Studies on Nitrosylruthenium Complexes in Nitric Acid Using Repeated Extractions

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Repeated extractions using the system tri-*n*-butyl phosphate (TBP) — nitric acid have been applied to the study of nitrosylruthenium nitrates. A detailed investigation of the partition coefficients has been carried out. The equilibrium composition of a solution of nitrosylruthenium nitrates in aqueous nitric acid has been determined, and the kinetics of the interchange between the complexes have been studied.

In the presence of oxides of nitrogen, ruthenium easily forms strong nitroso complexes. These complexes have recently attracted much attention because some of them are effectively extracted by tributyl phosphate. The extraction with tributyl phosphate from nitric acid solutions is a method often used for the separation of uranium and plutonium from fission products. There are two ruthenium isotopes with long half-lives and high fission yields among the fission products¹, namely ¹⁰³Ru and ¹⁰⁶Ru, and ruthenium therefore causes difficulties in the separation process.

Several investigations of the nitrate complexes of nitrosylruthenium have been published²⁻⁹. In the present investigation an extraction method has been worked out which makes accurate determinations of concentrations and partition coefficients possible. This technique has been used for a study of (a) the composition of a solution of nitrosylruthenium nitrates in aqueous nitric acid as a function of the acidity, (b) the kinetics of the interchange between the complexes, and (c) the dependence of the partition coefficients on various factors such as the tributyl phosphate concentration, the nitric acid concentration, and the temperature.

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THE METHOD OF REPEATED EXTRACTIONS

Independent constituents

A solution (water phase) containing i independent constituents of the concentrations c_i is extracted repeated times with the same volume of an immiscible liquid (organic phase). The coefficients for the partition of the constituents between the organic phase and the water phase are denoted by q_i . For the sake of simplicity, the symbols p_i are introduced by the relation

$$p_i = \frac{q_i}{1 + q_i} \quad (1)$$

The n :th organic phase will contain the compounds in the total concentration $(C_o)_n$:

$$(C_o)_n = \sum_i c_i q_i (1 - p_i)^n \quad (2)$$

For large values of n the constituent with the smallest partition coefficient ($= p_1$) will dominate. If $\log (C_o)_n$ is plotted *versus* n a straight line is then obtained:

$$\log (C_o)_n \rightarrow \log c_1 q_1 + n \log (1 - p_1) \quad (3)$$

This line has the slope $\log (1 - p_1)$, and its intercept with the $\log C_o$ -axis is equal to $\log c_1 q_1$. Thus q_1 and c_1 can be determined. By the subtraction of $c_1 q_1 (1 - p_1)^n$ from eqn. (2) a new function $(C_{o,d})_n$ is obtained. This function can be plotted *versus* n on a semilogarithmic scale and be used for a determination of the partition coefficient and the concentration of the constituent with the next smallest partition coefficient. The same procedure can be repeated to yield the partition coefficients and the concentrations of the remaining constituents of the solution provided that the partition coefficients are sufficiently different*.

If p_1 is very small, eqn. (3) corresponds to a line with a small slope, and it is difficult to determine the partition coefficient. For large values of n , however, one obtains

$$\frac{(C_o)_n}{(C_w)_n} \rightarrow q_1 \quad (4)$$

where $(C_w)_n$ is the total concentration in the water phase after the n :th extraction. The smallest partition coefficient q_1 is determined by plotting the concentration ratio *versus* n .

By repeated extractions of an organic phase with water phases (equal volumes) similar results are obtained:

$$(C'_w)_n = \sum_i \frac{c_i}{q_i} p_i^n \quad (5)$$

(Primed symbols refer in this work to repeated extractions of an organic phase).

* This method of analysis is analogous to the resolution of a complex decay curve of a number of radioactive isotopes into its components.

On a semilogarithmic scale, $(C'_w)_n$ can be resolved into a number of straight lines with their slopes equal to $\log p_i$ and their intercepts with the $\log C'_w$ -axis equal to $\log c_i/q_i$. The concentration ratio (eqn. (4)) gives in this case the largest partition coefficient.

Repeated extractions of a water phase containing dependent constituents (nitrosylruthenium nitrates)

If the constituents of a solution are dependent of each other, the method of analysis just outlined must be changed in order to take this into account. The nitrosylruthenium nitrates interchange rapidly, and they cannot be considered as independent.

In a solution, which is not too strongly acidified with nitric acid, mainly four different nitrosylruthenium complexes are found ⁶, namely the trinitrate (RuT), the dinitrate (RuD), the mononitrate (RuM), and a nitrate-free complex (RuN). (Obviously, the complex RuN is not a "nitrate" complex. It is closely related to the others, however, and will therefore be considered in this work). The following formulas have been proposed for these compounds:

These complexes interchange in the following way:

The symbols k_{XY} denote rate constants. The rates of these reactions are all of the first order with respect to ruthenium ⁶.

In the present investigation the time for each complete extraction step (1 min) was kept short in comparison to the half-time of the reactions. Thus, it is appropriate to assume that the amount of the complex X which is converted into the complex Y during one extraction step is given by the product of its concentration and the "effective" rate constant k_{XY} (in min^{-1}). The actual complex will be found partly in the organic phase and partly in the water phase during the extraction. This is taken into account by using an effective rate constant computed from the partition coefficient and the rate constants in both phases.

Immediately after the n :th extraction the total concentration of nitrosylruthenium nitrates in the water phase and in the organic phase can be written as follows:

$$\left. \begin{aligned}(C_w)_n &= B_{\text{Tn}}(1-p_{\text{T}}) + B_{\text{Dn}}(1-p_{\text{D}}) + B_{\text{Mn}}(1-p_{\text{M}}) + B_{\text{Nn}}(1-p_{\text{N}}) \\ (C_o)_n &= B_{\text{Tn}}p_{\text{T}} + B_{\text{Dn}}p_{\text{D}} + B_{\text{Mn}}p_{\text{M}} + B_{\text{Nn}}p_{\text{N}}\end{aligned} \right\} \quad (6)$$

Since the actual rate constants are fairly small ($<0.1 \text{ min}^{-1}$), all terms which are small of the third or higher orders, *i.e.* which contain more than two rate constants as factors, are now neglected. The following expressions for the B_{Xn} 's can then be deduced:

$$\left. \begin{aligned} B_{Tn} &= c_T(1-k_T)Q_T^{n-1} + c_D k_{DT} S_{DTn} + c_T P_{TDT} U_{DTn} + c_M P_{MDT} V_{MDTn} \\ B_{Dn} &= c_D(1-k_D)Q_D^{n-1} + c_M k_{MD} S_{MDn} + c_T k_{TD} S_{TDn} + c_D(P_{DMD} U_{MDn} + \\ &\quad + P_{DTD} U_{TDn}) + c_N P_{NMD} V_{NMDn} \\ B_{Mn} &= c_M(1-k_M)Q_M^{n-1} + c_N k_{NM} S_{NMn} + c_D k_{DM} S_{DMn} + c_M(P_{MNM} U_{NMn} + \\ &\quad + P_{MDM} U_{DMn}) + c_T P_{TDM} V_{TDMn} \\ B_{Nn} &= c_N(1-k_N)Q_N^{n-1} + c_M k_{MN} S_{MNn} + c_N P_{NMN} U_{MNn} + c_D P_{MDN} V_{MDNn} \end{aligned} \right\} \quad (7)$$

The concentration symbols c_T , c_D , c_M , and c_N appearing in eqns. (7) denote the concentrations of RuT, RuD, RuM, and RuN, respectively, at the beginning of the experiment. The other symbols have the following meaning:

$$k_T = k_{TD}; \quad k_D = k_{DM} + k_{DT}; \quad k_M = k_{MN} + k_{MD}; \quad k_N = k_{NM}$$

$$Q_X = (1-k_X)(1-p_X)$$

$$P_{XYZ} = k_{XY}(1-p_Y)k_{YZ}$$

$$S_{XYn} = \frac{Q_X^n - Q_Y^n}{Q_X - Q_Y}$$

$$U_{XYn} = \frac{1}{(Q_X - Q_Y)^2} \left[(n-1)Q_Y^n - nQ_Y^{n-1}Q_X + Q_X^n \right]$$

$$V_{XYZn} = \frac{1}{Q_X - Q_Y} \left[Q_X \frac{Q_X^{n-1} - Q_Z^{n-1}}{Q_X - Q_Z} - Q_Y \frac{Q_Y^{n-1} - Q_Z^{n-1}}{Q_Y - Q_Z} \right]$$

The partition coefficients q_M and q_N are very small (<0.01) for extractions with tributyl phosphate. They will therefore be neglected in this work.

For large values of n both Q_T^n and Q_D^n become negligible. (At the extraction of 1 M HNO_3 with 30 % TBP at 20° , Q_T is about 0.02 and Q_D about 0.75.) In this case the following approximation holds:

$$\begin{aligned} (C_o)_n \rightarrow Q_M^n &\left[\frac{c_M k_{MD} p_D}{Q_M - Q_D} + \frac{c_M P_{MDT} p_T}{(Q_M - Q_D)(Q_M - Q_T)} + \frac{c_D P_{DMD} p_D}{(Q_M - Q_D)^2} - \frac{c_N P_{NMD} p_D}{(Q_N - Q_M)(Q_M - Q_D)} \right] + \\ &+ Q_N^n \frac{c_N P_{NMD} p_D}{(Q_N - Q_M)(Q_N - Q_D)} \end{aligned} \quad (8)$$

The last term in eqn. (8) is usually small. For this reason $\log(C_o)_n$ will tend to a straight line when plotted *versus* n . From the slope of this line, Q_M is determined. A more accurate value of Q_M can be obtained as a second approximation by taking the last term of eqn. (8) into account.

For somewhat smaller values of n , Q_T^n is still negligible but not Q_D^n . In this case the following difference is obtained by subtracting eqn. (8) (right part) from $(C_o)_n$:

$$(C_o)_n \rightarrow Q_D^n \left[c_D q_D - \frac{c_M k_{MD} p_D}{Q_M - Q_D} + \frac{c_T k_{TD} p_D}{Q_D - Q_T} + \frac{c_D k_{DT} p_T}{Q_D - Q_T} + \right. \\ \left. + \frac{c_N P_{NMD} p_D}{(Q_M - Q_D)(Q_N - Q_D)} - \frac{c_M P_{MDT} p_T}{(Q_M - Q_D)(Q_D - Q_T)} + \frac{c_T P_{TDT} p_T}{(Q_D - Q_T)^2} + \right. \\ \left. + \frac{c_D P_{DMD} p_D}{(Q_M - Q_D)^2} \left(n - 1 - n \frac{Q_M}{Q_D} \right) + \frac{c_D P_{DTD} p_D}{(Q_D - Q_T)^2} \left(n - 1 - n \frac{Q_T}{Q_D} \right) \right] \quad (9)$$

The last two terms within the square brackets are small. Therefore, $\log (C_o)_n$ gives a straight line when plotted *versus* n , and Q_D can be determined from the slope of this line.

By subtraction of the right part of eqn. (9) from $(C_o)_n$ a new difference is obtained:

$$(C_o)_n = Q_T^n \left[c_T q_T - \frac{c_D k_{DT} p_T + c_T k_{TD} p_D}{Q_D - Q_T} + \right. \\ \left. + \text{smaller terms} \right]. \quad (10)$$

If $\log (C_o)_n$ is plotted *versus* n a straight line is obtained with the slope equal to $\log Q_T$. The line is very steep, however, and it is better to determine Q_T by other experiments (repeated extractions of an organic phase).

As an illustration C_o , $C_{o,d}$ and $C_{o,d,d}$ have been plotted *versus* n on a semi-logarithmic scale in Fig. 1.

If the partition coefficients and the rate constants are known, eqn. (10) can be used for a determination of c_T (the term containing c_D is very small and can be neglected).

$$c_T = \frac{(C_o)_n}{Q_T^n} \left[q_T - \frac{k_{TD} p_D}{Q_D - Q_T} \right] \quad (11)$$

For the determination of the relative concentrations c_D , c_M and c_N the following relationships are chosen: (a) the value A_o of the right part of eqn. (9) for n equal to zero as determined by extrapolation of the straight line, and (b) the ratio $(C_o)_n / (C_w)_n = q_n$ for a large value of n (the value $n = 25$ was used). The former relationship depends essentially on the concentration of the dinitrate and the latter on the ratio between the concentrations of the mononitrate and the nitrate-free complex. Besides, all concentrations add up to unity so that a system of equations of the following type is obtained:

$$\left. \begin{array}{l} c_N + c_M + c_D = 1 - c_T \\ \text{(a) } \alpha_1 c_N + \alpha_2 c_M + \alpha_3 c_D = A_o - \alpha_4 c_T \\ \text{(b) } (\beta_1 - q_n \gamma_1) c_N + (\beta_2 - q_n \gamma_2) c_M + (\beta_3 - q_n \gamma_3) c_D = (q_n \gamma_4 - \beta_4) c_T \end{array} \right\} \quad (12)$$

Fig. 1. The activity (proportional to the total concentration of nitrosylruthenium nitrates) of the organic phase *versus* the number of extractions for repeated extractions of a water phase. Circles: $(C_o)_n$; Squares: $(C_{o,d})_n$; Triangles: $(C_{o,d,d})_n$.

Fig. 2. The ratio between the activity of the organic phase and that of the water phase *versus* the number of extractions for repeated extractions of an organic phase. Curve A: The activity was originally in the water phase. Curve B: The activity was originally in the organic phase.

The α 's, β 's and γ 's depend only on the partition coefficients and the rate constants. They are easily calculated from eqns. (6), (7), and (9). The expressions are somewhat lengthy, however, and they are therefore not written out here.

Repeated extractions of an organic phase containing dependent constituents (nitrosylruthenium nitrates)

For repeated extractions of an organic phase eqns. (6) and (7) are valid if the factor $(1-p_x)$ is changed into p_x in the expressions for Q_x and P_{xyz} . Thus

$$Q'_x = p_x (1 - k'_x)$$

$$P'_{xyz} = k_{xy} p_y k'_{yz}$$

The rate constants, which appear here, differ from the corresponding ones in the preceding section. Since they turn out to be considerably smaller, terms which are small of the second order, *i. e.* terms containing P'_{xyz} as a factor, can be neglected. Besides, Q'_N and Q'_M are negligible.

For large values of n , $Q_D'^n$ can be neglected, and the following relation is obtained:

$$\frac{(C_o')_n}{(C_w')_n} \rightarrow q_T (1 - \delta) \quad (13)$$

with

$$\delta \sim \frac{k_{TD}'}{Q_T' - Q_D'} \left[q_T (1 - p_D) - p_D \right]$$

From eqn. (13) q_T is determined by successive approximations.

The ratio $(C_o')_n / (C_w')_n$ has been plotted *versus* n in Fig. 2. It tends to become a constant after 4–5 extractions.

For large values of n , $(C_o')_n$ can be written:

$$(C_o')_n \rightarrow c_T Q_T'^n (1 + \varepsilon) \quad (14)$$

with

$$\varepsilon \sim \frac{p_T \left[k_{TD}' \frac{p_D}{p_T} + k_{DT}' \frac{c_D}{c_T} \right]}{Q_T' - Q_D'}$$

The right part of eqn. (14) corresponds to a straight line when plotted *versus* n on a semilogarithmic scale. The intercept for n equal to zero can be used for a determination of c_T .

If $\log (C_w')_n$ is plotted *versus* n , a straight line is obtained for large values of n . By a subtraction procedure similar to the one leading to $(C_{o,d})_n$ (eqn. (9)), the following difference results:

$$(C_{w,d})_n = Q_D'^n \left[\frac{c_D}{q_D} + \frac{c_M k_{MD}'}{q_D (1 - k_D')} - \frac{c_T k_{TD}' (1 - p_D) + c_D k_{DT}' (1 - p_T)}{Q_T' - Q_D'} \right] \quad (15)$$

A straight line results when $\log (C_{w,d})_n$ is plotted as a function of n . The line has the slope $\log Q_D'$ and can be used for a determination of Q_D' . An approximate value of c_D is also obtained.

The accuracy of the determinations. The reproducibility of the determinations is high, especially with regard to RuT. Thus it is possible to determine c_T with an accuracy of better than 1 %, and the q_T -values are in many cases accurate to ± 2 %. The determinations of q_D are reliable to ± 5 –10 %.

The accuracy of the determinations of c_D , c_M , and c_N depends essentially upon how well the rate constants are determined. It is probably not better than ± 10 –20 %.

EXPERIMENTAL

Solutions. The nitrosylruthenium nitrate contained tracer of ^{106}Ru . A stock solution in 8 M nitric acid was prepared as described in Ref.⁹. The stock solution was carrier-free. An analysis was performed using the dithio-oxamide method¹⁰ after the distilla-

tion of ruthenium as the tetroxide. The analysis showed that the ruthenium concentration of the samples was less than 10^{-7} M.

The tri-*n*-butyl phosphate was first washed with a 5 % solution of sodium carbonate and then distilled at vacuum. After the distillation it was diluted with an inert mixture of hydrocarbons.* The concentration of tributyl phosphate was determined analytically by the method of Allen and DeSesa¹¹.

The experimental procedure. Repeated extractions of a water phase were carried out using an extraction apparatus (Fig. 3) where the lighter organic phase could be easily removed after each extraction. The extractions were performed by stirring for 30 sec. After this, the phases were separated and a new portion of tributyl phosphate was added. The time allowed for this was also 30 sec. so that the time interval between two successive extractions was exactly 1 min. The experiment was usually carried out at 20° with 0.95 M nitric acid as the water phase and 30 % tributyl phosphate as the organic phase. The volume of each phase was 5 ml, and the number of extractions was 25–35. The activities of all organic phases and the water phase were measured with a scintillation counter. The activity was used as a measure of the concentration.

At the experiments with repeated extractions of an organic phase, a separation funnel was used. The number of extractions was 10.

The acidity of the water phases was determined by titration after the extractions.

RESULTS

Dependence on the extraction time

In a series of experiments with repeated extractions of an organic phase (30 % TBP) with 1 M nitric acid at 20°, the extraction time was varied. The partition coefficients obtained are tabulated in Table 1.

* Nysolvin 160/200, a mainly paraffinic kerosene fraction from Nynäs-Petroleum AB.

Fig. 3. Extraction apparatus for repeated extractions of the heavier phase.

Table 1. The dependence of the partition coefficients on the extraction time.

Extraction time	q_T	q_D
15 sec.	46.9	0.28
30 »	47.9	0.28
40 »	47.4	0.32

The partition coefficients are independent of the extraction time in the interval studied. Thus stirring for 30 sec is adequate for the equilibrium between the phases to be reached. Similar results regarding RuT have been obtained by Brown *et al.*⁶

Studies on the kinetics of the interchange between the nitrosylruthenium nitrates

(a) *Rate constants in 0.95 M nitric acid.* In order to make a determination of partition coefficients and concentrations from the extraction data possible, the rate constants must be known. Kinetic experiments are therefore essential. Since the analyses by the method of repeated extractions were usually carried out at 20° and with the system 0.95 M HNO₃—30 % TBP, it was of primary interest to determine the rate constants corresponding to these conditions.

In a series of experiments a pure solution of RuT in 30 % tributyl phosphate was first prepared by removing all other complexes by repeated extractions with 1 M nitric acid. The trinitrate was then reextracted into 8 M nitric acid, and the solution was diluted to 0.95 M with water. It was kept at 20° in a thermostat. Samples were taken at different times for repeated extractions, and the quantities $(C_{o,d,d})_{n=1}$, A_o , and q_{25} (eqns. (11) and (12)) were measured.

Starting from the approximations $k_{TD} = k_{NM} = 0$ and $Q_M = 1 - k_{MD}$, the constants of eqns. (12) were calculated and the concentrations determined. Next, new rate constants were determined from the concentrations just obtained. The kinetic equations are of the following form:

$$\left. \begin{aligned} \frac{dc_T}{dt} &= -k_{TD}c_T + k_{DT}c_D \\ \frac{dc_N}{dt} &= -k_{NM}c_N + k_{MN}c_M \end{aligned} \right\} \quad (16)$$

Now, k_{DT} can be expressed in k_{TD} and k_{MN} in k_{NM} using the concentrations at equilibrium. The derivatives in eqns. (16) are then replaced by the differences $\frac{\Delta c_T}{\Delta t}$ and $\frac{\Delta c_N}{\Delta t}$, and the rate constants k_{TD} and k_{NM} are determined graphically. They are combined with the relation $Q_M = 1 - k_M$ and all equilibrium concentrations to yield the remaining rate constants, and the "effective" rate con-

stants are calculated. These are used for new determinations of the concentrations c_x . By successive approximations, values of c_x and k_{xy} are finally found which are not changed by further approximations. The final values of the rate constants in 0.95 M nitric acid and at the temperature 20° are tabulated in Table 2.

Table 2. Rate constants in 0.95 M HNO₃.

k_M	0.051 min ⁻¹ *
k_{TD}	0.025 »
k_{DT}	0.0024 »
k_{DM}	0.084 »
k_{MD}	0.047 »
k_{MN}	0.0041 »
k_{NM}	0.0025 »

* This value was obtained from $Q_M = 0.949 \pm 0.002$, average of 34 determinations.

The following value of Q_D (average of 34 determinations) has been obtained:

$$Q_D = (1 - k_D) (1 - p_D) = 0.742 \pm 0.007$$

The effective value of k_D is found to be 0.078 min⁻¹ from the appropriate rate constants in 0.95 M nitric acid and tributyl phosphate. With this k_D -value one obtains

$$p_D = 0.195; q_D = 0.242$$

Fig. 4. Relative concentrations of nitrosylruthenium nitrates versus time starting from a solution of pure RuT in 0.95 M nitric acid. Temperature: 20°.

Filled circles: c_T
 Crosses: c_D
 Squares: c_M
 Triangles: c_N
 Open circles: c_T

From repeated extractions of a water phase.

From repeated extractions of an organic phase.

Fig. 5. $\frac{\Delta c_T}{\Delta t}$ versus $c_T - c_D \left(\frac{c_T}{c_D}\right)_{eq}$ for RuT in 0.95 M nitric acid. Temperature: 20°.

Fig. 6. Relative concentration of RuT versus time starting from a solution of pure RuT in 30 % tributyl phosphate. Temperature: 20°.

The concentrations of the nitrosylruthenium nitrates in 0.95 M nitric acid are plotted *versus* time in Fig. 4.

As an example of the rate constant analyses, $\frac{\Delta c_T}{\Delta t}$ has been plotted *versus* $c_T - c_D \left(\frac{c_T}{c_D}\right)_{eq}$ in Fig. 5. The slope of the straight line corresponds to k_{TD} . The value 0.025 min⁻¹ is found.

(b) *Rate constants in 30 % tributyl phosphate saturated with 0.95 M nitric acid.* The decrease of c_T in a solution of RuT in 30 % tributyl phosphate (saturated with 0.95 M nitric acid) has also been studied. The temperature was 20°. In this case only two components have to be considered, namely RuT and RuD. The following rate constants were obtained:

$$k_{TD,o} = 0.00067 \text{ min}^{-1}$$

$$k_{DT,o} = 0.0059 \text{ min}^{-1}$$

Fig. 6 shows c_T as a function of time.

A conversion of the aquo-complexed nitrosylruthenium trinitrate into the corresponding TBP-complexed compound has been proposed to occur in tributyl phosphate solutions⁶. The latter compound is thought to have a much higher partition coefficient ($> 10^3$) than the former. The half-time of the reaction is estimated to be about 3 min and that of the reverse reaction to be about 6 min. In this work a great number of experiments with repeated extractions of organic phases have been performed in which the ruthenium was originally in the water phase. The experiments cover the temperature range

0°–50° and the acidity range 0.165 M–3.25 M (water phase). In all these experiments results similar to those in Fig. 2 were found. The activity ratio reaches a constant value after 4–5 extractions, *i. e.* after 4–5 min. The same results were obtained also in experiments where the ruthenium was originally in the TBP-phase, in some cases for as long as 18 days. This is not in accord with the hypothesis mentioned above. The conversion proposed would cause the activity ratio to approach a constant value much more slowly. On the other hand, it is quite possible that a more rapid interchange takes place. If this is the case, a measured q_T -value will be a function of the true partition coefficient of the aquo-complex and the rate constants of the interchange.

(c) *The temperature dependence of the rate constants in 0.95 M nitric acid.* Kinetic experiments have been carried out at three different temperatures: 10°, 20°, and 30°. The nitric acid concentration of the solutions was 0.95 M. The results are given in Table 3 and shown in Fig. 7.

Table 3. The temperature dependence of the rate constants.

Temperature	k_{TD} , min ⁻¹	k_{DT} , min ⁻¹	k_{MN} , min ⁻¹	k_{NM} , min ⁻¹
10°	0.0065	0.00096		
20°	0.025	0.0024	0.0041	0.0025
30°	0.068	0.0058	0.012	0.0085

An increase of the temperature by 10° corresponds to a threefold increase of the rate constants. Jenkins and Wain⁵ have carried out a series of rate constant determinations. Their results for the rate constant k_{TD} in 0.7–0.8 M nitric acid obtained at 0°, 25°, and 35° have also been plotted in Fig. 7.

(d) *The acidity dependence of the rate constants.* The dependence of the rate constants on the acidity of the water phase has been studied at the temperature 20°. The results are given in Table 4 and shown in Fig. 8.

Fig. 7. The temperature dependence of the rate constants in 0.95 M nitric acid. Circles: k_{TD} ; Crosses: k_{DT} ; Squares: k_{MN} ; Triangles: k_{NM} ; Dotted circles: k_{TD} from Ref.⁵.

Table 4. The acidity dependence of the rate constants.

Acidity	k_{TD} , min ⁻¹	k_{DT} , min ⁻¹	k_{MN} , min ⁻¹	k_{NM} , min ⁻¹
0.95 M	0.025	0.0024	0.0041	0.0025
1.92 M	0.019	0.0058	0.0046	0.014
3.80 M	0.018	0.013		
7.11 M	0.020	0.053		

The rate constant k_{TD} is almost independent of the acidity. This is in agreement with the results by Jenkins and Wain⁵.

In Fig. 9 c_T has been plotted *versus* time for different acidities.

Relative concentrations of the nitrosylruthenium complexes at equilibrium in aqueous nitric acid solutions

A series of nitrosylruthenium solutions of varying nitric acid concentration were prepared and analysed after about one week by repeated extractions of an organic phase (determination of c_T and c_D) or repeated extractions of a water phase (determination of c_T , c_D , c_M , and c_N). The results are tabulated in Tables 5 and 6, respectively, and plotted *versus* the acidity in Fig. 10.

Fig. 8. The acidity dependence of the rate constants. Temperature: 20°. Circles: k_{TD} ; Crosses: k_{DT} ; Squares: k_{MN} ; Triangles: k_{NM} .

Fig. 9. Relative concentration of RuT *versus* time starting from a solution of pure RuT in aqueous nitric acid. Temperature: 20°. Circles: 0.95 M HNO₃; Crosses: 1.92 M HNO₃; Squares: 3.80 M HNO₃; Triangles: 7.11 M HNO₃.

Table 5. Relative concentrations of nitrosylruthenium nitrates.

Acidity, M	c_D	c_T
0.316	0.00305	0.16
0.517	0.00655	0.21
0.747	0.0115	0.18
1.37	0.0288	0.22
2.03	0.0611	0.27
2.73	0.109	0.26
3.31	0.154	
3.64	0.182	
4.13	0.232	
5.54	0.383	
6.61	0.481	
8.15	0.640	
10.2	0.785	
12.4	0.882	
13.5	0.923	

Table 6. Relative concentrations of nitrosylruthenium nitrates.

Acidity, M	c_T	c_D	c_M	c_N
0.316	0.0028	0.076	0.20	0.72
0.506	0.0069	0.13	0.29	0.58
1.01	0.025	0.19	0.31	0.48
1.94	0.063	0.24	0.36	0.33
2.84	0.124	0.27	0.41	0.20
4.63	0.269	0.28	0.37	0.077
5.96	0.417	0.24	0.30	0.037
8.15	0.582	0.16	0.24	0.014
10.3	0.709	0.11	0.18	0
12.4	0.757	0.084	0.16	0

Fig. 10. The concentrations at equilibrium of nitrosylruthenium nitrates in aqueous nitric acid *versus* the acidity. Circles: c_T ; Crosses: c_D ; Squares: c_M ; Triangles: c_N .

Studies on the partition coefficients of the nitrosylruthenium nitrates

(a) *Dependence on the tributyl phosphate concentration.* Tributyl phosphate solutions with the concentration varying from 10 % to 50 % were extracted at 20° with 1 M nitric acid. The measured partition coefficients are tabulated in Table 7 and plotted *versus* the tributyl phosphate concentration in Fig. 11.

Table 7. Partition coefficients for different concentrations of tributyl phosphate.

Concentration of TBP, %	q_T	q_D
10.0	2.4	
15.6	8.5	0.13
21.0	19.5	0.18
25.9	33.2	0.23
31.2	45.1	0.39
36.1	67.5	0.56
40.9	88	0.54
45.4	113	0.52
50.0	150	0.63

As found by other investigators⁶ a plot of $\log q_T$ *versus* $\log C_{TBP}$ gives a straight line with the slope about 2 (the value 2.3 is obtained from Fig. 11).

Fig. 11. The dependence of the partition coefficients on the tributyl phosphate concentration for extractions with 1 M nitric acid. Temperature: 20°. Circles: q_T ; Crosses: q_D .

Fig. 12. The temperature dependence of the partition coefficients for extractions of 1 M nitric acid with 30 % tributyl phosphate. Circles: q_T ; Crosses: q_D .

(b) *Dependence on the temperature.* The partition coefficients q_T and q_D were determined in experiments with repeated extractions of organic phases (30 % TBP) with 1 M nitric acid at different temperatures. Eqn. (13) was used for the evaluation of q_T . The effective rate constant k'_{TD} , which forms part of the correction factor δ , contains $k_{TD,w}$ and $k_{TD,o}$. The temperature dependence of $k_{TD,w}$ is obtained from Fig. 7. Only one $k_{TD,o}$ -value has been determined, namely that for 20°. The temperature dependence is assumed to be the same as for $k_{TD,w}$, i. e. a temperature increase of 10° corresponds to a threefold increase of $k_{TD,o}$.

For the determination of q_D from the experimental values of $Q'_D = p_D(1 - k'_D)$, the effective rate constant k'_D must be known. This contains $k_{DT,w}$, $k_{DT,o}$, and $k_{DM,w}$. The first of these three rate constants is obtained from Fig. 7. The others are assumed to vary with temperature in the same way as $k_{TD,w}$. Their values at 20° are known.

The resulting determinations of q_T and q_D are tabulated in Table 8 and plotted *versus* temperature in Fig. 12.

Table 8. The temperature dependence of the partition coefficients.

Temperature, °C	q_T	q_D
1.0	116	0.37
5.0	94	0.29
9.6	75	0.28
14.0	63	0.24
20.0	48.1	0.22
26.5	29.6	0.10
32.6	19.2	0.11
37.6	14.4	
42.8	10.9	
47.2	7.6	
52.0	6	

Table 9. The acidity dependence of the partition coefficients.

Acidity, M	q_T	q_D
0.165	120	0.27
0.326	102	0.24
0.506	94	0.35
0.817	62	0.30
0.937	45	0.19
1.00	39	
1.01	38	
1.22	27.5	
1.62	16.7	
2.06	7.3	
2.37	3.0	
2.79	2.7	
3.25	2.0	

(c) *Dependence on the acidity of the water phase.* The acidity dependence of the partition coefficients was studied using two different methods for both q_T and q_D . First repeated extractions of an organic phase (30 % TBP) were carried out at the temperature 20° with water phases of the desired acidity. The results are tabulated in Table 9.

In the second method for the determination of q_T , a pure solution of the trinitrate in 30 % tributyl phosphate was prepared by 8–10 extractions with 1 M nitric acid. The organic solution was then extracted at 20° with nitric acid of the desired strength (the acidity was measured after the experiment), and the partition coefficient was determined from the ratio between the activities in the phases after a correction for the formation of dinitrate during the experiment. The results are given in Table 10.

Table 10. The acidity dependence of q_T .

Acidity, M.	q_T
0.0003	24.5
0.0040	63
0.456	92
0.691	79
0.815	66
1.01	44.7
1.34	25.6
1.66	15.6
1.93	7.10
2.28	5.24
2.63	3.02
3.43	0.84
5.30	0.117
7.22	0.073
10.3	0.073
13.5	0.022

The partition coefficient of RuD was also determined by a method similar to the second one for RuT. A solution of nitrosylruthenium nitrates in 1 M nitric acid was extracted four times with 30 % tributyl phosphate. Since q_T is high, all RuT is effectively removed. The solution was then extracted once more, and the organic phase, containing essentially pure RuD, was removed and extracted at 20° with nitric acid of the desired strength. The partition coefficient q_D was obtained from the ratio between the activities in the phases after due correction for the formation of RuT and RuM during the experiment. The results are tabulated in Table 11.

All the data from these experiments have been plotted *versus* the acidity of the water phase in Fig. 13. The agreement with other investigations is reasonable with respect to q_T . The values of q_D are in agreement with measurements using repeated extractions of a water phase (page 1490).

(d) *The stability of nitrosylruthenium dinitrate in 30 % tributyl phosphate.* A solution of RuD in 30 % tributyl phosphate (saturated with 0.95 M nitric acid) was prepared in the way described in the preceding section. The solu-

Table 11. The acidity dependence of q_D .

Acidity, M	q_D
0.182	0.302
0.396	0.341
0.602	0.304
0.794	0.258
1.42	0.141
1.86	0.079
2.70	0.023
3.50	0.013
5.46	0
7.48	0

tion was kept at 20°. Samples were taken for extraction with 0.95 M nitric acid, and the ratio between the activity of the organic phase and that of the water phase was determined. This ratio is shown in Fig. 14 as a function of the time between the preparation of the solution and the extraction.

If it is assumed that the solution contains only RuT and RuD, their concentrations can be calculated from the activity ratios. From the time-dependence of the concentrations, the rate constant $k_{TD,0} = 0.0067 \text{ min}^{-1}$ is obtained. This agrees well with the value 0.0059 min^{-1} determined earlier.

Fig. 13. The acidity dependence of the partition coefficients for extractions with 30 % tributyl phosphate at 20°. Circles: q_T ; Crosses: q_D .

Fig. 14. The ratio between the activity of the organic phase and that of the water phase *versus* time for extractions of a solution of originally pure RuD in 30 % tributyl phosphate with 0.95 M nitric acid.

(e) *Upper limits for q_M and q_N .* A large number of experiments concerning the partition coefficients q_M and q_N have been performed. The experiments were carried out at 20° with the system 30 % tributyl phosphate — 0.95 M nitric acid. Upper limits of the partition coefficients are immediately obtained from repeated extractions of water phases. For large values of the extraction number n , the ratio between the activity of the organic phase and that of the water phase varies from 0.03 for solutions containing much RuM and little RuN to less than 0.005 for solutions containing mainly RuN. Thus

$$q_M < 0.03 \text{ and } q_N < 0.005$$

Fig. 15. The ratio between the activity of the organic phase and that of the water phase at the 25th extraction of a water phase with 30 % tributyl phosphate *versus* $C_M/(C_M + C_N)$. Temperature: 20°.

The activity ratio for n equal to 25 has been plotted *versus* the ratio $c_M/(c_M + c_N)$ in Fig. 15. By extrapolation the upper limit 0.001 is obtained for q_N .

A better estimate of the upper limit of q_M can be made. A solution of nitrosylruthenium nitrates in 0.95 M nitric acid was extracted four times with 30 % tributyl phosphate. The fourth organic phase was extracted with 0.95 M nitric acid at 20°, and the ratio between the activities of the phases was measured. Four determinations gave the value 0.260 ± 0.006 as an average. This corresponds to a q_D -value of 0.245, in excellent agreement with earlier results. In another series of experiments carried out at the same conditions, a water phase was extracted 25 times with 30 % tributyl phosphate, and the 25th organic phase was extracted with 0.95 M nitric acid. The activity ratio 0.237 ± 0.013 was obtained as an average of seven determinations. This is close to the q_D -value at the given conditions, and the conclusion can be drawn that almost all extracted ruthenium is in the form of RuD. The observed difference between 0.260 and 0.237 corresponds to a q_M -value of 0.003. It should be safe to estimate the upper limit of q_M to 0.01.

Since both q_M and q_N are small, their neglect in this work is justified.

DISCUSSION

The method of repeated extractions has proved to be very useful for the study of the nitrate complexes of nitrosylruthenium. Owing to the possibility of taking the interchange between the complexes during the experiment into account, reliable determinations of concentrations and partition coefficients can be made.

The values determined for rate constants, equilibrium concentrations, and partition coefficients make possible predictions of the behaviour of the nitrosylruthenium nitrates at different conditions with respect to the tributyl phosphate concentration, the nitric acid concentration, the temperature, and the time schedule followed during the experiment. Such predictions are of value in connection with those separation procedures for plutonium and uranium which are based on extractions with tributyl phosphate.

It must be pointed out that the present work has not been concerned with any confirmation of the formulas of the nitrosylruthenium complexes. The trinitrate has been identified merely by its partition coefficient and by comparison with other experiments^{6,8}. The identities of the other complexes found have been inferred from their relationships (for instance: a solution of RuD in tributyl phosphate is converted into RuT; a solution of RuM in dilute nitric acid is converted into RuD and not directly into RuT). Furthermore, RuT is probably the most nitrate-rich complex since it dominates at high nitric acid concentrations. Thus, if the identification of RuT as the trinitrate is correct, the identification of the other complexes as the dinitrate, the mononitrate and a nitrate-free complex seems plausible.

The technique of repeated extractions should be useful also for other investigations where a complex mixture of extractable compounds is to be analysed.

Acknowledgements. The author wishes to express his gratitude to Professor The Svedberg for his interest in this work.

Thanks are due to Mrs. Carina Kjellson for her valuable help in carrying out the experiments.

The investigation has been financially supported by AB Atomenergi, which is gratefully acknowledged.

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Received May 12, 1959.