Thermochemistry of Ammonium and Rubidium Perrhenates, and the Effect of Hydrogen Bonding on the Solubilities of Ammonium Salts

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The standard enthalpies of formation of ammonium and rubidium perrhenate have been determined, and the difference between them, 132.8 ± 1.5 kJ mol^{-1} is, as previously predicted, consistent with the observed barrier to ammonium ion rotation of 9—10 kJ mol^{-1}. New thermodynamic properties are proposed for the perrhenate ion, including S°_{m} (ReO_4^-, aq) = 198.1 ± 3 J K^{-1} mol^{-1}, and derived values consistent with these are $\Delta_f H^{\circ}_{m}$(NH_4ReO_4, s) = −975 kJ mol^{-1}, $\Delta_f H^{\circ}_{m}$($RbReO_4$, s) = −1 108 kJ mol^{-1}, and S°_{m}($RbReO_4$, s) = 182 J K^{-1} mol^{-1}. As with several other anions which provide relatively little resistance to ammonium ion rotation, the solubility of the ammonium salt exceeds that of the rubidium compound. This may be attributable to hydrogen bonding of the ammonium ion in aqueous solution.

Two recent papers[1,2] have established a linear correlation between the energy barrier opposing cation reorientation in a compound $(NH_4)_nX$, and the quantity $\Delta(X^{n-})$ [equation (1)].

$$\Delta(X^{n-}) = \frac{1}{n}\{\Delta_f H^{\circ}_{m}[(NH_4)_nX, s] - \Delta_f H^{\circ}_{m}[Rb_nX, s]\} \quad (1)$$

This correlation however, is not consistent with National Bureau of Standards (NBS) data[3] on the thermodynamic properties of ammonium and rubidium perrhenates. In particular, the correlation implies that $\Delta(X^{n-})$ should have a maximum value of 143 kJ mol^{-1}, but the NBS enthalpies of formation yield $\Delta(ReO_4^-)$ = 157 kJ mol^{-1}. Given that the barrier to ammonium ion rotation in NH_4ReO_4 is 9—10 kJ mol^{-1},[4] the Figure in ref. 5 implies that $\Delta(ReO_4^-)$ should be about 133 kJ mol^{-1}. Inspection of the NBS data on ammonium perrhenate suggests that they rely on Smith and Long's value[6] for the enthalpy of solution of NH_4ReO_4. For reaction (2),

$$NH_4ReO_4(s) \longrightarrow NH_4^+(aq) + ReO_4^-(aq) \quad (2)$$

Smith and Long[6] give ΔH°_{m} (2) = 26.0 kJ mol^{-1}, a value which is derived from the variation in the solubility of ammonium perrhenate with temperature. On the other hand, combination of S°_{m}(NH_4ReO_4, s)[7] with the solubility of the compound[6] gives ΔH°_{m}(2) = 45.1 kJ mol^{-1}.[2] The latter calculation, however, assumes that the activity coefficients of NH_4ReO_4 and NH_4ClO_4 are identical. This paper describes a direct calorimetric determination of ΔH°_{m}(2) which discriminates between the two competing figures. A value of $\Delta_f H^{\circ}_{m}$($RbReO_4$, s) has also been obtained.

Results

Unless otherwise stated, all auxiliary data have been taken from ref. 3. The enthalpies of solution of ammonium perrhenate were determined to dilutions between 1 450 and 6 000 H_2O at temperatures in the range 20—26 °C. Small corrections of the results to T = 298.15 K of <0.4 kJ mol^{-1} were made using the value of ΔC°_{p}(2), the figure for C°_{p}(NH_4ReO_4, s) being that given by Weir and Staveley.[7] Corrections to infinite dilution of <0.2 kJ mol^{-1} were made using data on $KMnO_4$, whose enthalpies of solution differ from those of NH_4ReO_4 by <1 kJ mol^{-1}. The data are given in Table 1.

Table 1. Determination of the standard enthalpy of solution of ammonium perrhenate at 298.15 K from the enthalpy of solution [equation (2)] in 100 g of water

Mass / g	Dilution / H_2O	T / °C	ΔH / J	$\Delta H_m(2)$ / kJ mol^{-1}	$\Delta H^{\circ}_{m}(2)$* / kJ mol^{-1}
0.2508	5 936	21.3	40.92	43.77	43.46
0.2508	5 936	22.7	40.87	43.68	43.49
0.2508	5 936	23.1	41.67	44.56	44.40
0.3893	3 824	23.8	63.92	44.05	43.95
0.4701	3 167	26.3	78.01	44.50	44.62
0.5033	2 936	22.0	82.13	43.77	43.56
0.6180	2 409	24.2	102.16	44.34	44.34
0.6625	2 247	20.6	109.06	44.15	43.86
0.8695	1 712	22.2	144.44	44.55	44.43
1.0263	1 450	22.7	169.10	44.19	44.12

* At 298.15 K; calculated from the figures in the preceding column using the corrections described in the text.

The 10 results span <1 kJ mol^{-1}, and the average ΔH°_{m}(2) is 44.0 kJ mol^{-1} to which an uncertainty of ±1 kJ mol^{-1} is assigned. The value differs substantially from the result of Smith and Long,[6] in part, it seems, because they determined their value from a plot of the logarithm of the solubility, rather than of the solubility product, against $1/T$. The value obtained here is close to that which was previously obtained[2] from the independent values of ΔG°_{m}(2) and ΔS°_{m}(2).

Attempts to obtain $\Delta_f H^{\circ}_{m}$($RbReO_4$, s) by measuring ΔH°_{m} [equation (3)] were unsuccessful because the dissolution of this

$$RbReO_4(s) \longrightarrow Rb^+(aq) + ReO_4^-(aq) \quad (3)$$

sparingly soluble salt was slow and incomplete within a reaction time with which the calorimeter could cope. Such experiments led only to a minimum value of the enthalpy of solution expressed as $\Delta H^{\circ}_{m}(3) > 55$ kJ mol^{-1}. However, the compound dissolves much more quickly in a solution of tetraphenylarsonium chloride, when $AsPh_4ReO_4$ is precipitated. This observation was therefore exploited to determine ΔH°_{m}(4) [equation (4)]. The calorimeter contained 100 cm^3 of 0.019 mol

$$RbReO_4(s) + NH_4Cl(s) \longrightarrow RbCl(s) + NH_4ReO_4(s) \quad (4)$$

dm^{-3} $AsPh_4Cl$, and the heat of solution of an equimolar mixture of $RbReO_4$ and NH_4Cl was determined in this medium. The

Table 2. Determination of $\Delta H_m^\ominus$ for reaction (4) at 298.15 K from the enthalpies of solution of the mixtures NH_4ReO_4–RbCl and $RbReO_4$–NH_4Cl in 100 cm^3 of $AsPh_4Cl$ solution

Substances	Amount/mol	ΔH/J	T*/°C	$\Delta H_m^\ominus(4)$/kJ mol^{-1}
NH_4ReO_4–RbCl	0.001 04	9.16		
$RbReO_4$–NH_4Cl	0.001 04	21.04	22.2	11.4
NH_4ReO_4–RbCl	0.001 18	10.67		
$RbReO_4$–NH_4Cl	0.001 18	25.57	22.2	12.6
NH_4ReO_4–RbCl	0.001 34	11.02		
$RbReO_4$–NH_4Cl	0.001 34	27.83	22.5	12.5
NH_4ReO_4–RbCl	0.001 39	13.14		
$RbReO_4$–NH_4Cl	0.001 39	28.99	22.1	11.4
NH_4ReO_4–RbCl	0.001 53	11.93		
$RbReO_4$–NH_4Cl	0.001 53	29.64	23.5	11.6

* Mean of the two reaction temperatures, typically differing by less than 0.2 °C.

Table 3. Thermodynamic properties of some key rhenium compounds and ions at 298.15 K

Substance	State	$\Delta_f H_m^\ominus$/kJ mol^{-1}	$\Delta_f G_m^\ominus$/kJ mol^{-1}	$S_m^\ominus$/J K^{-1} mol^{-1}
Re	s	0	0	36.53[a]
ReO_2	s	−448.3[b]	−390.5[c]	47.82[d]
Re_2O_7	s	−1 263.1[e]	−1 089.0[e]	207.1[f]
ReO_4^-	aq	−798.9[g]	−705.3[c]	198.1[e]
$KReO_4$	s	−1 108.7[h]	−1 005.5[h]	164.7[i]
NH_4ReO_4	s	−975.4[h]	−793.3[h]	193.1[i]
$RbReO_4$	s	−1 108.2[j]	−1 006.5[e]	182.5[c]

[a] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, 'Selected Values of the Thermodynamic Properties of the Elements,' American Society for Metals, Metals Park, Ohio, 1973. [b] Mean of the two values in the text. [c] Calculated from the two other values in this row. [d] Ref. 17. [e] See text. [f] Ref. 3. [g] Calculated from the heat of solution of Re_2O_7(s) implied by ref. 3. [h] Fitted to the energies of solution in the text and $S_m^\ominus(ReO_4^-$, aq). [i] Ref. 7. [j] Calculated from $\Delta H_m^\ominus(4)$ = 11.9 kJ mol^{-1}.

measurement was then repeated with the same mass of an equimolar mixture of RbCl and NH_4ReO_4, the reaction temperatures of the two measurements typically differing by less than 0.2 °C. When pairs of such reaction mixtures were stirred in beakers for 20 min, cooled in ice and filtered, the two masses of $AsPh_4ReO_4$ lay within 0.5% of each other, and of the theoretical weight. The value of $\Delta H_m^\ominus(4)$ at 298.15 K was therefore calculated from the difference in the two heats of solution, assuming that the correction to 25 °C for such a reaction is negligible. The results are shown in Table 2. The average $\Delta H_m^\ominus(4)$ is 11.9 kJ mol^{-1} to which an uncertainty of ±1.5 kJ mol^{-1} is assigned.

Previous predictions[2] of the enthalpies of formation of ammonium and rubidium perrhenates relied upon the accuracy of the NBS data[3] for ReO_4^-(aq). With this proviso, the $\Delta H_m^\ominus$ values for reactions (2) and (4) lead to $\Delta_f H_m^\ominus(NH_4ReO_4$, s) = −963.9 kJ mol^{-1}, $\Delta_f H_m^\ominus(RbReO_4$, s) = −1 096.7 kJ mol^{-1}, and $\Delta(ReO_4^-)$ = 132.8 kJ mol^{-1}, in excellent agreement with the predictions. However, in the course of this work, it became clear that the NBS data for ReO_4^-(aq), and therefore for other rhenium compounds, needed reassessment. The next section turns to this problem. Unless otherwise stated, all thermodynamic data are from ref. 3.

Thermochemistry of Rhenium.—The thermochemistry of rhenium lacks a firm foundation because $\Delta_f H_m^\ominus(Re_2O_7$, s) and $\Delta_f H_m^\ominus(ReO_4^-$, aq), upon which much of the data on other rhenium compounds depend, are uncertain. To improve matters, new values of $S_m^\ominus(ReO_4^-$, aq) were calculated. When the heats of solution of $KReO_4$ of Roth and Becker[8] are extrapolated to 25 °C and infinite dilution, $\Delta H_m^\ominus$ = 57.4 kJ mol^{-1} is obtained for reaction (5).

$$KReO_4(s) \longrightarrow K^+(aq) + ReO_4^-(aq) \qquad (5)$$

From the solubility data of Smith and Long,[6] the solubility of $KReO_4$ at 298.15 K is 0.0410 mol kg^{-1}, and activity coefficient data on $TlClO_4$[9] suggest that at this concentration $\gamma\pm$ = 0.809. Hence $\Delta G_m^\ominus(5)$ = 16.89 kJ mol^{-1}, $\Delta S_m^\ominus(5)$ = 135.9 J K^{-1} mol^{-1} and, using $S_m^\ominus(KReO_4$, s) = 164.7 J K^{-1} mol^{-1} as determined by Weir and Staveley,[7] $S_m^\ominus(ReO_4^-$, aq) = 198.1 J K^{-1} mol^{-1}.

A second value can be obtained from $\Delta H_m^\ominus(2)$ = 44.0 kJ mol^{-1}. At saturation, the solubility[6] of ammonium perrhenate is 0.274 mol kg^{-1} at 298.15 K, and the activity coefficient, obtained from NH_4ClO_4,[9] is 0.629. Hence, $\Delta G_m^\ominus(2)$ = 8.72 kJ mol^{-1} and $\Delta S_m^\ominus$ = 118.3 J K^{-1} mol^{-1}. Combining the latter with $S_m^\ominus(NH_4ReO_4$, s),[7] gives $S_m^\ominus(ReO_4^-$, aq) = 198.0 J K^{-1} mol^{-1}. This is almost identical with the figure based on reaction (5), but it is noted here that data on NH_4^+(aq) more recent than that of the NBS[10,11] would increase the value by about 2 J K^{-1} mol^{-1}. Here however, consistency with other data and previous papers in this series[1,2] is maintained by using NBS values for NH_4^+(aq). Thus $S_m^\ominus(ReO_4^-)$ = 198.1 ± 3 J K^{-1} mol^{-1}.

The values of $\Delta_f H_m^\ominus(Re_2O_7$, s) are now considered. The NBS value of −1 240 kJ mol^{-1} was obtained from combustion data,[12,13] and differs substantially from results derived by solution calorimetry.[14] Moreover, the latter work requires a value of $\Delta_f H_m^\ominus$(CuO, s), and this quantity apparently depends upon the state of division and mode of preparation of the compound.[15] The value used by King *et al.*[14] was −155.8 kJ mol^{-1}; those recommended by Nunez *et al.*[15] for powdered and granulated CuO are −157.1 and −161.7 kJ mol^{-1} respectively. The corresponding values of $\Delta_f H_m^\ominus(Re_2O_7$, s) are −1 263.1, −1 272.3, and −1 304.8 kJ mol^{-1}. Some guidance of the choice between these possibilities is provided by the high-temperature cell measurements of Franco and Kleykamp[16] whose accuracy is vouched for by their values of $S_m^\ominus(ReO_2$, s) which agree closely with those obtained by heat capacity measurements.[17] When their data are combined with the heat capacities of Stuve and Ferrante,[17] $\Delta_f H_m^\ominus(ReO_2$, s) = −447.7 kJ mol^{-1} is obtained. This is close to $\Delta_f H_m^\ominus(ReO_2$, s) = −448.9 kJ^{-1}, calculated by King *et al.*[14] from $\Delta H_m^\ominus(6)$ [equation (6)], which

$$Re(s) + 2CuO(s) \longrightarrow ReO_2(s) + 2Cu(s) \qquad (6)$$

suggests that their choice of $\Delta_f H_m^\ominus$(CuO, s) was appropriate for their sample. The preferred value of $\Delta_f H_m^\ominus(Re_2O_7$, s) is therefore −1 263.1 kJ mol^{-1}. This is in reasonable accord with the high-temperature equilibrium data reviewed by Oppermann,[18] but a precise comparison cannot be made because of the absence of high-temperature heat capacity data for Re_2O_7(g).

Table 3 summarizes the resulting data on key rhenium species, together with the thermochemical properties of ammonium and rubidium perrhenates that have been calculated from that data, and from the measurements made in this paper. The value of $\Delta_f G_m^\ominus(RbReO_4$, s) was obtained from $\Delta G_m^\ominus(3)$ = 17.25 kJ mol^{-1} which was calculated from the solubility[6] of 0.0378 mol kg^{-1} at 298.15 K, and the $TlClO_4$ activity coefficient[9] of 0.816 at that concentration. The resulting entropy of $RbReO_4$(s) is 17—18 J K^{-1} mol^{-1} greater than that of the potassium salt. This increment is fairly reasonable: the values for the halides, perchlorates, nitrates, and hydrogenfluorides cover the range 10—16 J K^{-1} mol^{-1}.

The values in Table 3 are given to one decimal place so that

Table 4. Thermochemistry of the dissolution of some potassium, rubidium, and ammonium salts in water at 298.15 K *

Salt	Solubility mol kg^{-1}	ΔH°_{m} kJ mol^{-1}	ΔG°_{m} kJ mol^{-1}	ΔS°_{m} J K^{-1} mol^{-1}
$KReO_4$	0.0410	57.4	16.9	135.9
$RbReO_4$	0.037	58.1	17.3	137.1
NH_4ReO_4	0.274	44.0	8.7	118.3
$KClO_4$	0.150	51.0	11.3	133.5
$RbClO_4$	0.072	56.7	14.4	142.2
NH_4ClO_4	2.12	33.5	0.9	109.2
KCl	4.81	17.2	−5.5	76.4
RbCl	7.81	17.0	−7.4	82.0
NH_4Cl	7.34	14.8	−7.7	75.3

* Data on perrhenates from this work; all other solubilities are from ref. 25.

their origins can be traced. However, the uncertainties in the ΔH and ΔG values are much larger than this precision implies, and are almost entirely due to that in $\Delta_f H^{\circ}_{m}(Re_2O_7, s)$. An error margin of ± 15 kJ mol^{-1} per rhenium atom is probably safe. Independent corroboration of the value of $\Delta_f H^{\circ}_{m}(Re_2O_7, s)$ is badly needed, and any revision would shift all energy values in Table 3 in the same sense. The equivalent uncertainties in the entropy values are very much smaller, much the largest being that in $S^{\circ}_{m}(RbReO_4, s)$ which is taken to be ± 8 J K^{-1} mol^{-1}. The data in Table 3 suggest that $E^{\circ}(ReO_4^{-}\text{–}ReO_2) = 0.55$ V in acid solution. This differs significantly, but not substantially from the unpublished value of 0.51 V which was obtained by Hugus and cited by Latimer.[19] The difference is equivalent to one of about 11 kJ mol^{-1} in $\Delta_f H^{\circ}_{m}(ReO_4^{-}, aq)$, but may not be relevant because there seems to be an uncertainty[20,21] as to whether the reduced phase in Hugus' measurements was anhydrous or hydrated ReO_2.

Discussion

The enthalpies of formation of ammonium and rubidium perrhenates in Table 3 yield $\Delta(ReO_4^{-}) = 132.8$ kJ mol^{-1}, in excellent agreement with the prediction made earlier; $\Delta(ReO_4^{-})$ falls below the upper threshold of $\Delta(X^{n-})$ values by 10 kJ mol^{-1}, a quantity that elsewhere has been called the *stabilisation due to lowered cation symmetry* (s.l.c.s.) in the ammonium salt.[2] For substances which conform to the correlation between $\Delta(X^{n-})$ and the barrier to ammonium ion reorientation, the s.l.c.s. is close to the barrier height which, in NH_4ReO_4, is 9.3 kJ mol^{-1}.[4] As now shown, the influence of the s.l.c.s. can be detected during comparisons of the chemistry of ammonium and alkali metal salts.

Textbooks of inorganic chemistry often point to the frequent similarities in the solubilities of ammonium and rubidium or potassium salts, arguing that it is a reflection of the similarity in cation radii.[22,23] The perrhenate data are used here to pilot a closer analysis of the phenomenon. Table 4 contains the solubilities, and the energies and entropies of solution of NH_4ReO_4, $RbReO_4$, and $KReO_4$. The solubility of ammonium perrhenate is considerably greater than that of both the potassium and rubidium salts, a result that is to be expected given the less positive ΔG°_{m} value for this compound. The data show that this difference in ΔG°_{m} arises from the less positive value of ΔH°_{m} for ammonium perrhenate, rather than from the entropies of solution which, by themselves, work in favour of the opposite result.

The ionic radii of NH_4^{+} and Rb^{+} are very similar.[2] If the ammonium ion is regarded as spherical, ionic models, expressed for example by the Born equation for Gibbs energies of hydration, and by lattice energy calculations,[2,24] then suggest that energies of solution of ammonium and rubidium salts should be very similar. The differences evident in Table 4 can then be attributed to the different s.l.c.s. values of the ammonium ion in the solid compound and in solution. As noted above, the s.l.c.s. for the ammonium ion in an environment of perrhenate ions is 10 kJ mol^{-1}, a value that falls in the lower part of the observed range[2] of 1—49 kJ mol^{-1}. To obtain an s.l.c.s. value for the ammonium ion in water, the scope of equation (1) is extended to include solutions as well as solid compounds, and $\Delta(H_2O)$ is calculated from equation (7) to be 118.7 kJ mol^{-1}.

$$\Delta(H_2O) = \Delta_f H^{\circ}_{m}(NH_4^{+}, aq) - \Delta_f H^{\circ}_{m}(Rb^{+}, aq) \quad (7)$$

This is equivalent to an s.l.c.s. value of 24 kJ mol^{-1}. If the s.l.c.s. values are taken to be a measure of hydrogen bonding, it suggests that the hydrogen bonding of the ammonium ion in water is a little stronger than in NH_4Cl, but considerably weaker than in NH_4F where the s.l.c.s. value is 49 kJ mol^{-1}. According to this analysis, it is the difference in the s.l.c.s. values for $NH_4^{+}(aq)$ and NH_4ReO_4 which accounts for the 14 kJ mol^{-1} difference in the ΔH°_{m} values for NH_4ReO_4 and $RbReO_4$ in Table 4. Because this difference is largely retained in the ΔG°_{m} values and thereby influences the relative solubilities, it can be argued that the greater solubility of the ammonium compound is caused by hydrogen bonding of NH_4^{+} which is greater in solution than in the solid salt.

Table 4 also contains data on perchlorates and chlorides, two other strong acid systems where solubilities should not be much affected by hydrolysis. In NH_4ClO_4, the barrier to ammonium ion rotation is < 2 kJ mol^{-1}, and the s.l.c.s. value is very close to zero, so hydrogen bonding can be regarded as very weak. Its strengthening when NH_4ClO_4 dissolves in water is therefore even greater than for NH_4ReO_4, and the excess solubility of the ammonium salt is all the greater. By contrast, in ammonium chloride, the rotational barrier and s.l.c.s. values are both about 21 kJ mol^{-1}, very close to the s.l.c.s. value of $NH_4^{+}(aq)$. The strengths of the hydrogen bonding in the solid and in solution are similar, and this accounts for the similar solubilities and energies of solution of NH_4Cl and RbCl. Most ammonium salts, however, have rotational barriers and s.l.c.s. values which are smaller than those of ammonium chloride, so the perchlorate/perrhenate case is by far the most common: ammonium salts are usually more soluble than the corresponding rubidium salts. This is true, for example, of the bromides, iodides, sulphates, nitrates, dichromates, hexachloroplatinates(IV), hexafluorosilicates(IV), and hexafluorotitanates(IV).[25]

Finally, recent work on the rotational motion of the ammonium ion in aqueous solution necessitates a comment. The barrier to rotation of the ammonium ion in water is 6—12 kJ mol^{-1},[26] a value which lies well below the s.l.c.s. value of 24 kJ mol^{-1}, so it is clear that the usual correlation between $\Delta(X^{n-})$ and the barrier height does not hold for this system. This indicates that the barrier is less than the directional interaction between the ammonium ion and its environment would normally suggest, and is a further justification of the surprise occasioned by the barrier measurement. The low barrier has been explained by special rotational mechanisms made available by the mobile co-ordination sphere of the ammonium ion in aqueous solution.[27,28] They involve synchronized N–H–O bond formation and bond rupture during rotational motion.

There is an analogy here with the explanation proposed elsewhere[2] for the low rotational barrier in the room-temperature form of NH_4I. There, too, the barrier lies well below the s.l.c.s., and this may be because the symmetry of the rock salt lattice favours a reorientation different from the usual rotation[29] about the C_2 axes. In the two low-temperature forms of NH_4I, by contrast, based upon the CsCl structure, the s.l.c.s. values and the barrier heights are similar.

Experimental

Enthalpies of reaction were determined in a Parr 1451 solution calorimeter. The initial volume of liquid in the Dewar was 100 cm^3, and temperatures were measured with a thermistor, in appropriate cases to 0.0005 °C. The calorimeter was calibrated chemically, according to the manufacturer's instructions, using the heat of solution of tris(hydroxymethyl)aminomethane in 0.1 mol dm^{-3} HCl. Since all reactions were endothermic, the calibration was checked by determining the enthalpy of solution of potassium chloride to a dilution of 700 H_2O (17.56; lit.,[3] 17.54 *kJ* *mol*$^{-1}$). Ammonium perrhenate (Johnson and Matthey, 99.5%) was recrystallized from water and dried in a vacuum desiccator. Rubidium perrhenate was obtained by adding a slight excess of rubidium hydroxide solution to a solution of ammonium perrhenate, and boiling until ammonia evolution had ceased. The solution was cooled in ice, and the white product recrystallized from water. Rhenium was determined gravimetrically as $AsPh_4ReO_4$.[30] The perrhenates were dissolved in 25 cm^3 of warm 0.05 mol dm^{-3} NaCl solution, and treated with an excess of 1.5% $AsPh_4Cl$ solution. The suspension was cooled in ice for 3 h prior to filtration, and the filtered precipitate washed with saturated $AsPh_4ReO_4$ solution prior to oven-drying at 110 °C (Found for NH_4ReO_4: 69.4. Calc.: 69.45. Found for $RbReO_4$: 55.5. Calc.: 55.45%).

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