

372. *Solvent-extraction of Septivalent Rhenium. Part II.¹ Heterogeneous Equilibria in the System, Aqueous Nitric Acid–Potassium Perrhenate—“Tri-iso-octylamine.”*

By A. S. KERTES and A. BECK.

The distribution of rhenium in its highest oxidation state between aqueous nitric acid and tris-(2,2,4-trimethylpentyl)amine has been investigated. The variation in the rhenium molarity in the organic phase with nitric acid concentration shows that the rhenium species extracted is free perrhenic acid, HReO_4 . Job's method of continuous variations indicated $\text{NR}_3\cdot\text{HReO}_4$ as the species present in the organic phase. Some information on the similar distribution mechanisms for rhenium(VII) in this amine system and in that of Dowex-1, an anion-exchange resin, is also obtained. Evidence is presented which indicates that the affinity of the amine for ReO_4^- is higher than for NO_3^- .

THE usefulness of long-chain amines of high molecular weight for the extraction of strong mineral acids²⁻⁴ suggests that it might be advantageous to employ them in the extraction of metals in a high valency state, *i.e.*, those forming strong metal oxyacids of the type HMO_4 . “Tri-iso-octylamine” was selected for the present work which involved studying the behaviour of a metal as anion rather than as cation. No previous investigations seem to have been reported on the extraction of rhenium by amines.

Experimental.—The amine, which was 92.4% pure as determined titrimetrically,⁴ was obtained from Union Carbide Chemicals Co., and was used without purification. Carbon tetrachloride was of the grade used in Part I.¹ Fresh organic solvents were prepared every few days. The other reagents were of the standard reagent grade.

Equilibration techniques, experimental procedures, and analyses used were as described in Part I.

RESULTS AND DISCUSSION

It has been shown (see, *e.g.*, ref. 3) that the heterogeneous equilibria in solvent-extraction processes with long-chain amines are by no means simple. With these two completely immiscible phases there are some “side processes” in amine–metal or amine–acid

¹ Part I, preceding paper.

² (a) Moore, *Analyt. Chem.*, 1957, **29**, 1660; Schindewolf, *Z. Elektrochem.*, 1958, **62**, 335; Bizot and Trémillon, *Bull. Soc. chim. France*, 1959, 122; (b) Allen, *J. Phys. Chem.*, 1956, **60**, 239, 943.

³ Coleman, Brown, Moore, and Allen, Proc. Internat. Conf. Peaceful Uses of Atomic Energy, U.N. 1958, Vol. XXVIII, p. 278.

⁴ Boirie, *Bull. Soc. chim. France*, 1958, 980, 1088; Thesis, Paris, and C.E.A. Report No. 1262, 1960.

extraction that are not general for other classes of solvents; the two chief side reactions are the formation of high polymeric aggregates of the amine salt in the organic layer^{2b,3,5} and of stoichiometrically undefined amine-nitrate compounds, the latter caused by the varying and irregular solubility of the acid in the normal amine nitrate, R_3N, HNO_3 .^{6,7} These factors must be taken into account as causing a variation in the extraction mechanism expected. On the other hand, the species soluble in the organic phase was not hydrated in the amine-nitrates system,⁷ as determined by direct Karl Fischer analysis of the equilibrated organic layer, and this factor could be ignored.

(a) *Stoichiometry between $KReO_4$ and HNO_3 in the Extracted Species.*—Variation in the extraction of perrhenate by the amine in carbon tetrachloride as a function of the molar $KReO_4:HNO_3$ ratio in the initial aqueous solution was studied under three sets of conditions: (1) Job's method of continuous variations; (2) changing the nitric acid concentration in the initial aqueous solution at constant perrhenate concentration; and (3) changing the perrhenate concentration in the initial aqueous solution at constant nitric acid content; the amine concentration in the organic layer was kept constant.

Job's method (curve 1, Fig. 1) indicated a molar $KReO_4:HNO_3$ ratio of $\sim 1.2:1$. Additional evidence was obtained from two series of experiments. In the first, with a constant concentration (0.024M) of potassium perrhenate in the initial aqueous solution, the nitric acid concentration was varied and, in the second, the concentration of perrhenate was varied from zero to 0.024M at a constant concentration of nitric acid of 0.024M; in both series the amine concentration in the organic layer was constant at 0.024M. Fig. 2 shows the graph of molar concentration of perrhenate in the equilibrated organic layer plotted against the molar $KReO_4:HNO_3$ ratio (for the wide range of ratios 0.05—20) in the initial aqueous solutions. As shown, the maximum rhenium content in the organic phase appears at a $KReO_4:HNO_3$ ratio of unity. In Fig. 3 the perrhenate molarity of the equilibrated organic layer is plotted against the nitric acid concentration in the initial aqueous solution. The straight line for initial acid concentration, up to $\sim 0.015M$, with unit slope predicts the transfer of one mole of perrhenic acid to the organic phase per mole of nitric acid in the initial aqueous solution. The departure from the unit slope at higher acid concentrations will be dealt with below. These experiments indicate that the perrhenic acid must be the only extractable septivalent rhenium species. Perrhenate is not extracted in the absence of acid.

(b) *Stoichiometry between $HReO_4$ and Amine.*—In experiments by Job's method the initial nitric acid concentration was kept constant, and the initial perrhenate concentration and the amine concentration in the organic layer were varied. In the plot of these results (Fig. 4), the extremum appears at a molar $KReO_4$:Amine ratio of unity, suggesting a solvation number of one. It has recently been shown⁸ that the only anionic rhenium species present in the aqueous solution for a very wide range of acid concentrations is the normal perrhenate ion, ReO_4^- , of tetrahedral symmetry, and that perrhenic acid is $HReO_4$ and not H_3ReO_5 or H_5ReO_6 . It seems evident that the normal amine salt of a strong monobasic acid, such as perrhenic, must have the stoichiometric composition of $R_3N, HReO_4$.

(c) *Relative Affinities of $HReO_4$ and HNO_3 for the Extractant.*—Of the mineral acids so far investigated,³ perchlorate will probably have the highest affinity for the amines. The order of affinities shown in acid extraction by amines is generally similar to that shown by anion-exchange resins, namely, $ClO_4^- > NO_3^- > Cl^- > HSO_4^- > F^-$ (the order of exchange of one anion for another). If in the aqueous phase the nitric acid concentration is less than that of perrhenate, the perrhenate concentration in the equilibrated organic

⁵ Allen, *J. Phys. Chem.*, 1958, **62**, 1119; *J. Amer. Chem. Soc.*, 1958, **80**, 4133; McDowell and Baes, jun., *J. Phys. Chem.*, 1958, **62**, 777; McDowell and Allen, *ibid.*, 1959, **63**, 747.

⁶ Carswell and Lawrance, *J. Inorg. Nuclear Chem.*, 1959, **11**, 69.

⁷ Platzner, M.Sc. Thesis, Hebrew University, 1960.

⁸ Earley, Fortnum, Wojcicki, and Edwards, *J. Amer. Chem. Soc.*, 1959, **81**, 1295.

layer appears to approach a constant limiting value which depends on the nitric acid concentration; one g.-ion of H^+ in the initial aqueous solution increases the perrhenate content of the organic layer by one mole, before any nitric acid passes into the organic phase, as shown by results presented in Fig. 3. On the other hand, with an excess of nitric acid, increasing the perrhenate concentration leads to almost 100% extraction, as shown in Fig. 5. The unit slope of the curves in Figs. 3 and 5 at lower electrolyte level

FIG. 1. Plot of (I) $[ReO_4^-]_o$ and (II) $[NO_3^-]_o$ (perrhenate and nitrate content in the organic layer) against the molar composition of the initial aqueous solutions in experiments with continuous variations (amine concentration 0.03M).

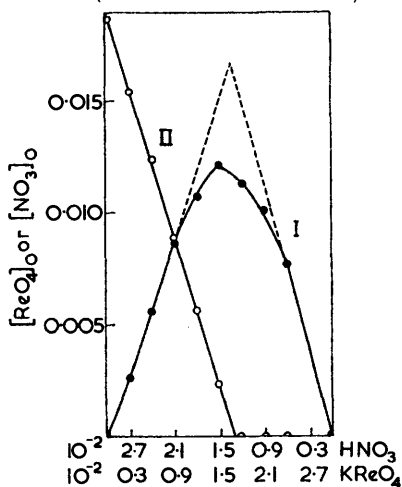


FIG. 3. Perrhenate concentration in the equilibrated organic layer plotted against the concentration of nitric acid in the initial aqueous solution (initial aqueous $KReO_4$ concentration 0.024M; initial amine concentration in CCl_4 0.024M).

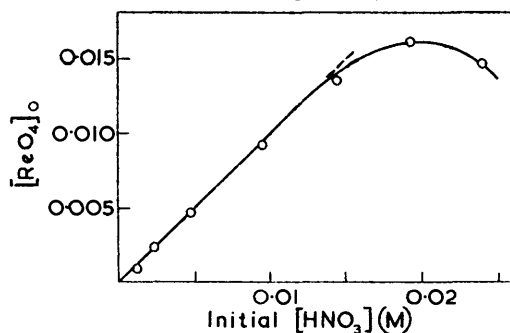


FIG. 2. Rhenium concentration in the equilibrated organic layer plotted against the molar $KReO_4 : HNO_3$ ratio of the initial aqueous solution (initial amine concentration in CCl_4 0.024M).

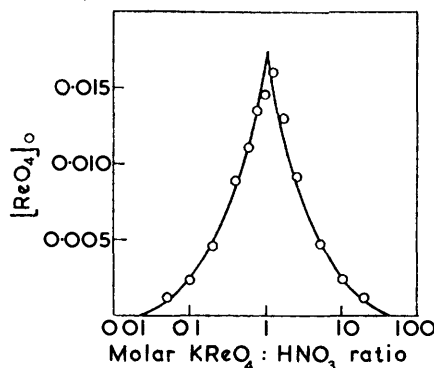
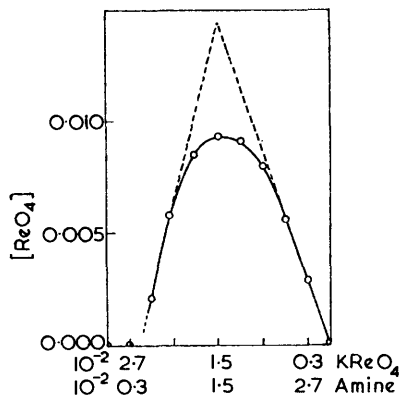


FIG. 4. Plot of $[ReO_4]_o$ (perrhenate molarity in the organic layer) against the molar ratio $KReO_4$: amine at constant nitric acid concentration (0.03M) in the initial aqueous layer.



indicates a first-power dependence of $[ReO_4]_o$ on either the initial nitric acid or the initial perrhenate concentration when the initial aqueous solution contains an excess of nitric acid. This simple proportionality does not hold for the higher range of total electrolyte concentrations (see Figs. 3 and 5), where the latter concentration approaches the "saturation" of the amine. For the results shown in Fig. 6, the total electrolyte concentration of the aqueous layer was chosen so as not to reach the saturation region of the amine; here, for both ions, the slope of unity, up to complete extraction, shows a first-power dependence on the amine concentration in the organic phase. As the hydrogen

ions in the organic phase are due either to the nitric acid or to the perrhenic acid extracted, the differences between $[H^+]_o$ and $[NO_3^-]_o$ represent the amount of perrhenic acid extracted. The analytical results confirmed this argument: perrhenic acid is the first species passing into the amine phase from an aqueous solution containing nitric and perrhenic acid in

FIG. 5. Perrhenate concentrations in the equilibrated organic layer plotted against its concentration in the initial aqueous solution (initial HNO_3 concentration 0.024M in the aqueous layer; initial amine concentration in CCl_4 0.024M).

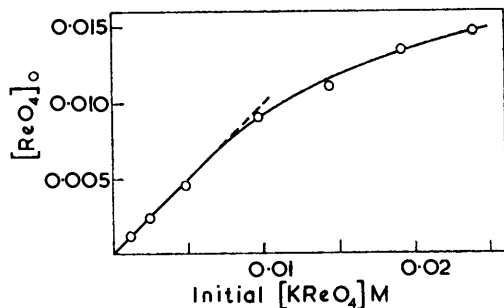


FIG. 6. Plot of $[H^+]_o$ and $[NO_3^-]_o$ (hydrogenion and nitrate concentrations in the organic layer) against initial amine concentration in the organic phase at constant initial concentration of nitric acid (0.215M) and perrhenate (0.024M) in the aqueous layer.

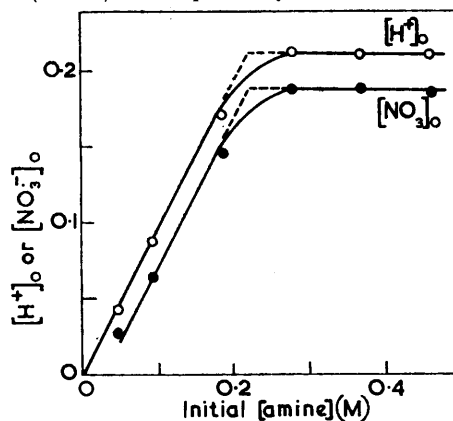
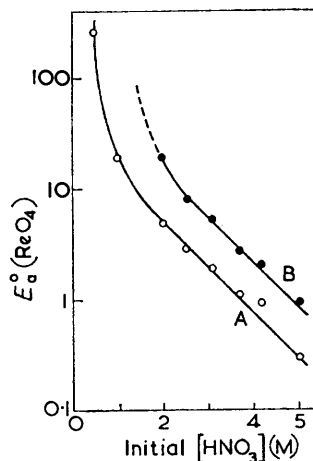


FIG. 7. Semi-log plot of the extraction ratio of perrhenate with changing nitric acid concentration in the initial aqueous solution [initial perrhenate concentration 0.012M in the aqueous layer, and initial amine concentration in CCl_4 (A) 0.23 and (B) 0.46M].



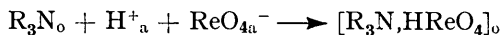
equimolar, or nearly equimolar, concentrations. When perrhenic acid has been completely extracted, extraction of nitric acid starts, provided enough amine is available. Further evidence for the stronger perrhenic acid-amine complex is shown in Fig. 1 where curve II represents the nitric acid concentration in the equilibrated organic layer as determined by Job's method. When the ratio $KReO_4 : HNO_3$ exceeds unity, no nitrate is found in the organic phase, and when this ratio is less than unity rhenium is almost completely extracted.

(d) *Effect of High Acid Concentration.*—To extend the concentration ranges studied, the variation of $E_a(ReO_4)$ with higher concentrations of nitric acid was measured for constant amine concentrations. In Fig. 7, the calculated extraction ratio has been plotted against initial nitric acid concentrations. The results suggest a trend towards lower perrhenate

extraction as the concentration of nitric acid in the aqueous layer increases. Chu and Diamond⁹ have found that the distribution ratio of traces of ReO_4^- , as measured on a Dowex-1 anion-exchange resin, decreased with increasing nitric acid concentration in the eluant. The general similarity of amine extraction to resin sorption of anions (compare our Fig. 7 with Fig. 4 of ref. 9) is supported by this comparison. Thus it appears that the conclusions reached for the previous tributyl phosphate system are valid also for the system now under consideration.

The effect of the concentration of the macroelectrolyte in this system should be less pronounced than in the tributyl phosphate system, principally because of the different solvation numbers of perrhenic and nitric acid extracted by tributyl phosphate and by the amine. The solvation number of nitric acid is unity in both systems, in contrast to the perrhenic acid tetrasolvate in tributyl phosphate and the monosolvate in the amine. It is obvious^{4,10} that a highly solvated complex in the organic phase, such as the perrhenic acid-tetrakis(tributyl phosphate) solvate, must be more easily destroyed by the extraction-competition of the macroelectrolyte, nitric acid, forming a lower (mono) solvate, than is a solvate which is itself a monosolvate, such as our perrhenic acid-amine compound.

(e) *Calculation of the Equilibrium Constant.* According to the reaction



the equilibrium constant

$$K = \frac{[\text{R}_3\text{N},\text{HReO}_4]_o}{[\text{H}^+]_a[\text{ReO}_4^-]_a[\text{R}_3\text{N}]_o}$$

was calculated. The fraction of the initial free amine concentration (*i.e.*, that not engaged as nitrate-amine or perrhenate-amine complex) is taken as $[\text{R}_3\text{N}]_o$. The ratio $[\text{R}_3\text{N},\text{HReO}_4]_o/[\text{ReO}_4^-]_a$ represents the gross extraction ratio of perrhenic acid. No calculations could be made for experiments carried out with nitric acid concentration in the initial aqueous solution so low or so high as to preclude formation of extractable perrhenic acid or lead to the saturation of the extractant, respectively. With the above limitation, the K values have been calculated and found to be about 1×10^5 . The divergencies are due more to inaccuracies in the measurements than to the non-ideality of the solutions in the activity relation assumed. The calculations were made with the assumption of true solution behaviour and unit activity coefficients for the carbon tetrachloride-amine soluble species and free amine. With reasonable assumptions as to the appropriate activities in the equilibrated aqueous phase, and by neglecting the solubility of the amine in it, the values could probably be somewhat corrected, in spite of the fact that, for the actual range of acid concentrations in the equilibrated aqueous layer, the deviation of the activity coefficient from unity must be negligibly small. However, in view of the non-ideality of the organic phase in all cases where the amine molarity is greater than 0.01, it is doubtful whether such corrections would change the results to a significant extent.

DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY,
THE HEBREW UNIVERSITY OF JERUSALEM,
JERUSALEM, ISRAEL.

[Received, August 18th, 1960.]

⁹ Chu and Diamond, *J. Phys. Chem.*, 1959, **63**, 2021.

¹⁰ Hesford and McKay, *Trans. Faraday Soc.*, 1958, **54**, 573.