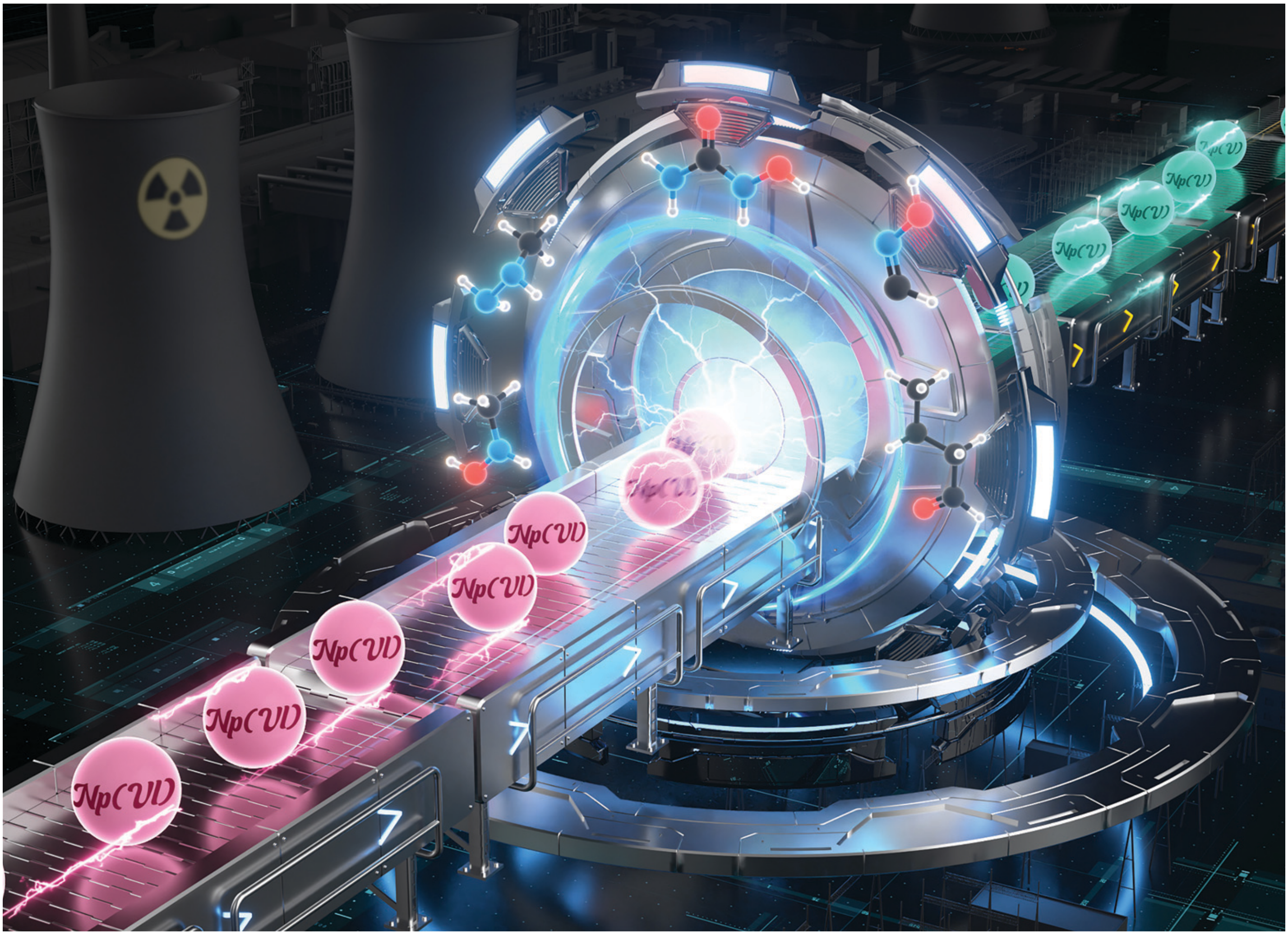

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Experimental and theoretical progress on the reduction of Np(VI) with salt-free reagents in the PUREX process

This review summarizes the reduction reaction of Np(VI) to Np(V) by hydrazine, hydroxylamine, aldehydes, oximes, hydroxamic acids and their derivatives as well as the reaction kinetics, reaction mechanism and electronic structures.

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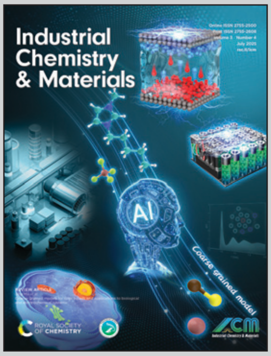
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Experimental and theoretical progress on the reduction of Np(VI) with salt-free reagents in the PUREX process

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Effectively controlling the oxidation state of neptunium (Np) is crucial for the separation of Np during the advanced plutonium uranium reduction extraction process. The reduction reactions and kinetics of Np(VI) with salt-free reagents were explored by applying experimental and theoretical studies. This review summarizes the reduction reaction, kinetics, mechanism and electronic structures as well as the potential energy surfaces of Np(VI) to Np(V) using salt-free reagents, such as hydrazine, hydroxylamine, aldehydes, oximes, hydroxamic acids and their derivatives. This review will hopefully serve as a useful resource to inspire further research on the reduction of Np(VI) using salt-free reagents.

Keywords: Reduction kinetics; Reduction mechanism; Np(VI); Salt-free reagents; Theoretical simulation.

1 Introduction

The plutonium uranium reduction extraction (PUREX) process is effectively applied in the commercial scale reprocessing of spent nuclear fuel (SNF). In the PUREX process, U and Pu are separated from HNO_3 solution to the organic phase using tri-*n*-butyl phosphate (TBP). The extraction performance of U, Np and Pu is significantly sensitive to their oxidation states in the PUREX process. Generally, hexavalent and tetravalent actinide ions exhibit higher extractability compared with trivalent and pentavalent ones. Therefore, the extractability of these actinides can be changed by oxidation or reduction, which achieves independent separation of U, Np and Pu in the different flowsheets. Actinides are very difficult to separate because they are similar in many respects.[1,2] Thus, an advanced PUREX process is desired to achieve comprehensive control of U, Np, and Pu extraction in a single extraction cycle. ^{237}Np has an exceptionally long half-life of 2.14×10^6 years[3] and

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poses significant environmental hazards and radiotoxicity.[4] Furthermore, ^{237}Np serves as a key precursor in the production of ^{238}Pu, an essential component in the manufacture of nuclear-powered batteries.[5] Therefore, the separation of Np is very crucial and urgent. Np exhibits three oxidation states during the PUREX process, and their extractability by TBP follows the sequence of Np(VI) > Np(IV) ≫ Np(V).[6–8] The valence state of Np in aqueous nitric acid depends on the concentration of HNO_2.[9–11] At low concentrations of HNO_2, Np(V) is rapidly oxidized to Np(VI), while at high concentrations of HNO_2, Np(VI) is reduced to Np(V). HNO_2 exhibits a dual role in equilibrium reactions. At low concentrations, it acts as a catalyst, facilitating the oxidation of Np(V). Conversely, at high concentrations, it acts as a reductant, converting Np(VI) to Np(V). The redox reaction between Np(VI) and Np(V) is quasi-reversible and has simple one-electron transfer characteristic:

$$\mathrm{Np(VI)} + \mathrm{e} \longleftrightarrow \mathrm{Np(V)} \tag{1}$$

In addition, Np(V) slowly disproportionates, generating Np(VI) and Np(IV) in highly acidic solution though the following reaction. The extent of the disproportionation is promoted when the acidity of the solution and the concentration of Np(V) are high:

$$2\mathrm{Np(V)} + 4\mathrm{H}^+ \longleftrightarrow \mathrm{Np(IV)} + \mathrm{Np(VI)} + 2\mathrm{H_2O} \tag{2}$$

The valence state of Np ions in the different stages of the PUREX process is displayed in Fig. 1. The most of Np in the co-decontamination step is oxidized to Np(VI) by nitric acid and is extracted to the organic solvent accompanied with U(VI) and Pu(IV). In the U/Pu partition step, Np(VI) is reduced to Np(IV) or Np(V) by reductants and Np is distributed to the U and the Pu purification cycles. It is essential to isolate Np ions from Pu and U ions before the U/Pu split stream to simplify the PUREX process. In the advanced PUREX, it is necessary to effectively control the oxidation state of Np ions.[6,12]

Extensive studies have been conducted with the aim of developing an advanced PUREX process involving an efficient precise control of the Np oxidation state. There are several methods to control the Np oxidation state in the flowsheet of the PUREX process: Np can be entirely directed to (1) the high-level liquid waste (HLLW) stream, (2) the Pu purification stage, or (3) the U purification stage before the separation of the U and Pu stream. Np speciation in HNO_3 solution is dominated by the Np(VI)/Np(V) equilibrium, which is a very complex process due to the interactions among reaction kinetics, chemical equilibria, acidity, temperature and the presence of other ions.[9–11] In particular, the Np(VI)/Np(V) equilibrium is sensitive to the $HNO_3:HNO_2$ ratio and temperature. For example, the concentration of Np(VI) is enhanced at higher HNO_3 concentrations, lower HNO_2 concentrations and higher temperatures.[9] Salt-free reagents are considered to be promising for Np(VI) reduction because they can be decomposed into gases, such as N_2, CO_2 and H_2O.[13] The reduction behaviors of Np(VI) with many salt-free reagents have been explored by the groups of Taylor,[1,6,14,15] Uchiyama,[16,17] Koltunov[18,19] and Ye.[20,21] A variety of salt-free reductants can effectively reduce Np(VI) to Np(V), such as hydrazine,[14,22–25] aldehydes,[16,17] hydroxylamine,[26–30] oxime,[31–34] hydroxamic acid[15,35] and their derivatives. Recently, we systematically explored the Np(VI) reduction using hydrazine, hydroxylamine and its derivatives and elucidated their reduction mechanisms by employing density functional theory (DFT).[36–45] Koltunov and co-workers reported the reaction kinetics of Np and Pu ions using hydrazine, organic nitriles, hydroxylamine, monoximes, diaziridinylethane and their derivatives.[18,20,21] Marchenko *et al.* described the characteristics of organic reductants that can keep Np and Pu in a specific oxidation state.[46] Although much research has focused on Np(VI) reduction by salt-free reagents, there is no review on the subject. Noticeably, some salt-free reagents can reduce Np(VI) to Np(V) and reduce Np(V) to Np(IV). In this review, we mainly elucidate the experimental and theoretical progress on the reduction of Np(VI) to Np(V) by salt-free reagents. We hope that this review will serve as a useful resource to inspire further research on Np(VI) reduction by salt-free reagents in the reprocessing of SNF.

Wei-qun Shi

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2 Experimental progress on the reduction of Np(VI) to Np(V) by salt-free reagents

2.1 Hydrazine and its derivatives

Hydrazine and its derivatives can reduce Np(VI) to Np(V), which enables the separation of Np in SNF.[14,22–25,47] There are about 20 types of hydrazine and its derivatives studied in

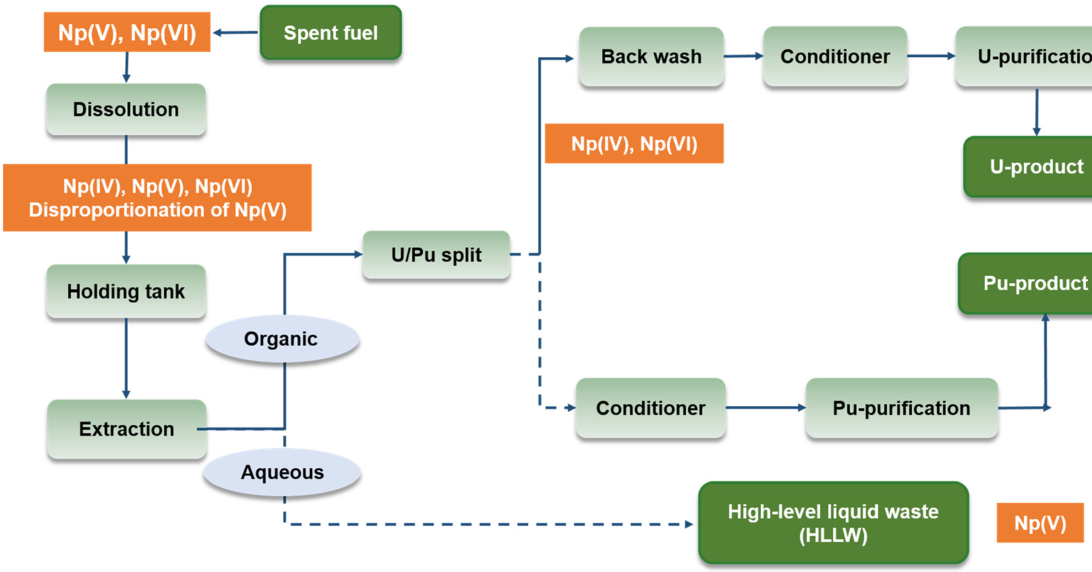

Fig. 1 Distribution of Np(VI,V,IV) in the PUREX process.

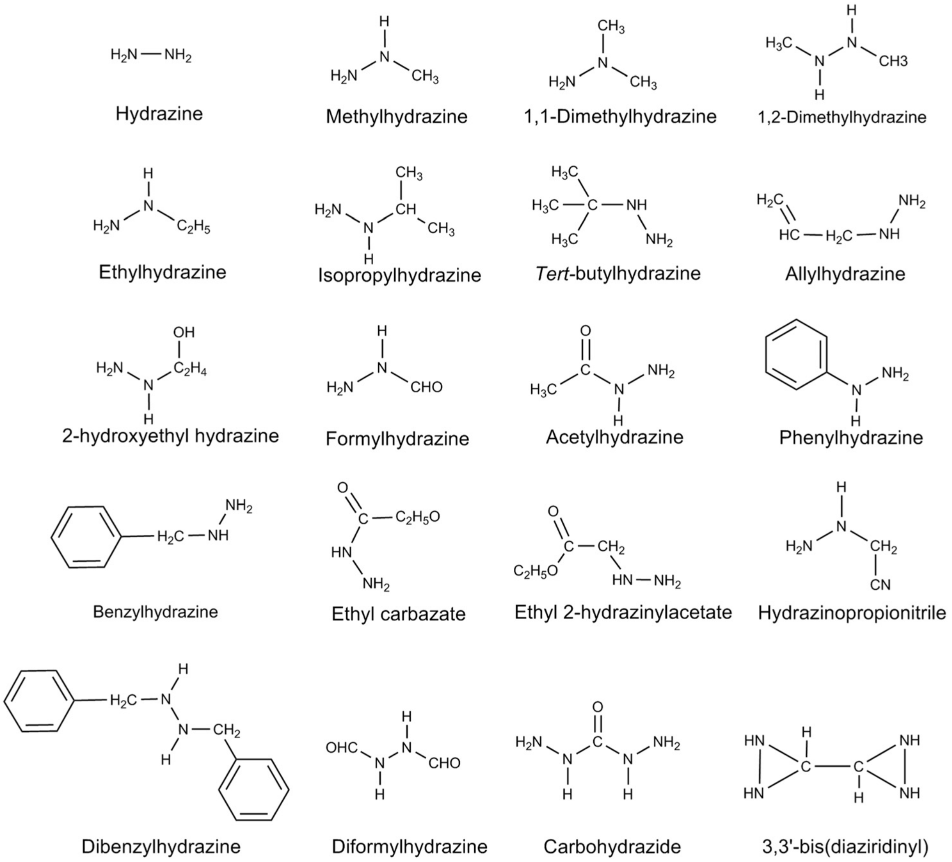

Fig. 2 Structures of hydrazine and its derivatives for Np(VI) reduction studies.

the experiment presented in Fig. 2, some of which can reduce four Np(VI) ions such as hydrazine, carbohydrazide, and 3,3′-bis(diaziridinyl), while the others only enable the reduction of two Np(VI) ions. The total reaction equation for excess Np(VI) and hydrazine, carbohydrazide and 3,3′-bis(diaziridinyl) is expressed in eqn (3)–(5), respectively.

$$4\mathrm{Np(VI)} + N_2H_4 \rightarrow 4\mathrm{Np(V)} + N_2 + 4H^+ \quad (3)$$

$$4\mathrm{Np}(\text{VI}) + \mathrm{CO(N_2H_3)_2} \rightarrow 4\mathrm{Np}(\text{V}) + \mathrm{HCOH} + 2\mathrm{N_2} + 4\mathrm{H^+} \quad (4)$$

$$4\mathrm{Np}(\text{VI}) + \mathrm{H_2N_2HCCHN_2H_2} \rightarrow 4\mathrm{Np}(\text{V}) + \mathrm{N_2HCCHN_2} + 4\mathrm{H^+} \quad (5)$$

Taking hydrazine as an example, the reduction mechanisms for the excess Np(VI) and N_2H_4 are shown in eqn (6)–(9).[22]

$$\mathrm{Np}(\text{VI}) + \mathrm{N_2H_4} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{N_2H_4}^{+\bullet} \quad (6)$$

$$\mathrm{Np}(\text{VI}) + \mathrm{N_2H_4}^{+\bullet} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{N_2H_2} + 2\mathrm{H^+} \quad (7)$$

$$\mathrm{Np}(\text{VI}) + \mathrm{N_2H_2} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{N_2H_2}^{+\bullet} \quad (8)$$

$$\mathrm{Np}(\text{VI}) + \mathrm{N_2H_2}^{+\bullet} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{N_2} + 2\mathrm{H^+} \quad (9)$$

Hydrazine can react with nitric acid and form hydrazinium nitrate, which is often used as a scavenging agent for nitrous acid (HNO_2) in the PUREX process. The reaction rate for the reduction of Np(VI) is enhanced by increasing the hydrazinium nitrate concentrations.[24] The kinetics of the reaction of hydrazinium nitrate and HNO_2 in eqn (10) is very fast. Moreover, the HN_3 product can react with HNO_2 in eqn (11) as soon as all the $N_2H_5^+$ has disappeared.[48]

$$\mathrm{N_2H_5^+} + \mathrm{HNO_2} \rightarrow \mathrm{HN_3} + 2\mathrm{H_2O} + \mathrm{H^+} \quad (10)$$

$$\mathrm{HN_3} + \mathrm{HNO_2} \rightarrow \mathrm{N_2O} + \mathrm{N_2} + \mathrm{H_2O} \quad (11)$$

The total reaction equation for Np(VI) with excess RN_2H_3 and $R_2N_2H_2$ is given in eqn (12) and (13), respectively.

$$2\mathrm{Np}(\text{VI}) + \mathrm{RN_2H_3} \rightarrow 2\mathrm{Np}(\text{V}) + \mathrm{RH} + \mathrm{N_2} + 2\mathrm{H^+} \quad (12)$$

$$2\mathrm{Np}(\text{VI}) + \mathrm{R_2N_2H_2} \rightarrow 2\mathrm{Np}(\text{V}) + \text{products} + 2\mathrm{H^+} \quad (13)$$

where R is a substituent group of hydrazine.

The reaction mechanism of eqn (12) is shown in eqn (14)–(16)

$$\mathrm{Np}(\text{VI}) + \mathrm{RN_2H_3} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{RN_2H_3}^{+\bullet} \quad (14)$$

$$\mathrm{Np}(\text{VI}) + \mathrm{RN_2H_3}^{+\bullet} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{RN_2H} + 2\mathrm{H^+} \quad (15)$$

$$\mathrm{RN_2H} \rightarrow \mathrm{RH} + \mathrm{N_2} \quad (16)$$

The reaction mechanism of eqn (13) corresponds to eqn (17)–(19)

$$\mathrm{Np}(\text{VI}) + \mathrm{R_2N_2H_2} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{R_2N_2H_2}^{+\bullet} \quad (17)$$

$$\mathrm{Np}(\text{VI}) + \mathrm{R_2N_2H_2}^{+\bullet} \rightarrow \mathrm{Np}(\text{V}) + \mathrm{R_2N_2} + 2\mathrm{H^+} \quad (18)$$

$$\mathrm{R_2N_2} \rightarrow \text{products} \quad (19)$$

We summarized temperature, equation of the reaction rate, activation energy (E) and rate constant for the reaction of Np(VI) reduction with hydrazine and its derivatives in Table 1. The oxidation rate of hydrazine and its derivatives in the HNO_3 solution follows the first-order kinetic equation, while its order with respect to H^+ is about −1. These results indicate that the reaction rate is not sensitive to the ionic strength. The activation energy for phenylhydrazine and hydrazinopropionitrile is smaller than that of other hydrazine derivatives.[18,49] Koltunov *et al.* first studied the kinetics of Np(VI) reduction using different hydrazine derivatives,[22,47] and revealed that the reduction by these derivatives exhibits a significant difference. Their reduction ability in HNO_3 solution, judged by the reaction rate, follows the order of

Table 1 Temperature (t), kinetic equation, rate constant (k) and activation energy (E) for the Np(VI) reduction reaction with hydrazine and its derivatives

Reductants (R)	t (°C)	$-\frac{\mathrm{d[Np(VI)]}}{\mathrm{d}t} = \frac{k\mathrm{[Np(VI)][R]}^e}{\mathrm{[H^+]}^n}$	k (min^{-1})	E (kJ mol^{-1})	Ref.
N_2H_4	25	$e = 1, n = 1.24$	14.0	78.7	50
$CH_3N_2H_3$	25	$e = 1, n = 1$	52.7	58.6	50
$(CH_3)_2N_2H_2$	25	$e = 1, n = 0.9$	55.3 (L mol^{-1})$^{0.1}$	47.2	51
$CH_3N_2H_2CH_3$	25	$e = 1, n = 0.8$	118	50.2	18, 22
$C_2H_5N_2H_3$	25	$e = 1, n = 1$	30	61.5	18, 22
$(CH_3)_2CHN_2H_3$	25	$e = 1, n = 0.9$	19.3	69.4	18
$(CH_3)_3CN_2H_3$	25	$e = 0.9, n = 1$	2.18 ± 0.19 (L mol^{-1})$^{0.1}$	63.1 ± 2.7	14
$(CH_3)_3CN_2H_3$	25	$e = 0.9, n = 0.75$	5.4 (L mol^{-1})$^{0.15}$	61.2	52
$CH_2CHCH_2N_2H_3$	25	$e = 1, n = 1$	46	63.6	18, 22
$HO(CH_2)_2N_2H_3$	25	$e = 1, n = 1$	391	56.6	53
$HCON_2H_3$	25	$e = 1, n = 1$	7.95	85.2	18, 22
$CH_3CON_2H_3$	25	$e = 1, n = 1.2$	7.52	76.5	18, 22
$C_6H_5N_2H_3$	25	$e = 1, n = 0.4$	3000	31.4	18
$C_6H_5CH_2N_2H_3$	25	$e = 1, n = 1$	53.2	98.2	18
$C_2H_5COON_2H_3$	25	$e = 1, n = 1.2$	19.3	65.4	18, 22
$C_2H_5COOCH_2N_2H_3$	25	$e = 1, n = 1.1$	97.6	70.1	18
$NCCH_2N_2H_3$	25	$e = 1, n = 1$	920 ± 38 (L mol^{-1})$^{0.1}$	38.7 ± 1.3	49
CHONHNHCHO	15	$e = 1.3, n = 1.55$	10.4 ± 0.3 (L mol^{-1})$^{0.25}$	85 ± 10	54
$N_2H_3(CO)N_2H_3$	15	$e = 1.15, n = 1.35$	39.7 ± 2.7 (L mol^{-1})$^{0.2}$	85 ± 20	55
$H_2N_2HCCHN_2H_2$	35.7	$e = 1, n = 1$	132 ± 10	73.1 ± 4.6	56

$CH_3CON_2H_3 < HCON_2H_3 < N_2H_4 < C_2H_5OCON_2H_3 < C_2H_5N_2H_3 < CH_2CHCH_2N_2H_3 < CH_3N_2H_3 < C_6H_5CH_2N_2H_3 < C_2H_5OCOCH_2N_2H_3 < CH_3N_2H_2CH_3 < HOC_2H_4N_2H_3$. The reduction rate of Np(vi) is enhanced by some hydrazine derivatives modified by electron-donating groups, which is ascribed to the increase of the electron density around the N atom by introducing electron-donating groups. Oppositely, some hydrazine derivatives modified by electron-withdrawing groups will make the Np(vi) reduction more difficult. In the reaction process, the free radical ion $RN_2H_3^{+\bullet}$ is an intermediate product of the first Np(vi) reduction by RN_2H_3, which can result in the second Np(vi) reduction.

Koltunov reported the rate constants, mechanisms, activation energies, and kinetic equations for Np(vi) reduction with sixteen kinds of hydrazine derivatives in HNO_3 solution.[18] Xiao *et al.* obtained a quantitative correlation between the molecular structures of hydrazine derivatives with the Np(vi) reduction rate.[21] They concluded that the reduction rates are mainly related to the molecular dipole moment, the level of LUMO as well as hydrophobic parameters.

Taylor *et al.*[14] investigated the solvent extraction of Np ions by selective reduction of Np(vi) using salt-free reagents and found that *tert*-butylhydrazine can be a potential candidate for the selective reduction of Np(vi) in certain conditions.[57] The reaction kinetics for Np(vi) with *tert*-butylhydrazine were explored using spectrophotometry in HNO_3 solution.[52] The reduction rate of Np(vi) by *tert*-butylhydrazine in TBP/HNO_3 solution is similar to that by dibenzylhydrazine.[58] Subsequently, Koltunov and coworkers explored the kinetic behavior and mechanisms of Np(vi) reduction by dibenzylhydrazine in TBP/HNO_3 solution and revealed the final reaction products, kinetic equation, and activation energy with an excess of the reductant.[59]

The separation of Np from Pu was explored using hydrazine as a stripping reductant in a single-stage extraction experiment and the Np/Pu separation efficiency is enhanced by elevating the concentrations of hydrazine, nitric acid, and temperature.[24] The feasibility of the Np/Pu separation with methylhydrazine was also assessed by a single-stage extraction device, which suggested that the separation ability of Np(vi)/Pu(iv) becomes weaker as the reaction time gets longer, which is similar to hydrazine.[24,25] The Np(vi) selective reduction by *N*,*N*-dimethylhydrazine within a TBP/*n*-dodecane HNO_3 solution including Pu(iv), U(vi) and Np(vi) was explored by spectrophotometry and numerical simulation.[23] The kinetic behavior for the Np(vi) reduction with $CH_3N_2H_3$ and $HOC_2H_4N_2H_3$ and their application in U/Np separation were investigated by Zhang *et al.*[53,60–62] Yin and coworkers also explored the reduction kinetics of Np(vi) by $(CH_3)_2N_2H_2$, which enables $(CH_3)_2N_2H_2$ as selective reductant of Np(vi) for U/Np separation.[51,63] The rate-determining step for Np(vi) reduction by $HOC_2H_4N_2H_3$, $(CH_3)_2N_2H_2$, and $CH_3N_2H_3$ in the kerosene-30% TBP/HNO_3 solution is the back-extraction of Np(v) from the kerosene-30% TBP into the HNO_3 solution,[64] which is important to separate Np in the SNF reprocessing. Carbohydrazide is an effective reductant of Np(vi) in high-burn-up SNF. Volk *et al.* found that Np(vi) is quickly reduced to Np(v) using carbohydrazide, but the reduction rate of Np(v) to Np(iv) is very slow.[65] Subsequently, Zavalina and coworkers examined the kinetic behavior of Np(vi) reduction to Np(v) using carbohydrazide in HNO_3 solution,[55] and Shilov and Fedoseev explored the corresponding reduction in $HClO_4$ solution.[66] The reduction rate for Np(vi) to Np(v) *via* carbohydrazide improves with increasing temperature, the concentration of carbohydrazide, and lowering the concentration of HNO_3. The activation energy for the corresponding reduction reaction is 85 kJ mol^{-1} in HNO_3 solution at 15 °C and 86 ± 5 kJ mol^{-1} in $HClO_4$ solution at 25 °C.

2.2 Hydroxylamine and its derivatives

In the PUREX process, a strategy for controlling Np separation includes the extraction of U(vi), Np(vi), and Pu(iv) together and the separation of Pu(iii) and Np(v) from U(vi). Effective and rapid reduction of Np(vi) to Np(v) and Pu(iv) to Pu(iii) necessitates the application of a suitable reductant. Hydroxylamine (HA) and its derivatives have been extensively explored for this purpose. Notably, HA enables rapid reduction of Np(vi) to Np(v).[46,57] HA is further able to reduce Np(v) to Np(iv) with increasing acidity and temperature.[1,57] The reduction equations of Np(vi) with HA are followed as eqn (20)–(22):[26,67]

In excess Np(vi),

$$2NpO_2^{2+} + 2NH_3OH^+ \rightarrow 2NpO_2^+ + N_2 + 2H_2O + 4H^+ \tag{20}$$

In excess HA,

$$4NpO_2^{2+} + 2NH_3OH^+ \rightarrow 4NpO_2^+ + N_2O + H_2O + 6H^+ \tag{21}$$

$$2NpO_2^+ + 2NH_3OH^+ + 4H^+ \rightarrow 2Np^{4+} + N_2 + 6H_2O \tag{22}$$

The reduction rate constant of Np(vi) by HA is 3.5 s^{-1} in HNO_3 solution with $\mu = 2$ at 22 °C.[19] HA is quite stable at low acidity and room temperature. However, it can decompose into N_2O as the HNO_3 concentration and/or temperature increase, which is enhanced under the catalysis of Fe.[68] Additionally, the reduction of Np(vi) by HA in 0.5 M HNO_3 solutions with a high U concentration of 850 g L^{-1} at 60 °C predominantly produces Np(v), while in 0.33 M HNO_3 solutions under the same temperature and uranium concentration conditions, the reduced products consist of a mixture of Np(v) and Np(vi).[20]

Most hydroxylamine derivatives exhibit a high reduction rate for Pu(iv) and Np(vi) (Fig. 3), making them suitable for the co-extraction of Np and Pu from U.[19,58] The reaction rates of Np(vi) reduction by HA and its derivatives are presented in Table 2. HA derivatives avoid additional stabilizers due to their rapid reactivity with HNO_2, which precludes the production of HN_3 and NH_4NO_3.[46] At moderate acidity and room temperature, HA derivatives can reduce Np(vi) to Np(v), but they cannot further reduce Np(v) to Np(iv) in the absence

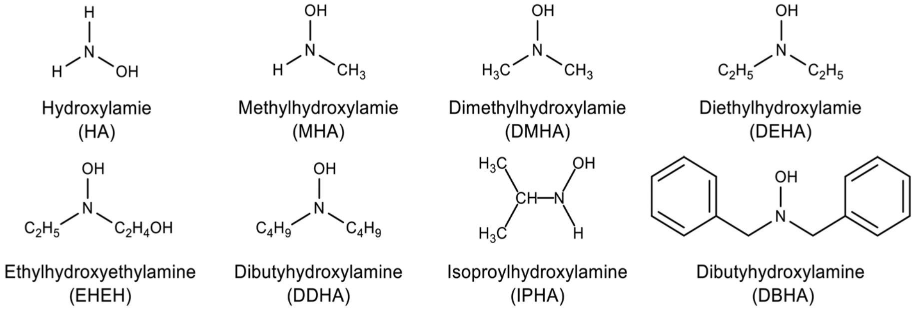

Fig. 3 Structures of hydroxylamine and its derivatives.

Table 2 Temperature (*t*), kinetic equation, rate constant (*k*), activation energy (*E*) for Np(VI) reduction by hydroxylamine and its derivatives at μ = 2

Reductants (R)	t (°C)	The kinetic equation $-\frac{\mathrm{d}[\mathrm{Np(VI)}]}{\mathrm{d}t}=\frac{k[\mathrm{Np(VI)}][\mathrm{R}]^e}{[\mathrm{H}^+]^n}$	k (min^{-1})	E (kJ mol^{-1})	Ref.
NH_2OH (HA)	15	$e = 1$, $n = 1$	92.1 ± 1.0	82.00	26
CH_3NHOH (MHA)	25	$e = 0.7$, $n = 0.4$	35.0 ± 0.9 (L mol^{-1})$^{0.3}$ min	63.6 ± 3	19
$(CH_3)_2NOH$ (DMHA)	25	$e = 1$, $n = 0.65$	24.2 ± 11 (L mol^{-1})$^{0.35}$ min	60.03 ± 0.02	70
$(C_2H_5)_2NOH$	25.2	$e = 1$, $n = 1$	23.0 ± 1.8	69.1	28
C_2H_5 $(HOC_2H_4)NOH$ (EHEH)	25.6	$e = 1$, $n = 0.8$	334 ± 12 (L mol^{-1})$^{0.2}$ min	42.3 ± 2.7	27
$CH_3CH(CH_3)NHOH$ (IPHA)	25.8	$e = 1$, $n = 0.8$	41.8 ± 1.0 (L mol^{-1})$^{0.2}$ min	58.20 ± 0.03	71
$(C_4H_9)_2NOH$ (DDHA)	25.5	$e = 1$, $n = 1$	15.6 ± 1.1	45.8 ± 0.8	72
$(C_6H_5CH_2)_2NOH$ (DBHA)	25	$e = 1$, $n = 1$	1.8	—	58

of catalysts,[30,69] and the reaction products are mainly alcohols and aldehydes.[19]

The stoichiometry of the Np(VI) reaction with HA derivatives is determined by the starting concentrations of the reactants. In cases where there is an excess of Np(VI) ions, the stoichiometric coefficient for Np(VI) : HA derivatives is (6–8) : 1. However, the corresponding stoichiometric coefficient decreases to (0.5–2) : 1 when the HA derivatives are in excess.[57]

The reaction order relative to hydrogen ion ranges from 0.4 to 1.0.[18] These reactions occur through different mechanisms, which contain several parallel pathways with R′RNOH and R′RNHOH$^+$.[26,70–72] The mechanisms of Np(VI) reduction by mono- and disubstituted hydroxylamines are different. For the disubstituted hydroxylamines, the rate-determining step is the decomposition reaction of the activated complex including the nitroxyl radical, which undergoes further oxidation to nitron, then forms aldehyde and monoalkyl hydroxylamine, or nitrosoalkyl and alcohol. In the case of monosubstituted hydroxylamine, it forms nitroxide radical, which oxidizes to alcohol and nitrosoalkyl, with the nitrosoalkyl further forms HNO_3.

The reduction rates of Np(VI) by most hydroxylamine alkyl derivatives are slower compared with that of HA,[57,67] except for *N*,*N*-ethyl(hydroxyethyl)hydroxylamine (EHEH) and *N*,*N*-dimethylhydroxylamine (DMAH). The reduction rate of Np(VI) by EHEH is much faster than that by *N*,*N*-diethylhydroxylamine (DEHA).[57] τ_{99} for the Np(VI) reduction by HA,[26] DMHA,[19] DEHA[19] and EHEH[73] is 0.12, 0.18, 0.15, and 0.14 min in 1.0 M HNO_3 and 0.01 M Np(VI) solution at 25 °C, respectively. Koltunov *et al.*[57,67,74] studied the reduction kinetics of Np(VI) by *N*-methylhydroxylamine (MAH) and DMAH in 2.0 M HNO_3 at 22 °C, and the τ_{99} values are 1.13 and 0.38 min, respectively, while the corresponding τ_{99} values change to 0.65 min and 0.18 min in 2.0 M HNO_3 at 25 °C. These values indicated that the reduction rate of Np(VI) by DMAH is much faster compared with that of MAH under the same conditions.[57,67,68,70]

Np(VI) is quickly reduced to Np(V) by DEHA in HNO_3 solution,[28] τ_{99} value for the reaction of DEHA and HNO_2 is 0.15 min at 1 M HNO_3 and 0.1 M DEHA solution.[75] DEHA is a better stabilizer compared with HA, The presence of U(VI) (up to 0.5 M) does not affect Np(VI) reduction by DEHA.[19,28] That is, DEHA is a more effective reductant than HA as an antinitrite. Zhang *et al.* applied DEHA to isolate Np and Pu from U for the U(VI) purification cycle step in the PUREX process and suggested that DEHA can quickly reduce over 99% of Np(VI) to Np(V).[29] Moreover, the cascade experiment and the cascade extraction separation demonstrate that DEHA is a promising reductant for the PUREX process. The combination of DEHA with hydrazine derivatives like 2-hydroxyethylhydrazine or 1,1-dimethylhydrazine enables the reprocessing process to be carried out without the presence of salts.[76]

The kinetics of Np(VI) by extraction mass transfer and reversible redox reaction by DEHA were examined. Zhang *et al.* discovered that the rate of Np(VI) transfer is obviously

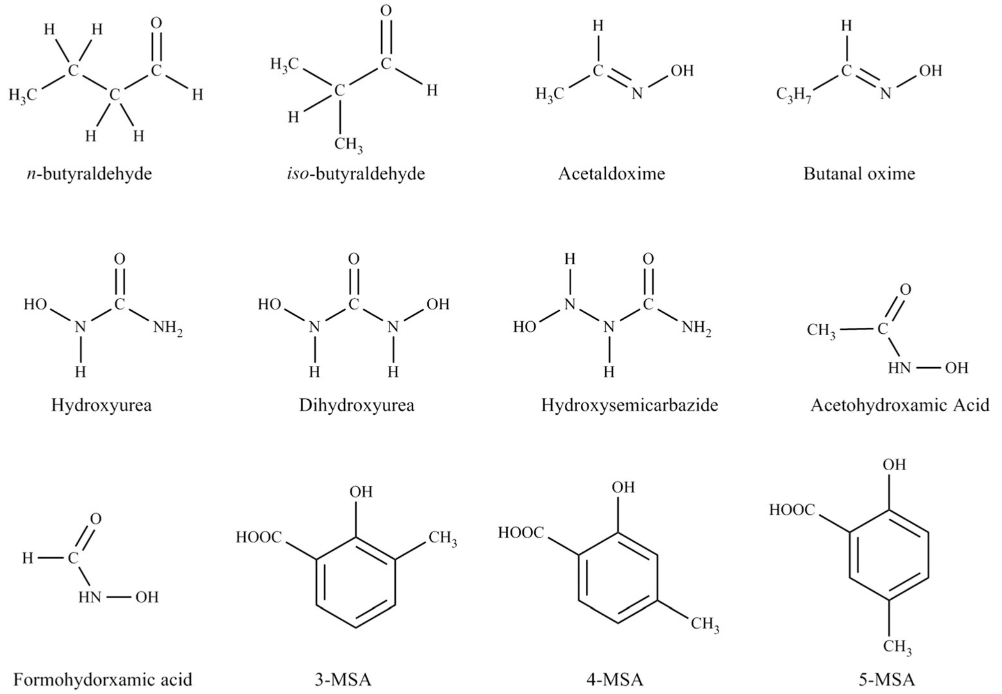

Fig. 4 Some structures of aldehydes, oxime, hydroxyurea, hydroxamic acid and methylsalicylic acids.

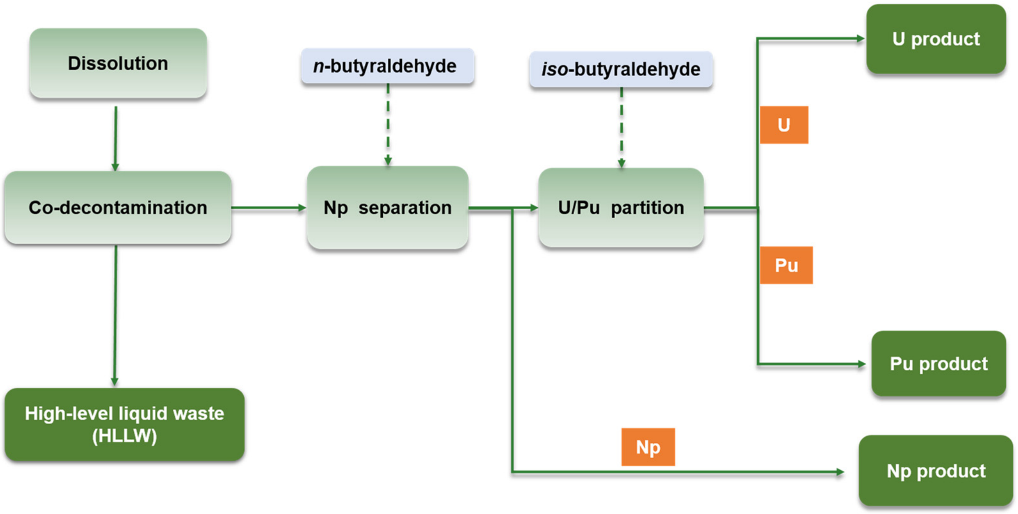

Fig. 5 U, Np, and Pu separation using *n*- and iso-butyraldehydes.

faster than that of the redox reaction.[76] Li's group further determined that the reduction rate of Np(VI) depends on the rate of Np(V) transfer from the kerosene-30% TBP organic phase to HNO_3 solution.[7] EHEH is DEHA modified by a hydroxyl group, which can enhance the reduction rate of Np(VI).[19] The reaction of Np(VI) with EHEH is:[64,73]

$$4NpO_2^{2+} + HOC_2H_4(C_2H_5)NHOH^+ + 3H_2O \rightarrow 4NpO_2^+ + 2C_2H_5OH + HNO_3 + 5H^+ \quad (23)$$

This rate constant is much larger than that of Np(VI) reduction by DEHA (Table 2). EHEH exhibits adequate stability in less than 3–4 M HNO_3 solution, even in the presence of Tc(VII) ions.[27] Moreover, the reaction of EHEH with HNO_2 is very slow, which eliminates the need for an additional scavenging agent.[19] Therefore, the rapidity of the reduction renders EHEH an ideal candidate for application in the U/Pu split process.

2.3 Aldehyde

Uchiyama *et al.* introduced an innovative method for separating Np/Pu/U by utilizing *n*- and iso-butyraldehyde, which are illustrated in Fig. 4, capitalizing on their distinct reduction capabilities.[17] Both *n*- and iso-butyraldehydes are favorable reductants for selective Np(VI) reduction in the presence of Pu(IV) and/or U(VI). Moreover, *n*-butyraldehyde has much higher selectivity and a much lower reduction rate compared with iso-butyraldehyde. Therefore, *n*-butyraldehyde can selectively reduce Np(VI), while iso-butyraldehyde is utilized to reduce both Np(VI) and Pu(IV). According to the different reduction abilities of *n*- and iso-butyraldehyde, the selective Np, Pu and U separation process in the PUREX is proposed (Fig. 5). *n*-Butyraldehyde can extract and reduce about 99.98% Np in the Np separation process, and iso-butyraldehyde is employed for reducing Pu(IV) during the U/Pu split stage.

Subsequently, Uchiyama *et al.* conducted a more in-depth study on the reduction kinetics of Np(VI) by both iso- and *n*-butyraldehyde in HNO_3 solution.[16] Iso-butyraldehyde shows superior performance for reducing Np(VI) compared with *n*-butyraldehyde. Np(VI) is totally converted to Np(V) in 0.069 M iso-butyraldehyde and 3 M HNO_3. This work showed that *n*-butyraldehyde appears to be a potential reagent for Np separation in the PUREX process. Subsequently, the reduction kinetics of Np(VI) with *n*-butyraldehyde in *n*-dodecane/30% TBP solution were examined with spectrophotometry.[77] The rate constant is about $10–10^5$ smaller in *n*-dodecane than that in aqueous solution, suggesting that the Np(VI) reduction process with *n*-butyraldehyde primarily occurs in aqueous solution at 294 ± 1 K.

2.4 Oxime

Monomimes are known to be weakly acidic and basic, which have strong reducing abilities towards Np(VI) ions owing to the –C═N– double bond (Fig. 4). Acetaldoxime is an example of the monoximes, which is considered a valuable reagent for Np/U separation in the advanced PUREX process. Koltunov and coworkers investigated the reduction rate for the reaction of Np(VI) and acetaldoxime in HNO_3 solution:

$$-\mathrm{d}[\mathrm{Np(VI)}]/\mathrm{d}_t = k[\mathrm{Np(VI)}][\mathrm{CH_3CHNOH}]/[\mathrm{HNO_3}] \tag{24}$$

where $k = 254 \pm 10\ \mathrm{min^{-1}}$ with $\mu = 2$ at 26.0 °C as well as the activation energy of $62.6 \pm 2.6\ \mathrm{kJ\ mol^{-1}}$.[31] They also suggest that Np(VI) reduction by acetaldoxime may proceed *via* an intermediate $CH_3CH\dot{N}O$ radical and the hydrolysis product. Extraction studies show that Np(VI) is reduced to Np(V), which is stripped from 30% TBP/*n*-dodecane solution bearing U(VI). After studying the Np(VI) reduction with acetaldoxime, they show the advantages of acetaldoxime in that it reduces Np(VI) to Np(V) but does not form Np(IV).[34] Subsequently, Koltunov *et al.* reported that the reduction rate of Np(VI) by butanal oxime is $230 \pm 15\ \mathrm{min^{-1}}$ with $\mu = 2$ at 25.0 °C and the activation energy in 1 M HNO_3 is $69.4 \pm 12.4\ \mathrm{kJ\ mol^{-1}}$.[33] The results indicated that Np(VI) reduction by butanal oxime and acetaldoxime is a first-order reaction. The reduction kinetics of Np(VI) by butanal oxime were further studied in undiluted TBP in the presence of HNO_3. The reaction rate constant is $0.058 \pm 0.007\ \mathrm{L^{2.5}\ mol^{-2.5}\ min^{-1}}$ between 0.01 to 0.27 M HNO_3 solution with the activation energy of $79 \pm 9\ \mathrm{kJ\ mol^{-1}}$ at T = 25.0 °C.[32] Noticeably, oxime can act as a scavenging agent for HNO_2. For example, butanal oxime can react with HNO_2 and obtain N_2O and N_2 as shown in eqn (25)–(27). The NO_2^+ formed in eqn (27) can be quickly eliminated by reaction with HNO_2 as shown in eqn (28).[78]

$$\mathrm{H^+ + HNO_2 \leftrightarrow H_2NO_2^+ \leftrightarrow H_2O + NO^+} \tag{25}$$

$$\mathrm{C_3H_7CHNOH + NO^+ \rightarrow C_3H_7CHO + N_2O + H^+} \tag{26}$$

$$\mathrm{C_3H_7CHNOH + 2NO^+ \rightarrow C_3H_7CHO + N_2 + NO_2^+ + H^+} \tag{27}$$

$$\mathrm{NO_2^+ + HNO_2 \rightarrow N_2O_4 + H^+} \tag{28}$$

2.5 Hydroxyurea

Hydroxyurea (HU) presented in Fig. 4 is also a potential salt-free reagent for U/Np separation. Zhu and coworkers reported that Np(VI) is reduced to Np(V) with HU, in which Np(V) is effectively transferred from TBP to the aqueous phase.[79] Noticeably, the effectiveness of Np stripping is weakened in HNO_3 solution since the Np(VI) reduction is impeded at higher acidity.

Spectrophotometric analysis was applied to study the Np(VI) reduction by dihydroxyurea (DHU).[80] The reduction rate of Np(VI) by DHU is quick, which makes it suitable for the U/Np separation. The rate constant for the above reaction is $1.86\ \mathrm{s^{-1}}$ in 7.5×10^{-2} M DHU and 0.44 M HNO_3 solution at 4 °C. Under the given experimental conditions, 98% of Np(VI) was quickly stripped to the aqueous phase. The stripping ability decreases with increasing $[HNO_3]$, while it increases with increasing [DHU], so DHU can be used to separate Np in the advanced PUREX process. The reduction rate of Np(VI) by hydroxysemicarbazide (HSC) is also quick with a rate constant of $1037 \pm 60\ \mathrm{M^{-1.40}\ s^{-1}}$ at 4.0 °C;[81] it is positively influenced by increasing [HSC] or temperature and decreasing $[HNO_3]$ or ionic strength.

2.6 Hydroxamic acids

Hydroxamic acids with the general formula RCONHOH illustrated in Fig. 4 are excellent chelating reagents, which provides great benefits in separating Np in advanced PUREX. Furthermore, hydroxamic acids are easily decomposed to gases and consume HNO_2 without an additional reagent. Formohydroxamic acid (FHA) and acetohydroxamic acid (AHA) are hydrophilic ligands that do not enter into TBP. Hydroxamic acids undergo hydrolysis in less than 3 M HNO_3 and result in the formation of hydroxylamine and carboxylic acid. Taylor and co-workers found that Np(VI) is reduced to Np(V) by AHA and FHA in nitric acid.[15] They verified that Np(VI) is effectively reduced and removed from the solvent phase bearing U(VI) by AHA and FHA in laboratory scale experiments.[35] Subsequently, further investigation of the reduction kinetics of Np(VI) by FHA in HNO_3 solution shows that it is rapidly reduced within a few seconds and is first order with respect to Np(VI) by stopped-flow spectrophotometry with a rate constant of $1.17 \times 10^3\ M^{-1}\ s^{-1}$ in 2 M HNO_3 solution at 22 °C.[67]

Chung and Lee investigated the reduction of Np(VI) by AHA in HNO_3 solution.[82] The reduction reaction is first-order relative to the concentration of Np(VI) and AHA with the rate constant of $191.2 \pm 11.2\ M^{-1}\ s^{-1}$ at 25 ± 0.5 °C and 1.0 M HNO_3 solution. Investigation of the reduction stripping behavior of Np(VI) by AHA from kerosene/30% TBP organic phase to HNO_3 solution[83] shows that the stripping rate is dominated by the kinetic process at the interface. In addition, the reduction kinetics of Np(VI) with AHA was studied with infrared spectroscopy in 1 M $HClO_4$ media.[84] When AHA is in excess, the reduction rate equation of Np(VI) is shown below:

$$-d[Np(VI)]/d_t = k[Np(VI)][AHA] \tag{29}$$

where $k = 2.57 \times 10^3\ M^{-1}\ s^{-1}$ at 10 °C.

When Np(VI) is in great excess relative to AHA, the mechanism of Np(VI) reduction is controlled by two different reactions. The reaction rate is 3.7×10^{-4} and $1.0 \times 10^{-3}\ s^{-1}$ for the first order mechanism at 10 °C and 22 °C, respectively.

2.7 Others

Rao and Choppin explored the reduction kinetics of Np(V) with three methylsalicylic acids (MSA) as shown in Fig. 4 using spectrophotometry.[85] Their rate constants decrease in the order of 5-MSA > 3-MSA > 4-MSA, which is attributed to the electronic effect of substituents. Humic acid (HA) is one of the significant species in groundwater. The rate constant for Np(VI) reduction by HA is $59 \pm 6\ M^{0.1}\ min^{-1}$ at 10 °C and $\mu = 0.41$.[86] Additionally, the reduction kinetics of Np(VI) by H_2O_2 was studied in a perchloric acid–sodium perchlorate solution.[87] The stoichiometric equation was established to be $2Np(VI) + H_2O_2 = 2Np(V) + 2H^+ + O_2$. The respective rate of Np(VI) reduction by H_2O_2 is $(2.19 \pm 0.01) \times 10^3$ in 0.05 M Na_2CO_3 at 25 °C.[88] In addition, ethylenediaminetetraacetic acid (EDTA) is a common organic chelating reagent that was studied to reduce Np(VI) in low ionic strength media.[89] EDTA can effectively reduce Np(VI) to Np(V) in the presence of organic complexes.

3 Theoretical progress on the reduction of Np(VI) to Np(V) by salt-free reagents

Simulation for accurate prediction of electronic structures and properties as well as the reaction mechanics of actinide systems is one of the most challenging issues in computational chemistry. Nevertheless, significant advances were achieved in the last few decades owing to the development of electronic structure methods for actinides and improvement in computational speed. Our group has theoretically explored the extraction behaviors of the actinide systems and the corresponding electronic structures as well as the bonding characters.[90–109] Recently, we have focused on exploring the mechanisms of Np(VI) reduction by some salt-free reagents using scalar-relativistic DFT calculations. All calculations of Np(VI) systems were performed using the B3LYP hybrid functional[110,111] within the Gaussian 16 program.[112] The scalar-relativistic effective core potentials (RECPs)[113] and the ECP60MWB-SEG valence basis set[114,115] were applied for Np. The solvation effect was considered by implicit solvation models, solvation model density (SMD)[116] or the conductor-like polarizable continuum model (CPCM) approach with Klamt's radii.[117,118] Transition states (TSs), initial complexes (ICs) and intermediates (INTs) were confirmed by the harmonic frequency calculations. The calculations of the intrinsic reaction coordinate were carried out to verify the ICs and INTs. The bonding change of the reduction process was analyzed using the quantum theory of atoms-in-molecules (QTAIM),[119,120] electron localization function (ELF),[121–123] and localized molecular orbitals (LMOs)[124] using the Multiwfn.[125,126] Analysis of spin density uncovered the oxidation state of the metal atom for ICs, TSs, and INTs, which can elucidate the nature of the reduction reaction.

3.1 Introduction to transition state theory and method

The studies on the mechanisms of Np(VI) reduction by salt-free reagents essentially depend on the transition state theory, which has been successfully applied to actinide systems.[38,127–131] Here, we briefly introduce transition state theory. The concepts of potential energy surface and saddle point were originally introduced by Pelzer and Wigner.[132] Later, Erying and Polanyi proposed the transition state theory (TST) based on quantum mechanics and statistical mechanics when they studied organic reactions from reactants to products in 1935.[133,134] TST includes classic and generalized TSTs. Classic TST is a statistical-mechanical

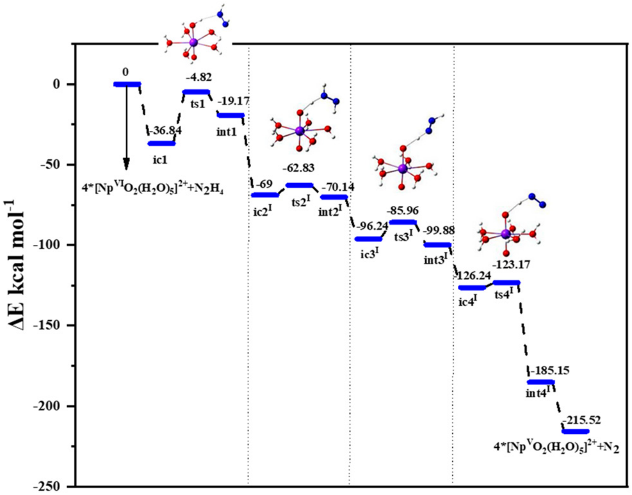

Fig. 6 PEP and four TS structures for $[Np^{VI}O_2(H_2O)_5]^{2+}$ reduction by N_2H_4.

theory of chemical reaction rate according to the no-return assumption and the quasi-equilibrium assumption. That is, transition states are in local equilibrium with reactant molecules and do not return to the reaction region once they fall into the product region. The generalized TST defines the transition state as a hypersurface in phase space and no longer localizes the transition state to the saddle point of the reaction pathway.

3.2 Hydrazine and its derivatives

Hydrazine and its derivatives reduce Np(VI) to Np(V) in the PUREX process, while their reduction mechanisms remain unclear. Therefore, studies on their reduction mechanism of Np(VI) to Np(V) using theoretical approaches are needed. The reduction mechanism of Np(VI) by hydrazine was explored theoretically and three reaction pathways were obtained.[36] A free radical mechanism is thermodynamically and kinetically feasible based on the results for energy barrier and thermodynamic energy (Fig. 6). Np(VI) reduction by N_2H_4 accompanies dissociation of the N–H bond and formation of the O_{yl}–H bond. To investigate the influence of substituent effects of hydrazine on the reducing ability of Np(VI), the mechanisms of Np(VI) by $CHON_2H_3$, $HOC_2H_4N_2H_3$ and $CH_3N_2H_3$ were explored.[43] Their reduction mechanisms are similar, based on the potential energy profiles (PEPs), the order of the energy barrier follows $HOC_2H_4N_2H_3$ (15.15) < $CH_3N_2H_3$ (16.57) < $CHON_2H_3$ (25.73 kcal mol^{-1}) for the free radical ion mechanism, which agrees with the rates of reduction observed in the experiments.

Carbohydrazide ($CO(N_2H_3)_2$) appears significant for potential applications in reducing Np(VI) to Np(V) in high-burn-up SNF. The mechanism of Np(VI) reduction by $CO(N_2H_3)_2$ is shown in Fig. 7.[45] The calculated energy barrier agrees with the experimental activation energy.[66] The value of spin density (Fig. 8) shows that the reduction nature is outer-sphere electron transfer and hydrogen transfer.

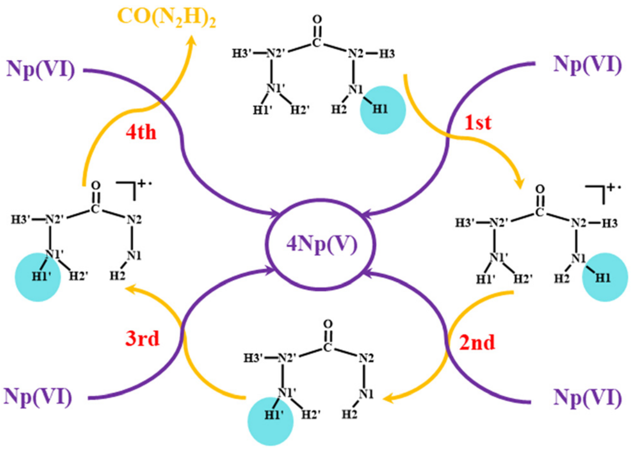

Fig. 7 Mechanism of Np(VI) reduction by $CO(N_2H_3)_2$. Reprinted with permission from ref. 45. Copyright 2023, American Chemical Society.

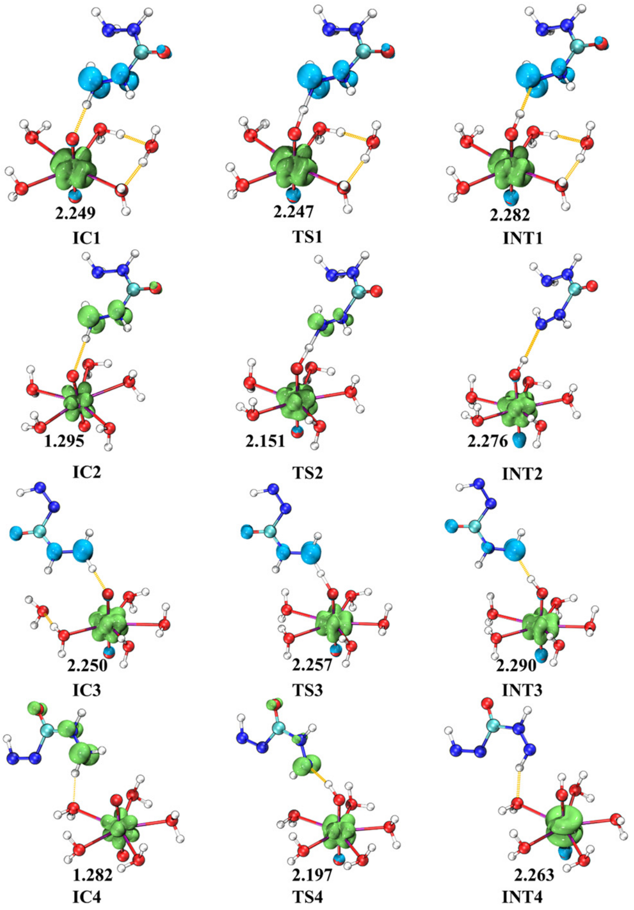

Fig. 8 Diagrams and value of spin density on the Np atom for the ICs, TSs and INTs of Np(VI) reduction by $CO(N_2H_3)_2$. Yellow dashed lines depict H-bonds. Reprinted with permission from ref. 45. Copyright 2023, American Chemical Society.

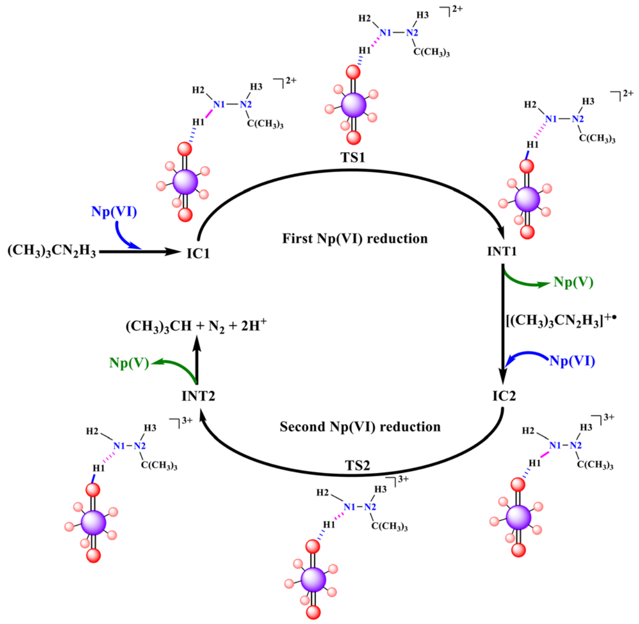

Fig. 9 Reduction processes of Np(VI) ions by $(CH_3)_3CN_2H_3$. Reprinted with permission from ref. 41. Copyright 2024, Springer Nature.

Tert-butylhydrazine ($(CH_3)_3CN_2H_3$) has exceptional selectivity in the reduction of Np(VI) in experiments, and the reduction reaction of Np(VI) with $(CH_3)_3CN_2H_3$ was explored using scalar-relativistic DFT.[41] During Np(VI) reduction, the free radical ion $[(CH_3)_3CN_2H_3]^{+\bullet}$ intermediate can achieve another Np(VI) reduction (Fig. 9). The first Np(VI) reduction in pathway I and the second Np(VI) reduction in pathway III is kinetically optimal based on the energy barrier of the pathways. The reduction nature of the first and second Np(VI) reduction for the three pathways is outer-sphere electron transfer and hydrogen transfer, respectively. Moreover, the optimal reduction process from IC2 to TS2 is probably due to the existence of water-mediated proton transfer.

The short τ_{99} for the Np(VI) reduction by phenylhydrazine ($C_6H_5N_2H_3$) and hydrazinopropionitrile ($NCCH_2N_2H_3$) indicates that they quickly reduce Np(VI) to Np(V), which was confirmed by theoretical investigations.[37,44] Pathways I and II are the free radical ion mechanism and pathway III is the free radical mechanism for Np(VI) reduction by $C_6H_5N_2H_3$ (Fig. 10(a)). The first Np(VI) reduction by $C_6H_5N_2H_3$ is the rate-determining step with an energy barrier of 12.89 kcal mol^{-1}. LMOs of the structures for pathway II reveal N–H bond dissociation and O_{yl}–H bond formation. The reduction kinetics of Np(VI) by $NCCH_2N_2H_3$ was studied. Each $NCCH_2N_2H_3$ molecule can reduce two Np(VI) ions and the second Np(VI) reduction is the rate-determining step, with an energy barrier of 14.36 kcal mol^{-1}. This is attributed to water-mediated proton transfer.[37] The fast reduction kinetics of Np(VI) by $NCCH_2N_2H_3$ and $C_6H_5N_2H_3$ is attributed to the σ–π hyperconjugation effect and delocalized π-orbital, respectively. The spin density of the Np atom indicates that the reduction of Np(VI) by $NCCH_2N_2H_3$ arises from outer-sphere electron transfer and hydrogen transfer.

The stable Np(VI) species are $[Np^{VI}O_2(H_2O)_5]^{2+}$, $[Np^{VI}O_2(NO_3)(H_2O)_3]^+$ and $[Np^{VI}O_2(NO_3)_2(H_2O)]$ in 0–14 M HNO_3 solution.[135] The reduction mechanisms of $[Np^{VI}O_2(NO_3)(H_2O)_3]^+$ by $CH_3N_2H_3$[136] and $[Np^{VI}O_2(NO_3)_2(H_2O)]$ by N_2H_4, $CHON_2H_3$, and $HOC_2H_4N_2H_3$[42] were also explored. The reduction of $[Np^{VI}O_2(H_2O)_5]^{2+}$ by $CH_3N_2H_3$ has a lower energy barrier compared with that of $[Np^{VI}O_2(NO_3)(H_2O)_3]^+$ due to the coordination of nitrate ions (Fig. 10(b)). To further explore the influence of nitrate ions on the energy barrier of Np(VI) reduction, the reactions for $[Np^{VI}O_2(NO_3)_2(H_2O)]$ with N_2H_4, $CHON_2H_3$, and $HOC_2H_4N_2H_3$ were also investigated. $[Np^{VI}O_2(NO_3)_2(H_2O)]$ reduction by the three reductants needs to overcome the higher energy barrier. Overall, the reduction of Np(VI) becomes more difficult when the nitrate ion coordinates Np(VI).

3.3 Hydroxylamine and its derivatives

Hydroxylamine derivatives are promising salt-free reductants that can reduce Np(VI) to Np(V) in nitric acid solution and their kinetic behavior of Np(VI) to Np(V) were studied experimentally. The reduction mechanism of Np(VI) by diethylhydroxylamine (DEHA) in aqueous solution was explored using scalar-relativistic DFT.[39] The whole reduction process of Np(VI) to Np(V) by DEHA occurs *via* four stages (Fig. 11). For the first stage, the Ho atom of DEHA contacts the O_{yl} atom of $[Np^{VI}O_2(H_2O)_5]^{2+}$ and forms Np(V) and free radical $(C_2H_5)_2\dot{N}O$. Subsequently, the H_C atom of free radical $(C_2H_5)_2\dot{N}O$ contacts the O_{yl} atom of $[Np^{VI}O_2(H_2O)_5]^{2+}$ and obtains Np(V) and $(C_2H_5)_2N(O)C_2H_4$ for the second stage. Then, $(C_2H_5)_2N(O)C_2H_4$ is quickly hydrolyzed to mono-substituted C_2H_5NHOH, which can further reduce Np(VI) *via* two reaction pathways due to the different participating position of the H atom. The largest energy barrier among the four Np(VI) reduction processes is 12.23 kcal mol^{-1} for the third stage of pathway I, which indicates that the reduction rate of Np(VI) by DEHA is rapid, agreeing with the

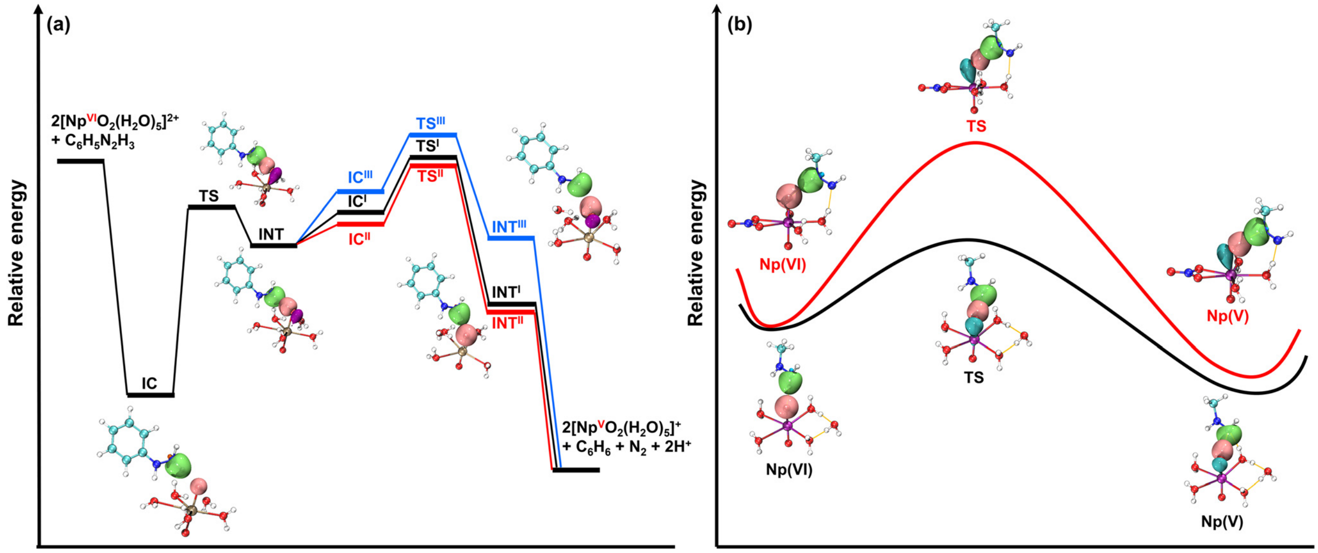

Fig. 10 Three PEPs for Np(VI) reduction with $C_6H_5N_2H_3$ and LMOs for the structures of pathway II (a). Reprinted with permission from ref. 45. Copyright 2023, American Chemical Society. PEPs for $[Np^{VI}O_2(H_2O)_5]^{2+}$ and $[Np^{VI}O_2(NO_3)(H_2O)_3]^+$ reduction by $CH_3N_2H_3$ (b).

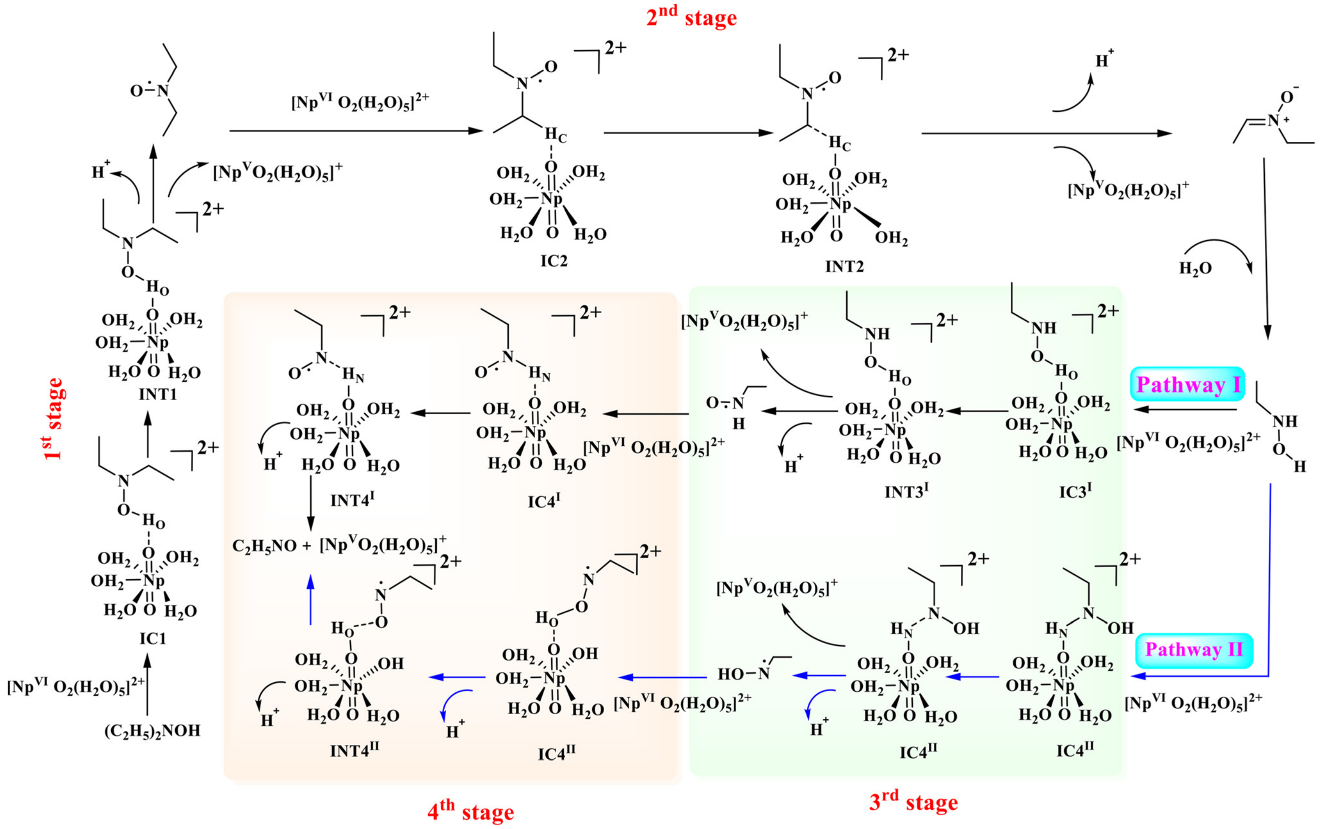

Fig. 11 Reaction of Np(VI) with DEHA. Reprinted with permission from ref. 39. Copyright 2024, The Royal Society of Chemistry.

experimental observations. The Np–O_{yl} bond distances and spin density on Np elucidate the reduction essence, including outersphere electron transfer or hydrogen atom transfer.

The reduction rates of Np(VI) by hydroxylamine (HA), monomethyl substituted *N*-methylhydroxylamine (MHA) and dimethyl substituted *N*,*N*-dimethylhydroxylamine (DMHA) are different. To evaluate the impact of methyl substitution on the reduction mechanism, the Np(VI) reduction reactions by HA, MHA and DMHA were theoretically investigated (Fig. 12).[40] The electron density results indicate that the nature of Np(VI) reduction by HA and the first Np(VI) reduction by methyl-substituted MHA and DMHA are hydrogen atom transfer processes. Meanwhile, the second Np(VI) reduction is outersphere electron transfer, probably due to the electronic effect of methyl substitution. The rate-determining step for MHA and DMHA is the first Np(VI) reduction, Moreover, the energy barrier for the Np(VI) reduction by DMHA is lower than that by MHA, which reflects that the reaction rate of the former is faster than that of the latter. This work provided a kinetic insight into the effect of methyl substitution on the reduction of Np(VI) by hydroxylamine.

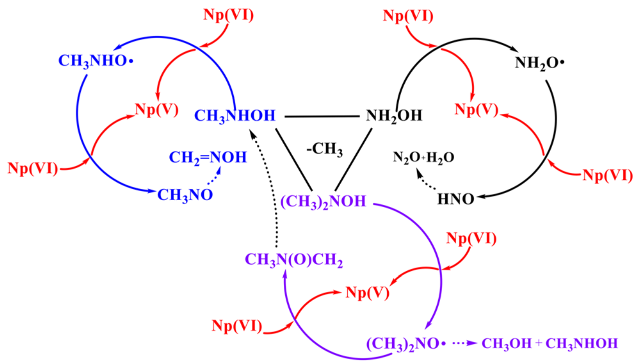

Fig. 12 Redox process of Np(VI) with HA, MHA and DMHA. Reprinted with permission from ref. 40. Copyright 2025, The Royal Society of Chemistry.

3.4 Other related reactions of Np(VI)

As far as we know, there are no theoretical investigations on the Np(VI) reduction by other reductants, except for hydrazine and hydroxylamine and their derivatives as discussed above. Some relevant Np(VI) reactions were explored by applying theoretical approaches, including the water exchange mechanism of neptunyl(VI) aqua ion[38,130] and the hydrolysis mechanism of $[(CH_3)Np^{VI}O_2(O_2C{-}CH_3)_2]^-$.[129] The water exchange of the $[Np^{VI}O_2(H_2O)_5]^{2+}$ complex can be achieved by dissociative-, associative-, and interchange mechanisms.[38] The reaction pathway and the corresponding structures are presented in Fig. 13(a and b). As for the dissociative water exchange mechanism, the water molecule in the second shell gradually deviates from the neptunyl ion in the structure of IC to INT. Concurrently, a water molecule coordinated to

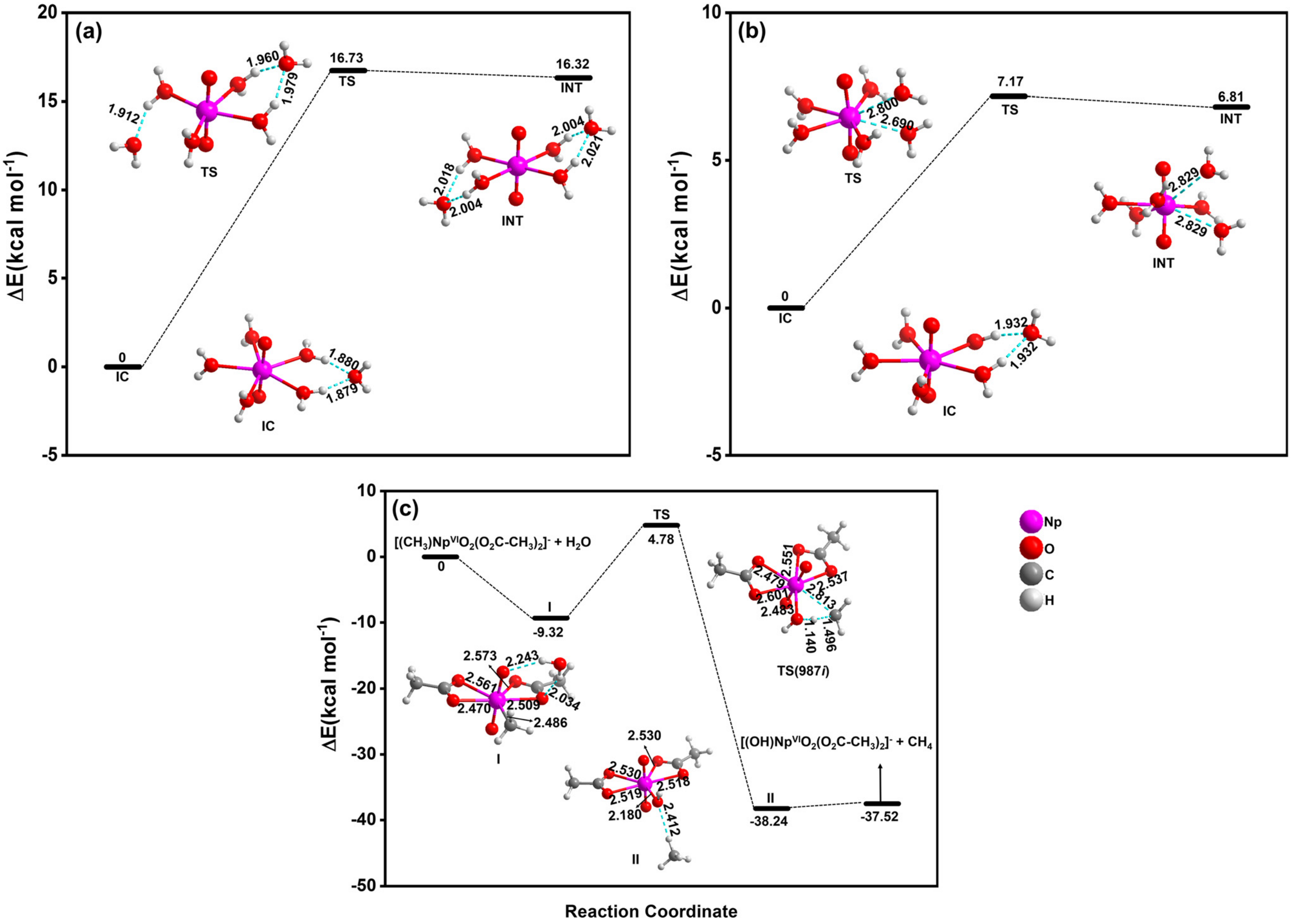

Fig. 13 Reaction pathway and the corresponding structures for the dissociative (a) and associative (b) water exchange mechanisms for the $[Np^{VI}O_2(H_2O)_5]^{2+}$ complex. Reprinted with permission from ref. 38. Copyright 2004, American Chemical Society. PEP and the corresponding structures for the $[(CH_3)Np^{VI}O_2(O_2C–CH_3)_2]^-$ hydrolysis reactions (c). Reprinted with permission from ref. 130. Copyright 2018, American Chemical Society.

Np(VI) shifts out of the initial coordination sphere and forms two hydrogen bonds in the INT with four-coordinated Np(VI) (Fig. 13(a)). As for the associative water exchange mechanism in Fig. 13(b), the six-coordinated Np(VI) complex was formed. The energy barrier for the dissociative water mechanism is 16.73 kcal mol^{-1}, which is obviously larger than that for the associative one (7.17 kcal mol^{-1}), indicating that the latter is more feasible kinetically. The hydrolysis reaction of $[(CH_3)Np^{VI}O_2(O_2C–CH_3)_2]^-$ was investigated in Fig. 13(c).[129] $[(CH_3)Np^{VI}O_2(O_2C–CH_3)_2]^-$ with one water molecule forms structure **I** by two hydrogen bonds, which is characterized as the exothermic reaction with the energy of 9.32 kcal mol^{-1}. Structure **I** overcomes the energy barrier of 14.10 kcal mol^{-1} and forms structure **II**. In this process, the H atom from the H_2O molecule transfers to the CH_3^- fragment coordinated with Np(VI), which leads to the coordination of the hydroxyl group (OH^-) with Np(VI) and formation of the methane molecule. Essentially, the hydrolysis reaction of $[(CH_3)Np^{VI}O_2(O_2C–CH_3)_2]^-$ was achieved by the dissociation of the water molecule, leading to the exchange of ligands from the CH_3^- to OH^- group.

4 Conclusions and outlook

An important aim of the future advanced PUREX process is to create a single cycle reprocessing flowsheet that streamlines plant size, simplifies operations, and minimizes waste. The effective control of the valence state of Np is an important factor in the single cycle design. Although many salt-free reagents have been studied for the Np(VI) reduction, it is not easy to accomplish within the simplified flowsheets favored for an advanced reprocessing plant. Hydrazine and its derivatives, as well as *n*-butyraldehyde effectively reduce Np(VI) to Np(V) and do not reduce U(VI) and Pu(IV) under specific experimentally conditions, which are suitable for the Np separation. Hydroxylamine and its derivatives, as well as iso-butyraldehyde efficiently and quickly reduce Pu(IV) to Pu(III) and Np(VI) to Np(V), so they are applied to separate Np and Pu from U. The reduction ability of Np(VI) with different salt-free reagents are suitable for different flowsheets, but no single reductant has been applied for the Np(VI) reduction in a single cycle reprocessing flowsheet.

Therefore, it is essential to develop effective reductants for the U/Np and Np/Pu separation during SNF reprocessing.

Generally, experimental techniques for the investigation of Np(VI) reduction by salt-free reagents are difficult or dangerous; therefore, theoretical simulation seems to be an effective method to obtain reliable predictions. However, computational approach for accurate prediction of electronic structures and mechanisms of Np(VI) reduction remains a scientific challenge due to their relativistic and electron correlation effects. It requires intensive algorithms and available computational power for large actinide systems. Fortunately, with the rapid development of artificial intelligence, machine learning (ML) and the improvement of computational power, *ab initio* molecular dynamics (AIMD) and quantum mechanics/molecular mechanics (QM/MM) is applied for Np(VI) reduction by salt-free reagents. ML facilitates high-throughput screening and can obtain the key descriptors between molecular structures and the reduction rate of Np(VI). AIMD can investigate the effect of temperature, solvent and nitric acid concentration on the reduction rate of Np(VI) in the water/organic phase. The QM/MM approach can evaluate local electron transfer between Np(VI) and salt-free reagents. These methods synergistically uncover electronic structure, bonding evolution, thermodynamics and kinetics of Np(VI) reduction by salt-free reagents.

In summary, research on the reduction of Np(VI) by salt-free reagents still faces many challenges. (1) Finding stable efficient salt-free reagents could be achieved by conducting an in-depth study on the reduction mechanism and kinetics of Np(VI) by salt-free reagents, and accurately controlling the amount of salt-free reagents and reaction conditions such as temperature, pH value, reaction time, *etc.* for quantitative reduction of Np(VI). (2) Np(VI) may form various coordinated complexes in different solutions, which increases the complexity of the Np(VI) reduction process. (3) Np is radioactive: special radioactive analysis techniques and equipment are required. Although the research on the reduction of Np(VI) by salt-free reagents faces many challenges, with the rapid development of science and technology, (1) it is expected to develop more salt-free reagents with excellent performance to achieve accurate and efficient reduction of Np(VI); (2) with the help of advanced spectroscopy technology and actinide quantum chemical calculations, the reaction mechanism of Np(VI) reduction by salt-free reagents is studied in depth, revealing the electron transfer and chemical bond evolution; (3) the environmentally friendly process of Np(VI) reduction by salt-free reagents is optimized to reduce the amount of radioactive substances. In conclusion, the design and development of a new and environmentally friendly process for Np(VI) reduction by salt-free reagents is one of the future directions for the nuclear fuel cycle. In conclusion, the design, synthesis and development of salt-free reagents that specifically reduce Np(VI) is one of the future directions for the nuclear fuel cycle.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Author contributions

Xin Huang and Xiao-Bo Li: writing – original draft. Qun-Yan Wu: writing – original draft, supervision. Wei-Qun Shi: supervision.

Conflicts of interest

There are no conflicts to declare.

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