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COMMUNICATION

Generation and Study of Am(IV) by Temperature-Controlled Electron Pulse Radiolysis

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First-of-a-kind temperature-controlled electron pulse radiolysis experiments facilitated the radiation-induced formation of Am(IV) in concentrated (6.0 M) HNO_3, and enabled the derivation of Arrhenius and Eyring activation parameters for the instigating radical reaction between $NO_3^{\bullet}$ and Am(III).

Americium (Am) marks the point in the actinide series where thermodynamic preference for a trivalent oxidation state dominates, owing to changes in the energy and bonding contributions of the 5*f* orbitals.[1] Despite the energetic barrier imposed by the Am(IV)/Am(III) redox couple (E^o = 2.62 V_{SCE}),[2] several techniques, including chemical[3-6] and photo-electrochemical oxidation,[7-10] have successfully generated the penta- and hexa- americyl states (AmO_2^{n+}, n = 1 or 2 for Am(V) and Am(VI), respectively). These non-equilibrium americium oxidation states have been extensively explored, due to their potential utilisation in the separation of Am(III) from trivalent lanthanide fission products and curium in used nuclear fuel (UNF) by solvent extraction technologies.[11-15] This separation remains an enduring challenge due to the similar chemical and physical properties of these trivalent *f*-elements, but is a critical step in reducing the radiotoxicity of nuclear waste and securing the long-term sustainability of nuclear power.

Unlike the americyl states, equivalent knowledge of the tetravalent state, Am^{4+}/Am(IV), has proven more elusive, given its tendency to spontaneously reduce or disproportionate in non-complexing solvents. Asprey and Penneman first stabilized Am(IV) in 1961 through dissolution of americium hydroxide in ammonium fluoride; proposing that Am(IV) was complexed by fluoride ions.[16] Since then, Am(IV) has so far mainly been studied in strongly complexing, alkaline media or phosphoric acid.[17-22] Although these studies were successful in generating Am(IV) at ambient temperature and measuring its absorption spectrum, the highly complexing conditions employed limited the extent to which the fundamental chemistry of this non-equilibrium Am oxidation state could be explored.

Alternatively, ambient temperature electron pulse radiolysis techniques have been shown to produce simple, highly oxidizing radicals that react with Am(III) to yield the desired Am(IV). For example, in the 1970s both Gordon[23, 24] and Pikaev[25, 26] reported the generation of Am(IV) by the reaction of Am(III) with the hydroxyl radical ($^{\bullet}OH$, E^o = 2.7 V_{NHE})[27] in perchloric acid ($HClO_4$, pH 0–6). Lierse *et al.* also demonstrated that the dichlorine radical anion ($Cl_2^{\bullet-}$, E^o = 2.13 V_{SHE})[28] could achieve the same goal in aqueous sodium chloride solution,[29] despite possessing a lower oxidation potential.

These initial radiolysis studies, however, were constrained to conditions less relevant to both the fundamental manipulation of heavy elements in a laboratory setting and UNF reprocessing formulations, namely elevated temperatures, and high concentrations of nitrate (NO_3^-) or nitric acid (HNO_3). Actinide nitrate complexes are amongst the most utilised starting materials in synthetic actinide chemistry, and thus NO_3^- is observed in the coordination sphere of many known actinide crystal structures. In UNF reprocessing, molar (3–8 M) amounts of HNO_3 are used for both the dissolution of UNF and the aqueous phase in subsequent solvent extraction cycles.[30] Furthermore, radiation heating affords elevated temperatures that impact separation efficiency[31] and the extent to which radiation-induced processes impact the longevity of chemical reagents. Therefore, under these very acidic and non-ambient temperature conditions, the speciation of actinide nitrate complexes is of great importance when optimizing extraction flowsheets, wherein resolving the role of Am(IV) in the reduction and disproportionation of Am(V) is of interest:[9, 32-34]

$$2AmO_2^+ + 4H_{aq}^+ \rightarrow AmO_2^{2+} + Am^{4+} + 2H_2O, \quad (1)$$

$$AmO_2^+ + Am^{4+} \rightarrow AmO_2^{2+} + Am^{3+}, \quad (2)$$

$$2Am^{4+} + 2H_2O \rightarrow Am^{3+} + AmO_2^+ + 4H_{aq}^+. \quad (3)$$

Understanding these proposed redox processes and their temperature dependence (**Eq. 1**–**3**) is essential for refining our ability to quantitatively predict radiation-induced americium redox chemistry, which is required for the accelerated development of innovative Am separation technologies.[12]

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Moreover, deeper knowledge of the formation and stabilization of Am(IV) is of fundamental interest to the ongoing investigation of unique *f*-element chemical properties and periodic trends.

Under high NO_3^-/HNO_3 concentration conditions, the typical suite of radicals and molecular products generated by the radiolysis of aqueous solutions:[27]

$$H_2O \rightsquigarrow e_{aq}^-, H^\bullet, {}^\bullet OH, H_2O_2, H_2, H_{aq}^+, \quad (4)$$

are transformed into reducing nitrous acid (HNO_2) and oxidizing nitrate radicals ($NO_3^\bullet$):[35-38]

$$HNO_3/NO_3^- \rightsquigarrow e_{aq}^-, NO_3^\bullet, HNO_2/NO_2^-, O^\bullet, H_{aq}^+, \quad (5)$$

$$NO_3^- + e_{aq}^-/H^\bullet \rightarrow\rightarrow\rightarrow\rightarrow HNO_2/NO_2^-, \quad (6)$$

$$HNO_3 + {}^\bullet OH \rightarrow NO_3^\bullet + H_2O. \quad (7)$$

Our previous work demonstrated that these two radiolysis products are predominantly responsible for the redox cycling between Am(V) and Am(VI) in irradiated HNO_3 systems.[11, 12] However, the reaction of Am(III) with $NO_3^\bullet$ has until now not been studied, having been discounted based on this radical's potential (E^o = 2.3–2.6 V_{SHE})[39] versus the Am(IV)/Am(III) redox couple, and the rapid reduction of Am(IV) by HNO_2 that is generated both as a product of water radiolysis and the reaction of highly reducing Am(IV) with water.[40] That said, more recent studies have shown that $NO_3^\bullet$ is capable of transiently oxidizing trivalent actinides with formally higher IV/III couples, such as curium (E^o = 3.1 V_{SHE}) and californium (E^o = 3.2 V_{SHE}).[24, 41, 42] Consequently, $NO_3^\bullet$ may have the capacity to transiently generate Am(IV), providing the opportunity to study this non-equilibrium oxidation state under conditions more frequently encountered in fundamental and applied americium manipulations.

To that end, we employed integrated electron pulse radiolysis and transient absorption spectroscopy techniques to generate $NO_3^\bullet$, observe the growth and decay of Am(IV), and elucidate the unprecedented associated reaction kinetics and activation parameters (Arrhenius and Eyring) for the instigating Am(III) oxidation mechanism in 6.0 M HNO_3 (pH = -0.78):

$$Am^{3+} + NO_3^\bullet \rightarrow Am^{4+} + NO_3^-. \quad (8)$$

Samples were prepared by the dilution of a stock solution of purified Am(III) nitrate in 6.0 M HNO_3, to achieve pseudo-first-order solute concentrations. Transient absorption spectra and temperature-controlled chemical kinetics—the first for an actinide element—were measured using a new, custom-built temperature controlled actinide sample holder (**Fig. S3**) installed at the Brookhaven National Laboratory (BNL) Laser Electron Accelerator Facility (LEAF).[43] Detailed experimental procedures can be found in the *Electronic Supplementary Information* (ESI).

Reaction of $NO_3^\bullet$ with Am(III) afforded the formation of Am(IV); the transient absorption spectra from these irradiations are shown in **Fig. 1**. The Am(IV) spectrum recorded at 10 µs after the electron pulse is the first of its kind in concentrated nitric acid media, and is characterized by a single absorption band that peaks at ~350 nm. At shorter timescales residual

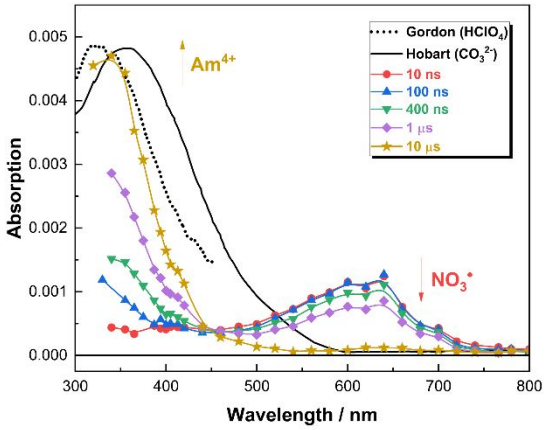

Fig. 1. Dose normalized transient absorption spectra from the electron pulse irradiation of 2.32 mM Am(III) in aerated 6 M HNO_3 at 21 ± 1 °C for several time slices after the electron pulse. Scaled ambient temperature Am(IV) spectra reported by Gordon[23] and Hobart[44] are shown as a dotted and solid black lines, respectively.

contributions from the absorption of $NO_3^\bullet$ are seen at ~450–750 nm. The Am(IV) spectrum shown here is in very good agreement with those reported by Gordon and Pikaev for the oxidation of Am(III) by $^\bullet OH$, and the more complete spectrum reported by Hobart and Peterson for the electrochemical generation of Am(IV) in aqueous carbonate solution, confirming our assignment.[23-26,44] For ease of comparison, the Gordon and Hobart spectra have been scaled and plotted alongside our data in **Fig. 1**. Both irradiation and electrochemical techniques afforded Am(IV) spectra with little-to-no fine structure after the initial absorption band, avoiding spectral complications from stabilizing additives (e.g. phosphotungstunate)[32] which is ideal for studying the chemistry of this unique oxidation state.

Chemical kinetics for the instigating oxidation of Am(III) by $NO_3^\bullet$ were explored as a function of temperature (8–40 °C, see ESI) to derive the associated rate coefficients and unprecedented activation parameters. Such data allows for a greater molecular level understanding of this system and the

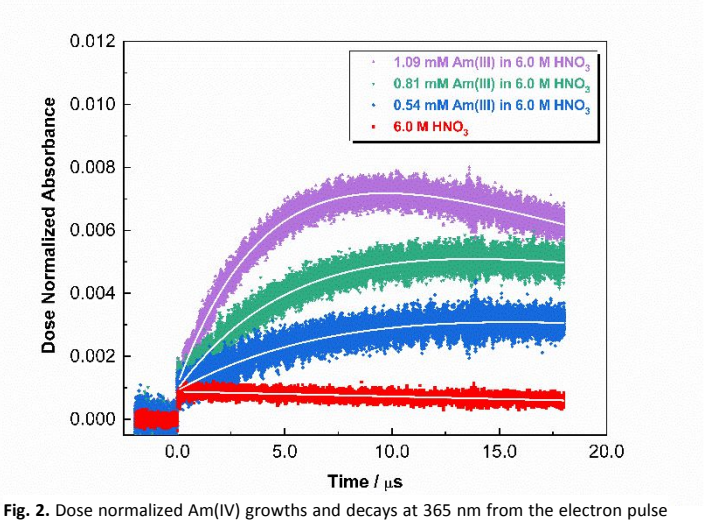

Fig. 2. Dose normalized Am(IV) growths and decays at 365 nm from the electron pulse irradiation of Am(III) in aqueous 6.0 M HNO_3 at 22 ± 1 °C. Solid white lines are exponential growth and decay fits to data. Calculated pseudo-first-order growth rates were used to derive the corresponding second-order rate coefficient, $k(Am(III) + NO_3^\bullet \rightarrow Am(IV) + NO_3^-) = (1.32 \pm 0.06) \times 10^8\ M^{-1}\ s^{-1}$, R^2 = 0.99 (ESI, **Fig. S10A**).

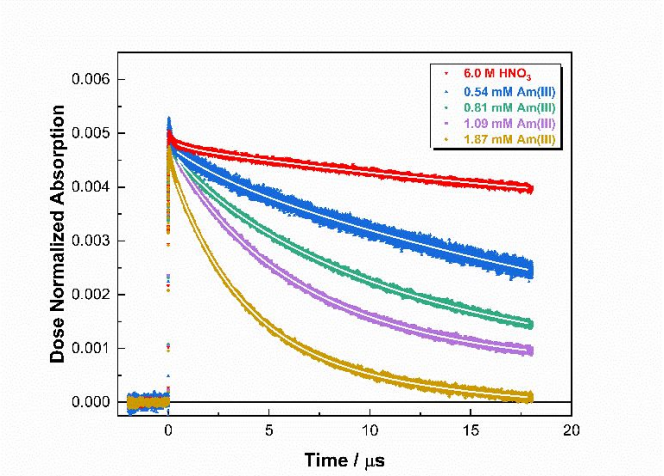

Fig. 3. Complementary dose normalized $NO_3^•$ decays at 632 nm from the electron pulse irradiation of Am(III) in aqueous 6.0 M HNO_3 at 22 ± 1 °C. Solid white lines are double exponential fits to data. Calculated pseudo-first-order decay rates were used to derive the corresponding second-order rate coefficient, k(Am(III) + $NO_3^•$ → Am(IV) + NO_3^-) = (1.38 ± 0.03) × 10^8 M^{-1} s^{-1}, R^2 = 0.99 (ESI, **Fig. S10B**).

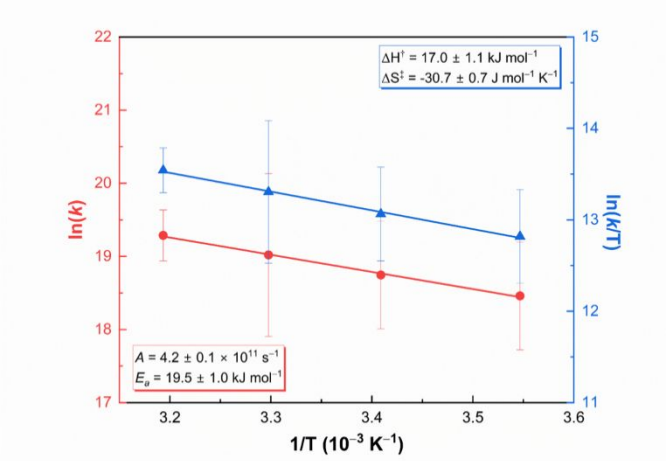

Fig. 4. Combined Arrhenius and Eyring plots utilizing second-order rate coefficient data from the reaction of Am(III) with $NO_3^•$ at 8, 22, 30, and 40 ± 1 °C.

development of quantitative models for the prediction of Am redox chemistry over a range of temperatures, alongside significant advances in our ability to probe the kinetics and reactivity of the actinide series as a whole.[11, 12]

Typical kinetic data are shown in **Figs. 2** and **3** for the growth and decay of Am(IV) and the complementary decay of $NO_3^•$, respectively, as a function of Am(III) concentration at ambient temperature (22 ± 1 °C). Plotting the pseudo-first-order component values derived from these exponential fits against solute concentration gave an average second-order rate coefficient of k = (1.35 ± 0.05) × 10^8 M^{-1} s^{-1} for the growth of Am(IV)/decay of $NO_3^•$ (ESI, **Fig. S16**). The ambient temperature rate for **Eq. 8** is consistent with those reported for the few other measured trivalent actinides: plutonium (2.50 × 10^8 M^{-1} s^{-1}),[45] curium ((4.83 ± 0.09) × 10^7 M^{-1} s^{-1}),[41] and californium ((1.78 ± 0.06) × 10^8 M^{-1} s^{-1}).[42, 46] Comparison of these values with the associated IV/III redox couples (ESI, **Fig. S13**)[2] demonstrates that single electron transfer to $NO_3^•$ becomes less energetically favourable with increasing reduction potential, as expected.

The radiolytically generated Am(IV) was unstable, and kinetic plots of absorbance versus time (**Fig. 2**) indicate that the species possessed a lifetime of ~16 µs, similar to that measured for transient tetravalent curium and californium ions.[41, 46] The lifetime of Am(IV) in 6.0 M HNO_3 is shorter than previously reported in less acidic media, which is consistent with Pikaev's observation of increased reduction of Am(IV) by radiolytically generated hydroperoxide radicals with decreasing pH.[17, 47] That said, 16 µs is sufficiently long-lived to study Am(IV)'s inherent chemistry, as evident from the wealth of literature on aqueous radiolysis products with similar lifetimes.[41, 46, 48-50] The decay of Am(IV) in the investigated systems was likely by a mixture of processes, including **Eqs. 1–3** and reactions involving HNO_2 and H_2O_2. The combination of these processes afforded a pseudo rate coefficient (k') of 10^5 s^{-1} for the loss of Am(IV).

The Arrhenius (activation energy, E_a, and pre-exponential factor, A) and Eyring (enthalpy of activation, $\Delta H^†$, and entropy of activation, $\Delta S^‡$) activation parameters calculated for **Eq. 8** from the temperature dependence of the second-order rate coefficients are: A = (4.2 ± 0.1) × 10^{11} s^{-1}, E_a = 19.5 ± 1.0 kJ mol^{-1}, $\Delta H^†$ = 17.0 ± 1.1 kJ mol^{-1}, and $\Delta S^‡$ = -30.7 ± 0.7 J mol^{-1} K^{-1}. The endothermic $\Delta H^†$ value indicates that the approach of $NO_3^•$ requires some perturbation of the Am(III) coordination sphere (H_2O or NO_3^-)[51] for electron transfer to occur. The negative $\Delta S^‡$ value determined denotes a decrease in entropy upon attaining this reaction's transition state of **Eq. 8**, which is indicative of an associative mechanism that generates a single transition state species. No equivalent temperature-dependent kinetic data exist for other actinide elements.

In conclusion, we have established unprecedented capability for temperature-dependent electron pulse radiolysis studies with actinide elements, and demonstrated that Am(III) oxidation is a mechanistically feasible reaction pathway under UNF reprocessing conditions, i.e., low pH, high HNO_3 concentrations, and varied temperature. The resulting Am(IV) is sufficiently long-lived (~16 µs) to play a critical mechanistic role in such processes. Kinetic measurements were also successfully performed using the sulfate radical anion ($SO_4^{•-}$, E^o = 2.5–3.1 V_{NHE})[52] in $HClO_4$ (pH = 1.2), see ESI **Figs. S14–16**, providing further evidence that a range of oxidizing agents not previously studied may be used to access non-equilibrium actinide oxidation states to study their fundamental reaction kinetics.

Author Contributions

A.E.K. sample preparation, experimental, data analysis, writing and editing, funding acquisition; T.S.G. lead sample preparation; S.P.M. data analysis; B.L. construction of temperature control cell; A.R.C. experimental assistance; B.M.R. experimental assistance; G.P.H. data analysis, writing and editing, funding acquisition, project conceptualization, supervision.

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Conflicts of interest

There are no conflicts to declare.

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