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

Authors: LIU Fang, WANG Hui, WEI Yan, JIA Yong-Fen

Date: 2023-06-18T00:00:00+00:00

Abstract

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 ℃ to 55 ℃ 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.

Full Text

Preamble

Modeling the Autocatalytic Reaction Between Tc(VII) and Methyl-Hydrazine in HNO_3 Solution

LIU Fang (刘方)[1], WANG Hui (王辉)[1], WEI Yan (魏艳)[1], and JIA Yong-Fen (贾永芬)[1]
[1]China Institute of Atomic Energy, Beijing 102413, China

(Received May 16, 2014; accepted in revised form August 9, 2014; published online December 20, 2014)

The reduction of Tc(VII) by methyl-hydrazine (MMH) in nitric acid aqueous solution was studied under various conditions. A logistic equation widely used for modeling autocatalytic reactions was adopted to simulate the target reaction. All experimental data were consistent with the proposed equation. Results showed that Tc(VII) was reduced by MMH through two pathways: stepwise

reduction by MMH and autocatalytic reduction by Tc(IV). Isothermal experiments were conducted at temperatures ranging from 40 °C to 55 °C, yielding activation energies of 31.51 kJ/mol and 65.68 kJ/mol for the stepwise and autocatalytic reductions, respectively.

Keywords: Technetium, Autocatalytic reaction, PUREX, Methyl-hydrazine, Logistic equation
DOI: 10.13538/j.1001-8042/nst.26.S10304

Introduction

An advanced salt-free PUREX process was developed by the China Institute of Atomic Energy, which employs N,N-dimethylhydroxylamine (DMHAN) as a reductant and methyl-hydrazine (MMH) as a stabilizer in the U/Pu splitting stage. DMHAN can rapidly reduce Pu(IV) to Pu(III), while MMH acts as an HNO_2 scavenger [1]. MMH is a moderate reductant that may reduce Tc(VII) to lower valence states, thereby influencing technetium distribution in the process. Previous studies indicated that DMHAN could not reduce Tc(VII) in HNO_3 solution [2]. However, technetium enters the aqueous solution mainly as Tc(IV) in the U/Pu splitting stage of the advanced PUREX process [3], suggesting that Tc(VII) is primarily reduced by MMH in this system.

The reaction between technetium and hydrazine has been extensively studied [4–6]. It is well established that technetium can catalyze the reduction of hydrazine by nitric acid. However, the reaction between technetium and MMH has not yet been investigated, and previous works on technetium have primarily focused on its effect on reductant consumption. In this paper, the reaction between technetium and MMH was studied in detail under different conditions, with Tc(VII) concentration monitored to elucidate technetium valence transformations. This investigation is valuable for understanding the mechanism of MMH over-consumption and technetium behavior in the advanced PUREX process.

Experimental Details

Reagents and Instruments

NH_4TcO_4 was purchased from Oak Ridge National Laboratory (ORNL) and dissolved in distilled water. 2,4,6-trimethylpyridine was obtained from Fluka chemical reagent company. A liquid scintillation spectrometer manufactured by Beckman was used for technetium measurement. The cocktail solution for liquid scintillation counting was prepared by dissolving 1 g triphosphoxane, 16 g 2,5-diphenyloxazole, and 300 g naphthalene in 2 L dioxane. All other chemicals used were of analytical grade.

Analysis

The concentrations of MMH and HNO_3 were determined by titration using a glass electrode to monitor pH. Tc(VII) concentration was detected via liquid scintillation after extraction with 2,4,6-trimethylpyridine in alkaline solution [7].

Procedure

All experiments were conducted in a 20 mL test tube immersed in a constant temperature bath. All reactants were preheated to the reaction temperature before mixing. After mixing, a small volume of solution was sampled immediately and at regular intervals throughout the experiment. The sampled solution was sealed and placed in an ice water bath to quench the reaction for subsequent analysis.

To predict technetium behavior in actual reprocessing conditions, the initial reactant concentrations in the experiments were similar to those in the U/Pu splitting stage of the advanced PUREX process. Since MMH and HNO_3 concentrations were hundreds of times higher than that of technetium and only small amounts were consumed during the reaction, their concentrations could be treated as constants in data processing.

Results and Discussion

Mechanism Consideration and Technetium Effect on the Reaction

The effect of initial Tc(VII) concentration on the reaction is shown in Fig. 1 [Figure 1: see original paper]. The curves exhibit a typical sigmoidal shape. Tc(VII) is reduced relatively slowly at the beginning, which is termed the induction period. Subsequently, Tc(VII) concentrations decline sharply, marking the transition to the fast reaction period. At the reaction's conclusion, the reduction rate slows again. A notable observation is that Tc(VII) is consumed much faster under higher initial Tc(VII) concentrations, suggesting that the reduction product of Tc(VII) may accelerate its own consumption. In all experiments, Tc(VII) could not be completely reduced, with approximately 10% remaining in solution.

Technetium is a polyvalent nuclide; tetravalent, pentavalent, hexavalent, and heptavalent technetium species may be involved in this reaction. Other potential reactions such as disproportionation of Tc(VI) and Tc(V), oxidation of Tc(VI) and Tc(V), and redox reactions between MMH and HNO_3 are not considered here. Reactions (3) and (5) mentioned above are dominant when MMH is in excess, while other reactions have minimal effect on Tc(VII) reduction. The intermediate-valence technetium species, Tc(VI) and Tc(V), are unstable in this system and rapidly transform to stable valences (Tc(IV) or Tc(VII)) after formation [9]; consequently, little Tc(VI) and Tc(V) remain in solution.

To simplify data processing, we neglected intermediate-valence technetium and assumed that only Tc(VII) and Tc(IV) exist in the system.

The dissociation of $CH_3N_2H_4^+$ in HNO_3 solution is expressed as:

$$CH_{3N_{2H}}4^+ \Leftrightarrow CH_{3N_{2H}}3 + H^+, \quad k_a = \frac{[CH_{3N_{2H}}3][H^+]}{[CH_{3N_{2H}}4^+]}$$

where k_a is the dissociation constant. The reported pK value is 7.87 [8], indicating that MMH exists primarily as $CH_3N_2H_4^+$ in this solution.

The reduction of Tc(VII) by MMH in HNO_3 aqueous solution is complex. Tc(VII) is reduced through two pathways, as shown in reactions (3) and (5): stepwise reduction by MMH and catalytic reduction by Tc(IV).

$$Tc(VII) + CH_{3N_{2H}}4^+ + H^+ \rightarrow Tc(VI)$$
$$Tc(VI) + CH_{3N_{2H}}4^+ \rightarrow Tc(IV)$$
$$Tc(IV) + Tc(VII) \rightarrow Tc(V) + Tc(VI)$$

The reduction of Tc(VII) can be expressed as:

$$-\frac{d[Tc(VII)]}{dt} = k_1[CH_{3N_{2H}}4^+][Tc(VII)][H^+] + k_2[Tc(VII)][Tc(IV)]$$

where k_1 and k_2 are the rate constants for reactions (3) and (5), respectively. Substituting $[Tc(IV)]$ with $[Tc(VII)]$, this equation transforms to:

$$-\frac{d[Tc(VII)]}{dt} = k_1[CH_{3N_{2H}}4^+][Tc(VII)][H^+] + k_2[Tc(VII)](c_0 - [Tc(VII)])$$

where c_0 represents the initial Tc(VII) concentration.

Let $k = k_1[CH_{3N_{2H}}4^+][H^+] + k_{2c}0$, so the above equation can be written as:

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

From this equation, we can easily derive the integral form:

$$\ln|[Tc(VII)] - \frac{k}{k_2}| - \ln[Tc(VII)] = kt + c$$

Since $\frac{k}{k_2} = \frac{k_1[CH_{3N_{2H}}4^+][H^+]}{k_2} + c_0 > [Tc(VII)]$, the modulus can be removed and the equation expressed in exponential form:

$$\frac{\frac{k}{k_2} - [Tc(VII)]}{[Tc(VII)]} = \exp(kt + c)$$

Thus, $[Tc(VII)]$ can be expressed as:

$$[Tc(VII)] = \frac{\frac{k}{k_2}}{1 + \exp(kt + c)}$$

It is evident that the mechanism equation has the same format as the logistic function. The logistic function used for fitting is:

$$y = \frac{a}{1 + \exp[-b(x - x_c)]}$$

Relationships between the logistic function and mechanism function are displayed in Table 1 . The fitting was performed using Origin 8 software. The fitting results and calculated k_1 and k_2 for reactions (3) and (5) are presented in Table 2 . When calculating k_1 and k_2, we assumed that the concentration of $CH_3N_2H_4^+$ equals the initial MMH concentration.

The Effect of MMH on the Reaction

The effect of initial MMH concentration on Tc(VII) reduction is presented in Fig. 2 [Figure 2: see original paper]. MMH concentration affects the induction period more distinctly than the fast reaction period. The length of the induction period decreases with increasing MMH concentration, but the fast reaction periods under different conditions show little variation. This is supported by the proposed mechanism: the stepwise reduction is dominant during the induction period, and since MMH is first-order for stepwise reduction, higher MMH concentrations favor Tc(VII) reduction. Once sufficient Tc(IV) is produced, the autocatalytic reaction becomes dominant and the reduction is influenced primarily by technetium concentration rather than MMH. Additionally, MMH concentration affects the reaction extent, with less Tc(VII) remaining at higher initial MMH concentrations.

The Effects of Acidity on the Reaction

The effect of initial HNO_3 concentration on Tc(VII) reduction is presented in Fig. 3 [Figure 3: see original paper]. HNO_3 has a similar effect as MMH on the reaction due to their analogous roles in Tc(VII) reduction. The fitting results and derived parameters are presented in Table 4 .

In the logistic function, when $x = x_c$, the second derivative of y equals zero, meaning x_c defines the time when the Tc(VII) reduction reaction accelerates. When $x = x_c$, $y = a/2$, and the calculated value of "a" is very close to the initial

Tc(VII) concentration, suggesting that Tc(VII) decreases most rapidly when its concentration is approximately half of the total technetium concentration. This confirms our hypothesis that mainly Tc(VII) and Tc(IV) exist in solution, with only trace amounts of other valence states.

From the rate constants k_1 and k_2 obtained in different experiments, we calculated the average k_1 to be 0.179 $M^{-2}h^{-1}$ with a standard deviation of 0.02, and the average k_2 to be 961 $M^{-2}h^{-1}$ with a standard deviation of 129. k_2 has a larger relative error than k_1 because we assumed that the activities of MMH and HNO_3 equal their initial concentrations in data processing, which introduces significant deviation. Based on this 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 during which Tc(VII) is stepwise reduced by $CH_3N_2H_4^+$ to Tc(IV). When sufficient Tc(IV) accumulates, the autocatalytic reaction becomes prominent and the reaction enters the fast reaction period. As Tc(VII) decreases, the reduction rate slows again.

Thus, both MMH concentration and acidity affect the induction period. Higher initial technetium concentration, higher $CH_3N_2H_3$ concentration, and higher acidity all facilitate passage through the induction period, but the fast reaction velocity is primarily determined by technetium concentration.

The Effects of Temperature on the Reaction

Temperature significantly affects reaction kinetics. This effect is typically expressed as a temperature dependence of kinetic parameters, which has been widely studied and can be generally described by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

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

The effect of temperature on this reaction is presented in Fig. 4 [Figure 4: see original paper]. The fitting results and derived parameters at different temperatures are displayed in Table 5 . Based on these 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).

Conclusion

The reduction of Tc(VII) by MMH in HNO_3 aqueous solution is a complex reaction. Tc(VII) is consumed through two pathways: reduction by MMH and catalysis by Tc(IV). The first is a termolecular reaction dominant during the induction period. When sufficient Tc(IV) is present in solution, the autocatalytic reaction becomes primary and the reaction enters the fast reaction period. Therefore, the induction period is affected by initial Tc(VII) concentra-

tion, MMH concentration, and acidity, while the fast reaction period is primarily controlled by technetium concentration.

Based on this mechanism, we derived the reaction rate equation and fitted it with a logistic function. The reaction rate equation for Tc(VII) reduction is:

$$-\frac{d[Tc(VII)]}{dt} = k_1[CH_{3N_{2H}}4^+][Tc(VII)][H^+] + k_2[Tc(VII)][Tc(IV)]$$

The rate constant k_1 is 0.179 $M^{-2}h^{-1}$ with a standard deviation of 0.02, and k_2 is 961 $M^{-2}h^{-1}$ with a standard deviation of 129. The apparent activation energy is 31.5 kJ/mol for reaction (3) and 65.68 kJ/mol for reaction (5), respectively.

References

[1] He H. Reductive back-extraction of Pu with N,N-dimethylhydroxylamine and the development of the corresponding computation modeling. J Nucl Radiochem, 2001, 2: 65-71. (in Chinese). DOI: 10.3969/j.issn.0253-9950.2001.02.001

[2] Wei Y. The research of reaction kinetics of heptavalent technetium and salting-free reagents in nitric acid medium. Master Thesis, China Institute of Atomic Energy, 2006. (in Chinese)

[3] Liu F, Wang H, Jia Y F, et al. Methyl-hydrazine deoxidize Tc(VII) in nitric acid in presence of U(VI) and behavior of technetium in the UPu splitting stage of APOR process. Energy Procedia 2013, 39: 358–364. DOI: 10.1016/j.egypro.2013.07.223

[4] Garraway J, Wilson P D. The technetium catalysed oxidation of hydrazine by nitric acid. J Less Common Met, 1984, 97: 191–203. DOI: 10.1016/0022-5088(84)90023-7

[5] Zhu Z X, Jia Y F, Wang F D. Study of the reaction between technetium and hydrazine in nitric acid medium. J Nucl Radiochem, 2003, 25: 129-134. (in Chinese) DOI: 10.3969/j.issn.0253-995

[6] Akopov G A, Krinitsyn A P, Tsarenko A F. Oxidation of hydrazine in nitric acid solutions in the presence of technetium. Radiokhimiya, 1982, 24: 529–532.

[7] Zhu G H, Huang H X. Determination of content for technetium in high level liquid waste (HLLW). At Energy Sci Technol, 1992, 26: 27–30. (in Chinese)

[8] Othmer K. Encyclopedia of Chemical Technology, Second Edition, Interscience Publishers a Division of John Wiley & Sons, Inc New York, London, Sydney, 1: 164–192.

[9] Rulfs C, Pacer R A, Hirsch R F. Technetium chemistry, oxidation states and species. J Inorg Nucl Chem, 1967, 29: 681–691. DOI: 10.1016/0022-1902(67)80323-3