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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Extraction of Complex Nitrosopentahalogenides of Ruthenium by Aliphatic Amines

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Long-chain aliphatic amines are widely used for the selective isolation and separation of various elements from complex mixtures. In recent years several papers have appeared in the literature on extraction from solutions containing indicator amounts of ruthenium nitrosonitrate complexes by trioctylamine (1–4). It is known (5,6) that in such solutions ruthenium occurs in various chemical forms, the equilibrium among which changes depending on the acid concentration, temperature, time of aging of the solutions, and other factors. Therefore the obtained distribution coefficients of ruthenium represent a total value characterizing the distribution of several different chemical forms of ruthenium simultaneously.

In the literature there are no data on the extraction of individual nitrosocomplex ruthenium compounds, or on the influence of the nature of acidoligands and amines on their extractability.

Fig. 1. Influence of the nature of the acidoligand on the extraction of nitrosoruthenium in the form of $[RuNO\Gamma_5]^{2-}$ complexes by $TOAHNO_3$, in benzene, from 1 M HNO_3.

The main objective of our work was to study the influence of the structure of amine molecules and the nature of acidoligands on the extraction of complex ruthenium compounds in the form of nitrosopentahalogenides. Extraction experiments were carried out in separatory funnels at room temperature and with a phase-volume ratio of 1 : 1. The concentration of ruthenium in the aqueous and organic phases was determined from the β-activity of $Ru \to Rh^{106}$. Centrifugation was used for better phase separation. The following extractants were used: $(n\text{-}C_8H_{17})_3N$, tri-*n*-octylamine (TOA), $(n\text{-}C_6H_{13})_2NH$, di-*n*-hexylamine (DHA), $(n\text{-}C_{12}H_{25})NH_2$, *n*-dodecylamine (DDA), in the appropriate diluent. To investigate the influence of the nature of the acidoligand, the following complex nitroso compounds of ruthenium, labeled with the radioactive isotope Ru^{106}, were synthesized: $(NH_4)_2[RuNOCl_5]$, $(NH_4)_2[RuNOBr_5]$, and $(NH_4)_2[RuNOJ_5]$.

Freshly prepared 0.005 M solutions of ammonium ruthenium nitrosopentahalogenides in 1 M acid were used as the aqueous phase. These compounds are sufficiently stable in aqueous solutions; therefore their hydrolysis during the experiment can be neglected, and the obtained distribution coefficients (K_p) may be ascribed to the initial chemical forms of ruthenium. Experimental data on the extraction of ruthenium nitrosopentahalogenides from 1 M solutions of the corresponding hydrohalic acids in za-

Table 1

Change in the extraction of nitrosoruthenium as a function of the structure and concentration of the amine

Ligand in the $[RuNO\Gamma_5]^{2-}$ complex	Amine concentration, mol	Ruthenium extraction, %	Ruthenium extraction, %	Ruthenium extraction, %	Ruthenium extraction, %	Ruthenium extraction, %	Ruthenium extraction, %
		0.01	0.025	0.05	0.1	0.2	0.4
Cl^-	DDA	59.1	75.0	85.9	87.8	89.5	89.7
Cl^-	DGA	64.9	87.1	88.9	92.6	92.0	93.1
Cl^-	TOA	99.5	99.6	99.3	99.8	99.7	99.5
Br^-	DDA	47.6	60.2	71.2	86.7	90.4	90.2
Br^-	DGA	62.4	74.5	84.7	91.4	91.8	92.6
Br^-	TOA	94.5	95.0	94.9	96.6	97.3	97.5
I^-	DDA	38.1	52.5	64.5	85.6	86.6	87.0
I^-	DGA	46.3	64.9	73.8	87.1	88.9	89.4
I^-	TOA	89.5	89.3	89.8	91.7	91.9	92.6

as a function of the amine concentration in n-hexane are given in Table 1. As can be seen from the data obtained, the extraction of ruthenium into the organic phase increases on going from primary (DDA) to secondary (DGA) and then to tertiary amines (TOA), irrespective of the nature of the acidoligand in the complex.

In experiments to study the effect of the nature of the acidoligand on the extractability of ruthenium nitroso complexes, 1 mol nitric-acid solutions of ammonium nitrosopentahaloruthenates were used as the aqueous phase. This excluded the influence of the nature of the acid anion in the aqueous phase on the extractability of the ruthenium nitroso complexes and the possibility of inner-sphere substitution reactions, since the complexing ability of the NO_3^- group, as our observations showed, is considerably lower for ruthenium nitroso complexes than that of $Cl < Br < J$.

Figure 1 presents the dependence of $\lg K_p$ on the logarithm of the equilibrium concentration of free $TOAHNO_3$ in the organic phase. From the data obtained it is evident that the extraction of nitrosoruthenium pentahalides increases in the series of $Cl < Br < J$ ligands. The tangents of the angles of inclination of these straight lines ($\operatorname{tg} \alpha$, equal to 1.3 for Cl, 1.2 for Br, and 0.65 for J), from which the number of extractant molecules associated with the metal atom in the extracted complex is usually determined ([2,5]), proved to be variable quantities and also dependent on the nature of the acidoligands. It seemed to us unlikely that these fractional values of $\operatorname{tg} \alpha$ could characterize the composition of the complex in the organic phase.

In order to obtain direct evidence for the composition of the compounds passing into the organic phase during extraction from acid solutions of ruthenium nitrosopentahalides by amines, we isolated these compounds in an individual state and analyzed them.

The following three compounds were obtained with TOA:

$$[(n\text{-}C_8H_{17})_3NH]_2[RuNOJ_5].$$

Found, %: Ru 6.73; N 2.92; C 37.6; H 6.7
Calculated, %: Ru 6.86; N 2.85; C 38.8; H 7.05

$$[(n\text{-}C_8H_{17})_3NH]_2[RuNOBr_5].$$

Found, %: Ru 7.65; N 3.69; C 48.1; H 8.25
Calculated, %: Ru 8.46; N 3.39; C 46.5; H 8.4

$$[(n\text{-}C_8H_{17})_3NH]_2[RuNOCl_5].$$

Found, %: Ru 9.24; N 4.31; C 56.68; H 9.56
Calculated, %: Ru 9.95; N 4.14; C 56.7; H 10.2

With DHA—three compounds:

$$[(n\text{-}\mathrm{C_6H_{13}})_2\mathrm{NH_2}]_2[\mathrm{RuNOJ_5}].$$

Found, %: Ru 8.46; N 3.78
Calculated, %: Ru 8.9; N 3.69

$$[(n\text{-}\mathrm{C_6H_{13}})_2\mathrm{NH_2}]_2[\mathrm{RuNOBr_5}].$$

Found, %: Ru 11.7; N 4.79
Calculated, %: Ru 11.2; N 4.65

$$[(n\text{-}\mathrm{C_6H_{13}})_2\mathrm{NH_2}]_2[\mathrm{RuNOCl_5}].$$

Found, %: Ru 15.0; N 6.0; C 41.5; H 7.6
Calculated, %: Ru 14.88; N 6.17; C 42.2; H 8.1

With DDA—two compounds:

$$[(n\text{-}C_{12}H_{25}NH_3)_2][RuNOBr_5].$$

Found, %: Ru 11.15; N 4.85; C 31.23; H 6.07
Calculated, %: Ru 11.20; N 4.66; C 31.9; H 6.2

$$[(n\text{-}C_{12}H_{25}NH_3)_2][RuNOCl_5].$$

Found, %: Ru 14.25; N 5.9; C 42.86; H 9.1
Calculated, %: Ru 14.82; N 6.18; C 42.4; H 8.24

In general form, the composition of the complexes can be represented by the following formula: $(AmH)_2[RuNO\Gamma_5]$, where Am denotes various amines.

The equilibrium of the complex-formation reaction in the systems studied by us can be represented by the following equation:

$$[RuNO\Gamma_5]^{2-}_{aq} + 2Am\,H\Gamma_{org} \rightleftharpoons (AmH)_2[RuNO\Gamma_5]_{org} + 2\Gamma^-_{aq}.$$

An increase in the electron-donor properties of the amines in the series DDA < DHA < TOA leads to a shift of the equilibrium of the complex-formation reaction to the right.

An increase in the electron-donor properties of the acidoligands (7) in the series Cl < Br < J also shifts the equilibrium of the complex-formation reaction to the right, which accounts for the increase in the extractability of ruthenium into the organic phase.

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Note: Figure translations are in progress. See original paper for figures.