Kinetics and Mechanism of Np and Pu Reactions with Organic Derivatives of Hydrazine*

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Investigation of the kinetics of the reactions of Np(VI) to Np(V) and Pu(IV) to Pu(III) reduction with organic derivatives of hydrazine is clearly of theoretical interest. This study shows that the reactions of this type proceed by a single mechanism and different reactivities of some derivatives of hydrazine correlate with a change in the basicity of those derivatives and with the induction effect of an organic radical – a substituent in a hydrazine molecule. On the other hand, the reactions are also interesting from the practical viewpoint and can be employed for reprocessing irradiated fuel of a nuclear power plant.

Results

Stoichiometry of Reactions

Analysis of the relative amounts of Np(V) or Pu(III) resulting from the full completion of the reactions with a reductant in deficit showed that the consumption of Np(VI) or Pu(IV) as calculated per mol of a hydrazine derivative varies from 2 to 4 mol with an increase in the ratio between the initial concentrations of an oxidant and a reductant. For example, for the Np(VI)–methylhydrazine reaction, the following data were found [1]:

$[Np(VI)]_0/[CH_3N_2H_4^+]_0$	2	4	6	10	20
$[Np(V)]/[CH_3N_2H_4^+]_0$	2.0	2.9	3.4	3.7	4.0

Reactions of the similar type are likely to proceed according to two maximum stoichiometric equations: in excess of a reductant, according to eqn. (1):

$$2NpO_2^{2+} + RN_2H_4^+ = 2NpO_2^+ + RH + N_2 + 3H^+ \qquad (1)$$

and in excess of an oxidant, according to eqn. (2):

$$4NpO_2^{2+} + RN_2H_4^+ + H_2O = 4NpO_2^+ + ROH + N_2 + 5H^+ \qquad (2)$$

Kinetics of Np(VI) Reactions

The kinetics of Np(VI) reactions were studied in perchloric and nitric acid media at the ionic strength $\eta = 1$–4, supported through the addition of sodium perchlorate or nitrate. Under conditions of a significant excess of a reductant the reactions proceed according to the kinetic equation of the first-order relative to Np(VI) (Fig. 1); the first-order rate constant k' increases in proportion to the concentration of hydrazine derivative. Hence,

$$-d[Np(VI)]/dt = k_1[Np(VI)][RN_2H_4^+] \qquad (3)$$

Hydrogen ions retard all the reactions studied, while the order relative to these ions is equal or close to −1. Thus, the general equation of the reaction rate is

$$-\frac{d[Np(VI)]}{dt} = k\frac{[Np(VI)][RN_2H_4^+]}{[H^+]^n} \qquad (4)$$

where $n \approx 1$. This dependence is illustrated by the data of Table I on the Np(VI)–1,1-dimethylhydrazine reaction at different temperatures and the ionic strength of the solution $\eta = 2$ as well as by Fig. 2 for the Np(VI)–ethylhydrazine reaction at $\eta = 1$.

It should be noted that the solution ionic strength, which can be changed through the addition of sodium perchlorate, does not affect (or it retards insignifi-

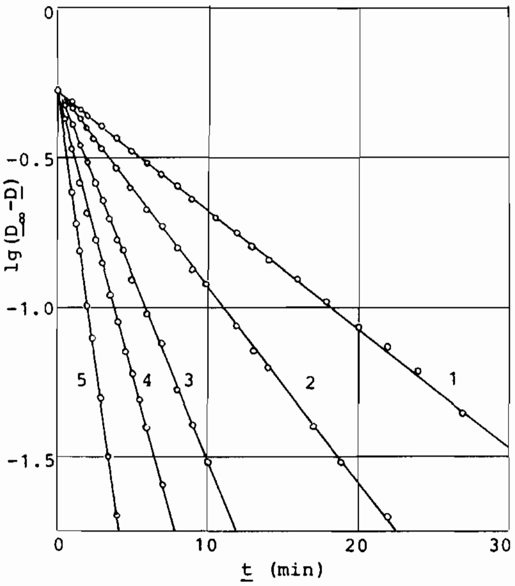

Fig. 1. Time dependence of $\log(D_\infty - D)$ on t for the reaction between Np(VI) and methylhydrazine in $HClO_4$ at $[H^+] = 1.5$ mol/l, $\eta = 2$ and 25 °C where: $[CH_3N_2H_4^+] = 4 \times 10^{-3}$ (1); 7×10^{-3} (2); 1.25×10^{-2} (3); 2.2×10^{-2} (4) and 4×10^{-2} mol/l (5). D_∞ and D are optical densities following the reaction and at time t.

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TABLE I. Dependence of the Second-order Rate Constant of Np(VI)–1,1-Dimethylhydrazine Reaction on the H^+ Ion Concentration and Temperature in $HClO_4$ + $NaClO_4$ Solution at $\eta = 2$

$[H^+]$ mol/l	k_1 (l/mol/min) (at given temperatures)			
	25.0 °C	30.8 °C	37.5 °C	40.7 °C
0.2	214	307	407	550
0.5	87.8	106	173	191
1.0	45.0	64.3	85.0	103
1.4	31.1	43.1	59.2	69.9
2.0	21.7	30.9	41.5	52.0

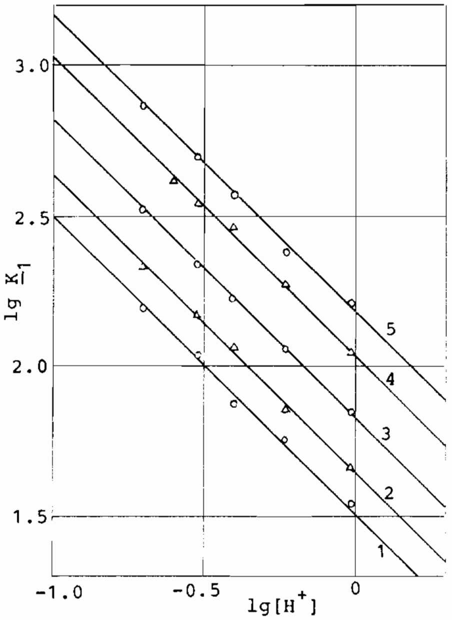

Fig. 2. Dependence of log k_1(l/mol/min) on log$[H^+]$(mol/l) for the reaction between Np(VI) and ethylhydrazine at $\eta = 1$ and temperatures: 25.0 (1); 30.7 (2); 36.4 (3); 41.0 (4) and 45.6 °C (5).

cantly) the reactions. When going from chloric to nitric acid medium the rate constant somewhat increases, with the exception of the Np(VI)–acetylhydrazine reaction where the rate constant retains its value.

Table II tabulates the general rate constants of all the Np(VI) reactions studied at 25 °C and $\eta = 2$ and the order of the reactions n relative to H^+ ions. For the sake of comparison, the data are also given on the hydrazine reaction [2, 3]. It can be seen that when the organic radicals studied are introduced into a hydrazine molecule the rate of Np(VI) ion reduction increases in some instances. At the same time, as compared to hydrazine, the introduction of radicals such as formyl and acetyl results in the reaction slowing down.

TABLE II. Rate Constants of Np(VI)–Hydrazine Derivative Reactions at 25 °C and $\eta = 2$

Reductant	Medium	n	k (min^{-1})
$N_2H_5^+$	$HClO_4$	1.25	10.4
	HNO_3	1.24	14.0
$CH_3N_2H_4^+$	$HClO_4$	1.0	32.1
	HNO_3	1.0	52.7
$C_2H_5N_2H_4^+$	HNO_3	1.0	30.0
$(CH_3)_2N_2H_3^+$	$HClO_4$	1.0	43.0
$CH_3N_2H_3CH_3^+$	$HClO_4$	0.8	88.0
	HNO_3	0.8	118
$CH_2CHCH_2N_2H_4^+$	HNO_3	1.0	46.0
$HC(O)N_2H_4^+$	HNO_3	1.0	7.95
$CH_3C(O)N_2H_4^+$	$HClO_4$	1.2	8.44
	HNO_3	1.2	7.52
$C_6H_5CH_2N_2H_4^+$	$HClO_4$	1.0	38.9
	HNO_3	1.0	54.4
$N_2H_4C_2H_4N_2H_4^{2+}$	$HClO_4$	1.0	41.0
$HOC_2H_4N_2H_4^+$	$HClO_4$	1.0	285
	HNO_3	1.0	302
$C_2H_5OC(O)N_2H_4^+$	HNO_3	1.2	19.3
$C_2H_5OC(O)CH_2N_2H_4^+$	HNO_3	1.1	97.0

TABLE III. Rate Constants of Reactions between Pu(IV) and Hydrazine Derivatives in HNO_3 Solution at $\eta = 2$

Reductant	t (°C)	n	k (min^{-1})
$N_2H_5^+$	50	1.0	0.361
$CH_3N_2H_4^+$	31	1.0	0.088
$CH_3N_2H_3CH_3^+$	25	1.0	0.15

Kinetics of Pu(IV) Reactions

The interaction of Pu(IV) with methylhydrazine and symmetrical 1,2-dimethylhydrazine has been studied. Both reactions were studied in HNO_3 solution and the results are summarized in Table III, together with the early data on the Pu(IV)–hydrazine reaction [4]. The investigations showed that the course of the reactions obeys the same kinetic regularities as the Np(VI) reactions. The general equation of the rate of the reactions is:

$$-\frac{d[Pu(IV)]}{dt} = k\,\frac{[Pu(IV)]\,[RN_2H_4^+]}{[H^+]} \qquad (5)$$

The introduction of various organic radicals into a hydrazine molecule increases the rate of Pu(IV) reduction. At the same time it should be noted that Pu(IV) reactions proceed at a significantly slower rate than the corresponding reactions of Np(VI). For example, in the case of methylhydrazine the rates of these two reactions differ by a factor of ~1000 (at

25 °C). This difference can be used in separation of Np and Pu on fuel reprocessing, if the corresponding conditions and reaction time are chosen so that Np(VI) could be fully reduced to the inextractable pentavalent state and Pu(IV) could remain tetravalent.

The reaction rates of Pu(IV) with hydrazine derivatives as well as those of Np(VI) are slightly dependent on the ionic strength of the solution. If this fact and eqns. (3) and (5) are taken into account one can assume the mechanisms of these reactions to be similar.

On account of the slow rate of Pu(IV) reactions it is of interest to discuss possible homogeneous catalysts of these reactions. It has been shown previously [5] that molybdenum(VI) salts accelerate the reduction of Pu(IV) with hydrazine. A similar action is also effected by Mo(VI) ions on the reaction between Pu(IV) and methylhydrazine. Since Mo(V) interacts with Pu(IV) at a fast rate [5] and Mo(VI) slowly reacts with methylhydrazine, at a fairly high catalyst concentration the general reaction proceeds according to the equation of the first-order relative to Mo(VI) and methylhydrazine, and zero-order relative to Pu(IV) and H^+ ions. When the catalyst concentration is not high enough, a certain contribution is made by a non-catalyzable reaction between Pu(IV) and methylhydrazine. Therefore, the general rate equation becomes eqn. (6).

$$-\frac{d[\mathrm{Pu(IV)}]}{dt} = k\,\frac{[\mathrm{Pu(IV)}][\mathrm{CH_3N_2H_4^+}]}{[\mathrm{H^+}]} + k_2[\mathrm{Mo(VI)}][\mathrm{CH_3N_2H_4^+}] \tag{6}$$

in which $k = (8.77 \pm 0.50) \times 10^{-2}$ min^{-1} and $k_2 = 1.50 \pm 0.06$ l/mol/min at $\eta = 2$ and 31 °C.

Activation Thermodynamics

The thermodynamic values of the process of activated complex formation in the reactions of Np(VI) studied are given in Table IV. Attention should be paid to two special features of variations in these values. First, all the reactions studied except for those of formyl-, acetyl- and benzyl-hydrazine, are characterized by the negative values of the activation entropy. Second, the higher ΔS^* value is in line with the higher ΔH^* value and thus, in the reactions discussed, a compensation effect is observed that is expressed by relation (7):

$$\Delta H^* = \alpha + \beta\Delta S^* \tag{7}$$

then for the Np(VI) reactions $\alpha = 73.5 \pm 1.7$ kJ/mol and $\beta = 310 \pm 30$ K.

It should also be noted that the free energy of activation of Pu(IV) reactions is 20–25 kJ/mol higher than that of the respective Np(VI) reactions. The significant difference between the rates of the reactions of these two types is due to a change in both enthalpy and entropy terms in the free energy of activation.

TABLE IV. Enthalpy, Free Energy and Entropy of Activation of Np(VI)–Hydrazine Derivative Reactions at 25 °C

Reductant	ΔH^* kJ/mol	ΔG^* kJ/mol	ΔS^* J/mol/K
$N_2H_5^+$	67.7	76.6	−30
$CH_3N_2H_4^+$	56.1	73.3	−58
$C_2H_5N_2H_4^+$	59.0	74.6	−52
$CH_3N_2H_3CH_3^+$	47.3	71.1	−80
$CH_2CHCH_2N_2H_4^+$	61.1	72.7	−42
$HC(O)N_2H_4^+$	82.7	78.0	16
$CH_3C(O)N_2H_4^+$	74.0	66.7	24
$C_6H_5CH_2N_2H_4^+$	95.7	73.3	75
$N_2H_4C_2H_4N_2H_4^{2+}$	62.9	73.9	−37
$HOC_2H_4N_2H_4^+$	54.2	69.0	−50
$C_2H_5OC(O)N_2H_4^+$	62.9	75.9	−44
$C_2H_5OC(O)CH_2N_2H_4^+$	62.0	71.7	−33

Discussion

When discussing the mechanism of reactions of Np(VI) and Pu(IV) reduction with hydrazine derivatives, attention should be paid to two experimental factors: (i) the order of the reactions relative to H^+ ions is equal or close to −1; (ii) the ionic strength of the solution does not practically affect the rate. It is likely that at the slow stages of these reactions one of the reacting ions interacts in a form the concentration of which is inversely proportional to the concentration of H^+ ions; in this case the form must be an electrically neutral particle. These two conditions are met by a mechanism in which a hydrated actinide ion interacts with a hydrazine derivative molecule at the slow stage, e.g.,

$$\mathrm{NpO_2^{2+} + RN_2H_3 \longrightarrow NpO_2^+ + RN_2H_3^{+\bullet}} \tag{8}$$

Since in acid solution hydrazine derivatives are available as protonated ions $RN_2H_4^+$, their concentration in the molecular form is equal to:

$$[\mathrm{RN_2H_3}] = \frac{K_a[\mathrm{RN_2H_4^+}]}{K_a + [\mathrm{H^+}]} \tag{9}$$

where K_a is the equilibrium constant for $RN_2H_4^+ \rightleftharpoons RN_2H_3 + H^+$.

The ion-radical $RN_2H_3^{+\bullet}$ that forms at stage (8) quickly oxidizes to a diazenium ion:

$$\mathrm{N_2H_3^{+\bullet} + NpO_2^{2+} \longrightarrow RN_2H_2^+ + NpO_2^+ + H^+} \tag{10}$$

The subsequent interaction of diazenium ions depends on the ratio between the concentrations of oxidant and reductant in solution: in excess actinide ions an oxidation reaction predominantly proceeds to form alcohol and nitrogen:

$$RN_2H_2^+ + 2NpO_2^{2+} + H_2O \longrightarrow ROH + 2NpO_2^+ + N_2 + 3H^+ \quad (11)$$

while with an oxidant deficit a diazenium ion decomposition reaction proceeds

$$RN_2H_2^+ \longrightarrow RH + N_2 + H^+ \quad (12)$$

If χ is a rate constant of slow stage (8), it is obvious that

$$-d[NpO_2^{2+}]/dt = \chi[NpO_2^{2+}][RN_2H_3] \quad (13)$$

or by substituting eqn. (9) into (13) one finds

$$-\frac{d[NpO_2^{2+}]}{dt} = \chi K_a \frac{[NpO_2^{2+}][RN_2H_4^+]}{[H^+]} \quad (14)$$

taking into account that $K_a \ll [H^+]$. Thus, the reaction rate must correlate with the basicity values of hydrazine derivatives which are really observed.

It is also interesting to note the symbate nature of a variation of reaction rates and the induction effect of a radical substituent in a hydrazine molecule. As for the reactivity of hydrazine derivatives with respect to the reaction with NpO_2^{2+} ions, all the substituents studied can be placed in a series (in HNO_3 solution):

$$CH_3C(O) < HC(O) < H < C_2H_5OC(O) < C_2H_5 < CH_2CHCH_2 < CH_3 < C_6H_5CH_2 < C_2H_5OC(O)CH_2 < CH_3{-}CH_3 < HOC_2H_4$$

It can be seen that radical substituents having a positive induction effect (*i.e.*, repulsing electrons and increasing the electron density on a nitrogen atom) accelerate Np(VI) reduction as compared to unsubstituted hydrazine. On the other hand, substituents having a negative induction effect retard this interaction. It is a pity that due to the lack of complete data on the induction constants of the substituents studied it is impossible to validate the quantitative correlation dependence of the indicated values.

As far as the mechanism of the Pu(IV)–methylhydrazine reaction catalysis with Mo(VI) ions is concerned, taking into account the first order of the catalyzed reaction relative to Mo(VI) and methylhydrazine, and the order equal to −1 relative to H^+ ions and zero relative to Pu(IV), one can assume that at the slow catalysis stage MoO_2^{2+} ions interact with $CH_3N_2H_3$ molecules, while the MoO_2^+ ions formed are quickly oxidized with Pu^{4+} ions.

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