Pulse radiolysis study on the reactivity of NO_3 radical toward uranous(iv), hydrazinium nitrate and hydroxyl ammonium nitrate at room temperature and at 45 °C

R. Musat, J.L. Marignier, C. Le Naour, S. Denisov, L. Venault, Ph. Moisy, M. Mostafavi

Pulse radiolysis study on the reactivity of $NO_3^{\bullet}$ radical toward Uranous (IV), hydrazinium nitrate and hydroxyl ammonium nitrate at room temperature and at 45 °C

R. Musat,[a,‡] J. L. Marignier[a], C. Le Naour[b], S. Denisov[a], L. Venault[c], Ph. Moisy[c,*], and M. Mostafavi[a,*]

[a] Institut de Chimie Physique CNRS-Université Paris-Saclay, 91405 Orsay, France

[‡] Present address : CEA, DEN/DANS/DPC/SECR/LRMO, 91191 Gif sur Yvette Cedex, France

[b] Institut de Physique Nucléaire, CNRS-IN2P3, Université Paris-Sud, Université Paris-Saclay, 91406 Orsay Cedex, France

[c]CEA, DEN, DMRC, Univ Montpellier, France

ABSTRACT

Concentrated nitric acid solutions subjected to radiation produce radicals of extreme importance in the reprocessing of spent nuclear fuel. Knowledge of the different rate constants of the reactions involved in this chemistry is needed to improve the efficiency of the process and to define safe operating practices. Pulse radiolysis measurements are performed to find the rate constant of the reaction between $NO_3^{\bullet}$ radicals and U(IV) in highly concentrated nitrate solution. The optimal stabilization conditions toward thermal oxidation are defined for the considered solutions at room temperature and at 45°C by adding the anti-nitrous agents such as hydrazinium nitrate (HN) and hydroxyl ammonium nitrate (HAN). The decay of the $NO_3^{\bullet}$ radical is monitored and its reaction rates with HN, HAN and U(IV) are found to be 1.3×10^5, 1.5×10^7 and 1.6×10^6 M^{-1} s^{-1} at room temperature. The latter value is more than 10 times lower than the one currently used in numerical codes for simulation of the long-term radiolytic degradation associated with the reprocessing and storage of spent nuclear waste. At 45°C, conditions similar to the reprocessing of spent fuel, the values of the rate constants of $NO_3^{\bullet}$ radical toward HN, HAN and U(IV) increase and are found to be 2.6×10^5, 2.9×10^7 and 9.3×10^6 M^{-1} s^{-1}.

Introduction

An increasing demand of energy in the XXI[st] century, combined with societal demands to preserve the livability of planet earth emphasizes the need for a consciously responsible energetic transition. Several countries have committed towards an enhanced deployment of renewable energy in order to reduce or eliminate the burning of fossil fuel for electricity, heat and transportation as the primary source of green gas emissions. As reform of the energy market is imminent, the nuclear energy still plays an important role as a virtually CO_2 benign source, providing access to clean, reliable and affordable energy, currently supplying 75% of the total electricity in France. Currently, 30 countries use nuclear power and about the same number are considering, planning or

actively working on including it in their energy mix, with an International Atomic Energy Agency (IAEA), Organization for Economic Cooperation and Development (OECD), International Energy Agency (IEA) and World Nuclear Association (WNA) projected global nuclear power capacity growth from its current level of 381.7 GW(e) to 600-700 GW(e) by 2030. Through the energy reform debate, and concerns over the risks associated with nuclear energy, constant efforts are made in the industry in order to guarantee safety, long functioning and performance of nuclear power plants. The major area of investigations, for more than a half of century, has been the separation and recovery of actinides from the spent nuclear fuel. These developments will open the way for differentiated management modes, which will contribute ultimately to downsizing the waste volume and reduce its intrinsic radiotoxicity levels.[1] The preferred industrial reprocessing technology is the hydrometallurgical one, with the PUREX process at its core, a liquid-liquid extraction processes, allowing the recovery and recycling of major actinides.[2,3] The MO_X (mixed oxide (U-Pu)O_2) fuel fabrication earned first place in the uranium and plutonium recycling industry, with a recycling success rate of 99.9%.[4]

The first step of PUREX processes consists of spent nuclear fuel dissolution in nitric acid, with subsequent uranium U(VI) ($U^{VI}O_2^{2+}$) and plutonium Pu(IV) (and a low fraction of Pu(VI)) co-extraction into an organic phase, usually consisting of diluted tri-n-butyl-phosphate (TBP). Subsequently, Pu partitioning into an aqueous stream is performed by reducing Pu(IV) to Pu(III) and purifying it. The chemical separation steps are carried out at room temperature or at 45°C, depending on the equipment used. The use of nitric acid as a reaction medium, for all nuclear fuel treatment operations is based on its redox, acido-basic and complexing properties.[5] Due to the oxidation of $U^{IV}O_2$ to $U^{VI}O_2^{2+}$, the instability of HNO_3 towards temperature and radiation,[6,7] from the first step of dissolution of fuel elements, accumulation of NO_2, HNO_2, and NO in solution (NOx) can occur, that affects the redox potential of the aqueous media.[8] Part of the HNO_2 produced can escape as NOx gases from the liquid, part is extracted into the TBP organic phase and part remains in the aqueous phase. Uranous (IV) nitrate aqueous solution that is used as a reductant of Pu(IV) to Pu(III) can also be oxidized into U(VI) in the presence of HNO_2.[9] The U(VI)/U(IV) couple (~0.33 V/SHE in $HClO_4$ 1 M[10]) is smaller than the one corresponding to HNO_2 in nitric acid media ($E^{\circ}(HNO_2/NO)$ = 0.996 V/SHE[11]), rending U(IV) unstable. Pu(III), also being an unstable species, can rapidly be re-oxidized into Pu(IV) in the presence of nitrous acid, leading to partitioning failure. This is a self-catalyzing reaction, as it leads to the production of more HNO_2 than it consumes.[12]

The most commonly used anti-nitrous agent in the PUREX process is hydrazinium nitrate (HN), as it is capable of rapidly destroying the nitrous acid in aqueous solution. In acidic media, hydrazinium exists under two protonated forms (pKa_1 = 7.9[13–15] 8.1[16] 8.23[17] and pKa_2 = -1[18]): $N_2H_5^+$ and $N_2H_6^{2+}$.[19] The interaction between nitrous acid and hydrazinium leads to the formation of hydrazoic acid as chemical intermediate.[20–23]

$$N_2H_5^+ + HNO_2 \rightarrow N_3H + H^+ + 2H_2O \quad (1)$$

$$N_3H + HNO_2 \rightarrow N_2O + N_2 + H_2O \quad (2)$$

Due to its Pu(IV) to Pu(III) reducing capacity and scavenging properties of nitrous acid and prevention of back-oxidation of Pu(III), hydroxyl ammonium nitrate (HAN) was proposed as a reducing agent in the PUREX process.[24–27] HAN exists in HNO_3 under its protonated form NH_3OH^+ ($pKa_1 = 5.96$[28]). However, the destruction of HNO_2 occurs much slower than in the presence of HN, according to reaction (3).[23,29,30] In 1970, Walser et al[21] showed the successful use of a hydroxyl ammonium nitrate-hydrazinium mixture as reducing agent to obtain an efficient U decontamination, Pu and Np recovery in the PUREX based process. The use of hydroxyl ammonium nitrate reduces the quantity of hydrazinium converted into hydrazoic acid from 5% to 30%, avoiding addition of supplemental chemical reductants such as U(IV) (or Fe(II)) to the process.

$$NH_3OH^+ + HNO_2 \rightarrow N_2O + H_2O + H_3O^+ \quad (3)$$

In sufficiently high concentrations of nitric acid an autocatalytic reaction can occur, which can lead to the formation of HNO_2, rather than its destruction:[31]

$$NH_3OH^+ + 2HNO_3 \rightarrow 3HNO_2 + H_3O^+ \quad (4)$$

Borderline conditions for the transition of HNA from a nitrous acid scavenger to a species responsible for the production of HNO_2 have been determined: a [HNO_3] and temperature increase and a decrease of [HAN], all favor reaction (4).[32,31]

The study of the effects of ionizing radiation on acidic solutions containing actinides provides information on their redox behaviors and their reactivities towards the free radicals issued from the radiolysis of HNO_3. It is therefore of extreme importance to fully understand and develop numerical models for the chemical process of actinides during the nuclear fuel reprocessing, and to do so, kinetic information on the reaction rates is needed. A few radiolytic models for U, Np, Pu and Am ions in concentrated nitric and perchloric acid solutions have already been proposed,[33–36] but questions still remain on the reaction rates involved in the process. Addition of stabilizing agents into the HNO_3 solutions can prevent U(IV) and Pu(III) oxidation by nitrous acid with an autocatalytic mechanism, and avoid partition failure in the PUREX process. Therefore the oxidation of U(IV) and Pu(III) by HNO_3/HNO_2 mixture is of extreme interest,[37–43] not only for maintaining and optimizing the currently operating process but also for developing more efficient methods. Predicting and controlling the reaction pathways of U(IV), HAN and HN in the PUREX process is important for defining safe operating conditions for the use and storage of these compounds, for improving the product separation and recovery and waste management process.

The radiolytic behavior of HNO_3 solutions[44–46,6,47–53] has been fully characterized, and the nitrate radicals ($NO_3^{\bullet}$) formation mechanism has been elucidated.[54,55,52,56] The nitrate radicals ($NO_3^{\bullet}$) are used in most investigations as a probe to monitor the radiation-induced changes in HNO_3 solutions,[57,46,49,58,54,50,55,59,56] as they are known to be key radiolytic intermediates and drivers of chemical changes through the formation of secondary radiolytic products or through the oxidation of important metal ions. The three reactions responsible for the production of nitrate radicals are presented in Table 1: the reaction between $^{\bullet}OH$ radicals and undissociated HNO_3 molecules (14),[49,60] the direct action of ionizing radiation on NO_3^- ions (6) and HNO_3

molecules[61,46] and oxidation of NO_3^- ions and undissociated acid molecules by the primary water cation radical $H_2O^{\bullet+}$ (11).[58]

Table 1. Main reactions occurring in the radiolysis of aqueous solutions of HNO_3 containing uranium, and associated reaction rate constants in M^{-1} s^{-1}.

$NO_3^- \rightarrow NO_3^{-*} \rightarrow NO_2^- + O$		*(5)*
$NO_3^- \rightarrow NO_3^{\bullet} + e^-$		*(6)*
$NO_3^- + e^-_{pre} \rightarrow NO_3^{\bullet 2-}$	*4.5 ×10[12];* [62]	*(7)*
$NO_3^- + e^-_{sol} \rightarrow NO_3^{\bullet 2-}$	*9.7 ×10[9];* [63]	*(8)*
$NO_3^- + H^{\bullet} \rightarrow HNO_3^{\bullet -}$	*1 ×10[7];* [64]	*(9)*
$H_2O^+ + H_2O \rightarrow OH^{\bullet} + H_3O^+$	*~10[13];* [65,66]	*(10)*
$H_2O^{\bullet +} + NO_3^- \rightarrow NO_3^{\bullet} + H_2O$		*(11)*
$H^+ + e^-_{pre} \rightarrow H^{\bullet}$		*(12)*
$H^+ + e^-_{sol} \rightarrow H^{\bullet}$	*2.3 ×10[10];* [67]	*(13)*
$OH^{\bullet} + HNO_3 \rightarrow NO_3^{\bullet} + H_2O$	*1.4 ×10[7];* [54] *9.03 ×10[7];* [49,68] *5.3 ×10[7];* [56,69] *8.6 ×10[7];* [70]	*(14)*
$NO_3^{\bullet} + {}^{\bullet}OH \rightarrow NO_2^{\bullet} + HO_2^{\bullet}$		*(15)*
$2UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O$	*3 ×10[3] ;* [71]	*(16)*
$UO_2^{2+} + e^-_{aq} \rightarrow UO_2^+$	*1.7 ×10[10];* [63]	*(17)*
$UO_2^{2+} + H^{\bullet} \rightarrow UO_2^+ + H^+$	*4.1 ×10[7];* [64,72]	*(18)*
$U^{4+} + H^{\bullet} \rightarrow U^{3+} + H^+$	*1 ×10[6];* [64,72]	*(19)*
$UO_2^+ + OH^{\bullet} \rightarrow UO_2^{2+} + OH^-$	*4 ×10[9];* [64,72]	*(20)*
$UO_2^+ + NO_3^{\bullet} \rightarrow UO_2^{2+} + NO_3^-$	*2×10[4];* [69]	*(21)*
$UO_2^+ + NO_2^{\bullet} \rightarrow UO_2^{2+} + NO_2^-$	*1 ×10[3];* [67,69]	*(22)*
$UO_2^+ + HNO_2 \rightarrow UO_2^{2+} + HNO_2^-$	*8.6 ×10[8];* [71]	*(23)*

$U^{4+} + NO_3^{\bullet} \rightarrow UO_2^{+} + NO_3^{-}$	*2 × 10⁷;* ([H⁺] = 1 M) [71]	*(24)*
$U^{4+} + NO_2^{\bullet} \rightarrow UO_2^{+} + NO_2^{-}$	*1 × 10²;* [71]	*(25)*
$U^{4+} + H_2O_2 \rightarrow UO_2^{+} + OH^{\bullet} + OH^{-}$	*11;* [71,72]	*(26)*

The oxidation of U(IV) in nitric acid exhibits an initial induction period, in which oxidation of HNO_3 occurs producing HNO_2, followed by an autocatalytic reaction, in which U(IV) is oxidized by the resulting HNO_2.[38,73,74]

$$U(IV) + HNO_3 + H_2O \rightarrow UO_2^{2+} + HNO_2 + 2H^{+} \quad (27)$$

$$U(IV) + 2HNO_2 \rightarrow UO_2^{2+} + 2NO + 2H^{+} \quad (28)$$

$$2NO + HNO_3 + H_2O \leftrightarrow 3HNO_2 \quad (29)$$

The activation energies of reactions (27) and (28) are E_{27} = 103 ± 15 and E_{28} = 93 ± 5 kJ mol^{-1}.[73,75] The induction period duration is reduced with increasing acidities,[76,77] and at high enough HNO_3 concentrations, reaction (28) rate is reduced, which is explained by U(IV) hydrolysis, favored as acidity decreases. The autocatalytic reaction occurs via the second hydrolysis product ($U(OH)_2^{2+}$):[73]

$$U(OH)_2^{2+} + NO_2^{+} \rightarrow UO_2^{+} + NO_2 + 2H^{+} \quad (30)$$

$$U(OH)_2^{2+} + HNO_2 \rightarrow UO_2^{+} + H_2O + H^{+} + NO \quad (31)$$

Ermolaev and Krot[78] suggested that the oxidation of U(IV) in HNO_3 after the induction period follows a first order reaction equation, depending on the temperature and H^+ and NO_3^- concentrations. However, more complex decay equations are given by Koltunov[75] and Matsumoto.[79] Some authors have extrapolated the reaction rate constant of U(IV) with $NO_3^{\bullet}$ radicals in aqueous solutions (24), based on the published reaction rates of other actinides with these radicals,[80] or have estimated this value from computer simulations,[34] or from the reaction of U(IV) with $OH^{\bullet}$ radicals (8.6×10^9 M^{-1} s^{-1}) and U(IV) with SO_4^- (1.2×10^7 M^{-1} s^{-1}) in acidic solutions.[71] The U(IV) reaction rate with $NO_2^{\bullet}$ radicals was estimated by comparison with that for $UO_2^+ + NO_2^{\bullet}$.

The purpose of the present work is to examine the radiation chemistry of uranium (IV) in nitric acid solution in presence of HN and HAN. Pulse radiolysis investigations allow us to determine the reaction rates of $NO_3^{\bullet}$ with U(IV), HN and HAN in HNO_3/$LiNO_3$ solutions at room temperature (22.5°C), as well as at elevated temperature (45°C), similar to the temperature under PUREX operating conditions. This is the first time these reactions have been looked into directly, as it involves safe handling of actinides in a low oxidation state. Working with actinides presents scientific challenges in itself, but especially when combined with state of the art experimental methods like pulse radiolysis. The methodology developed involved an incremental approach:

initially, determination of kinetic rates for anti-nitrous agents and once the solutions' stability conditions defined, experimental measurement of kinetic rate for uranium (IV).

Experimental

Nitric acid (69 wt.%) and lithium nitrate ultrapure grade (99.999%) were purchased from Sigma-Aldrich and VWR respectively, and used without further purification. Deionised water (18 MΩ cm and less than 10 ppb organic carbon) was used in all experiments. U(IV) stock solutions were prepared by catalytic hydrogenation of U(VI) nitrate in the presence of platinum. In order to prevent U(IV) hydrolysis and oxidation, nitric acid, hydrazinium or hydroxyl ammonium nitrate were added, yielding the following composition: U(IV) ~0.5 M, HNO_3 1 M, HN 0.1 M or HAN 0.2 M. U(IV) samples were prepared by dilution of an aliquot of the stock solution in the corresponding electrolyte containing HN or HAN. For pulse radiolysis measurements, the total NO_3^- concentration was set at 7 M, the solutions being formed by a mixture of $LiNO_3$ (6 M) and HNO_3 (1 M). An increase of the temperature from 25°C to 45°C leads to a reduction of the concentration of the species of 2% in molarity scale, due to the decrease of the density.[81] We took into account this variation in the spectrophotometric measurements for the calculations including the molar extinction coefficients. The stability of U(IV) solutions in these media at room temperature and 45°C was investigated by UV-Vis spectrophotometry (Shimadzu UV2501PC).

The decay of nitrate radicals in the presence of uranium (IV) with anti-nitrous agents was monitored using the pulse radiolysis system of ELYSE accelerator (Paris-Saclay University) that allows the generation and investigation of transient species with high time resolution, on time scales ranging from ps to ms. Laser (260 nm) driven Cs_2Te photocathode allows the production of short electron pulses with a typical half width of 7 ps, charge of ~ 6 nC, and energy of ~7.8 MeV, at a repetition rate of 5 Hz.[82] The experimental line used for these investigations employs a highly dynamic Hamamatsu C7700-01 streak camera, coupled to a Chromex 250 IS spectrograph for detection, while the analyzing light is delivered by a home built xenon flash lamp.[83] Optical quartz cells with a path length of 1 cm for room temperature experiments, and 0.5 cm for high temperature experiments, were placed as close as possible to the output window of the accelerator to minimize the divergence of the electron beam. All measurements were obtained as an average of 750 acquisitions per scan. The sample was continuously flown using a peristaltic pump (flow rate ca. 20 cm^3/min) for the high temperature experiments, in order to avoid degradation of the sample or accumulation of degradation products, and purged with argon gas continuously during the measurements. UV-Visible measurements were performed in the 400 to 700 nm wavelength range. The exploration of this wavelength domain made it possible to simultaneously follow the time evolution of nitrate radicals' spectrum intensity, and to verify that uranium in

our solutions is indeed in +IV oxidation state (Sup. Data-1). Quantification of the decay of the nitrate radical was carried out at 640 nm.

In order to reach the desired working temperature, we used a modified coil type condenser, placed before the entrance of the sample cell, equipped with an external heating cable, connected to a PID controller that allows the remote regulation of the temperature (with a precision of ± 0.5°C). The temperature was measured on the external surface of the quartz cell and inside the heating coil with Pt-100 temperature sensors. The measurements were performed at 22.5°C and 45°C. Details about the heating system are presented elsewhere.[56] Special materials that are both acid and temperature resistant were used for these investigations in order to insure safe operation. (e.g., MasterFlex Chem-Durance Bio tubing).

The dose deposited per pulse was determined from measurements of the absorbance of solvated electrons ($A_{e^-_{aq}}(\lambda, t)$) in water at 22.5°C and verified before each series of experiments, considering the initial yield of the solvated electrons, measured at 10 ps, to be G(10 ps) = 4.5×10^{-7} mol/J,[84] and its molar extinction coefficient ε_{715nm} = 19700 M^{-1} cm^{-1}.[85] The absorbance (A(λ, t)) measured for a given species in highly concentrated solutions depends on the dose (D), extinction coefficient (ε_λ) and the yield (G(t)) according to:

$$A(\lambda, t) = \varepsilon_\lambda \cdot l \cdot c(t) = \varepsilon_\lambda \cdot l \cdot D \cdot \rho \cdot G(t) \qquad \text{(Eq. 1)}$$

where *l* is the optical path-length, c(t) is the concentration of the investigated species at time t, ρ is the density of the solution. All results presented herein were measured at an absorbed dose in water of 50 Gy per pulse.

Methodology

The thermal instability and radio-sensitivity of HNO_3, leads to accumulation of HNO_2 in solution and NO_2 and NO (NOx) in gas phase, that affects the redox potential of the aqueous media. In order to prevent U(IV) oxidation in HNO_3 media hydrazinium nitrate and hydroxyl ammonium nitrate were used to stabilize uranium in the +IV oxidation state. Moreover, in order to prevent U(IV) hydrolysis, the HNO_3 concentration was fixed at 1 M. Simultaneously, to avoid a slow oxidation by oxygen, the atmosphere was controlled by bubbling Ar during all experiments.

The methodology developed for this study relies on the optimum choice of U(IV) and anti-nitrous agent concentrations in order to obtain a perfect stability of the U(IV) solution, especially at higher temperatures (45°C), and to ensure that nitrate radicals react with U(IV) and not with the anti-nitrous agent. Indeed, it has been confirmed during this work that these anti-nitrous agents react rapidly with the nitrate radical and these reactions will therefore be in competition with the oxidation of U(IV). Only scarce literature data exist on the stability of the U(IV) solutions (not relevant for our experimental conditions). It was therefore necessary, prior to the pulse radiolysis measurements, to establish the ratio between U(IV) to anti-nitrous agents concentrations that should be used. Spectrophotometric studies of U(IV) stability were performed for various ratios of [U(IV)] to anti-nitrous agents concentration. Preliminary work has

shown that it is necessary to use a mixture of both anti-nitrous agents hydroxyl ammonium and hydrazinium to obtain a solution of U(IV) stable at 45°C for at least 3 hours in HNO_3 medium (1 M) and $LiNO_3$ (6 M).

Results

Speciation of U(IV) in nitric acid media

The speciation of U(IV) chemical form was investigated by UV-Visible spectrophotometry. Figure 1A shows the absorption spectra of the solutions used in this work. These spectra exhibit the characteristic absorption band of U(IV) centered at 647 nm.[86–92] . A prior calibration of U(IV) in (H, Li)NO_3 7 M in the presence of HN and HAN was performed at 25°C, over the U(IV) concentration range $2.5 \times 10^{-3} – 5 \times 10^{-2}$ M, yielding a $\varepsilon_{647nm} = 21.4 \pm 0.1$ M^{-1} cm^{-1}. The spectrophotometric absorption measurements of the uranium (IV) solution at 25°C and 45°C are presented in Figure 1. These measurements show that the molar extinction coefficient and the absorption maximum values do not depend on the temperature. Comparison of our results with those of Ikeda-Ohno et al. (performed by spectrophotometry and EXAFS)[36] clearly shows that in (H, Li)NO_3 7 M medium, the uranium(IV) is complexed with 4 or 5 bidentate nitrate ions and that the coordination sphere is completed by 1 ($[U(NO_3)_5(H_2O)]^-$) or 2 water molecules ($[U(NO_3)_4(H_2O)_2]$). The presence of water molecules in the first coordination sphere of U(IV) is confirmed by the differences in the absorption spectra with those of the hexanitrate complex of U(IV) ($U(NO_3)_6^{2-}$).[93] The U(IV) solution is stable at least for a few hours during our experiments (Figure 1 Right). Performing the pulse radiolysis experiments, we verified the stability of the solutions by observing the absorption spectra of the solutions before and after the pulse.

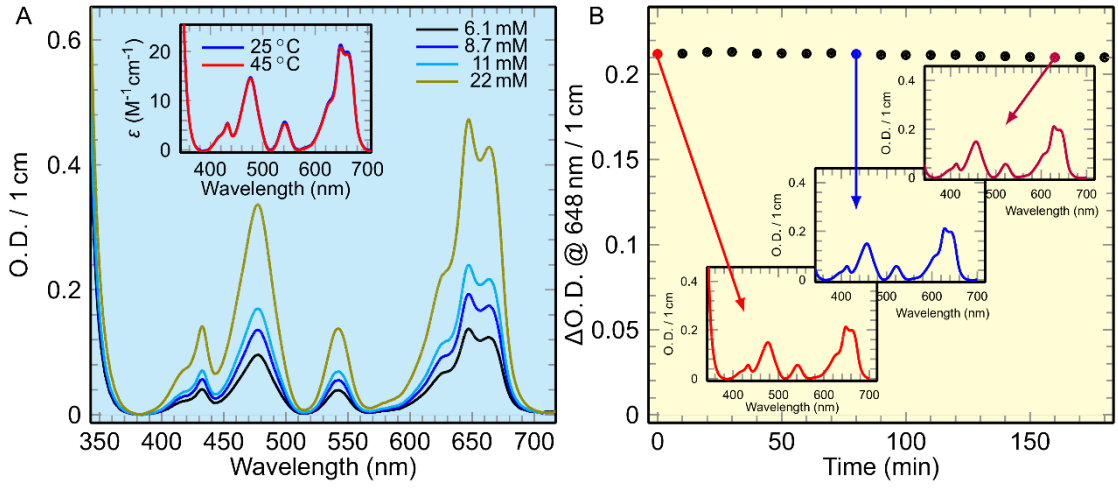


Figure 1. (Left) Absorption spectra of U(IV) at different concentrations at 25°C ($LiNO_3$ 6 M, HNO_3 1 M, HAN 7.7×10^{-3} M, HN 2.2×10^{-4} M); Inset :Absorption spectra of U(IV) 10^{-2} M at 25°C and 45°C ($LiNO_3$ 6 M, HNO_3 1 M, HAN 7.7×10^{-3} M, HN 2.2×10^{-4} M). (Right) Stability of the solutions over time.

Reaction between NO_3 radicals and HAN

In our experimental conditions, HAN exists under its protonated form NH_3OH^+ and in order to understand the $NO_3^{\bullet}$ radical reaction with HAN, we followed the time evolution of the absorption band of $NO_3^{\bullet}$ radical at 640 nm for solutions of different concentrations of HAN (Figure 2). The kinetics at 640 nm show a faster decay with increasing concentration, indicating the occurrence of the investigated reaction. *Ab initio* calculations showed that the radical – hydroxylamine reaction can occur either via the cleavage of O-H (32) bond and formation of O-N bond (33),[94] or via H atom abstractions, as suggested by Pembridge et al:[95,94]

$$NH_3OH^+ + NO_3^{\bullet} \rightarrow NH_2ONO_3^+ + H^{\bullet} \quad (32)$$

$$NH_3OH^+ + NO_3^{\bullet} \rightarrow NH_3O^+ + NO_3^- + H^+ \quad (33)$$

The decay of the nitrate radicals is extremely complex,[59] but in a first approximation, we consider the decay as a pseudo-first order and fit the recorded kinetics using a single exponential function. When adding HAN to the solution, we observe a faster decay, with a first order kinetics. The concentration of HAN is too low to be ionized directly and the main reactions of the radicals issued from radiolysis occur with HNO_3, H^+ and NO_3^-. By plotting the observed reaction rates as a function of the HAN concentration (Figure 2 right) we can determine the reaction rate. Based on our measurements, the reaction rate is 1.3×10^5 M^{-1} s^{-1} at 22.5 °C. As expected, at 45ºC, an acceleration of this decay is observed, yielding a reaction rate of 2.6×10^5 M^{-1} s^{-1}.

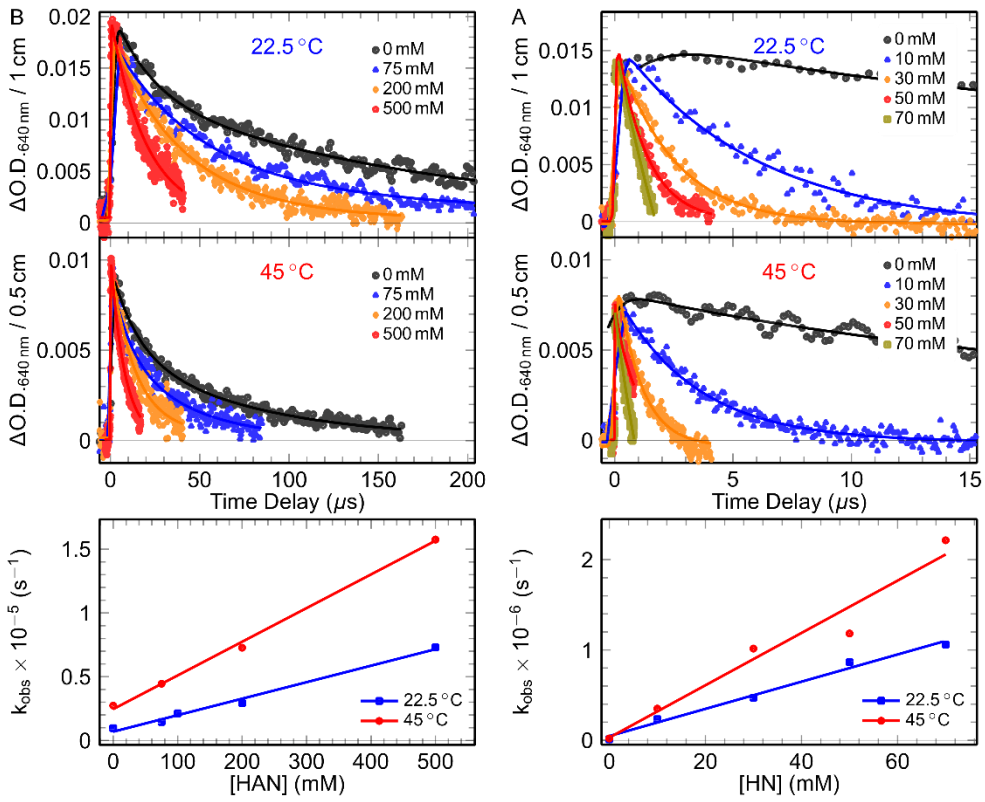


Figure 2. Time evolution of the absorbance at 640 nm, measured at 22.5°C (top image) and 45°C (middle image) in solutions containing different concentrations of hydroxyl ammonium (left) and hydrazinium (right), along with their pseudo-first order fit (Except for the decay at 22.5°C and 45°C in

the absence of HN. In these cases the solid line are drawn to guide the eyes). Observed reaction rates (bottom image) as a function of the concentration of HAN at 22.5°C (black) and 45°C (red).

Reaction between $NO_3^\bullet$ radicals and $N_2H_5^+$

Previous studies gave contradictory values for the reaction rate between hydrazine (N_2H_4) and nitrate radicals: 1.3×10^9 M^{-1} s^{-1};[96] 6.6×10^6 M^{-1} s^{-1}.[97] A previous pulse radiolysis investigation in our group of hydrazine reactivity towards $NO_3^\bullet$ radicals on in 7 M $LiNO_3$, 7 M $LiNO_3$ + 1×10^{-3} M HNO_3 and 6.9 M $LiNO_3$ + 0.1 M HNO_3 allowed the extrapolation of the reaction rates between the two protonated forms of N_2H_4 ($N_2H_5^+$ and $N_2H_6^{2+}$) and $NO_3^\bullet$ radicals: $k_{N_2H_5^+} = 2.9 \times 10^7$ M^{-1} s^{-1} and $k_{N_2H_6^+} = 1.3 \times 10^6$ M^{-1} s^{-1} at room temperature.[59]

The present conditions 1 M HNO_3 + 6 M $LiNO_3$ allow us to select only the $N_2H_5^+$ protonated form of hydrazine in our system, and investigate the reaction:

$$N_2H_5^+ + NO_3^\bullet \rightarrow N_2H_4^{\bullet+} + NO_3^- + H^+ \qquad (34)$$

Figure 2 left presents the change in the $NO_3^\bullet$ absorbance at 640 nm for 1 M HNO_3 + 6 M $LiNO_3$ in the absence and presence of hydrazine. As expected, $N_2H_5^+$ concentration and temperature increase lead to a faster decay of the nitrate radical. From exponential fits of this decay, assuming the decay to be a pseudo-first order decay in the presence of hydrazinium, we can extrapolate the reaction rate constant for this reaction. At room temperature, the reaction rate is 1.5×10^7 M^{-1} s^{-1}, while the temperature increase leads to an acceleration up to 2.9×10^7 M^{-1} s^{-1}. The values we determined are different from the ones previously reported by our group at room temperature (2.9×10^7 M^{-1} s^{-1}) and the differences can arise from the fact that the previous evaluations are based on calculations assuming an arbitrary value of 12.9 for the acid dissociation constant. At the same time, uncertainties over the pKa_2 value (-1) for hydrazine exists, which may have induced errors on the previously reported values. It is interesting to note that the rate constant of the $NO_3^\bullet$ decay is two orders of magnitude faster with hydrazinium (HN) than with HAN, showing a more powerful scavenging efficiency of hydrazinium.

Reaction between $NO_3^\bullet$ radicals and U(IV)

To bind nitrous acid and stabilize the solutions at 45°C, a mixture of 7.7 mM HAN and 0.22 mM HN was added to the solutions of U(IV) to study the reactivity of $NO_3^\bullet$ radicals towards U(IV) in six solutions all containing 1 M HNO_3 + 6 M $LiNO_3$ and with concentrations of U(IV) between 1×10^{-3} and 2×10^{-2} M at the two temperatures.

Following the absorbance decay of nitrate radicals at 640 nm, we observe its faster decay when increasing the U(IV) concentration, indicating the oxidation of U(IV) by nitrate radicals. Using the methodology describe above, we determined the reaction rate constant for this oxidation reaction to be 1.6×10^6 M^{-1} s^{-1}, and 9.3×10^6 M^{-1} s^{-1} at 22.5°C and 45°C, respectively. Note that this value found by direct observation at room temperature is

10 times smaller than previous reported values obtained by numerical simulations of the steady-state radiolytic yields measurements at room temperature (2×10^7 M^{-1} s^{-1}).[71]

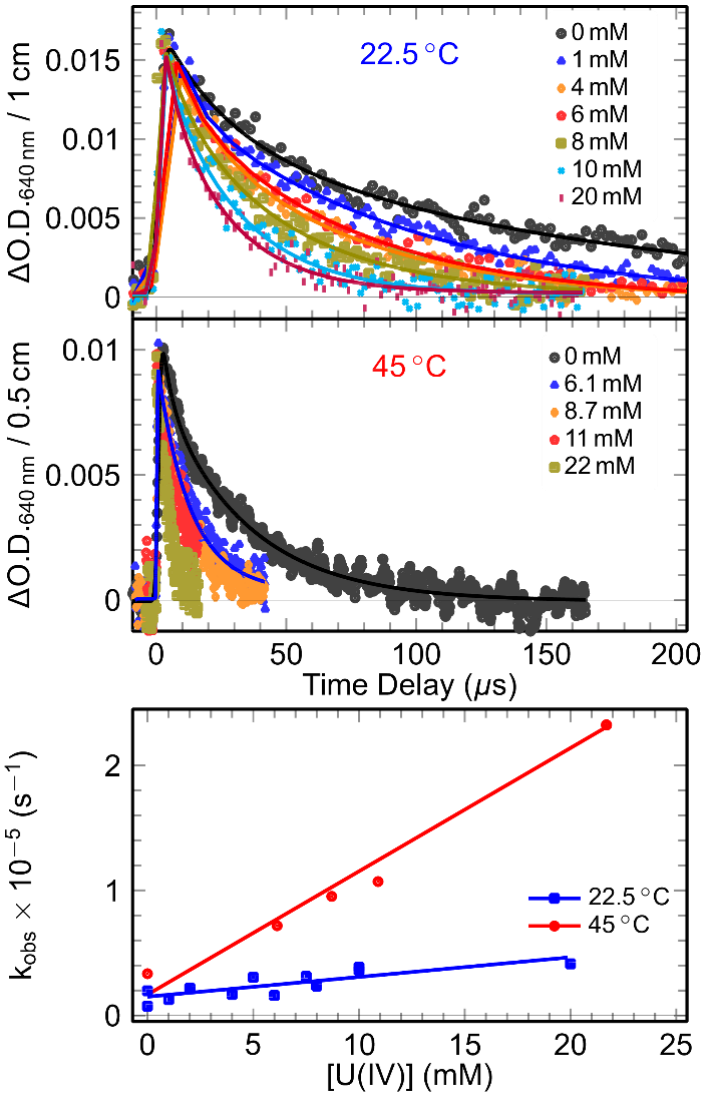


Figure 3. Absorption at 640 nm of $NO_3^{\bullet}$ radicals measured at 22.5°C (top image) and 45°C (middle image) as a function of time from radiolysis of deaerated 1 M HNO_3 + 6 M $LiNO_3$ + 7.7 mM HAN + 0.22 mM HN, with different concentrations of U(IV). Bottom image: observed reaction rates as a function of the concentration of U(IV) at 22.5°C (black) and 45°C (red).

Discussion and Concluding remarks

The behavior of nitric acid solutions under radiation is of great importance in the reprocessing of spent nuclear fuel, and based on the evaluated reaction rates, theoretical models, that can better predict the radiolytic process during the PUREX process, can be developed. These models are critical for defining safe operating practices and controls and engineered safety features. Knowledge gained from radiolytic experiments of HNO_3 solution provides insight on the role of these parameters and their interdependencies in promoting the reactions between $NO_3^{\bullet}$ radicals and the PUREX process main components. The detailed mechanism of nitrate radicals reaction with hydrazinium, hydroxyl ammonium and U(IV) has been elucidated through a pulse radiolysis investigation of HNO_3/$LiNO_3$ 1/6 M solutions at 22.5°C and 45°C. We defined the conditions to stabilize U(IV) in nitrate solution against thermal oxidation while using the smallest possible amounts of HN and HAN that allows us to observe directly the reaction between U(IV) and $NO_3^{\bullet}$ by pulse radiolysis at room temperature and at 45°C. The thus evaluated rate constants are summarized in Table 2.

Table 2. Reaction rate constants measured during this pulse radiolytic investigation of 1 M HNO_3 + 6 M $LiNO_3$ at 22.5 and 45 °C

Reaction	k (M^{-1} s^{-1})		Estimated activation energy (kJ/mol)
	22.5°C	45°C	
$NH_3OH^+ + NO_3^{\bullet}$	1.3×10^5	2.6×10^5	22
$N_2H_5^+ + NO_3^{\bullet}$	1.5×10^7	2.9×10^7	21
$U(IV) + NO_3^{\bullet}$	1.6×10^6	9.3×10^6	56.3

The radical $NO_3^{\bullet}$ is known to oxidize by a one electron transfer reaction. The rate constants obtained for the electron transfer between $NO_3^{\bullet}$ and the three scavengers are all lower that the diffusion limit by several orders of magnitudes, showing the presence of an activation barrier.

At room temperature hydrazinium scavenges the $NO_3^{\bullet}$ radical 100 times faster than hydroxyl ammonium. The reactivity of U(IV) towards $NO_3^{\bullet}$ is 10 time slower than that with hydrazinium and 10 times faster than that with hydroxyl ammonium. For these reasons, it was important to define the optimum concentration ratios to be used in order to observe experimentally the reaction of $NO_3^{\bullet}$ with U(IV).

The direct observation of radical $NO_3^{\bullet}$ in the presence of U(IV), gives us a rate constant at least 10 times lower than the value currently used, which has been estimated by comparing the oxidation rate with other oxidizing radicals. It is clear that this difference with the reported estimated rate constant value cannot be explained by the difference of the ionic strength, because this latter does not strongly affect the kinetics when the solutions have high ionic strength where the Debye law is no longer valid. It is important to note that the oxidation rate constant depends strongly on the complexation state of the ions. For example, it is reported that the rate constant of the oxidation reaction of U(IV) by $OH^{\bullet}$ radicals is 8.6×10^8 M^{-1} s^{-1}. However, it is not possible to

measure this rate constant in highly concentrated nitric solution because $OH^{\bullet}$ is almost entirely scavenged by HNO_3 and U(IV) is no longer in the +IV oxidation state in such solutions. However, it is interesting to compare the rate constant of oxidation by $NO_3^{\bullet}$ with that by $NO_2^{\bullet}$: the reaction rate constant is 10^4 times larger with $NO_3^{\bullet}$ than with $NO_2^{\bullet}$. Note that the oxidation potential of $NO_2^{\bullet}/NO_2^-$ is around 1 V/NHE[98] and that of $NO_3^{\bullet}/NO_3^-$ is close to 2.5 V/NHE.[99] It was reported that the oxidation rate of U(IV) by $SO_4^{\bullet}$ in sulfuric acid is 7×10^7 M^{-1} s^{-1}.[71] When comparing our results, we can conclude that U(IV) is complexed by nitrate ions which is different than complexion by in sulfuric acid, changing the redox potential.

Although reprocessing of spent nuclear fuel occurs at moderate temperatures (close to 45°C for separation steps), up to now, no data on the rate constants of U(IV) oxidation have been reported, due to the complex conditions for direct measurements. The reaction rate constant values are influenced by the temperature and these modification can impact the ratio of the competitive reactions. Therefore, it is important to measure the rate constants at temperatures simulating the separation process conditions. We found that at 45°C, the rate constant of the reaction with hydroxyl ammonium and hydrazinium, is increased by almost a factor of 2. The estimated activation energy should be larger for U(IV), because the rate constant becomes 6 times faster at 45°C compared to 22.5 °C (Table 2).

The results reported show the complexity of the solutions usually used in the spent nuclear fuel reprocessing. The reported data are key input information for the simulations codes dedicated to the radical chemistry of reprocessing process in nuclear industry. The similar approaches should be adapted to study the role of Pu and associated rate constants.

Conflicts of interest

There is no conflict to declare.

Notes and references

(1) Zilberman, B. Y. Application of Purex Process to Highly Burned-up NPP Fuel in Closed Nuclear Fuel Cycle from the Viewpoint of Long-Lived Radionuclide Localization. *Radiochemistry* **2000**, *42* (1), 1–14.

(2) Lee, J. S. *Status and Trends in Spent Fuel Reprocessing*; Nuclear Fuel Cycle and Materials Section; International Atomic Energy Agency: Vienna, Austria, **2005**.

(3) Lovasic, Z. *Spent Fuel Reprocessing Options*; Nuclear Fuel Cycle and Materials Section; International Atomic Energy Agency: Vienna, Austria, **2008**.

(4) *Spent Nuclear Fuel Reprocessing Flowsheet*; Nuclear Science; Technical Report NEA/NSC/WPFC/DOC(2012)15; Nuclear Energy Agency, **2012**; p 122.

(5) Stern, S. A.; Mullhaupt, J. T.; Kay, W. B. The Physicochemical Properties of Pure Nitric Acid. *Chem. Rev.* **1960**, *60* (2), 185–207. https://doi.org/10.1021/cr60204a004.

(6) Miner, F. J.; Kazanjian, A. R.; Brown, Alan K.; Hagan, P. G.; Berry, J. W. *Radiation Chemistry of Nitric Acid Solutions*; U.S. Atomic Energy Commission Contract AT(29-1)-1106; Technical Report RFP-1299; The Dow Chemical Company: United States, **1969**.

(7) *Treatment and Recycling of Spent Nuclear Fuel: Actinide Partitioning - Application to Waste Management*; Parisot, J.-F., France, Eds.; Nuclear Energy Division Monograph; Editions le Moniteur, for the Commissariat à l'Energie Atomique: Paris, France, **2008**.
(8) Lecomte, M.; Bonin, B. *Le traitement-recyclage du combustible nucléaire usé: La séparation des actinides – Application à la gestion des déchets*; CEA - Direction de l'Energie Nucleaire: France, **2015**.
(9) Bugrov, K. V.; Korotaev, V. G.; Korchenkin, K. K.; Logunov, M. V.; Lukin, S. A.; Mashkin, A. N.; Melentev, A. B.; Samarina, N. S. The Development and Testing of the New Flowsheets for the Plutonium Purification Cycle of the Purex Process. *Procedia Chem.* **2016**, *21*, 162–166. https://doi.org/10.1016/j.proche.2016.10.023.
(10) *Encyclopedia of Electrochemistry of the Elements. Vol. 9, Part B: Bi, Cr, Hf, U, Zr, Alkali Metals*; Bard, A. J., Ed.; Marcel Dekker Inc: New York, **1986**; Vol. 9.
(11) *Encyclopedia of Electrochemistry of the Elements. 8: Ag, Ga, Ng, N, Actinides*; Bard, A. J., Lund, H., Eds.; Dekker: New York, **1978**; Vol. 8.
(12) Miner, F. J.; Seed, J. R. Radiation Chemistry of Plutonium Nitrate Solutions. *Chem. Rev.* **1967**, *67* (3), 299–315. https://doi.org/10.1021/cr60247a003.
(13) Spulnik, J. B. The Determination of the Ionization Constant of Hydrazine Hydroxide with the Glass Electrode. Masters Thesis, Oregon State Agricultural College, USA, **1935**.
(14) Ware, G. C.; Spulnik, J. B.; Gilbert, E. C. The Ionization Constant of Hydrazinium Hydroxide. *J. Am. Chem. Soc.* **1936**, *58* (9), 1605–1606. https://doi.org/10.1021/ja01300a028.
(15) Audrieth, L. F.; Ogg, B. A. *The Chemistry of Hydrazine*; John Wiley & Sons, Inc: New York, USA, **1951**.
(16) Mezyk, S. P.; Tateishi, M.; MacFarlane, R.; Bartels, D. M. pK a of the Hydrazinium Ion and the Reaction of Hydrogen Atoms with Hydrazine in Aqueous Solution. *J. Chem. Soc. Faraday Trans.* **1996**, *92* (14), 2541. https://doi.org/10.1039/ft9969202541.
(17) Scharf, U.; Grabner, E. W. Electrocatalytic Oxidation of Hydrazine at a Prussian Blue-Modified Glassy Carbon Eelectrode. *Electrochimica Acta* **1996**, *41* (2), 233–239. https://doi.org/10.1016/0013-4686(95)00259-H.
(18) Neta, P.; Huie, R. E. Rate Constants for Reactions of Nitrogen Oxide (NO3) Radicals in Aqueous Solutions. *J. Phys. Chem.* **1986**, *90* (19), 4644–4648. https://doi.org/10.1021/j100410a035.
(19) Banerjea, D.; Singh, P. Studies on the Hydrazine Complexes of Some Bivalent Metal Ions in Aqueous Solution. *Z. Für Anorg. Allg. Chem.* **1967**, *349* (3–4), 213–219. https://doi.org/10.1002/zaac.19673490314.
(20) Higginson, W. C. E.; Sutton, D.; Wright, P. 282. The Oxidation of Hydrazine in Aqueous Solution. Part I. The Nature of 1- and 2-Electron-Transfer Reactions, With Particular Reference to the Oxidation of Hydrazine. *J. Chem. Soc. Resumed* **1953**, No. 0, 1380–1386. https://doi.org/10.1039/jr9530001380.
(21) Walser, R. L. *The Handford Purex Plant Experience with Reductants*; 1970.
(22) Harrison, J. A.; Khan, Z. A. The Oxidation of Hydrazine on Platinum in Acid Solution. *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, *28* (1), 131–138. https://doi.org/10.1016/S0022-0728(70)80288-1.
(23) Swanson, J. L. Destruction of Nitrous Acid and Hydrozoic Acid in Purex Systems, Pacific Northwest Laboratories, 1971.
(24) McKibben, M. J.; Bercaw, J. E. *Hydroxylamine Nitrate as a Plutonium Reductant in the Purex Solvent Extraction Process*; AEC Research and Development Report DP-1248; Savannah River Laboratory: United States, **1971**.
(25) McKibben, M. J.; Chostner, D. F.; Orebaugh, E. G. *Plutonium-Uranium Separation in the Purex Process Using Mixtures of Hydroxylamine Nitrate and Ferrous Sulfamate*; DE-AC09-76SR00001; Technical Report DP-1656; E. I. du Pont de Nemours & Co.; Savannah River Laboratory: United States, **1983**.
(26) McKibben, M. J. Chemistry of the Purex Process. *Radiochim. Acta* **1984**, *36* (1/2), 3–15.
(27) Harlow, D. G.; Felt, R. E.; Agnew, S.; Barney, S. G.; McKibben, M. J.; Garber, R.; Lewis, M. *Technical Report on Hydroxylamine Nitrate*; Technical Report DOE/EH-0555; US Department of Energy: United States, **1998**.

(28) McFarlane, J.; Delmau, L. H.; DePaoli, D. W.; Mattus, C. H.; Phelps, C. E.; Roach B. D. *Hydroxylamine Nitrate Decomposition under Non-Radiological Conditions*; Technical Report ORNL/TM-2015/156; Oak Rodge National Laboratory: United States, **2015**.
(29) Richardson, G. L.; Swanson, J. L. *Plutonium Partitioning in the Purex Process Qith Hydrazine-Stabilized Hydroxylamine Nitrate*; HEDL-TME--75-31; Hanford Engineering Development Laboratory: United States, **1975**; p 92.
(30) Bennett, M. R.; Maya, L.; Brown, G. M.; Posey, F. A. Oxidation of Hydroxylamine by Nitrous and Nitric Acids. *Inorg. Chem.* **1982**, *21* (6), 2461–2468. https://doi.org/10.1021/ic00136a066.
(31) Gowland, R. J.; Stedman, G. Kinetic and product studies on the decomposition of hydroxylamine in nitric acid RORY. *J. Inorg. Nucl. Chem.* **1981**, *43* (11), 2859–2862.
(32) Hughes, M. N. Kinetic Study of the Reaction Between Nitrous Acid and Sulphamic Acid. *J. Chem. Soc. Inorg. Phys. Theor.* **1967**, No. 0, 902–905. https://doi.org/10.1039/j19670000902.
(33) Vladimirova, M. V. Alpha Radiolysis of Aqueous Solutions. *Russ. Chem. Rev.* **1964**, *33* (4), 212–220.
(34) Vladimirova, M. V. Mathematical-modeling of the radiation-chemical oxidation of U(IV) in HCLO4. *Radiochemistry* **1995**, *37* (5), 422–428.
(35) Vladimirova, M. V.; Khaperskaya, A. V. Mechanism and Kinetics of Rh(IV) Radiation-Chemical Reduction in HNO3 Solutions. *Radiochemistry* **2003**, *45* (1), 33–39. https://doi.org/10.1023/A:1022313300868.
(36) Ikeda-Ohno, A.; Hennig, C.; Tsushima, S.; Scheinost, A. C.; Bernhard, G.; Yaita, T. Speciation and Structural Study of U(IV) and -(VI) in Perchloric and Nitric Acid Solutions. *Inorg. Chem.* **2009**, *48* (15), 7201–7210. https://doi.org/10.1021/ic9004467.
(37) Ondrejcin, R. S. *Preparation of Uranium (IV) Nitrate Solutions*; AT(07-2)-l; Technical Report DP-602; E. I. du Pont de Nemours & Co.; Savannah River Laboratory: United States, **1961**; p 13.
(38) Slade, A. L. *Oxidation of Uranium (IV) by Oxygen and Nitrous Acid*; **1961**.
(39) Schlea, C. S.; Caverly, M. R.; Henry, H. E.; Jenkins, W. J. *Uranium(IV) Nitrate as a Reducing Agent for Plutonium(IV) in the PUREX Process*; CONTRACT AT (07-2)-1; DP-808; Savannah River Laboratory: United States, **1963**.
(40) McKay, H. A. C.; Streeton, R. J. W. Extraction of Uranium (IV) Nitrate by Tri-N-Butyl Phosphate and by Dibutyl Carbitol. *J. Inorg. Nucl. Chem.* **1965**, *27* (4), 879–884. https://doi.org/10.1016/0022-1902(65)80450-X.
(41) Salomon, L.; Lopez-Menchero, E. Optimization of the Aqueous Processing of Irradiated Fuel from Nuclear Power Reactors. Use of Uranium(IV) Nitrate as Reductant in a Purex Type Processing Plant. *Ind. Eng. Chem. Process Des. Dev.* **1970**, *9* (3), 345–358. https://doi.org/10.1021/i260035a001.
(42) Zhou, Z.-M.; Zhang, Y.-J.; Du, H.-F. Kinetic Studies on the Oxidation of Uranium (IV) in Nitric Acid Solution. *J. Radioanal. Nucl. Chem.* **1994**, *188* (3), 177–187.
(43) Fedorov, Y. S.; Zilberman, B. Y.; Kopyrin, A. A.; Arkhipov, S. A. Uranium(IV) Complexes Formed in Extraction with Tributyl Phosphate from Nitric Acid Solutions. *Radiochemistry* **2001**, *43* (2), 166–171.
(44) Mahlman, H. A. The OH Yield in the Co60 γ Radiolysis of HNO3. *J. Chem. Phys.* **1961**, *35* (3), 936–939. https://doi.org/10.1063/1.1701241.
(45) Broszkiewicz, R. K. The Radiation-Induced Formation of NO_3 in Aqueous Solutions. *Int. J. Appl. Radiat. Isot.* **1967**, *18*, 25–32.
(46) Daniels, M. Radiation Chemistry of the Aqueous Nitrate System. III. Pulse Electron Radiolysis of Concentrated Sodium Nitrate Solutions. *J. Phys. Chem.* **1969**, *73* (11), 3710–3717. https://doi.org/10.1021/j100845a027.
(47) Kazanjian, A. R.; Miner, F. J.; Brown, A. K.; Hagan, P. G.; Berry, J. W. Radiolysis of Nitric Acid Solution : L.E.T. Effects. *Trans. Faraday Soc.* **1970**, *66*, 2192–2198. https://doi.org/10.1039/tf9706602192.
(48) Bhattacharyya, P. K.; Saini, R. D. Radiolytic Yields G(HNO2) and G(H2O2) in the Aqueous Nitric Acid System. *Int. J. Radiat. Phys. Chem.* **1973**, *5*, 91–99.
(49) Kozlowska-Milner, E.; Broszkiewicz, R. K. Pulse Radiolysis of HNO_3 and HNO_3(aq). *Radiat. Phys. Chem.* **1978**, *11*, 253–260.
(50) Nagaishi, R.; Jiang, P. Y.; Katsumura, Y.; Domae, M.; Ishigure, K. Radiolysis of Concentrated Nitric Acid Solutions. In *JAERI-conference*; **1995**; Vol. 1, pp 194–198.

(51) Mezyk, S. P.; Cullen, T. D.; Elias, G.; Mincher, B. J. Aqueous Nitric Acid Radiation Effects on Solvent Extraction Process Chemistry. In *Nuclear Energy and the Environment*; Wai, C. M., Mincher, B. J., Eds.; American Chemical Society: Washington, DC, **2010**; Vol. 1046, pp 193–203.
(52) Horne, G. P.; Donoclift, T. A.; Sims, H. E.; Orr, R. M.; Pimblott, S. M. Multi-Scale Modeling of the Gamma Radiolysis of Nitrate Solutions. *J. Phys. Chem. B* **2016**, *120* (45), 11781–11789. https://doi.org/10.1021/acs.jpcb.6b06862.
(53) Horne, G. P.; Gregson, C. R.; Sims, H. E.; Orr, R. M.; Taylor, R. J.; Pimblott, S. M. Plutonium and Americium Alpha Radiolysis of Nitric Acid Solutions. *J. Phys. Chem. B* **2017**, *121* (4), 883–889. https://doi.org/10.1021/acs.jpcb.6b12061.
(54) Katsumura, Y.; Jiang, P. Y.; Nagaishi, R.; Oishi, T.; Ishigure, K. Pulse Radiolysis Study of Aqueous Nitric Acid Solutions. Formation Mechanism, Yield, and Reactivity of ˙NO3 Radical. *J. Phys. Chem.* **1991**, *95* (11), 4435–4439. https://doi.org/10.1039/FT9949000093.
(55) Balcerzyk, A.; El Omar, A. K.; Schmidhammer, U.; Pernot, P.; Mostafavi, M. Picosecond Pulse Radiolysis Study of Highly Concentrated Nitric Acid Solutions: Formation Mechanism of $NO_3^{\bullet}$ Radical. *J. Phys. Chem. A* **2012**, *116* (27), 7302–7307. https://doi.org/10.1021/jp304429f.
(56) Musat, R.; Denisov, S. A.; Marignier, J. L.; Mostafavi, M. Decoding the Three-Pronged Mechanism of NO 3˙ Radical Formation in HNO3 Solutions at 22 and 80 °c Using Picosecond Pulse Radiolysis. *J. Phys. Chem. B* **2018**, *122* (7), 2121–2129. https://doi.org/10.1021/acs.jpcb.7b12702.
(57) Daniels, M. Radiolysis and Photolysis of the Aqueous Nitrate System. In *Radiation Chemistry*; Hart, E. J., Ed.; Advances in Chemistry; American Chemical Society: Washington, D. C., **1968**; Vol. 81, pp 153–163.
(58) Kozlowska-Milner, E. Réactivité de “trous” En Radiolyse Pulsée Des Solutions Nitrates En Présence D’acides. *Int. J. Rad. Appl. Instrum. [A]* **1987**, *38* (7), 517–520.
(59) Garaix, G.; Horne, G. P.; Venault, L.; Moisy, P.; Pimblott, S. M.; Marignier, J. L.; Mostafavi, M.; Michael G. MacNaughton, Gregory A. Urda, S. E. B.; Mezyk, S. P.; Tateishi, M.; et al. Decay Mechanism of NO3• Radical in Highly Concentrated Nitrate and Nitric Acidic Solutions in the Absence and Presence of Hydrazine. *J. Phys. Chem. B* **2016**, *120* (22), 5008–5014. https://doi.org/10.1021/acs.jpcb.6b02915.
(60) Broszkiewicz, R. K. The Radiation-Induced Formation of NO3 in Aqueous Solutions. *Int. J. Appl. Radiat. Isot.* **1966**, *18*, 25–32.
(61) Daniels, M. Pulse Radiolysis of the Aqueous Nitrate System. Formation of NO_3 in Concentrated Solutions and the Mechanism of “Direct Action” ^{1}. *J. Phys. Chem.* **1966**, *70* (9), 3022–3024. https://doi.org/10.1021/j100881a514.
(62) Pimblott, S. M.; LaVerne, J. A. On the Radiation Chemical Kinetics of the Precursor to the Hydrated Electron. *J. Phys. Chem. A* **1998**, *102* (17), 2967–2975. https://doi.org/10.1021/jp980496v.
(63) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (·OH/·O−in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, *17* (2), 513–886. https://doi.org/10.1063/1.555805.
(64) Loegager, T.; Sehested, K. Formation and Decay of Peroxynitric Acid: A Pulse Radiolysis Study. *J Phys Chem* **1993**, *97* (39), 10047–10052. https://doi.org/10.1021/j100141a025.
(65) Furuhama, A.; Dupuis, M.; Hirao, K. Reactions Associated with Ionization in Water: A Direct *Ab Initio* Dynamics Study of Ionization in (H2O)17. *J. Chem. Phys.* **2006**, *124* (16), 164310. https://doi.org/10.1063/1.2194904.
(66) Marsalek, O.; Elles, C. G.; Pieniazek, P. A.; Pluhařová, E.; VandeVondele, J.; Bradforth, S. E.; Jungwirth, P. Chasing Charge Localization and Chemical Reactivity Following Photoionization in Liquid Water. *J. Chem. Phys.* **2011**, *135* (22), 224510. https://doi.org/10.1063/1.3664746.
(67) Jonah, C. D.; Miller, J. R.; Matheson, M. S. The Reaction of Hydrated Electron + Oxonium. Concentration Effects of Acid or Salts. *J. Phys. Chem.* **1977**, *81* (9), 931–934. https://doi.org/10.1021/j100524a026.
(68) Johnston, H. S.; Chang, S.-G.; Whitten, G. Photolysis of Nitric Acid Vapor. *J. Phys. Chem.* **1974**, *78* (1), 1–7. https://doi.org/10.1021/j100594a001.
(69) Jiang, P. Y.; Katsumura, Y.; Ishigure, K.; Yoshidalb, Y. Reduction Potential of the Nitrate Radical in Aqueous Solution. *Inorg. Chem.* **1992**, *31* (24), 5135–5136. https://doi.org/10.1021/ic00050a038.

(70) Poskrebyshev, G. A.; Neta, P.; Huie, R. E. Equilibrium Constant of the Reaction ·OH + $HNO_3 \leftrightarrows H_2O + NO_3$. in Aqueous Solution. *J. Geophys. Res. Atmospheres* **2001**, *106* (D5), 4995–5004. https://doi.org/10.1029/2000JD900702.

(71) Nagaishi, R. A Model for Radiolysis of Nitric Acid and Its Application to the Radiation Chemistry of Uranium Ion in Nitric Acid Medium. *Radiat. Phys. Chem.* **2001**, *60* (4–5), 369–375. https://doi.org/10.1016/S0969-806X(00)00410-2.

(72) Shilov, V. P.; Gogolev, A. V; Fedoseev, A. M.; Pikaev, A. K. Rate Constant Evaluation for the Reaction of H Atoms with U(V) upon Radiolysis of Aqueous Acid Solutions of Uranium Ions. *Khimiya Vysok. Energii* **1994**, *28* (2), 114–116.

(73) Koltunov, V. S.; Taylor, R. J.; Marchenko, V. I.; Dvoeglazov, K. N.; Savilova, O. A.; May, I. The Oxidation of U(IV) by Nitric Acid in 30% Tri-Butyl Phosphate Solutions. *Radiochim. Acta* **1999**, *86*, 41–49. https://doi.org/10.1524/ract.1999.86.12.41.

(74) Taylor, R. J.; Koltunov, V. S.; Marchenko, V. I.; Denniss, I. S.; Broan, C. J.; Dvoeglazov, K. N.; Savilova, O. A. Studies of U(IV) Oxidation Kinetics in Nitric Acid and TBP Phases. *J. Nucl. Sci. Technol.* **2002**, *39* (sup3), 355–358. https://doi.org/10.1080/00223131.2002.10875482.

(75) Koltunov, V. S.; Marchenko, V. I.; Zhuravleva, G. I.; Savilova, O. A. Kinetics of Redox Reactions of U, Pu, and Np in TBP Solutions: VII. Kinetics of Reduction of Pu(IV) and Np(VI) with Butanal Oxime in Undiluted TBP. *Radiochemistry* **2001**, *43* (1), 334–337.

(76) Bhat, T. R.; Mathur, B. S. Studies on the Preparation and Properties of Uranium(IV) Nitrate. *Indian J. Technol.* **1963**, *1*, 14–19.

(77) Lopez-Menchero, E.; Salomon, L.; Bardone, G. *Study of Uranium (IV) as Reducing Agent for Plutonium IIa - Stability of Uranium (IV) in Solution*; Technical Report ETR No. 181; United States, **1966**.

(78) Ermolayev, N. P.; Krot, N. N. Some Data on Behaviour of U(IV) in Nitric Acid Solutions,. *Radiokhimiya* **1962**, *6* (4), 678--685.

(79) Honma, S.; Hashimoto, T.; Takanashi, M.; Koga, J.; Matsumoto, S. *Reaction D'oxydation de L'uranium Tetravalent Dans Les Solutions D'acide Nitrique*; Conference Report JAERI Conf. 96-013; Saitama University: Japon, **1996**.

(80) Pikaev, A. K.; Shilov, V. P.; Gogolev, A. V. Radiation Chemistry of Aqueous Solutions of Actinides. *Russ. Chem. Rev.* **1997**, *66* (9), 763–788. https://doi.org/10.1070/RC1997v066n09ABEH000284.

(81) National Research Council (U.S.); Washburn, E. W.; West, C. J.; Dorsey, N. E. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, 1st electronic edition.; Knovel: Norwich, N.Y., **1926**; Vol. 3.

(82) Belloni, J.; Monard, H.; Gobert, F.; Larbre, J.-P.; Demarque, A.; De Waele, V.; Lampre, I.; Marignier, J.-L.; Mostafavi, M.; Bourdon, J. C.; et al. ELYSE—A Picosecond Electron Accelerator for Pulse Radiolysis Research. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2005**, *539* (3), 527–539. https://doi.org/10.1016/j.nima.2004.11.006.

(83) Marignier, J.-L.; de Waele, V.; Monard, H.; Gobert, F.; Larbre, J.-P.; Demarque, A.; Mostafavi, M.; Belloni, J. Time-Resolved Spectroscopy at the Picosecond Laser-Triggered Electron Accelerator ELYSE. *Radiat. Phys. Chem.* **2006**, *75* (9), 1024–1033. https://doi.org/10.1016/j.radphyschem.2005.10.020.

(84) Muroya, Y.; Lin, M.; Wu, G.; Iijima, H.; Yoshii, K.; Ueda, T.; Kudo, H.; Katsumura, Y. A Re-Evaluation of the Initial Yield of the Hydrated Electron in the Picosecond Time Range. *Radiat. Phys. Chem.* **2005**, *72* (2–3), 169–172. https://doi.org/10.1016/j.radphyschem.2004.09.011.

(85) Torche, F.; Marignier, J.-L. Direct Evaluation of the Molar Absorption Coefficient of Hydrated Electron by the Isosbestic Point Method. *J. Phys. Chem. B* **2016**, *120* (29), 7201–7206. https://doi.org/10.1021/acs.jpcb.6b04796.

(86) Kraus, K. A.; Nelson, F. Hydrolytic Behavior of Metal Ions. I. The Acid Constants of Uranium(IV) and Plutonium(IV) [1]. *J. Am. Chem. Soc.* **1950**, *72* (9), 3901–3906. https://doi.org/10.1021/ja01165a020.

(87) Cohen, D.; Carnall, W. T. Absorption Spectra of Uranium(III) and Uranium(IV) in DClO4 Solution. *J. Phys. Chem.* **1960**, *64* (12), 1933–1936. https://doi.org/10.1021/j100841a031.

(88) Wilson, A. S.; Keder, W. E. The Extraction of Uranium(IV) from Nitric Acid by Tri-N-Octylamine. *J. Inorg. Nucl. Chem.* **1961**, *18*, 259–262. https://doi.org/10.1016/0022-1902(61)80395-3.

(89) Gutniak, S.; Taube, M. Electronic Absorption Spectra of Uranium (IV) Chlorides in Some Organic Solvents and Fused Chlorides. *Spectrochim. Acta* **1964**, *20* (10), 1627–1632. https://doi.org/10.1016/0371-1951(64)80142-9.

(90) Bagnall, K. W.; Brown, D. The Absorption Spectra of protactinium(IV) and uranium(IV) in Aqueous Hydrochloric Acid. *J. Chem. Soc. Inorg. Phys. Theor.* **1967**, 275–278. https://doi.org/10.1039/j19670000275.

(91) Bürck, J. Spectrophotometric Determination of Uranium and Nitric Acid by Applying Partial Least-Squares Regression to uranium(VI) Absorption Spectra. *Anal. Chim. Acta* **1991**, *254* (1–2), 159–165. https://doi.org/10.1016/0003-2670(91)90022-W.

(92) Tutschku, J.; Hennig, C.; Geipel, G.; Bernhard, G. *UV-Vis Measurements of Uranium(VI) and Uranium(IV) in Concentrated Chloride Solution Prepared with the Electrochemical Cell*; International Nuclear Information System; Annual Report FZR – IRC Annual Report 2004; International Atomic Energy Agency, **2004**.

(93) Takao, K.; Kazama, H.; Ikeda, Y.; Tsushima, S. Crystal Structure of Regularly Th-Symmetric [U(NO3)6]2− Salts with Hydrogen Bond Polymers of Diamide Building Blocks. *Angew. Chem.* **2019**, *131* (1), 246–249. https://doi.org/10.1002/ange.201811731.

(94) Raman, S.; Ashcraft, R. W.; Vial, M.; Klasky, M. L. Oxidation of Hydroxylamine by Nitrous and Nitric Acids. Model Development from First Principle SCRF Calculations. *J. Phys. Chem. A* **2005**, *109* (38), 8526–8536. https://doi.org/10.1021/jp053003c.

(95) Pembridge, J. R.; Stedman, G. Kinetics, Mechanism, and Stoichiometry of the Oxidation of Hydroxylamine by Nitric Acid. *J. Chem. Soc. Dalton Trans.* **1979**, No. 11, 1657. https://doi.org/10.1039/dt9790001657.

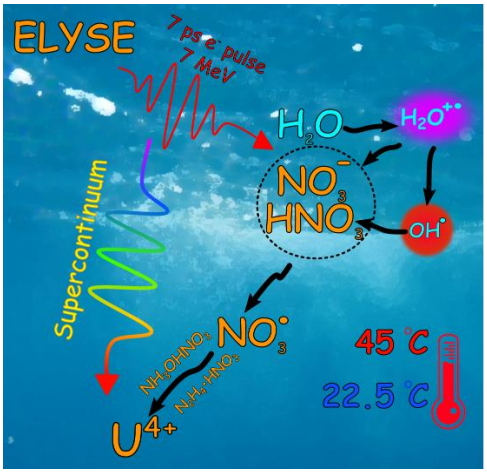
(96) Belova, E. V.; Egorov, G. F. Radiolytic Behaviour of Hydrazine Nitrate in Aqueous Solutions of Nitric Acid. *At. Energy* **1997**, *83* (2), 622–626.

(97) Protasova, E. L.; Khaikin, G. I. Nitrogen Trioxide in Irradiated Aqueous Nitric Acid Solutions of Hydrazine. *High Energy Chem.* **2001**, *35* (4), 219–223. https://doi.org/10.1023/A:1017676326298.

(98) Shafirovich, V.; Cadet, J.; Gasparutto, D.; Dourandin, A.; Geacintov, N. E. Nitrogen Dioxide as an Oxidizing Agent of 8-Oxo-7,8-Dihydro-2‘-Deoxyguanosine but Not of 2‘-Deoxyguanosine. *Chem. Res. Toxicol.* **2001**, *14* (2), 233–241. https://doi.org/10.1021/tx000204t.

(99) Armstrong, D. A.; Huie, R. E.; Koppenol, W. H.; Lymar, S. V.; Meréni, G.; Neta, P.; Ruscic, B.; Stanbury, D. M.; Steenken, S.; Wardman, P. *Standard Electrode Potentials Involving Radicals in 5 Aqueous Solution: Inorganic Radicals*; IUPAC Task Group on Radical Electrode Potentials; Technical Report BNL-111793-**2016**-JA; PAC-REP-14-05-02; IUPAC Technical Report: 5/12/2009.

TOC


ELYSE
7 ps e⁻ pulse
7 MeV
H2O
H2O+•
NO3−
HNO3
OH•
Supercontinuum
NO3•
NH4OH+NO3•
N2H4+HNO3•
U4+
45 °C
22.5 °C