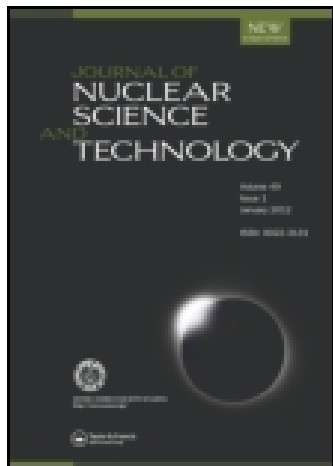


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Journal of Nuclear Science and Technology

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/tnst20>

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Published online: 27 Aug 2014.

To cite this article: Robin J. Taylor, Valentin S. Koltunov, Valery I. Marchenko, Iain S. Denniss, Chris J. Broan, Konstantin N. Dvoeglazov & Olga A. Savilova (2002) Studies of U(IV) Oxidation Kinetics in Nitric Acid and TBP Phases, Journal of Nuclear Science and Technology, 39:sup3, 355-358, DOI: [10.1080/00223131.2002.10875482](https://doi.org/10.1080/00223131.2002.10875482)

To link to this article: <http://dx.doi.org/10.1080/00223131.2002.10875482>

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Studies of U(IV) Oxidation Kinetics in Nitric Acid and TBP Phases

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U(IV) is an important reagent in current reprocessing plants since it is used to reduce Pu(IV) to Pu(III), therefore, allowing the efficient separation of U and Pu in multi-stage counter-current solvent extraction contactors. The benefits of U(IV) are that it is a kinetically fast reductant and it is a salt free reagent, since U(IV) is oxidised to U(VI) and so does not add to the aqueous waste volumes. Many kinetic reactions of U(IV) have been studied in the past and these are used by BNFL to model the behaviour of U(IV) in process flowsheets. However, some reactions have either not been studied or have been previously studied but without conclusive resolution. Therefore, to expand our understanding of U(IV) in the process and to generate data that underpins process models, we are studying a series of U(IV) reactions, and this paper will summarise the results of our kinetic and mechanistic studies.

KEYWORDS: *uranous nitrate, kinetics, oxidation, reduction, technetium, Purex process*

I. Introduction

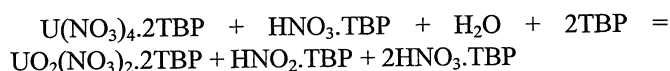
The reducing agent, uranous (IV) nitrate, is commonly used to separate U and Pu in Purex reprocessing flowsheets¹⁾. Separation is achieved by the reduction of Pu(IV) to Pu(III) by U(IV) and the consequent stripping of inextractable Pu(III) from the solvent tributyl phosphate phase to the aqueous nitric acid phase. A complicating factor is that Pu(III) is not stable and is reoxidised by nitric acid, in a process catalysed by nitrous acid, back to extractable Pu(IV). To prevent loss of Pu(III), a stabiliser such as hydrazine is also added to the system. This stabiliser removes nitrous acid rapidly thus interrupting the catalytic reoxidation. As well as reducing Pu(IV), U(IV) also reacts with other species which are present, including Np(VI) and Tc(VII). Like Pu(III), U(IV) can be oxidised by HNO₃ catalysed by HNO₂. It is also well known that hydrazine participates in catalytic reaction cycles with Tc²⁾. Finally, species are partitioned between aqueous and solvent phases and so kinetic reactions can occur in both phases. Although much data on the reactions of U(IV) are available, some reactions have either not been studied or studied without definitive conclusion. In order to improve our understanding of U(IV) systems and to provide data which underpins process models, BNFL and VNIINM in collaboration have undertaken a series of kinetic investigations. This paper summarises the results to date of this work³⁾.

II. EXPERIMENTAL METHODS

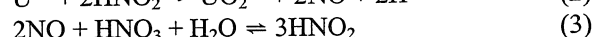
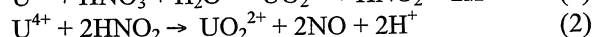
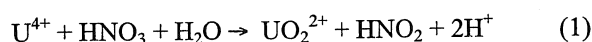
The experimental methods used have been described in detail elsewhere⁴⁻⁸⁾.

III. RESULTS AND DISCUSSION

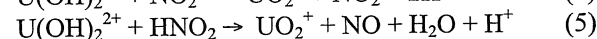
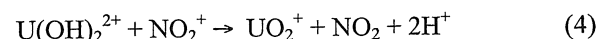
1. U(IV) Oxidation by HNO₃ in 30 % TBP Solution⁴⁾



In the oxidation of U(IV) by nitric acid in 30 % TBP there is an initial induction period, in which oxidation by HNO₃ occurs producing HNO₂, and then an autocatalytic reaction, in which U(IV) is oxidised by the resultant HNO₂. The reaction is represented by equations (1-3) below (ignoring TBP complexation).



The mechanism of the non-catalytic reaction (Eq. 1) is difficult to understand but it is possible that it involves the second hydrolysis product interacting with nitronium ions (NO₂⁺) [Eq. 4]. The rate of the autocatalytic reaction (Eq. 2) is reduced at increased [HNO₃] which can be explained by U(IV) hydrolysis, which increases as acidity decreases. The evidence is that the autocatalytic reaction is via the second hydrolysis product (U(OH)₂(NO₃)₂) [Eq. 5].



For the first time, reproducible and predictable data on U(IV) oxidation in TBP have been obtained and the rate equation is described by:

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$$-\frac{d[U(IV)]}{dt} = k_1[U(IV)][HNO_3]^2 + k \frac{[U(IV)][HNO_2]}{[HNO_3]^2 + \beta_1'[HNO_3] + \beta_2'}$$

Where: $k_1 \approx 0.3 \text{ M}^{-2}\text{min}^{-1}$; $k = 0.125 \pm 0.020 \text{ Mmin}^{-1}$; $\beta_1' = 0.03 \text{ M}$ and $\beta_2' = 0.006 \text{ M}^2$ at $T = 55 \text{ }^\circ\text{C}$; $[H_2O] = 0.44 \text{ M}$, within the acidity range $[HNO_3] = 0.05 - 0.3 \text{ M}$. The hydrolysis products are defined as $\beta_1' = \beta_1[H_2O]$; $\beta_2' = \beta_2[H_2O]^2$. Activation energies of reactions (1) and (2) are $E_1 = 103 \pm 15$ and $E_2 = 93 \pm 5 \text{ kJmol}^{-1}$. The calculated activation enthalpies and entropies at 298 K are given in Table 1. Attention is drawn to the fact that the activation entropies for both the U(IV) oxidation reaction routes are close to zero.

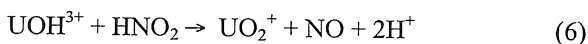
Table 1 Activation enthalpies and entropies at 298K

Reaction	ΔH^* (kJmol ⁻¹)	ΔS^* (Jmol ⁻¹ K ⁻¹)
U(IV) + HNO ₃ in 30 % TBP	101	~ -6
U(IV) + HNO ₂ (catalytically produced) in 30 % TBP	90	~ 4
U(IV) + HNO ₂ (direct reaction) in 30 % TBP	109	43
Np(VI) + U(IV) in HClO ₄ ¹²⁾	76.1	36
Np(VI) + U(IV) in HNO ₃	64.0	2
Np(VI) + U(IV) in 30 % TBP	64.1	- 26
Np(V) + U(IV) in 30 % TBP	86.5	~ 21

2. U(IV) Oxidation by HNO₂ in 30 % TBP Solution

To provide further information about the interaction of U(IV) and HNO₂ in TBP, this reaction was studied by introducing HNO₂ directly in to the reactive system, rather than just letting it accumulate through the autocatalytic reaction initiated by HNO₃. Except when $[HNO_2]$ was very low, no induction period was observed in these experiments. Kinetic analyses of the data showed that the reaction is first order with respect to U(IV) and HNO₂. The order relative to H₂O is 0.8, which is within the range suggested in the study of the reaction with HNO₃ above, i.e. 0.5 to 2.5 depending on HNO₃ concentration. A variable order between ~ -0.5 and ~ -0.85 was observed for HNO₃, which differs slightly from the situation observed in the autocatalytic reaction with HNO₃ where the order varied between ~ -0.8 and ~ -3.5.

These similarities and differences lead us to the hypothesis that the reaction mechanism has changed from proceeding via the second hydrolysis product (Eq. 5), in the HNO₃ autocatalytic oxidation, to one proceeding via the first hydrolysis product in this direct U(IV) – HNO₂ reaction (Eq. 6).



Accounting for this mechanism, ultimately, the rate equation was described by the equation:

$$-\frac{d[U(IV)]}{dt} = k \frac{[U(IV)][HNO_2][HNO_3][H_2O]}{[HNO_3]^2 + \beta_1[HNO_3][H_2O] + \beta_2[H_2O]^2}$$

The rate constant is $k = 0.405 \pm 0.055 \text{ M}^{-1}\text{min}^{-1}$ at $55 \text{ }^\circ\text{C}$ ($\beta_1 \approx 0.08$ and $\beta_2 \approx 0.007$) and the activation energy is $112 \pm 17 \text{ kJmol}^{-1}$, which is close to that previously determined ($93 \pm 5 \text{ kJmol}^{-1}$). However, as can be seen from Table 1, the activation entropy is higher.

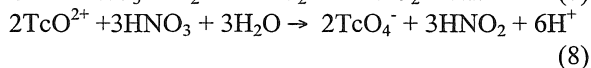
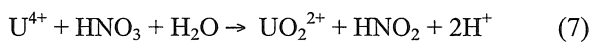
The overall conclusion to be drawn from this and the previous section is that the U(IV) – HNO₂ reaction proceeds in two parallel routes via UOH^{3+} or $U(OH)_2^{2+}$ species depending on the concentration of HNO₂. However, further analysis of this theory shows that the kinetics can not be wholly explained by this combination of reaction routes. It is tentatively suggested that the composition of the HNO₂.TBP complex is also important with cis and trans forms⁹⁾ having different reactivities for U(IV) ions. The fact that the activation energies determined in both studies are close supports the suggestion that the difference in rates is due to entropy changes governed by steric features of the reacting species.

3. U(IV) Oxidation in the Presence of Tc(VII) and Hydroxylamine (and NH₂OH/N₂H₄ Blends) in HNO₃

Previous papers have reported the reactions of Tc(VII) ions with hydroxylamine in HCl and HNO₃ – in the absence and presence of HNO₂⁵⁻⁷⁾. These reactions are very slow and are really governed by the well known oxidation reactions of hydroxylamine with HNO₃ and HNO₂ (see ⁷⁾ and references therein). Hence, at lower temperatures and acidities TcO_4^- is essentially stable in the presence of hydroxylamine. Furthermore, U(IV) solutions in HNO₃ are stabilised by hydroxylamine, and in perchloric acid U(IV) is known to rapidly reduce Tc(VII)¹⁰⁾. However, when Tc(VII) is added to solutions containing U(IV)/hydroxylamine in HNO₃, an unusual series of reactions are observed. Initially, there is a rapid oxidation of U(IV) followed by a slower zero order reaction which then speeds up towards the end of the oxidation. This situation is very different from the well known Tc(VII) catalysed oxidation of hydrazine²⁾. The addition of U(IV) to Tc – hydrazine solutions only eliminates the induction period by reducing Tc(VII) to a lower oxidation state more rapidly than N₂H₄. After this the reaction mechanism is essentially unchanged.

Clearly, this system is very complex¹¹⁾ but we have derived a kinetic equation for the slower zero order reaction under conditions in which hydroxylamine is a net scavenger of HNO₂ rather than a net generator. It is thought that HNO₂ is essentially unavailable at this point in the reaction schema, because it is scavenged by hydroxylamine, and that the U(IV) + Tc(VII) reaction is rapid. The slow rate determining reactions are, therefore, considered to be the HNO₃ oxidations of U(IV) and Tc(IV) (Eqs. 7-8). Kinetic analysis of the experimental data leads to the derivation of a rate

equation¹¹) where, respectively, $k_8 = (2.8 \pm 0.10) \times 10^{-3} \text{ l}^{1.05} \text{ mol}^{-1.05} \text{ min}^{-1}$; $k_9 = 123 \pm 10 \text{ l}^{2.4} \text{ mol}^{-2.4} \text{ min}^{-1}$ at 35 °C and $E_8 = 73 \pm 3$; $E_9 = 86 \pm 2 \text{ kJmol}^{-1}$. As the overall oxidation reaction proceeds, the initial U(IV) term in Eq. (9) decreases in importance, the Tc(IV) oxidation reaction becomes solely rate determining and the reaction tends towards zero order relative to U(IV).



$$-\frac{d[\text{U(IV)}]}{dt} = \frac{k_8[\text{U(IV)}][\text{HNO}_3]^{1.05}}{k_9[\text{Tc(IV)}]^{1.8}[\text{HNO}_3]^{1.6}} \quad (9)$$

One complicating factor is that if hydrazine is added to the U(IV) – Tc(VII) – hydroxylamine system then the rate of U(IV) oxidation is reduced. In particular, the initial rapid reaction is almost eliminated. It may be that hydrazine is interrupting the reaction cycles by rapidly scavenging HNO_2 , if HNO_2 is a reaction intermediate, or it may be that this system has a different set of reactions altogether. Much further work is needed to understand the complex reaction mechanisms of U(IV) – Tc – hydroxylamine reactions in the absence and presence of N_2H_4 , particularly the verification of reaction intermediates.

4. Np(VI) Reduction by U(IV) in HNO_3

Although this rapid reaction has been studied in perchloric acid¹², surprisingly, it has not previously been studied in nitric acid. Initially, a suitable anti-nitrite, i.e. one that did not react with U(IV) or Np(VI), had to be identified, since HNO_2 can cause interfering reactions. Sulphamic acid was found to be suitable, although high levels of sulphamic acid increased the observed reaction rate. This was most likely due to the catalytic effect of sulphate ions, which has also been observed previously in HClO_4 ¹². In a separate experiment, the addition of 0.0005M H_2SO_4 was shown to increase the reaction rate constant by a factor of ~2, thus confirming its catalytic effect. In order to minimise this effect in our experiments, sulphamic acid was used only at low concentrations.

Firstly, it was confirmed that the reaction stoichiometry was the same as for the reaction in HClO_4 , that is:



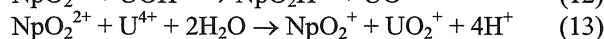
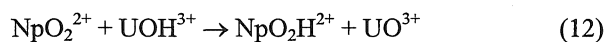
The rate of Np(VI) reduction in variable ionic strength solutions is expressed by Eq. (11), where $k = (696 \pm 20) \text{ M}^{-0.3} \text{ min}^{-1}$ at 10 °C and $[\text{NH}_2\text{SO}_3\text{H}] = 5 \times 10^{-4} \text{ M}$. The activation energy is $66.5 \pm 4.9 \text{ kJmol}^{-1}$ and the thermodynamic parameters are included in Table 1.

$$-\frac{d[\text{Np(VI)}]}{dt} = k[\text{Np(VI)}][\text{U(IV)}]/[\text{HNO}_3]^{0.7} \quad (11)$$

Next it was shown that increasing the ionic strength, by the addition of NaClO_4 , did not significantly change the rate

constant, indicating that the rate of reaction is independent of the ionic strength of the solution. Experiments at a constant nitrate ionic strength of 2, obtained by the addition of NaNO_3 , produced the same rate equation, indicating that the rate is not dependent on $[\text{NO}_3^-]$. Finally, an experiment in the presence of a ten-fold excess of U(VI) over U(IV), produced the same rate constant, which is consistent with the rate being independent of the ionic strength of the solution and indicates that it is not influenced by $[\text{U(VI)}]$ either.

Compared to the reaction in HClO_4 , the rate in HNO_3 is about 2.2 times quicker ($[\text{H}^+] = 1 \text{ M}$; $T = 25 \text{ °C}$); this is consistent with many other Np redox reactions¹³. The mechanism of the reaction in HClO_4 is suggested to proceed via charge transfer from hydrolysed U(IV) ions [Eq. 12]¹². This is consistent with the observed reaction order but, in HNO_3 , the order with respect to H^+ ions is fractional – 0.7. This suggests a parallel reaction route via non-hydrolysed U(IV) ions (Eq. 13)¹⁴.



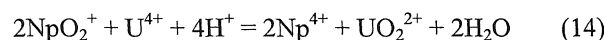
5. Np(VI) and Np(V) reduction by U(IV) in 30 % TBP

The reduction of Np(VI) in 30 % TBP follows the same stoichiometry as in the aqueous phase (Eq. 10) and the rate of reaction was shown¹⁵) to be given by:

$$-\frac{d[\text{Np(VI)}]}{dt} = k \frac{[\text{Np(VI)}][\text{U(IV)}][\text{H}_2\text{O}]^2}{[\text{HNO}_3]^2 + \beta_1[\text{HNO}_3][\text{H}_2\text{O}] + \beta_2[\text{H}_2\text{O}]^2}$$

Where $k = 59.3 \pm 1.7 \text{ M}^{-1} \text{ min}^{-1}$, $\beta_1 \approx 0.009$ and $\beta_2 \approx 0.1$ (hydrolysis constants) at 20.0 °C and the activation energy was the same as in the aqueous phase (HNO_3) – $E = 66.6 \text{ kJmol}^{-1}$. The mechanism involves the interaction of Np(VI) ions with twice hydrolysed U(IV) ions, U(OH)_2^{2+} .

The reduction of Np(V) (Eq. 14) was complicated by the formation of less reactive complexes between Np(V) and U(IV) and U(VI). The rate in the solvent phase is higher than in the aqueous phase and the rate equation was determined to be as given in Eq. (15), where $k = 23.8 \pm 0.7 \text{ M}^{-1} \text{ min}^{-1}$ at 35 °C and $E = 89.0 \pm 22.0 \text{ kJmol}^{-1}$. K is the equilibrium constant of the $[\text{NpO}_2 \cdot \text{U}(\text{NO}_3)_5]$ complex and was found to be equal to $\approx 400 \text{ M}^{-1}$ at 35 °C¹⁵.



$$\frac{d[\text{Np(V)}]}{dt} = k \frac{[\text{Np(V)}][\text{U}(\text{NO}_3)_4]}{1 + K[\text{U}(\text{NO}_3)_4]} \quad (15)$$

The role of H_2O was shown to be important, inhibiting the reduction of Np(VI) but catalysing the reduction of Np(V)¹⁵. The activation entropies are given in Table 1.

IV. Conclusions

Extending our knowledge of the redox chemistry of U(IV) is useful in improving our understanding and modelling of reprocessing flowsheets and it is also of intrinsic interest, particularly reactions in TBP phases. Hydrolysed species of U(IV) and activation entropies seem generally to be important factors, as are the roles of HNO₂ and H₂O in some of the reactions studied. Further kinetic studies of Tc and Pu catalysed U(IV) oxidation in TBP are ongoing and mechanistic studies are planned.

Acknowledgments

An earlier version of this paper was previously presented at the Atalante 2000 conference on the Back End of the Nuclear Fuel Cycle (Avignon, France)³.

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