects only the internal consistency of the data.	81A148
Bisoxalatodioxouranate(VI) ion					
$e_{aq}^- + UO_2(ox)_2^{2-} \rightarrow UO_2(ox)_2^{3-}$	5.0	$(2.8 \pm 0.13) \times 10^{10}$		p.r.; D.k. in soln. contg. 0.1 mol L^{-1} *tert*-BuOH and 0.01 mol L^{-1} oxalate and $0.4\text{–}7 \times 10^{-4}$ mol L^{-1} U(VI). The error is based on a least squares plot and reflects only the internal consistency of the data.	81A148

Table of rate constants — Continued

Reaction	pH	k(L mol^{-1}s^{-1})	I	Comment	Ref.
Iminodiacetatodioxouranium(VI)					
$e_{aq}^- + UO_2IDA \rightarrow UO_2IDA^-$	10.5	$(1.9 \pm 0.01) \times 10^{10}$		p.r.; D.k. in soln. contg. 0.1 mol L^{-1} *tert*-BuOH and 0.01 mol L^{-1} iminodiacetate and 0.4–7 × 10^{-4} mol L^{-1}U(VI); k increased to 3.87 and 3.1× 10^{10} resp. at concn. 0.05 and 0.25 mol L^{-1} iminodiacetate at pH 8. The error is based on a least squares plot and reflects only the internal consistency of the data.	81A148
Nitrilotriacetatodioxouranate(VI) ion					
$e_{aq}^- + UO_2NTA^- \rightarrow UO_2NTA^{2-}$	9.0	$(1.7 \pm 0.02) \times 10^{10}$		p.r.; D.k. in soln. contg. 0.1 mol L^{-1} *tert*-BuOH and 0.01 mol L^{-1} nitrilotriacetate and 0.4–7 × 10^{-4} mol L^{-1} U(VI); k increased to 1.9 and 2.4× 10^{10}, resp. at 0.05 and 0.25 mol L^{-1} nitrilotriacetate . The error is based on a least squares plot and reflects only the internal consistency of the data.	81A148

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