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Re-extraction Behavior of Nitrosyl Ruthenium Complex in Tributyl Phosphate-Dodecane Solvent System

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Synopsis. A re-extraction of the nitrosyl ruthenium complex from a tributyl phosphate-dodecane solvent system to a nitric acid solution was carried out. A longer aging of the organic phase before re-extraction lowered the re-extraction yield, while nitric acid extracted into the organic phase increased it. These results could be explained using a model with two organic species.

The extraction behavior of nitrosyl ruthenium has been studied for the past few years[1–7] owing to its presence in spent nuclear fuel. Ruthenium is distributed between the organic and aqueous phases and is a contamination during fuel reprocessing. Tributyl phosphate (TBP) is a common extraction reagent in nuclear fuel reprocessing. The extraction reaction in the system, nitrosyl ruthenium–nitric acid–TBP, was originally proposed as [8]

$$\mathrm{RuNO^{3+}(w.)} + m\mathrm{NO_3^-(w.)} + n\mathrm{TBP(w.)} \rightleftarrows \mathrm{RuNO(NO_3)}_m{}^{(3-m)+}\cdot\mathrm{(TBP)}_n\mathrm{(o.)}, \quad (1)$$

where (w.) and (o.) denote aqueous and organic phases. However, since it was pointed out that complex formation and deformation are very slow,[9] studies concerning the partition coefficients and formation-deformation reaction rate of each complex were necessary. The extraction reaction can be described in the following reaction scheme:

$$\mathrm{RuNO(NO_3)}_m{}^{(3-m)+}\mathrm{(w.)} + (m-x)\mathrm{NO_3^-(w.)} \rightleftarrows \mathrm{RuNO(NO_3)}_x{}^{(3-x)+}\mathrm{(w.)}, \quad (2)$$

$$\mathrm{RuNO(NO_3)}_x{}^{(3-x)+}\mathrm{(w.)} + y\mathrm{TBP(w.)} \rightleftarrows \mathrm{RuNO(NO_3)}_x\mathrm{(TBP)}_y{}^{(3-x)+}\mathrm{(w.)}, \quad (3)$$

and

$$\mathrm{RuNO(NO_3)}_x\mathrm{(TBP)}_y{}^{(3-x)+}\mathrm{(w.)} \rightleftarrows \mathrm{RuNO(NO_3)}_x\mathrm{(TBP)}_y{}^{(3-x)+}\mathrm{(o.)}. \quad (4)$$

However the only important species is RuNO $\mathrm{(NO_3)_3}$, since other anionic or cationic species are less extractable. Further, Prurtt[1] examined the extraction rate of mixtures of nitrosyl ruthenium nitrate complexes and found that the extraction was not completed within 4 hours. It was suggested that the slow extraction is due to a slow conversion of ruthenium complexes in the organic phase, but not the conversion of ruthenium species in the aqueous phase.[2] On the other hand, re-extraction behavior of nitrosyl ruthenium was not examined except for Maya's report.[2] In this paper we report on the effects of the re-extraction period, aging period of the organic phase before re-extraction, and acid concentration of the aqueous phase on the re-extraction rate.

Experimental

Preparation. An acid solution of nitrosyl ruthenium complexes was prepared by dissolving RuNO $\mathrm{(NO_3)_3}$ (α-products) in a 3 mol·dm^{-3} nitric acid solution. The acid solution was aged in a dark box for 6 months in order to equilibrate the reactions between the ruthenium complexes, such as in Eq. 2.[4] The acid solution contained 15.7×10^{-3} mol·dm^{-3} of the complexes. A solvent containing TBP was prepared by mixing 3:7 volume of reagent grade TBP and reagent grade dodecane (both Wako Chemical Co.).

Re-extraction. An organic phase containing ruthenium was obtained by the extraction of ruthenium from 20 cm^3 of the aged acid solution using 200 cm^3 of TBP solvent. The extraction was carried out for 5 min in a separatory funnel. The concentration of extracted ruthenium was about 1×10^{-3} mol·dm^{-3}. Then, the organic phase was aged from 5 min to 7 d before re-extraction. Ruthenium was re-extracted from 5 cm^3 of aged organic phase using 5 to 20 cm^3 of fresh aqueous phase containing 1 to 6 mol·dm^{-3} of nitric acid.

Analytical Method. Ruthenium concentration in the aqueous phase was measured by colorimetry.[10] The ruthenium in the organic phase was re-extracted into $\mathrm{Na_2SO_3}$ solution (0.5 mol·dm^{-3}) and measured by colorimetry.

Results and Discussion

First of all, the prepared organic phase was aged from 5 min to 24 h before a 2 min re-extraction into nitric acid solution. Since the nitric acid concentration in the aqueous phase after the extraction was 1 mol·dm^{-3}, ruthenium was re-extracted into nitric acid of the same concentration to avoid changing the acid concentration in the organic phase. The concentration ratio of ruthenium in the organic phase to the aqueous phase is plotted against the aging period before re-extraction in Fig. 1. The ratio increased with the aging period and depended on the volume ratio of organic and aqueous phases. However, a residual factor, R, defined as

$$R = \frac{\text{Organic Ru concentration after re-extraction}}{\text{Organic Ru concentration before re-extraction}}, \quad (5)$$

did not depend on the volume ratio (Fig. 2). This behavior was expected from the two species model.[2] The reaction is written as

$$\mathrm{Ru(s)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{Ru(r)}, \quad (6)$$

where Ru(s) and Ru(r) denote strippable and retained ruthenium species in the organic phase; k_1 and k_2 are rate constants. If the re-extraction period was

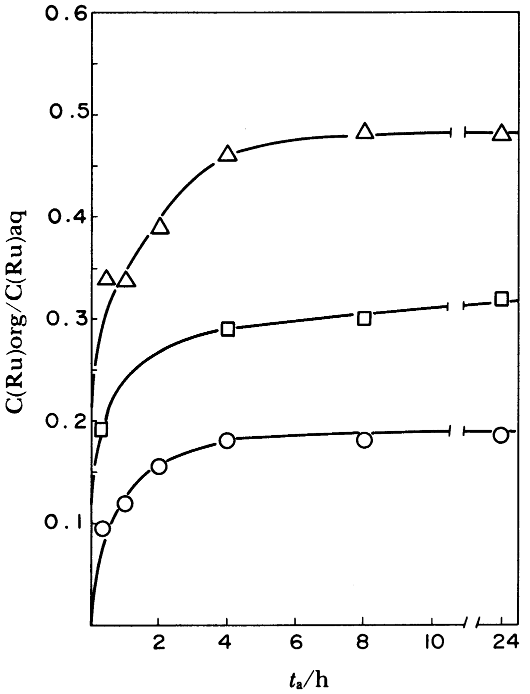

Fig. 1. Variation of ruthenium concentration ratio with organic phase aging period after 5 min extraction denoted as ta.
Aqueous volume/organic volume; Δ: 1, □: 2, O: 4. Concentration of aqueous nitric acid was 1 mol·dm^{-3} and re-extraction period was 2 min.

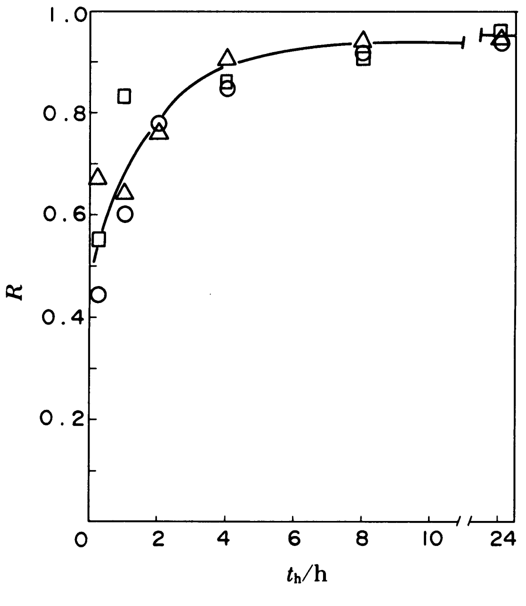

Fig. 2. Variation of ruthenium residual factor in organic phase with organic phase aging period.
Aqueous volume/organic volume; Δ: 1, □: 2, O: 4. Concentration of aqueous nitric acid was 1 mol·dm^{-3} and re-extraction period was 2 min.

sufficiently short to avoid conversion between Ru(r) and Ru(s) during re-extraction, the residual factor was equal to the mole ratio of Ru(r) to Ru(s) at the end of aging. Then, the residual factor was expected to be independent of the volume ratio. On the other hand, the Ru concentration in the aqueous phase was expected to decrease with increasing aqueous phase volume upon dilution. These predictions from this model agreed with the experimental results given in Figs. 1 and 2. Rate constants k_1 and k_2 were calculated from the dependency of residual factor on the aging period by using the rate equation of an "Opposing Reaction."[11] The estimated values of k_1 and k_2 were 5×10^{-1} and 4×10^{-2} h^{-1}, respectively.

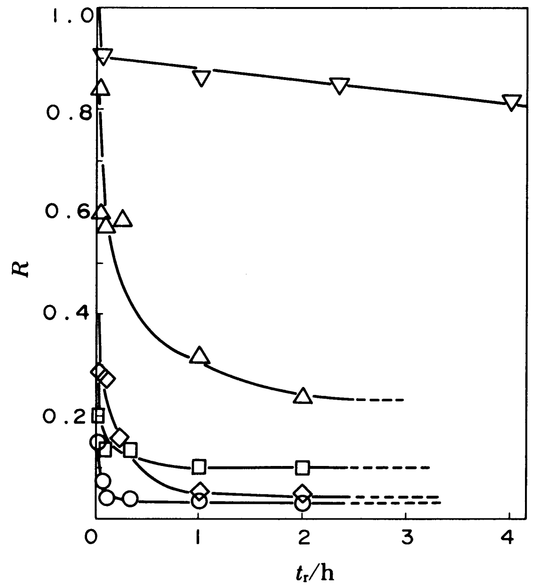

Fig. 3. Variation of ruthenium residual factor in organic phase, aged for 7 d, with re-extraction period denoted as t_r. Concentrations of aqueous nitric acid were ∇: 1, Δ: 2, □: 3, ◇: 4, O: 6 mol·dm^{-3}, respectively.

Next, the effect of the re-extraction period on the residual factor was measured. The used organic phase was aged for 7 d to equilibrate reaction 6. For a 2 min re-extraction into 1 mol·dm^{-3} nitric acid, the residual factor was equal to that of the organic phase aged 24 h, within the experimental error. The residual factor for re-extraction into 1 to 6 mol·dm^{-3} nitric acid is plotted against the re-extraction period in Fig. 3. For re-extraction into 1 mol·dm^{-3} nitric acid, it was observed that a rapid transfer of ruthenium into the aqueous phase was followed by a slow transfer. The former must be a stripping of species Ru(s) initially existing in the aged organic phase. The latter must be a stripping of Ru(s) formed from Ru(r) during re-extraction. The formation rate constant of Ru(s) calculated from the slope of slow transfer is shown in Table 1 as k(obs.). The calculated value agreed well with the value of k_2. For re-extraction into 2 mol·dm^{-3} nitric acid, ruthenium was transferred much more rapidly. For re-extraction into 3—6 mol·dm^{-3}, the partition equilibrium of ruthenium seemed to be established quickly. The nitric acid, extracted into the organic phase, would enhance the formation reaction of Ru(s) from Ru(r). The rate

Table 1. Rate Constant of Ru(s) Formation Reaction, *k*(obs.), Estimated from Re-extraction Rate

HNO_3 / $mol \cdot dm^{-3}$	*k*(obs.) / h^{-1}
1.0	4×10^{-2}
2.0	9×10^{0}
3.0	$\geqq 9\times10^{1}$
4.0	$\geqq 8\times10^{1}$
6.0	$\geqq 1\times10^{2}$

constants of the formation reaction of Ru(s) on the re-extraction into 2—6 $mol \cdot dm^{-3}$ nitric acid were calculated from the initial slopes of the residual factor versus the re-extraction period, and are shown in Table 1.

The two species model seemed to be a reasonable mechanism for the re-extraction of nitrosyl ruthenium complexes. However, further experiments would be required to clarify the mechanism of the conversion reaction between the two species of ruthenium in the organic phase.

References

1) D. J. Pruett, *Radiochim. Acta,* **27**, 115 (1980).

2) L. Maya, *J. Inorg. Nucl. Chem.,* **43**, 385 (1981).

3) L. Maya, *J. Inorg. Nucl. Chem.,* **41**, 67 (1979).

4) G. G. Boswell and S. Soentono, *J. Inorg. Nucl. Chem.,* **43**, 1625 (1981).

5) J. Blasius, J. P. Glatz, and W. Neumann, *Radiochim. Acta,* **29**, 159 (1981).

6) J. Blasius, H. J. Luxenburger, and W. Neumann, *Radiochim. Acta,* **36**, 149 (1984).

7) J. Blasius and K. Muller, *Radiochim. Acta,* **37**, 217 (1984).

8) E. Hallaba, R. Azzam, *Z. Phys. Chem.,* **237**, 177 (1966).

9) J. J. Diana, DP-TR-37 (1977).

10) G. R. Belew, *Anal. Chem.,* **33**, 886 (1961).

11) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw Hill, New York (1960), p. 29.