

Modeling the autocatalytic reaction between Tc(VII) and methyl-hydrazine in HNO₃ solution

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The reduction of Tc(VII) by methyl-hydrazine(MMH) in HNO₃ aqueous solution was studied under different conditions. A logistic equation widely used for modeling autocatalytic reaction was adopted to simulate the target reaction. All the experimental data were consistent with the proposed equation. Results showed that Tc(VII) was reduced by MMH in two ways, the stepwise reduced by MMH and the autocatalytic reduced by Tc(IV). Isothermal experiments were done at temperatures ranging from 40 °C to 55 °C and the activation energy were obtained to be 31.51 kJ/mol and 65.68 kJ/mol for the stepwise reduction and autocatalytic reduction, respectively.

Keywords: Technetium, Autocatalytic reaction, PUREX, Methyl-hydrazine, Logistic equation

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I. INTRODUCTION

An advanced salt-free PUREX process was developed by China Institute of Atomic Energy, which adopts *N,N*-dimethylhydroxylamine (DMHAN) as reductant and methyl-hydrazine (MMH) as stabilizer in U/Pu splitting stage. DMHAN can rapidly reduce Pu(IV) to Pu(III), and MMH acts as HNO₂ scavenger [1]. MMH is a moderate reductant, which may reduce Tc(VII) to lower valence so as to influence the distribution of technetium in the process. Previous works indicated that DMHAN could not reduce Tc(VII) in HNO₃ solution [2]. But technetium goes into aqueous solution mainly in Tc(IV) form in the U/Pu splitting stage of the advanced PUREX process [3], suggesting that Tc(VII) is mainly reduced by MMH in this system.

The reaction between technetium and hydrazine was studied in many papers [4–6]. It is well known that technetium can catalyze the reduction of hydrazine by nitric acid. So far the reaction between technetium and MMH has not been investigated yet, and previous works about technetium mainly focus on the effect of technetium on the consumption of reductant. In this paper, the reaction between technetium and MMH was studied in detail under different conditions and the concentration of Tc(VII) was inspected to discover the transformation of the technetium valence. So it is very helpful for uncovering the mechanism of the over-consumption of MMH and for understanding the behavior of technetium in the advanced PUREX process.

II. EXPERIMENTAL DETAILS

A. Reagents and instruments

NH₄TcO₄ was purchased from Oak Ridge National Laboratory (ORNL) and dissolved in distilled water. 2,4,6-trimethylpyridine was bought from Fluca chemical reagent company. Liquid scintillation spectrometer manufactured by

Beckman was used for the measurement of technetium. The cocktail solution used in the liquid scintillation measurement was prepared by dissolving 1 g triphosphoxane, 16 g 2,5-diphenyloxazole and 300 g naphthalene in 2 L dioxane. All the other chemicals used were of analytical grade.

B. Analysis

The concentrations of MMH and HNO₃ were determined by titration method using a glass electrode to monitor the pH value. Tc(VII) concentration was detected using liquid scintillation method after it was extracted by 2,4,6-trimethylpyridine in alkaline solution [7].

C. Procedure

All the experiments were carried out in a 20 mL test tube, which was set in a constant temperature bath pot. All the reactants were preheated to keep the reaction temperature. After the reactants were mixed together, a tiny volume of solution was sampled immediately and at regular intervals in the whole experiment course. The sampled solution was kept in a sealed tube and put in ice water bath to freeze the reaction for latter analysis.

To predict technetium behavior in the real reprocessing process, the initial concentrations of all the reactants in the experiments are similar as their concentrations in the U/Pu splitting stage of the advanced PUREX process. The concentrations of MMH and HNO₃ are hundreds times as high as that of technetium and only a little MMH and HNO₃ is consumed in reaction process, so the concentrations of MMH and HNO₃ can be treated as constants in data processing.

III. RESULTS AND DISCUSSION

A. Mechanism consideration and technetium effect on the reaction

The effect of initial Tc(VII) on the reaction is shown in Fig. 1. The curves present a typical sigmoid shape. Tc(VII)

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is reduced relatively slow at the beginning, which is called induction period. Then Tc(VII) concentrations decline sharply, the reaction turns into fast reaction period. At the end of the reaction, the reduction of Tc(VII) becomes slow again. A remarkable phenomenon is that Tc(VII) is consumed much faster in the condition of higher initial Tc(VII) concentration at the experiment conditions, which suggests that the reduced product of Tc(VII) may accelerate the consume of Tc(VII). In all experiments Tc(VII) could not be reduced completely, about 10% remained in the solution.

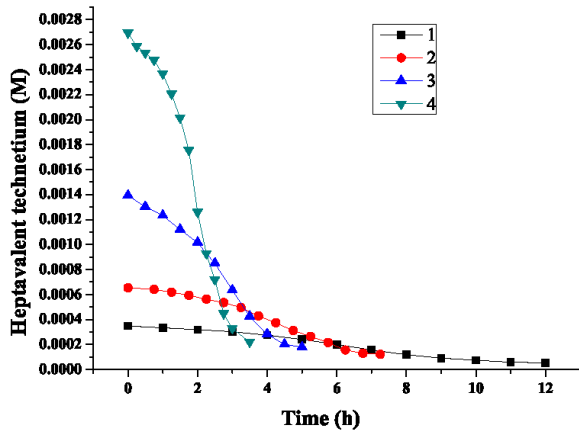
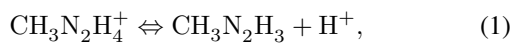


Fig. 1. (Color online) Tc(VII) concentration versus time under different initial Tc(VII) concentrations 40 °C, $c_0(\text{HNO}_3) = 1.5 \text{ M}$, $c_0(\text{MMH} \cdot \text{HNO}_3) = 0.15 \text{ M}$, $c_0(\text{Tc(VII)})$: 1: $3.48 \times 10^{-4} \text{ M}$, 2: $6.55 \times 10^{-4} \text{ M}$, 3: $1.39 \times 10^{-3} \text{ M}$, 4: $2.69 \times 10^{-3} \text{ M}$.

The dissociation of $\text{CH}_3\text{N}_2\text{H}_4^+$ in HNO_3 solution is expressed as

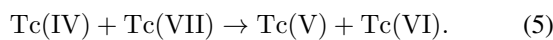
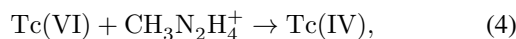
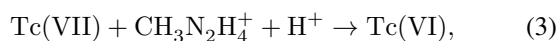


$$k_a = ([\text{CH}_3\text{N}_2\text{H}_3][\text{H}^+])/[\text{CH}_3\text{N}_2\text{H}_4^+], \quad (2)$$

where the k_a is dissociation constant.

It was reported that $\text{p}K_a$ value is 7.87 [8], which means that MMH exists in the form of $\text{CH}_3\text{N}_2\text{H}_4^+$ in this solution.

The reduction of Tc(VII) by MMH in HNO_3 aqueous solution is very complicated. Tc(VII) is reduced in two ways, as shown in reaction (3) and reaction (5), the stepwise reduced by MMH and catalytic reduced by Tc(IV).



Technetium is a polyvalent nuclide, there may be tetravalent, pentavalent, hexavalent and heptavalent technetium involved in this reaction. Other reactions such as the disproportionation of Tc(VI) and Tc(V), the oxidation of Tc(VI) and Tc(V), and the redox reactions between MMH and HNO_3 are not presented here. The reaction (3) and (5) mentioned above are dominant when MMH is excess in situation. Other reactions will have little effect in reduction of Tc(VII). The interim-valence technetium, Tc(VI) and Tc(V), are not stable in this system and tend to transform to stable valence, Tc(IV) or Tc(VII), very quickly after their emergence [9]. So little Tc(VI) and Tc(V) will exist in the solution. To simplify the data processing, we neglect the interim-valence technetium and suppose that only Tc(VII) and Tc(IV) exist in this system. So the reduction of Tc(VII) can be expressed as

$$-\frac{d[\text{Tc(VII)}]}{dt} = k_1[\text{CH}_3\text{N}_2\text{H}_4^+][\text{Tc(VII)}][\text{H}^+] + k_2[\text{Tc(VII)}][\text{Tc(IV)}], \quad (6)$$

where k_1 and k_2 are the rate constants of reaction (3) and (5) respectively. Substituting $[\text{Tc(IV)}]$ with $[\text{Tc(VII)}]$, this equation can be transformed as follows

$$-\frac{d[\text{Tc(VII)}]}{dt} = k_1[\text{CH}_3\text{N}_2\text{H}_4^+][\text{Tc(VII)}][\text{H}^+] + k_2[\text{Tc(VII)}](c_0 - [\text{Tc(VII)}]), \quad (7)$$

where c_0 represents the initial Tc(VII) concentration.

Let $k = k_1[\text{CH}_3\text{N}_2\text{H}_4^+][\text{H}^+] + k_2c_0$, so the above equation can be written as

$$-\frac{d[\text{Tc(VII)}]}{dt} = k[\text{Tc(VII)}] - k_2[\text{Tc(VII)}]^2. \quad (8)$$

From above equation, we can easily get the integral form

$$\ln |[\text{Tc(VII)}] - k/k_2| - \ln[\text{Tc(VII)}] = kt + c, \quad (9)$$

where $k/k_2 = k_1[\text{CH}_3\text{N}_2\text{H}_4^+][\text{H}^+]/k_2 + c_0 > [\text{Tc(VII)}]$, so the modulus can be taken away and the equation can be expressed as an exponential form

$$(k/k_2 - [\text{Tc(VII)}])/[\text{Tc(VII)}] = \exp(kt + c). \quad (10)$$

So, $[\text{Tc(VII)}]$ can be expressed as

$$[\text{Tc(VII)}] = (k/k_2)/[1 + \exp(kt + c)]. \quad (11)$$

It is obvious that the mechanism equation has the same format as logic function. The logic function used in fitting is $y = a/\{1 + \exp[-b(x-x_c)]\}$. Relationships between the logic function and mechanism function are displayed in Table 1. The fitting job was done by using the software Origin 8.

The fitting result and the calculated k_1 and k_2 of reaction (3) and (5) are presented in Table 2. When calculating k_1 and k_2 , we make the hypothesis that the concentration of $\text{CH}_3\text{N}_2\text{H}_4^+$ is equal to the initial MMH concentration.

B. The effect of MMH on the reaction

The effect of initial MMH concentration on the reduction of Tc(VII) is presented in Fig. 2. MMH concentration affects

TABLE 1. Relationship between the logic function and mechanism function

Function	Logic function	Mechanism function
Parameters	a, b, x_c	k_1, k_2, c
Relationship	$k_1 = b(c_0 - a)/(a[\text{CH}_3\text{N}_2\text{H}_4^+][\text{H}^+])$ $k_2 = -b/a$ $c = bx_c$	

the induction period more distinctly than the fast reaction period. The length of the induction periods decreases with the increment of MMH concentration, but the fast reaction periods under different conditions present little difference of each other. It can be supported by the proposed mechanism. The stepwise reduction is dominant in the induction period, and MMH is first order for the stepwise reduction, so a higher MMH concentration is favorable for reduction of Tc(VII). Once enough Tc(IV) is produced, the fast reaction will take charge of the reaction, the reduction will be influenced mainly by the concentration of technetium but MMH. Meanwhile the MMH concentrations influence the extent of the reaction and less Tc(VII) remained in a higher initial MMH concentration condition.

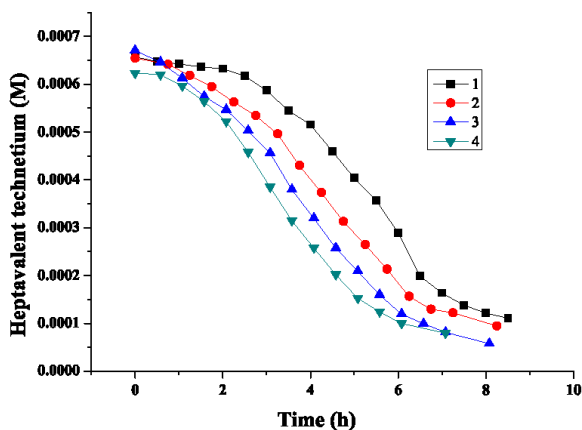


Fig. 2. (Color online) Tc(VII) concentration versus time under different initial MMH concentrations. 40 °C, $c_0(\text{Tc(VII)}) = 6.57 \times 10^{-4} \text{ M}$, $c_0(\text{HNO}_3) = 1.5 \text{ M}$, $c_0(\text{MMH} \cdot \text{HNO}_3)$, 1: 0.068M, 2: 0.15M, 3: 0.225M, 4: 0.34M.

C. The effects of acidity on the reaction

The effect of initial HNO_3 concentration on the Tc(VII) reduction is presented in Fig. 3. HNO_3 has a similar effect as MMH on the reaction because of their analogical role in the reduction of Tc(VII).

The fitting result and deducted parameters are presented in Table 4.

In the logic function, if $x = x_c$, the second derivative of y equals 0. That means, the x_c defines the time when

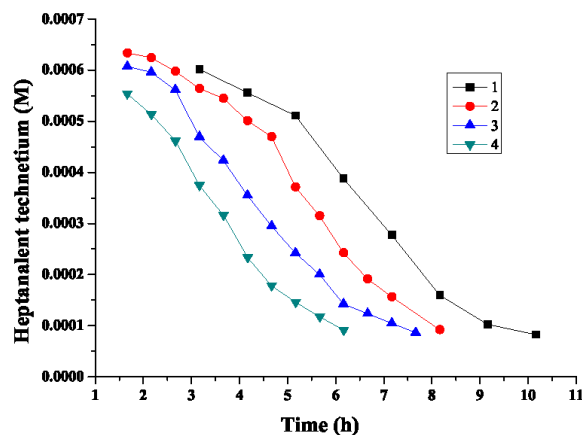


Fig. 3. (Color online) Tc(VII) concentration versus time under different initial HNO_3 concentration. 40 °C, $c_0(\text{Tc(VII)}) = 6.57 \times 10^{-4} \text{ M}$, $c_0(\text{MMH} \cdot \text{HNO}_3) = 0.15 \text{ M}$, $c_0(\text{HNO}_3)$, 1: 0.40M, 2: 0.80M, 3: 1.50M, 4: 2.20M.

the reaction of Tc(VII) reduction gets fast. When $x = x_c$, $y = a/2$ and the calculated value of “ a ” is very close to the initial Tc(VII) concentration, it suggests that Tc(VII) decreases most quickly when Tc(VII) concentration is nearly half of total technetium concentration. It confirms our hypothesis that there are mainly Tc(VII) and Tc(IV) in the solution, only a little other valent technetium exists in this system.

From the rate constant k_1 and k_2 obtained in different experiments, we calculated the average of k_1 to be $0.179/(\text{M}^2 \text{ h})$ with a standard deviation 0.02 and the average of k_2 to be $961/(\text{M}^2 \text{ h})$ with a standard deviation 129. k_2 has a bigger relative error than k_1 , because we assume that the activity of MMH and HNO_3 is equal to their initial concentration in data processing, but it has a distinct departure. Based on above discussion, it can be concluded that this reaction is very similar to the reaction between TcO_4^- and hydrazine [4]. There is a long induction period while the Tc(VII) is reduced by $\text{CH}_3\text{N}_2\text{H}_4^+$ stepwisely to Tc(IV). When there is enough Tc(IV) accumulated and the autocatalytic reaction becomes prominent. The reaction turns into the fast reaction period. With the decrement of Tc(VII), the reduction of Tc(VII) turns to slow again.

So the MMH concentration and the acidity all have effects on the induction period. A higher initial technetium concentration, higher $\text{CH}_3\text{N}_2\text{H}_3$ concentration, and acidity are all propitious to get through the inducing period. But the velocity of fast reaction is mainly determined by technetium concentration.

D. The effects of temperature on the reaction

Temperature is known to have a significant effect on reaction kinetics. This effect is often translated into a dependence of the kinetic parameters on temperature, which has

TABLE 2. Relationship between the logic function and mechanism function

Experiment conditions (M)			Fitting results				Parameters of the hypothesis mechanism		
$c_0(\text{Tc(VII)})$	$c_0(\text{MMH})$	$c_0(\text{H}^+)$	a	b	x_c	R^2	k_1 ($/(\text{M}^2 \text{ h})$)	k_2 ($/(\text{M}^2 \text{ h})$)	c
3.48×10^{-4}	0.15	1.5	3.82×10^{-5}	-0.38	6.25	0.9951	0.15	1002	-2.39
6.55×10^{-4}	0.15	1.5	6.93×10^{-5}	-0.65	4.53	0.9978	0.16	944	-2.96
1.39×10^{-3}	0.15	1.5	1.45×10^{-4}	-1.04	2.76	0.9959	0.18	718	-2.87
2.69×10^{-3}	0.15	1.5	2.74×10^{-4}	-2.05	1.99	0.9961	0.15	748	-4.08

TABLE 3. The fitting result of experiments under different initial MMH concentrations

Experiment conditions (M)			Fitting results				Parameters of the hypothesis mechanism		
$c_0(\text{Tc(VII)})$	$c_0(\text{MMH})$	$c_0(\text{H}^+)$	a	b	x_c	R^2	k_1 ($/(\text{M}^2 \text{ h})$)	k_2 ($/(\text{M}^2 \text{ h})$)	c
6.57×10^{-4}	0.068	1.5	6.74×10^{-4}	-0.71	5.59	0.9947	0.17	1052	-3.96
6.55×10^{-4}	0.15	1.5	7.03×10^{-4}	-0.63	4.48	0.9956	0.19	889	-2.80
6.71×10^{-4}	0.225	1.5	7.34×10^{-4}	-0.66	3.75	0.9983	0.17	902	-2.48
6.23×10^{-4}	0.34	1.5	7.08×10^{-4}	-0.73	3.42	0.9944	0.17	1026	-2.48

TABLE 4. The fitting result of experiments under different HNO₃ concentrations

Experiment conditions (M)			Fitting results				Parameters of the hypothesis mechanism		
$c_0(\text{Tc(VII)})$	$c_0(\text{MMH})$	$c_0(\text{H}^+)$	a	b	x_c	R^2	k_1 ($/(\text{M}^2 \text{ h})$)	k_2 ($/(\text{M}^2 \text{ h})$)	c
6.57×10^{-4}	0.068	1.5	6.74×10^{-4}	-0.71	5.59	0.9947	0.17	1052	-3.96
6.55×10^{-4}	0.15	1.5	7.03×10^{-4}	-0.63	4.48	0.9956	0.19	889	-2.80
6.71×10^{-4}	0.225	1.5	7.34×10^{-4}	-0.66	3.75	0.9983	0.17	902	-2.48
6.23×10^{-4}	0.34	1.5	7.08×10^{-4}	-0.73	3.42	0.9944	0.17	1026	-2.48

TABLE 5. The fitting result of experiments at different temperatures

$T(\text{K})$	Experiment conditions (M)			Fitting results				Parameters of the hypothesis mechanism		
	$c_0(\text{Tc})$	$c_0(\text{MMH})$	$c_0(\text{H}^+)$	a	b	x_c	R^2	k_1 ($/(\text{M}^2 \text{ h})$)	k_2 ($/(\text{M}^2 \text{ h})$)	c
313	6.55	0.15	1.5	6.89	-0.60	4.45	0.9964	0.21	850	-2.69
318	6.68	0.15	1.5	7.02	-1.10	3.09	0.9986	0.24	1572	-3.41
323	6.68	0.15	1.5	6.94	-1.47	2.07	0.9988	0.28	2108	-3.04
328	6.77	0.15	1.5	6.88	-1.95	1.13	0.9862	0.33	2771	-2.20

been widely studied, and can be generally expressed with an Arrhenius type equation as below

$$\ln k = \ln A - E_a / RT,$$

(12)

where k is a kinetic parameter, E_a is activation energy, R represents the universal gas constant, and T is standard temperature.

The effect of temperature on this reaction is presented in Fig. 4. The fitting result and the deduced parameters at different temperatures are displayed in Table 5. Based on the deduced parameters, the apparent activation energy (E_a) is calculated to be 31.51 kJ/mol for reaction (3) and 65.68 kJ/mol for reaction (5), respectively.

IV. CONCLUSION

The reduction of Tc(VII) by MMH in HNO₃ aqueous solution is a complicated reaction. Tc(VII) is consumed in two ways. One is reduced by MMH, and the other is catalyzed by Tc(IV). The first is a tri-molecule reaction, and it is dominant in the inducing period. When there is enough Tc(IV) in the

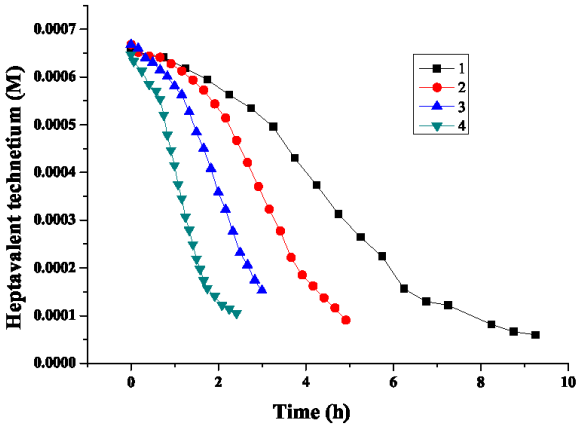


Fig. 4. (Color online) The effect of temperature on the reaction. $c_0(\text{Tc}) = 6.70 \times 10^{-4} \text{ M}$, $c_0(\text{HNO}_3) = 1.5 \text{ M}$, $c_0(\text{MMH} \cdot \text{HNO}_3) = 0.15 \text{ M}$. 1: 40 °C, 2: 45 °C, 3: 50 °C, 4: 55 °C.

solution, the autocatalytic reaction becomes primary. The reaction turns into fast reaction period. So the induction period is affected by the initial Tc(VII) concentration, MMH concentration and acidity, but the fast reaction period is mainly charged by the technetium concentration.

Based on the above mechanism, we deduced the reaction rate equation and fitted it with logic function. The reaction

rate equation for reduction of Tc(VII) is $-d[\text{Tc(VII)}]/dt = k_1[\text{CH}_3\text{N}_2\text{H}_4^+][\text{Tc(VII)}][\text{H}^+] + k_2[\text{Tc(VII)}][\text{Tc(IV)}]$.

The rate constant k_1 is $0.179/(\text{M}^2 \text{ h})$ with a standard deviation 0.02, and k_2 is $961/(\text{M}^2 \text{ h})$ with a standard deviation 129. The apparent activation energy is 31.5 kJ/mol for reaction (3) and 65.68 kJ/mol for reaction (5), respectively.

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