CHEMISTRY

L. N. KOMISSAROVA, M. B. VARFOLOMEEV, V. I. IVANOV,

1965

SovietRxiv

Abstract

Full Text

CHEMISTRY

L. N. KOMISSAROVA, M. B. VARFOLOMEEV, V. I. IVANOV,
V. E. PLYUSHCHEV

ON THE PREPARATION AND SOME PROPERTIES OF SCANDIUM PERRHENATES

(Presented by Academician V. I. Spitsyn, 24 VII 1964)

Scandium perrhenates had not previously been obtained. Meanwhile, they are of definite interest for the chemistry of the little-studied element scandium and for revealing possible areas of application of its compounds.

We have synthesized crystalline hydrates of scandium perrhenate, as well as the anhydrous compound of composition $Sc(ReO_4)_3$, and have studied some of their properties.

As starting materials we used scandium oxide containing less than 0.01% impurities and ammonium perrhenate with an impurity content of less than 0.02%, from which metallic rhenium was obtained. Directly for the synthesis we used perrhenic acid, which was obtained from metallic rhenium after its refining and dissolution in concentrated chemically pure nitric acid. The $HReO_4$ solution was evaporated on a water bath until HNO_3 had been completely removed. Control was carried out by the formation of a green precipitate of a mixture of lower rhenium oxides; to convert these into solution, H_2O_2 and water were added to the precipitate. When the concentration of $HReO_4$ in the solution thus obtained reached 240 g/l, it was filtered and used for synthesis. Details concerning the preparation of $HReO_4$ from NH_4ReO_4 through metallic rhenium have been described earlier (1).

Crystalline hydrates of scandium perrhenate were synthesized by the direct interaction of perrhenic acid with scandium oxide. The use of the latter has considerable advantages over scandium hydroxide, which, although it dissolves readily in $HReO_4$ even in the cold, is obtained in pure form only with great difficulty because of its high adsorption capacity. Dissolution of Sc_2O_3 in $HReO_4$ solutions proceeds rather slowly on heating and in the presence of hydrogen peroxide.

The amounts of starting substances for the synthesis were taken both from the calculation for formation of the normal perrhenate $Sc(ReO_4)_3$ and with deviations from the stoichiometrically required amount. With a 20–30% excess of $HReO_4$, during evaporation of the solution the crystals that separated became

Fig. 1. Crystals of $Sc(ReO_4)_3 \cdot 3H_2O$. 100×

Figure 1: Fig. 1. Crystals of $Sc(ReO_4)_3 \cdot 3H_2O$. 100×

covered with a blue coating of lower rhenium oxides. If an analogous excess of Sc_2O_3 was taken, it remained in the precipitate. In both cases, a compound of one and the same composition—$Sc(ReO_4)_3 \cdot 3H_2O$—crystallized from the solution. Consequently, for carrying out the synthesis it is advisable to use an excess of Sc_2O_3, which ensures completion of the reaction in a sufficiently short time, while the excess Sc_2O_3 is readily removed by filtration.

The synthesis of scandium perrhenate was carried out according to the following procedure. A weighed portion of Sc_2O_3 was dissolved in $HReO_4$, taken in an amount insufficient to dissolve the oxide, in the presence of hydrogen peroxide and with heating. The course of the reaction was monitored by the change in the acidity of the solution. The interaction proceeded practically to completion at pH $\sim$ 4.5. The end of the reaction was detected with methyl orange, which was added after decomposition of H_2O_2. The resulting solution of scandium perrhenate was filtered from excess Sc_2O_3 and then evaporated at a temperature of 75–80° to an almost saturated state. The solution was then cooled, and at 22–25° crystallization of the salt occurred. The crystals obtained were anneal-

evaporated to dryness and analyzed for the content of Re_2O_7, Sc_2O_3, and H_2O. For this purpose, a weighed portion of the salt (0.8–1.0 g) was dissolved in a 100-ml volumetric flask and, for the determination of rhenium, 10 ml was taken; the solution was diluted with water to 50 ml, heated to 70–80°, acidified with 0.5 ml of 6 N acetic acid, and precipitated with a 5% aqueous solution (20 ml) of nitron acetate. The precipitated nitron perrhenate, after precipitation, was aged for 2 hours at 6–8° and filtered through a No. 3 filter with a porous bottom. The precipitate was dried at 110° to constant weight and weighed. To determine Sc_2O_3, 20 ml of solution was taken, diluted to 50 ml, 2 g of NH_4NO_3 was added, the solution was heated almost to boiling, and scandium hydroxide was precipitated with a 25% aqueous ammonia solution. The solution with the precipitate was slightly heated, then filtered through a dense filter, washed with cold 2% NH_4NO_3 solution, and the precipitate was ignited at 900° to constant weight. Water was determined by the difference method, by chromatography (2), and by isothermal dehydration. On the basis of the data obtained (Table 1), it was established that at 25° scandium perrhenate trihydrate crystallizes, with a composition corresponding to the formula $Sc(ReO_4)_3 \cdot 3H_2O$.

Fig. 1. Crystals of $Sc(ReO_4)_3 \cdot 3H_2O$. 100×

Scandium perrhenate trihydrate is a colorless, slightly hygroscopic compound, very readily soluble in water (70.5 wt.% $Sc(ReO_4)_3$ at 25°), which crystallizes in the form of prisms (Fig. 1). Its crystals were studied by X-ray methods. Laue patterns taken along all important directions had only a center of symmetry. In the KFOR camera,

Table 1

Results of analysis of scandium perrhenate and its crystalline hydrates (wt.%)

Compound	Theoretical Sc_2O_3	Theoretical Re_2O_7	Theoretical H_2O	Found Sc_2O_3	Found Re_2O_7	Found H_2O*
$Sc(ReO_4)_3 \cdot 3H_2O$	8.02	85.51	6.37	8.29	85.80	6.29
$Sc(ReO_4)_3 \cdot H_2O$	8.48	89.30	2.22	8.60	89.45	2.12
$Sc(ReO_4)_3$	8.66	91.34	–	8.82	91.55	–
fused $Sc(ReO_4)_3$				10.73	89.09	–

* The water content is given as the average of results obtained using three determination methods.

were obtained rotation photographs of the 0th, 1st, and 2nd layer planes of the reciprocal lattice of the crystal about an axis coinciding with the longest edge of the crystal (the b axis). On the rotation photograph of the 0th plane there was only a center of symmetry; on the other rotation photographs, no symmetry elements of any kind were present. These facts indicate that $Sc(ReO_4)_3 \cdot 3H_2O$ possesses a triclinic primitive cell. The axes of the triclinic cell were chosen parallel to the edges of a typical prismatic crystal. The unit-cell parameters were determined by rotation and oscillation methods:

Some physicochemical constants of $Sc(ReO_4)_3 \cdot 3H_2O$

Density (g/cm^3) theor.	Density (g/cm^3) exp.	N_p^{**}	N_m^{**}	N_g^{**}	a, Å	b, Å	c, Å	α°	β°	γ°
4.490	4.397	1.688	1.704	1.724	8.00± 0.1	7.75± 0.05	22.5± 0.5	103± 1	110± 1	96 ± 1

* The density was measured by the pycnometric method at 25° in CCl_4; accuracy ±0.005 g/cm^3.
** The refractive indices were measured by the immersion method; accuracy ±0.003.

Careful measurements of the piezoelectric effect on single crystals and powder gave a negative result. Therefore, the centrosymmetric space group $P\bar{1}$ may be considered more probable, which is also consistent with the pinacoidal habit of the crystals.

Fig. 2. Left—thermogram and weight-change curve of $Sc(ReO_4)_3 \cdot 3H_2O$. Heating rate 8°/min; right—thermogram of $Sc(ReO_4)_3$ (cooling curve)

Fig. 2. Left: thermogram and weight-change curve of Sc(ReO4)3 · 3H2O. Heating rate 8°/min; right: thermogram of Sc(ReO4)3 (cooling curve)

Figure 2: Fig. 2. Left: thermogram and weight-change curve of Sc(ReO4)3 · 3H2O. Heating rate 8°/min; right: thermogram of Sc(ReO4)3 (cooling curve)

The thermal stability of scandium perrhenate trihydrate was studied by the methods of isothermal dehydration, thermography, and thermogravimetry (Table 2). To carry out isothermal dehydration, a sample

Table 2

Comparison of data from isothermal dehydration, thermography, and thermogravimetry for the compound
$Sc(ReO_4)_3 \cdot 3H_2O$

Isothermal dehydration	Thermography	Thermogravimetry	Notes
50°	60–120°	50–150°	Loss of 2 molecules of H_2O
140–150°	230–310°	230–320°	Loss of the 1st molecule of H_2O
–	448°	–	I polymorphic transformation of the anhydrous salt
550°	–	600°	Beginning of decomposition of the anhydrous salt
–	640°	–	II polymorphic transformation of the anhydrous salt
–	735°	–	Melting of the anhydrous salt

weighing 0.3–0.4 g was placed in a drying oven (range 30–200°) or in a muffle

Fig. 3

Figure 3: Fig. 3

furnace (range 200–550°). The accuracy of temperature regulation in the drying oven was ±1°, and in the muffle furnace ±20°.

The sample was kept at the specified temperature until constant weight was attained, after which the temperature was raised to the next step.

Dehydration of $Sc(ReO_4)_3 \cdot 3H_2O$ begins at 50°; the compound loses 2 molecules of water and is converted into $Sc(ReO_4)_3 \cdot H_2O$; scandium perrhenate monohydrate is stable up to 140°. In the interval 140—150° the latter is completely dehydrated. Anhydrous scandium perrhenate is stable up to 550°. Above this temperature it slowly decomposes with formation of Sc_2O_3 and Re_2O_7.

Fig. 3. Powder X-ray diffraction patterns:
a –$Sc(ReO_4)_3 \cdot 3H_2O$;
b –$Sc(ReO_4)_3 \cdot H_2O$;
c –$Sc(ReO_4)_3$;
d –$Sc(ReO_4)_3$, recorded at 490°;
e –$Sc(ReO_4)_3$, recorded at 670°.

The results of thermographic and thermogravimetric analysis (Fig. 2, left) agree well with the data of isothermal dehydration (Table 2). All dehydration stages and the onset of decomposition are clearly marked on the corresponding curves. As was to be expected, the temperature intervals, which depend on the heating rate, differ somewhat. On heating at a rate of 7–8 deg/min, the removal of 2 molecules of water proceeds stepwise in the interval 50—150°, complete dehydration occurs at 230—320°, decomposition begins above 650°, and, finally, at 735° the compound melts. The endothermic effects in the regions of ∼ 450 and 640° correspond to polymorphic transformations of anhydrous scandium perrhenate, which are reversible (Fig. 2b).

The formation of scandium perrhenate monohydrate, of the anhydrous compound, and all its transformations at high temperatures were confirmed by chemical and X-ray phase-analysis data (Table 1 and Fig. 3). It should be noted that the composition of the sample obtained after melting is close to the theoretical composition of anhydrous scandium perrhenate. The X-ray diffraction patterns of the anhydrous compound and of the remelted sample are identical. The melt, like the anhydrous salt, is readily soluble in water, but upon its dissolution a small precipitate of Sc_2O_3 appears.

For the monohydrate and anhydrous scandium perrhenate obtained by thermal decomposition of $Sc(ReO_4)_3 \cdot 3H_2O$, the refractive indices were determined and the density was measured by the pycnometric method at 25° in CCl_4. For $Sc(ReO_4)_3 \cdot H_2O$: $d = 4.800 \pm 0.005$ g/cm^3; $N_g = 1.735 \pm 0.003$; $N_p = 1.730 \pm 0.003$; for $Sc(ReO_4)_3$: $d = 4.891 \pm 0.005$ g/cm^3; $n_{\text{av}} = 1.745 \pm 0.003$.

Anhydrous scandium perrhenate, in contrast to its crystal hydrates, is extremely hygroscopic and in air very rapidly passes into the monohydrate.

Thus, scandium forms stable hydrated perrhenates, which upon heating are dehydrated with formation of the anhydrous compound, decomposing at a temperature above 550°. Under equilibrium conditions the process is described by the scheme:

$$Sc(ReO_4)_3 \cdot 3H_2O \xrightarrow{50^\circ} Sc(ReO_4)_3 \cdot H_2O \xrightarrow{150^\circ} Sc(ReO_4)_3 \xrightarrow{>550^\circ} Sc_2O_3 + Re_2O_7.$$

Moscow State University
named after M. V. Lomonosov

Received
7 VII 1964

REFERENCES

1. V. E. Plyushchev, V. M. Amosov, M. B. Varfolomeev, *DAN*, **150**, 105 (1963).

2. I. B. Gol' dman, I. N. Nikol' skaya, *Proceedings of the Donetsk Industrial Institute*, issue 39, 33 (1959–1960).

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