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Gaseous products of aqueous N, N-dimethyl hydroxylamine degraded by radiation

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Abstract In this work, the 0.1–0.5 mol·L^{-1} N, N-dimethylhydroxylamine (DMHA) were irradiated to 5–25 kGy, and gaseous products of mainly hydrogen, methane, ethane and n-butane were measured by gas chromatography. The results show that the volume fraction of hydrogen and methane increases with the concentration of DMHA and dose, and the latter does not change markedly at high doses.

Key words N, N-dimethyl hydroxylamine, Radiation degradation, Gaseous product, Spent fuel reprocess

1 Introduction

The PUREX process is a popular choice for nuclear fuel reprocessing. U(VI) and Pu(IV) are co-extracted from nitric acid to tri-butyl-phosphate(TBP) solution, and Np(VI) is suitable in the adjusted solution. The Pu(IV) is selectively reduced to the poorly extractable Pu(III) by a reducing agent. A sulfamate-stabilized Fe(II) used in early plants is preferred into hydrazine-stabilized U(IV). Sulphamate or hydrazine is used to remove infinitesimal nitrous acid, which initiates the oxidation of Pu(III)[1].

However, neither sulphamate nor hydrazine is appreciably extracted into the TBP phase. They cannot destroy nitrous acid in organic phase and lead to the oxidation of Pu(III) in the organic phase. This is why a large of excess reductant is required for acceptable Pu separation[2–5]. The excessive sulphamate ferrous consumption causes a great problem of radioactive wastes. The complex of Pu with sulfate produced from sulphamate contributes to the Pu loss, and sulfate also accelerates the evaporator corrosion. In the case of U(IV), the excessive U(IV) increase U loss in the Pu product[2,6], because the extractable U(IV) is one-tenth equivalent to U(VI). It is important to suppress oxidation of Pu(III) in the aqueous or organic phase.

The Np content increases with burning-up of the spent fuel[7], but the Fe(II) and U(IV) cannot control the Np valence, and Np goes to different streams. Koltunov *et al*[8–11] and Zhang *et al*[12–16] studied the reaction of N,N-diethylhydroxylamine (DEHA), N, N-dimethylhydroxylamine (DMHA) with Np(VI) and Pu(IV), and found that DEHA and DMHA could reduce Np(VI) and Pu(VI) to Np(V) and Pu(III). The DEHA and DMHA, which is extractable with TBP, can destroy nitrous acid and suppress oxidation of Pu(III) in organic phase[2], However, organic phase is degraded in the separation process due to its radiation sensitivity. This affects its reductive efficiency and partition of nuclides. In our previous papers[17–23], we studied the radiation stability and radiolysis product of DEHA. In this paper, we report the gaseous products of aqueous 0.1–0.5 mol·L^{-1} DMHA generated by γ-ray irradiation to 5–25 kGy.

2 Experimental

2.1 Main equipment and accessories

A 1.295×10^{17} Bq ^{60}Co irradiator (Shanghai Institute of Applied Physics, Chinese Academy of Sciences), a

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GC900A gas chromatograph, 2 m×3 mm packed column with 0.5 nm molsieve (Shanghai Ke Chuang Chromatograph Instruments Co., Ltd.), and a 50 m× 0.53 mm capillary column with aluminum oxide (Lanzhou Institute of Chemistry and Physics, Chinese Academy of Sciences) were used in this study.

2.2 Standard gas mixture

The contents of gas mixture in volume percentage (Shanghai Institute of Measurement and Testing Technology) were H_2 (0.5), CH_4 (0.03), C_2H_6 (0.03), C_2H_4 (0.03), C_3H_8 (0.03), C_3H_6 (0.03), n-C_4H_{10} (0.03), and N_2 (99.32).

2.3 Sample preparation and irradiation

DMHA (98%, China Institute of Atomic Energy) was analyzed by gas chromatography and prepared into 0.1, 0.2, 0.3 and 0.5 $mol \cdot L^{-1}$ using pure water. For each concentration, 4 mL was transferred into a 7-mL penicillin bottle, and sealed. They were irradiated to doses of 5, 10, 15, 20 or 25 kGy, which were monitored by dichromate dosimeters.

3 Results and discussion

3.1 Hydrogen produced by degradation of DMHA

The H_2 and CO evolved from the irradiated DMHA were analyzed by gas chromatography with a packed 0.5-nm molsieve column and a thermal conductivity detector[24], indicating that the volume fraction of H_2 was higher than that of CO.

As shown in Fig.1, the volume fractions of H_2 made by 0.1–0.5 $mol \cdot L^{-1}$ DMHA increased from 2.2×10^{-3} at 5 kGy to 26.5×10^{-3} at 25 kGy. The volume fraction is lower than that in Ref.[24], where the solutions of the same concentration were irradiated up to 1000 kGy, and at high doses the volume fraction increased with the DMHA concentration. At low doses, however, the volume is independent of the DMHA concentration.

The dilute solution under γ-ray irradiation mainly produces the following active species[25,26],

$$H_2O \rightarrow H^{\cdot},\ e_{aq}^{-},\ H_2,\ H_2O_2,\ H^{+} \qquad (1)$$

The H_2 is produced by the $H^{\cdot}$ reaction with DMHA, and the $H^{\cdot}$ concentration increases with the dose, so the volume fraction of H_2 increases with the dose and DMHA concentration.

$$(CH_3)_2NOH + H^{\cdot} \rightarrow (CH_3)_2NO^{\cdot} + H_2 \qquad (2)$$

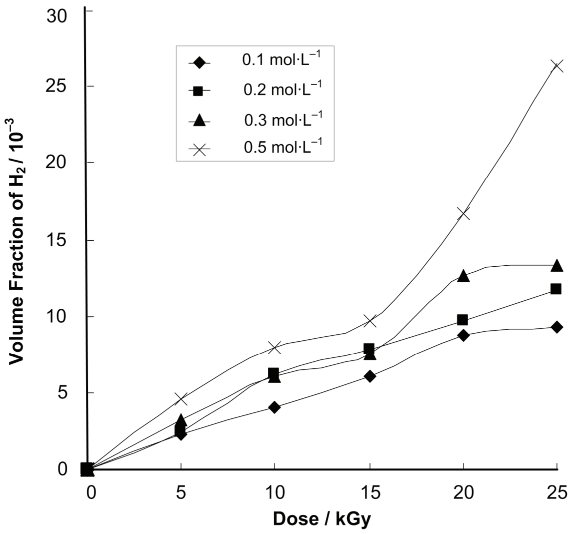

Fig.1 Volume fraction of H_2 in aqueous DMHA of 0.1–0.5 $mol \cdot L^{-1}$ irradiated to different doses.

3.2 Gaseous hydrocarbons

The gaseous products, methane, ethane, ethene, propane, propene and n-butane were analyzed by gas chromatography with an Al_2O_3 capillary column and a flame-ionization detector[27]. As shown in Fig.2, in the 0.1–0.5 $mol \cdot L^{-1}$ DMHA irradiated to 5–25 kGy, the volume fraction of methane, ethane and n-butane were $(12.5–89.4) \times 10^{-6}$, $(2.3–8.0) \times 10^{-6}$ and $(2.0–6.4) \times 10^{-6}$, respectively, increasing with the dose until being stabilized at a high dose. It was found that the volume fraction of methane increased obviously with the DMHA concentration. The volume fraction of ethane was the highest at 0.5 $mol \cdot L^{-1}$ DMHA. But the volume fraction of n-butane was not related to the DMHA concentration directly. The active $^{\cdot}CH_3$ may result from the C-N bond breaking with the excited DMHA[28], and abstract $H^{\cdot}$ from DMHA to give methane. The $^{\cdot}CH_3$ may also couple itself to form ethane. Therefore, the $^{\cdot}CH_3$ concentration increases with the DMHA concentration and the dose, as shown in Eqs.(3)–(5).

$$(CH_3)_2NOH \rightarrow \text{C-N break: } {}^{\cdot}CH_3 \qquad (3)$$

$${}^{\cdot}CH_3 + (CH_3)_2NOH \rightarrow CH_4 + (CH_3)_2NO^{\cdot} \qquad (4)$$

$${}^{\cdot}CH_3 + {}^{\cdot}CH_3 \rightarrow CH_3CH_3 \qquad (5)$$

At high dose, the methane and ethane is decomposed into $^{\cdot}CH_3$ and $.CH_3CH_3$, which further react with each other to form propane and n-butane as shown in Eqs.(6) and (7). Because the reaction of DMHA with $^{\cdot}CH_3$ is dominant, the volume fraction of methane is the highest among the products.

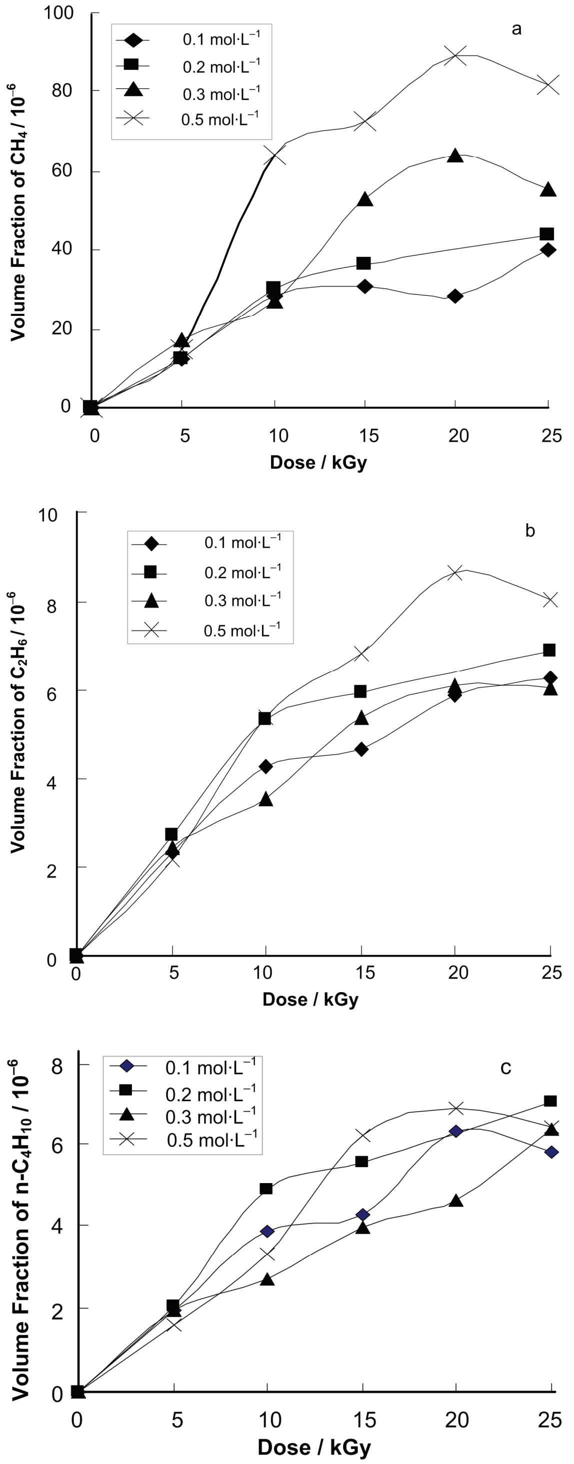

Fig.2 Volume fraction of (a) methane, (b) ethane and (c) n-butane in aqueous DMHA of 0.1–0.5 mol·L^{-1}, as a function of the irradiation dose.

$$^{\cdot}CH_3 + {}^{\cdot}CH_2CH_3 \rightarrow CH_3CH_2CH_3 \quad (6)$$

$$^{\cdot}CH_2CH_3 + {}^{\cdot}CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3 \quad (7)$$

By comparing Fig.1 with Fig.2, the volume fraction of H_2 is higher than those of methane, ethane and butane. This is because the $H^{\cdot}$ concentration is far higher than that of $^{\cdot}CH_3$ and $^{\cdot}CH_2CH_3$ in the aqueous DMHA.

4 Conclusions

The 0.1–0.5 mol·L^{-1} DMHA is degraded by γ-ray irradiation of 5–25 kGy. The gaseous products are mainly methane, hydrogen, ethane and n-butane. The volume fraction of hydrogen is higher than those of methane, ethane and n-butane, and increases with the dose and DMHA concentration. The volume fraction of methane is higher than those of ethane and n-butane, and increases with DMHA concentration and the dose at low doses.

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