

## 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]



Moreover, Martin and Eldau [2] found that  $\text{UCl}_5$  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  $\text{UCl}_6$  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  $\text{UCl}_5$  and  $\text{UCl}_6$  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  $\text{UCl}_5$  and  $\text{UCl}_6$  as a function of time was carried out.

## EXPERIMENTAL

### *Materials*

Uranium pentachloride was prepared by the liquid-phase chlorination of  $\text{UO}_3$  with  $\text{CCl}_4$  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  $\text{UCl}_5$  and  $\text{UCl}_4$ . It is assumed that the primary product of the reaction of  $\text{UO}_3$  with  $\text{CCl}_4$  is  $\text{UCl}_6$  and that  $\text{UCl}_5$  and  $\text{UCl}_4$  arise by successive decomposition reactions [1d]. Heating of the ampoule at 115°C for 4 h yielded a product

that, besides  $\text{UCl}_5$ , contained  $\text{UCl}_6$  as an impurity. The molar composition was  $\text{UCl}_5 \cdot (0.080 \pm 0.020)\text{UCl}_6$ .

Uranium hexachloride was prepared by disproportionation of  $\text{UCl}_5$  into  $\text{UCl}_4$  and  $\text{UCl}_6$  at  $80\text{--}125^\circ\text{C}$  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  $\text{UCl}_6$  was collected on a cold finger filled with a mixture of acetone and solid carbon dioxide. Since the starting material,  $\text{UCl}_5$ , is also notably volatile at the temperatures mentioned, the  $\text{UCl}_6$  sample contained  $\text{UCl}_5$  as an impurity and had the molar composition  $\text{UCl}_6 \cdot (0.019 \pm 0.019)\text{UCl}_5$ . Since it is difficult, if not impossible, to separate  $\text{UCl}_5$  and  $\text{UCl}_6$  by sublimation [1e], further purification of the  $\text{UCl}_6$  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  $\text{UCl}_5$  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  $\text{I}_2$  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.

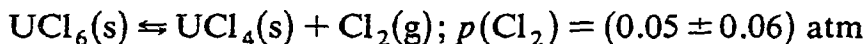
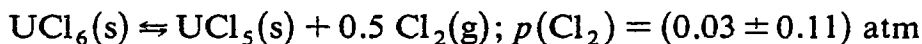
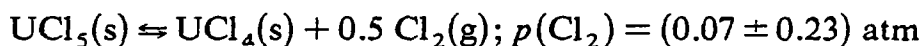
The room-temperature stability of  $\text{UCl}_6$  was investigated by the same procedure. Even after 1 month, measurable amounts of free chlorine could not be detected.

### DISCUSSION

The only important difference between our experiments with  $\text{UCl}_5$  and those of Martin and Eldau [2] lies in the preparation of the samples. Martin and Eldau prepared  $\text{UCl}_5$  by high-temperature chlorination of  $\text{UCl}_4$  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  $\text{UCl}_5$  and  $\text{UCl}_6$  or non-stoichiometric  $\text{UCl}_5$ ?).

Until further evidence is available the discrepancy concerning the room-temperature stability of  $\text{UCl}_5$  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  $\text{UCl}_5$  and  $\text{UCl}_6$  at  $25^\circ\text{C}$  with respect to  $\text{UCl}_4$  were calculated, using our recent values for the standard enthalpies of formation of  $\text{UCl}_5$  and  $\text{UCl}_6$  [3], the value for  $\text{UCl}_4$  assessed by Parker [6], and the standard entropies of  $\text{UCl}_4$ ,  $\text{UCl}_5$ ,  $\text{UCl}_6$  [6],  $\text{U}$  [7] and  $\text{Cl}_2$  [8]. The Gibbs energies of formation  $\Delta G_f^\circ$  (298 K) of  $\text{UCl}_4(\text{s})$ ,  $\text{UCl}_5(\text{s})$ , and  $\text{UCl}_6(\text{s})$  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  $25^\circ\text{C}$  calculated for the corresponding dissociation reactions are



The small differences between the free energies of formation of  $\text{UCl}_4$ ,  $\text{UCl}_5$ , and  $\text{UCl}_6$  and the corresponding (rather high) equilibrium chlorine pressures are in agreement with the reported low thermal stability of  $\text{UCl}_5$  and  $\text{UCl}_6$  with respect to  $\text{UCl}_4$  at temperatures round about  $100^\circ\text{C}$ . However, from a thermodynamic point of view it is astonishing that both  $\text{UCl}_5$  and  $\text{UCl}_6$  exist at all and that loss of chlorine at room temperature is hardly detectable ( $\text{UCl}_5$ ) and even appears to be absent ( $\text{UCl}_6$ ).

#### ACKNOWLEDGEMENT

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#### REFERENCES

- 1 J.J. Katz and E. Rabinowitch, *The Chemistry of Uranium*, McGraw-Hill, New York, 1951, (a) p. 496; (b) p. 505; (c) p. 490; (d) p. 491; (e) p. 493; (f) p. 489.
- 2 H. Martin and K.H. Eldau, *Z. Anorg. Allg. Chem.*, 251 (1943) 295.
- 3 E.H.P. Cordfunke, W. Ouweltjes, and G. Prins, *J. Chem. Thermodyn.*, in press.
- 4 A. Michael and A. Murphy, Jr., *Am. Chem. J.*, 44 (1910) 365.
- 5 O. Johnson, T. Butler and A.S. Newton, in J.J. Katz and E. Rabinowitch (Eds.), *USAEC Report TID-5290* (1958). p. 1.
- 6 V.B. Parker, *Natl. Bur. Stand. U.S. Interim Report NBSIR 80-2029* (1980).
- 7 F.L. Oetting, M.H. Rand and R.J. Ackermann, *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 1: The Actinide Elements*, IAEA, Vienna, 1976.
- 8 CODATA Bulletin No. 28, ICSU CODATA, Paris, 1978.

\* 1 kcal = 4.184 kJ.