Acetaldoxime – a Promising Reducing Agent for Pu and Np Ions in the Purex Process

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This paper discusses the properties of acetaldoxime as an example of a novel class of salt-free organic reductants for Np and Pu ions, the monoximes. The products of its reactions with Np(VI) and Pu(IV) are Np(V), Pu(III), N₂O, CH₃CHO and CH₃COOH. The rate of the Np(VI) – CH₃CHNOH reaction is first order relative to both reagents and negative first order relative to HNO₃. The rate constant is k₁ = 254 ± 10 min⁻¹ at 26 °C and the activation energy is E = 62.6 ± 2.6 kJ/mol. The orders of the Pu(IV) – CH₃CHNOH reaction for Pu(IV), Pu(III), CH₃CHNOH and HNO₃ are equal to 2, -1, 1.1 and -2.2, respectively, and the rate constant is k₂ = 25.3 ± 1.9 M⁻¹ min⁻¹ at 19.5 °C. The activation energy is 87.7 ± 2.8 kJ/mol. The likely mechanisms of these reactions are reviewed. Acetaldoxime is stable in HNO₃ solutions when [HNO₃] <~ 3 M and temperature <~ 35 °C. When so-called “critical” conditions are reached (e.g., [HNO₃] = 3.8 – 3.9 M at 35.5 °C) a rapid process of HN₂O₂ formation and acetaldoxime oxidation occurs. Investigations were implemented to study the kinetics of the acetaldoxime oxidation with HNO₂ when [HNO₃] < 1.4 M as well as with HNO₃ under “critical” conditions.

INTRODUCTION

In the reprocessing of irradiated nuclear fuel by the Purex process, the separation of U and Pu is a major stage. This is commonly achieved by a redox process, in which a reducing agent (e.g. U⁴⁺ or Fe²⁺) and a stabiliser (e.g. N₂H₄ or NH₂SO₃H) are added to reduce extractable Pu⁴⁺ to inextractable Pu³⁺. The stabiliser prevents the nitrous acid catalysed re-oxidation of Pu(III) back to Pu(IV). Np, which is present as extractable NpO₂²⁺, is also reduced – ultimately to extractable Np⁴⁺. Further purification of the U bearing solvent stream from Np is, therefore, needed.

In the development of advanced Purex processes, which have reduced costs and lesser environmental impact, one of the key objectives is to reduce both the number of solvent extraction cycles and the waste stream volumes [1]. One option for Advanced Purex flowsheets is to adopt a new reductant in the U/Pu split which routes Np with the Pu stream. This reagent would need the following properties (i) it does not form salts in waste treatment; (ii) it does not reduce Np to Np⁴⁺; (iii) it does not detrimentally interact with Tc(VII) ions; (iv) it has good kinetics for Np(VI) and Pu(IV) reduction compatible with the use of centrifugal contactors; (v) it scavenges nitrous acid rapidly. Therefore, it is of interest to search for and study novel salt-free agents, which may be good reductants for Np and Pu ions [1].

In our previous work [2-8] we have reported results of studies with some classes of organic compounds, namely, substituted derivatives of hydrazine and hydroxylamine and hydroxamic acids. Some of those reductants, specifically, substituted derivatives of hydrazine, may be used to selectively reduce Np(VI) to Np(V) without substantial effect on the Pu(IV) valence state; while others, e.g., some substituted derivatives of hydroxylamine, are capable of converting both Np(VI) to Np(V) and Pu(IV) to Pu(III), thus providing a high degree of separation of these elements from uranium. Hydroxamic acids are unusual in that they both reduce Np(VI) (very rapidly) and Pu(IV) (less rapidly) and form chelate complexes with Pu(IV) ions.

This paper considers the reductive properties of acetaldoxime, which is representative of another novel class of salt-free nitrogen containing organic reductants – the monoximes.

EXPERIMENTAL METHODS

These are described in detail elsewhere [2-7,9].

RESULTS AND DISCUSSION

Np(VI) – Acetaldoxime Reaction [9]

Spectrophotometric studies of the reaction solution show that the final product of the Np(VI) – CH₃CHNOH reaction is Np(V). The yield of Np(V) calculated per 1 mole of oxidized acetaldoxime, when Np is present in excess, increases from 3 to 4 moles as the ratio between the initial concentrations of reagents increases. This is evident from the following data:

EXP1-06
Based on these data it can be assumed that the reaction proceeds according to two limiting stoichiometric equations, namely, (a) at a high excess of Np(VI), via the equation:

$$8\text{NpO}_2^{2+} + 2\text{CH}_3\text{CHNOH} + 3\text{H}_2\text{O} = 8\text{NpO}_2^+ + \text{N}_2\text{O} + 2\text{CH}_3\text{COOH} + 8\text{H}^+$$ (1)

and (b) in excess acetaldoxime via the equation:

$$4\text{NpO}_2^{2+} + 2\text{CH}_3\text{CHNOH} + \text{H}_2\text{O} = 4\text{NpO}_2^+ + \text{N}_2\text{O} + 2\text{CH}_3\text{CHO} + 4\text{H}^+$$ (2)

<table>
<thead>
<tr>
<th>[CH$_3$CHNOH] (x10$^{-3}$ M)</th>
<th>[H$^+$]* (M)</th>
<th>k' (min$^{-1}$)</th>
<th>k** (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.98</td>
<td>0.122</td>
<td>240</td>
</tr>
<tr>
<td>1.0</td>
<td>0.98</td>
<td>0.278</td>
<td>272</td>
</tr>
<tr>
<td>2.0</td>
<td>0.98</td>
<td>0.513</td>
<td>252</td>
</tr>
<tr>
<td>4.0</td>
<td>0.98</td>
<td>1.14</td>
<td>279</td>
</tr>
<tr>
<td>10.0</td>
<td>0.98</td>
<td>2.22</td>
<td>218</td>
</tr>
<tr>
<td>1.0</td>
<td>0.31</td>
<td>0.704</td>
<td>218</td>
</tr>
<tr>
<td>1.0</td>
<td>0.50</td>
<td>0.403</td>
<td>202</td>
</tr>
<tr>
<td>1.0</td>
<td>0.77</td>
<td>0.325</td>
<td>250</td>
</tr>
<tr>
<td>1.0</td>
<td>1.17</td>
<td>0.218</td>
<td>255</td>
</tr>
<tr>
<td>1.0</td>
<td>1.94</td>
<td>0.103</td>
<td>200</td>
</tr>
</tbody>
</table>

Mean 238 ± 20

* Accounting for the degree of HNO$_3$ dissociation.
** k = k'[H$^+$]/[CH$_3$CHNOH]

Investigations of the reaction kinetics show that the reaction proceeds via an equation of the first order relative to the oxidant and reductant while the order for H$^+$ ions in a mixed HNO$_3$ and NaNO$_3$ medium is $-1$, at a constant ionic strength of $\mu = 2$ (Table 1). Hence, the reaction rate is described by the equation:

$$\frac{d[Np(VI)]}{dt} = k\frac{[Np(V)][CH_3CHNOH]}{[H^+]}$$ (3)

where $k = 238 \pm 20$ min$^{-1}$ at 24.5 °C. The form of the kinetic equation does not change at variable concentrations of HNO$_3$ and variable ionic strengths, that is, in a series of experiments implemented in HNO$_3$ solutions without NaNO$_3$. In this instance, the rate constant is determined as $254 \pm 10$ min$^{-1}$ at 26.0 °C. The activation energy of the reaction, $E_i = 62.6 \pm 2.6$ kJ/mol, is calculated on the basis of the following data (at [CH$_3$CHNOH]$_0 = 9 \times 10^{-4}$ M, [HNO$_3$] = 1 M, $\mu = 2$):

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>k' (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.4</td>
<td>0.152</td>
</tr>
<tr>
<td>24.4</td>
<td>0.220</td>
</tr>
<tr>
<td>30.4</td>
<td>0.345</td>
</tr>
<tr>
<td>35.4</td>
<td>0.532</td>
</tr>
<tr>
<td>40.8</td>
<td>0.808</td>
</tr>
</tbody>
</table>

The subsequent Np(V) → Np(IV) conversion is not observed for at least 6 hours in 2 and 3 M HNO$_3$ at [CH$_3$CHNOH] = 0.05 M and 35 °C. Under more severe conditions, this reaction was observed to proceed at a very low rate, e.g. at 50 °C, [CH$_3$CHNOH] = 0.5 M, [HNO$_3$] = 4 M, the first order rate constant is $2.5 \times 10^{-5}$ min$^{-1}$.

Pu(IV) – Acetaldoxime Reaction [9]

As with the Np(VI) reaction, the Pu(IV) – acetaldoxime reaction proceeds via two stoichiometric equations, namely, (a) in excess CH$_3$CHNOH:

$$4\text{Pu}^{4+} + 2\text{CH}_3\text{CHNOH} + \text{H}_2\text{O} = 4\text{Pu}^{3+} + \text{N}_2\text{O} + 2\text{CH}_3\text{CHO} + 4\text{H}^+$$ (4)

and (b) in excess Pu$^{4+}$ ions:

$$8\text{Pu}^{4+} + 2\text{CH}_3\text{CHNOH} + 3\text{H}_2\text{O} = 8\text{Pu}^{3+} + \text{N}_2\text{O} + 2\text{CH}_3\text{COOH} + 8\text{H}^+$$ (5)
These conclusions are reached based on the Pu(III) yield calculated per 1 mole of oxidized reductant:

\[
\begin{array}{ccccccc}
\text{[Pu(IV)]}_0 / [\text{CH}_3\text{CHNOH}] & 2 & 4 & 6 & 8 & 12 & 20 & 25 \\
\text{[Pu(III)]}_i / [\text{CH}_3\text{CHNOH}] & 2.0 & 3.3 & 3.7 & 3.8 & 3.8 & 3.9 & 4.0
\end{array}
\]

The notable feature of this reaction is the fact that it does not obey a first order relationship with [Pu(IV)], which is distinct from the similar reaction with Np(VI) above. In the initial stages the reaction approximately obeys a second order equation; however, after it is completed to 30-40% it deviates from this equation by decelerating. It can be shown that the mode of the kinetic curves is adequately represented by the equation:

\[
-\frac{d[\text{Pu(IV)}]}{dt} = k[\text{Pu(IV)}]^2[\text{Pu(III)}]
\]

From this it is evident that the reduction of Pu(IV) is slowed down over time as the reaction product, Pu(III) ions, inhibiting the reaction, are formed. In this respect the reaction under study is similar to reactions between Pu(IV) ions and N-methylhydroxylamine [10].

Integration of equation (6) results in the straight line equation:

\[
\frac{a}{a-x} - \ln\frac{a}{a-x} = 1 + k't
\]

where \(a=[\text{Pu(IV)]}_0; (a-x)=\text{[Pu(IV)]; x=[Pu(III)]. The tangent of the angle of the straight line inclination to the time axis is numerically equal to the pseudo-first order rate constant \(k'\) in eq.(6). The values of \(k'\), acquired in experiments under different conditions are listed in Table 2. The values were calculated by a PC based on the concentrations of Pu(IV) as a function of time. It is evident from Table 2 that the rate constant, \(k'\), increases in proportion to the acetaldoxime concentration to the 1.1 power.

The reaction rate is sharply slowed down as the solution acidity increases. The reaction order in relation to HNO\(_3\) is equal to \(-2.2\) at a variable ionic strength of the solution (see Table 2). Hence, the overall rate equation takes the form:

\[
-\frac{d[\text{Pu(IV)}]}{dt} = k[\text{Pu(IV)}]^2[\text{CH}_3\text{CHNOH}]^{1.1}\frac{1}{[\text{Pu(III)}][\text{HNO}_3]^{2.2}}
\]

where \(k = 25.3 \pm 1.9 \text{ mol}^{-1/2}\text{ l}^{-1/2}\text{ min}\) at 19.5°C.

<table>
<thead>
<tr>
<th>([\text{CH}_3\text{CHNOH}]) (M)</th>
<th>([\text{HNO}_3]) (M)</th>
<th>(k') (min(^{-1}))</th>
<th>(k^*) (mol(^{-1/2})l(^{1/2})min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>1.00</td>
<td>0.47</td>
<td>22.3</td>
</tr>
<tr>
<td>0.06</td>
<td>1.00</td>
<td>0.95</td>
<td>21.0</td>
</tr>
<tr>
<td>0.08</td>
<td>1.00</td>
<td>1.55</td>
<td>24.9</td>
</tr>
<tr>
<td>0.10</td>
<td>1.00</td>
<td>2.02</td>
<td>25.4</td>
</tr>
<tr>
<td>0.20</td>
<td>1.00</td>
<td>3.98</td>
<td>23.4</td>
</tr>
<tr>
<td>0.08</td>
<td>0.47</td>
<td>8.45</td>
<td>25.8</td>
</tr>
<tr>
<td>0.08</td>
<td>0.63</td>
<td>5.40</td>
<td>31.4</td>
</tr>
<tr>
<td>0.08</td>
<td>0.70</td>
<td>3.72</td>
<td>27.3</td>
</tr>
<tr>
<td>0.08</td>
<td>1.00</td>
<td>1.55</td>
<td>25.4</td>
</tr>
<tr>
<td>0.08</td>
<td>1.25</td>
<td>0.93</td>
<td>24.5</td>
</tr>
<tr>
<td>0.08</td>
<td>2.00</td>
<td>0.36</td>
<td>26.6</td>
</tr>
<tr>
<td>mean</td>
<td></td>
<td></td>
<td>25.3 ± 1.9</td>
</tr>
</tbody>
</table>

\(k^* = k_1[\text{HNO}_3]^{2.2} / [\text{CH}_3\text{CHNOH}]^{1.1}\)

To determine the activation energy, the reaction was investigated at various temperatures in 1.5 M HNO\(_3\), [CH\(_3\)CHNOH] = 0.8 M and at the ionic strength \(\mu = 2\). The resultant rate constants below were used to calculate the activation energy, \(E_2 = 87.7 \pm 9.8 \text{ kJ/mol}\), by the least squares method.

\[
\begin{array}{cccc}
\text{T (°C)} & 19.5 & 25.5 & 30.5 & 35.0 \\
\end{array}
\]
The unusual kinetic characteristics of the Pu(IV) - acetaldoxime reaction provide evidence of an intricate reaction mechanism. Taking into account that the reaction order in relation to Pu(IV) (+2) and the product, Pu(III), (-1) is consistent with the similar data on the Pu(IV) - N-methylhydroxylamine reaction [10], the mechanisms of those two reactions may be assumed to be similar. Based on this analogy, we postulate that the first stage of the reaction is a reversible interaction between reagents that results in the formation of a CH₃CHN-O radical.

$$\text{Pu}^{4+} + CH_3CHNO \leftrightarrow \text{Pu}^{3+} + CH_3CHN-O + H^+ \quad (9)$$

This is subsequently oxidized with hydrolyzed ions of Pu(IV) in the slow stage (10).

$$\text{PuOH}^{3+} + CH_3CHN-O \rightarrow \text{Pu}^{3+} + CH_3CHO + HNO \quad (10)$$

The reaction terminates in a quick stage (11).

$$2HNO \rightarrow N_2O + H_2O \quad (11)$$

As for Np(VI), being a thermodynamically stronger oxidant, the equilibrium of the reaction analogous to eq. (9) is displaced to the right, the rate of the stage of type (10) is high and reaction (12) in the forward direction is rate limiting.

$$\text{NpO}_2OH^+ + CH_3CHNOH \rightarrow \text{NpO}_2^+ + CH_3CHN-O + H_2O \quad (12)$$

These suggested mechanisms of the Np(VI) and Pu(IV) reactions can be shown to be consistent with the experimentally found kinetic equations (3) and (8) [9].

Acetaldoxime Stability in HNO₃ solutions

Acetaldoxime is adequately stable in solutions of HNO₃ at reasonably low concentrations (<~3.5M) and low temperatures (<~35 °C). However, as these parameters increase and the so-called “critical” conditions are attained, acetaldoxime is observed to oxidize quickly with HNO₂ autocatalytically formed. This can be represented by the reaction scheme below.

$$2CH_3CHNOH + 2HNO_3 \rightarrow 2CH_3CHO + 2HNO_2 + N_2O + H_2O \quad (13)$$

$$CH_3CHNOH + HNO_2 \rightarrow CH_3CHO + N_2O + H_2O \quad (14)$$

Reaction (13) proceeds slowly and (14) proceeds quickly.

According to this schema, in the acetaldoxime - HNO₃ reaction an induction period is present, the duration (τ) of which decreases as [HNO₃] and temperature increase and [CH₃CHNOH] decreases. For example, at 35.5 °C and [CH₃CHNOH] = 0.05 M, the values of τ are equal to:

<table>
<thead>
<tr>
<th>HNO₃ (M)</th>
<th>3.60</th>
<th>3.65</th>
<th>3.70</th>
<th>3.85</th>
<th>3.90</th>
<th>4.00</th>
<th>4.10</th>
<th>4.18</th>
<th>4.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ (min)</td>
<td>&gt;420</td>
<td>220</td>
<td>140</td>
<td>27</td>
<td>18</td>
<td>9.4</td>
<td>6.0</td>
<td>1.8</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Following the induction period, the concentration of HNO₂ increases quickly to reach a maximum and then slowly diminishes. A simultaneous quick oxidation of acetaldoxime via reaction (14) is observed.

The mechanism of acetaldoxime oxidation with HNO₃ in the presence of HNO₂ is similar to the mechanism of hydroxylamine oxidation [11] and involves the stages (15-18).

$$HNO_2 + HNO_2 \leftrightarrow N_2O_4 + H_2O \quad (15)$$

$$CH_3CHNOH + N_2O_4 \rightarrow CH_3CHO + HNO + N_2O_3 \quad (16)$$

$$2HNO \rightarrow N_2O + H_2O \quad (17)$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2 \quad (18)$$

Of these stages, reaction (16) is slow. According to this mechanism the rate of reaction (13) is expressed by:

$$-d[CH_3CHNOH]/dt = k_1[CH_3CHNOH][HNO_2][HNO_3] \quad (19)$$

On the other hand, it will be shown below that the rate of reaction (14) is described by a similar equation and, hence, the observed rate of HNO₂ formation is equal to the difference between the rates of reactions (13) and (14). The processing of the experimentally acquired data reveals that under the “critical” conditions the second order rate constant, k₁, of
reaction (13) increases very sharply indeed with [HNO$_3$]. For instance, at 35.5 °C and [CH$_3$CHNOH]$_0$ = 0.05 M the following values of $k_1'$ were calculated:

<table>
<thead>
<tr>
<th>[HNO$_3$] (M)</th>
<th>3.65</th>
<th>3.85</th>
<th>3.90</th>
<th>4.05</th>
<th>4.10</th>
<th>4.18</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1'$ (M$^{-1}$min$^{-1}$)</td>
<td>50</td>
<td>100</td>
<td>140</td>
<td>220</td>
<td>410</td>
<td>480</td>
</tr>
</tbody>
</table>

Under these conditions, the overall equation of the acetaldoxime oxidation rate takes the form of:

$$-d[CH_3CHNOH]/dt = k[CH_3CHNOH][HNO_2][HNO_3]^{17}$$

(20)

where $k = (1.28 \pm 0.20) \times 10^8$ M$^{-1}$min$^{-1}$ at 35.5 °C. The unusual high formal order of reaction with respect to [HNO$_3$], which we apparently experimentally observe, is not understood and also it seems to vary depending on temperature (e.g. $n \sim 7$ at 50.6 °C). One observation, however, is that the value of the order relative to HNO$_3$ ($n$) appears to increase as [HNO$_3$] increases and this is not temperature dependent. This is evidenced by the following data:

<table>
<thead>
<tr>
<th>[HNO$_3$] (M)</th>
<th>0.2-1.4</th>
<th>1-3</th>
<th>2.5-3.1</th>
<th>3.6-4.0</th>
<th>&gt;3.2</th>
<th>&gt;4.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>13</td>
<td>13</td>
<td>50.6</td>
<td>35.5</td>
<td>50.6</td>
<td>35.5</td>
</tr>
<tr>
<td>$n$</td>
<td>~1</td>
<td>2.8</td>
<td>7</td>
<td>17</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

This suggests that the increasing thermodynamic activity of HNO$_3$ as [HNO$_3$] is a factor. Since the ionic strength of the solution was not constant, the rate of the reaction is proportional to [HNO$_3$]$^2$Y$_{HNO_3}$. The activity coefficient of HNO$_3$ (Y$_{HNO_3}$) is known to increase strongly with [HNO$_3$] and temperature in the same [HNO$_3$] range at which the "critical" conditions are observed (~3 M) [12].

**Acetaldoxime – HNO$_2$ Reaction**

At a comparatively low acidity ([HNO$_3$] <~ 1.4 M), 1 mole of HNO$_2$ is consumed per 1 mole of acetaldoxime, which corresponds to the stoichiometric equation of reaction (14). In the higher range of HNO$_3$ concentrations, the HNO$_2$ consumption is reduced since it is not only lost through reaction (14) but it is also formed via reaction (13).

The rate of reaction (14) is described by the equation ([HNO$_3$] <~ 1.4 M):

$$-d[CH_3CHNOH]/dt = k_2[CH_3CHNOH][HNO_2][HNO_3]$$

(21)

where $k_2 = 830 \pm 80$ M$^{-2}$min$^{-1}$ at 13 °C. The activation energy of reaction (14) is found equal to $E_2 = 33.3 \pm 6.4$ kJ/mol.

At [HNO$_3$] > 1.4 M the observed rate of the HNO$_2$ consumption is in fact a difference between the rates of reactions (14) and (13). In view of this, the second order rate constant of HNO$_2$ consumption, $k_1'$, is a maximum function of [HNO$_3$] – e.g. at 13 °C:

<table>
<thead>
<tr>
<th>[HNO$_3$] (M)</th>
<th>0.2</th>
<th>0.4</th>
<th>0.8</th>
<th>1.0</th>
<th>1.4</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1'$ (M$^{-1}$min$^{-1}$)</td>
<td>170</td>
<td>330</td>
<td>720</td>
<td>770</td>
<td>990</td>
<td>630</td>
<td>330</td>
<td>270</td>
</tr>
</tbody>
</table>

Under the "critical" conditions, the rates of the HNO$_2$ formation via reaction (13) and the CH$_3$CHNOH oxidation via reaction (14) are close.

**Acetaldoxime stability in HNO$_3$ in the presence of Tc(VII) ions**

It is well known that Tc(VII) ions can catalyse the oxidation of some species by HNO$_3$; for instance, hydrazine [13]. On the introduction of TcO$_4^-$ in to a nitric acid solution of acetaldoxime, however, there is neither evidence that the induction period before oxidation is decreased nor that the rate constants of reactions (13) and (14) are increased (Table 3).

**Table 3. The effect of Tc(VII) ions on the induction period and rate constants of CH$_3$CHNOH (0.05 M) oxidation with HNO$_3$ and HNO$_2$**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>[HNO$_3$] (M)</th>
<th>[Tc(VII)] (M)</th>
<th>[HNO$<em>3$]$</em>{max}$ (x10$^{-5}$ M)</th>
<th>$\tau$ (min)</th>
<th>$k_1'$ (l/mol.min)</th>
<th>$k_2'$ (l/mol.min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-20</td>
<td>3.00</td>
<td>2.00</td>
<td>-</td>
<td>&gt;1500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>35.5</td>
<td>3.65</td>
<td>0.01</td>
<td>5.54</td>
<td>220</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>3.65</td>
<td>0.01</td>
<td>5.65</td>
<td>200</td>
<td>90</td>
<td>70</td>
</tr>
</tbody>
</table>
This is also indirect evidence that the rate of the reaction between Tc(VII) and acetaldoxime (possibly expressed by Eq. 22) is very low.

\[
\text{TcO}_4^- + \text{CH}_3\text{CHNOH} \rightarrow \text{TcO}_3^{2-} + \text{CH}_3\text{CHO} + \text{HNO}
\]  \hspace{1cm} (22)

**CONCLUSION**

These studies have shown that acetaldoxime is a good reducing agent for Np(VI) and Pu(IV) ions. It is, therefore, a potentially useful reagent in advanced Purex processes in which the separation of Np and Pu from U is required. In this task it exhibits several advantages over conventional combinations of reagents, such as: (a) the selective reduction of Np(VI) to Np(V) without the formation of Np(IV); (b) the adequate stability of the reductant under the standard conditions and the easy removal of its excess (through increasing [HNO₃] or temperature) (c) there is no need to introduce a stabilising agent, i.e., antinitrite and (d) no significant interactions with Tc(VII) ions. Furthermore, it has been shown [14] that acetaldoxime is partially extractable and so stabilises Pu(III) in the TBP phase as well as the aqueous phase. Other oximes, such as butyraldoxime, have been shown to have similar chemical properties. However, much further development work would need to be done before acetaldoxime could be considered for process applications.

**REFERENCES**

FOOTNOTES

a "o" and "f" indices denote the initial and final concentrations.
b Gas chromatographic analysis established that CH$_3$CHO and N$_2$O were formed as products of the CH$_3$CHNOH – Ce(IV) interaction in HClO$_4$ solution. Nitrate ions were not found.