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Note

THE STABILITY OF URANIUM PENTACHLORIDE AND URANIUM HEXACHLORIDE AT ROOM TEMPERATURE

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Uranium pentachloride is not very stable; some thermal decomposition occurs already at 75°C at atmospheric pressure and the rate of decomposition increases rapidly at 175°C [1a]

$$2\ UCl_5(s) \rightarrow 2\ UCl_4(s) + Cl_2(g)$$

Moreover, Martin and Eldau [2] found that UCl_5 dissociates slowly even at room temperature: a sample of about 0.5–1 g lost 0.01–0.05 mg chlorine/h in a stream of dry nitrogen at 16–23°C, totalling 1.3 mg of chlorine after 52 h.

No exact statements on the thermal stability of UCl_6 are given in the literature. The compound is probably stable up to 120–150°C [1b]. A determination of the enthalpy of formation of both UCl_5 and UCl_6 by means of solution calorimetry at 25°C was planned at this laboratory [3], and since considerable time might be expected to elapse between the preparation of the samples, the various chemical analyses, and the actual measurements, decomposition at room temperature would result in unknown errors in the calorimetric data. For this reason a determination of the loss of chlorine by UCl_5 and UCl_6 as a function of time was carried out.

EXPERIMENTAL

Materials

Uranium pentachloride was prepared by the liquid-phase chlorination of UO_3 with CCl_4 in a sealed ampoule [1c,4]. Preliminary experiments showed that the reaction temperature of 250°C [1c,4] is too high; according to the X-ray diagram the product obtained proved to be a mixture of UCl_5 and UCl_4. It is assumed that the primary product of the reaction of UO_3 with CCl_4 is UCl_6 and that UCl_5 and UCl_4 arise by successive decomposition reactions [1d]. Heating of the ampoule at 115°C for 4 h yielded a product that, besides UCl_5, contained UCl_6 as an impurity. The molar composition was $UCl_5 \cdot (0.080 \pm 0.020)UCl_6$.

Uranium hexachloride was prepared by disproportionation of UCl_5 into UCl_4 and UCl_6 at 80–125°C in a high vacuum. The apparatus used was essentially identical with that described by Johnson et al. [5]; however, electrical heating was applied instead of using a sulphuric acid heating bath. The volatilized UCl_6 was collected on a cold finger filled with a mixture of acetone and solid carbon dioxide. Since the starting material, UCl_5, is also notably volatile at the temperatures mentioned, the UCl_6 sample contained UCl_5 as an impurity and had the molar composition $UCl_6 \cdot (0.019 \pm 0.019)UCl_5$. Since it is difficult, if not impossible, to separate UCl_5 and UCl_6 by sublimation [1e], further purification of the UCl_6 was not attempted.

The compounds were characterized by X-ray diffraction and chemical analysis. All handlings of the very hygroscopic chlorides were performed in a glove box filled with dry recirculating argon.

Method

About 1 g of freshly prepared UCl_5 was kept in a closed Erlenmeyer flask filled with purified argon of atmospheric pressure; the flask was fitted with glass inlet and outlet tubes. This storage condition simulated that of the samples used for the enthalpy-of-solution measurements; the latter samples were kept in stoppered vials in an argon-filled dry box. The amount of chlorine evolved was determined at regular intervals by passing purified argon through the Erlenmeyer flask, allowing the gas stream from the flask to bubble through a solution of KI and titrating I_2 with thiosulphate solution. After 4 weeks the total amount of free chlorine measured was less than 10^{-5} g, which corresponds to a decrease of less than 0.001 wt.% of the original sample. The error caused by this loss of chlorine may be neglected.

The room-temperature stability of UCl_6 was investigated by the same procedure. Even after 1 month, measurable amounts of free chlorine could not be detected.

DISCUSSION

The only important difference between our experiments with UCl_5 and those of Martin and Eldau [2] lies in the preparation of the samples. Martin and Eldau prepared UCl_5 by high-temperature chlorination of UCl_4 under a chlorine pressure of 3–4 atm. They did not carry out a chemical analysis of their product, but it is known that the Cl/U ratio of the product obtained under the conditions mentioned may be as high as 5.5 [1f]. More details concerning the true chemical composition are lacking (mixture of UCl_5 and UCl_6 or non-stoichiometric UCl_5?).

Until further evidence is available the discrepancy concerning the room-temperature stability of UCl_5 must be attributed to the different modes of preparation of the compound, probably resulting in different compositions.

In order to check the experimental results, the thermodynamic stabilities of UCl_5 and UCl_6 at 25°C with respect to UCl_4 were calculated, using our recent values for the standard enthalpies of formation of UCl_5 and UCl_6 [3], the value for UCl_4 assessed by Parker [6], and the standard entropies of UCl_4, UCl_5, UCl_6 [6], U [7] and Cl_2 [8]. The Gibbs energies of formation ΔG_f^0 (298 K) of $UCl_4(s)$, $UCl_5(s)$, and $UCl_6(s)$ obtained from these data are $-(222.2 \pm 0.6)$ kcal mole^{-1}, $-(223.0 \pm 0.8)$ kcal mole^{-1}, and $-(224.0 \pm 0.5)$ kcal mole^{-1}, respectively*. The equilibrium chlorine pressures at 25°C calculated for the corresponding dissociation reactions are

$$UCl_5(s) \rightleftharpoons UCl_4(s) + 0.5\ Cl_2(g);\ p(Cl_2) = (0.07 \pm 0.23)\ \text{atm}$$

$$UCl_6(s) \rightleftharpoons UCl_5(s) + 0.5\ Cl_2(g);\ p(Cl_2) = (0.03 \pm 0.11)\ \text{atm}$$

$$UCl_6(s) \rightleftharpoons UCl_4(s) + Cl_2(g);\ p(Cl_2) = (0.05 \pm 0.06)\ \text{atm}$$

The small differences between the free energies of formation of UCl_4, UCl_5, and UCl_6 and the corresponding (rather high) equilibrium chlorine pressures are in agreement with the reported low thermal stability of UCl_5 and UCl_6 with respect to UCl_4 at temperatures round about 100°C. However, from a thermodynamic point of view it is astonishing that both UCl_5 and UCl_6 exist at all and that loss of chlorine at room temperature is hardly detectable (UCl_5) and even appears to be absent (UCl_6).

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* 1 kcal=4.184 kJ.