Inorganica Chimica Acta, 128 (1987) 7–9

The Reaction of Zirconium Oxide Chloride Octahydrate with Thionyl Chloride

I. BUSCAGLIONE, C. STABLES and H. SUTCLIFFE

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

(Received July 12, 1986)

Abstract

The dehydration of zirconium oxide chloride by thionyl chloride gives the products $ZrOCl_2 \cdot 3H_2O$ and $ZrCl_4 \cdot SOCl_2$ in a two-stage process. IR, DTA and TG data are presented.

Introduction

Several studies have been made of the thermal dehydration of zirconium oxide chloride [1–5] of which the most thorough is probably that of Powers and Gray [2]. By contrast there are only two reports of the dehydration of this compound by chemical means, and both of these lack experimental detail [6, 7].

Hardy *et al.* report a partially dehydrated compound having a zirconium to water ratio of 1:1.6–2.0, and that this residual water may be removed by vacuum treatment [6]. Paul *et al.* claim the formation of the compound $ZrOCl_2 \cdot SOCl_2$ when zirconium oxide chloride is treated with a large excess of thionyl chloride from which the thionyl chloride may be removed by ether treatment to leave anhydrous zirconium oxide chloride; amide complexes are also reported but without supporting elemental analysis data [7].

Experimental

Many of the materials used in this work are moisture sensitive and were handled either in a conventional dry box or in Schlenk tubes. Infrared spectra were measured as mulls using a Perkin-Elmer Model No 1710 FT–IR spectrophotometer. Zirconium was determined by precipitation as the tetramandelate followed by pyrolysis to zirconium dioxide [8]. Chloride was determined by standard gravimetric techniques, by chloride ion electrode, or by combustion (Butterworths Laboratories). Thermal gravimetric analysis was carried out using a Stanton-Redcroft TG 750 at a heating rate of 10° min^{-1}.

The Reaction of Zirconium Oxide Chloride with Thionyl Chloride

(a) Short reaction time

Zirconium oxide chloride (3.0 g, 0.01 mol) was stirred with excess thionyl chloride (50 cm^3, 0.69 mol) at room temperature until gas evolution ceased. The product (Yield 2.28 g. *Anal.* Found: Zr, 39.8. Calc. for $ZrOCl_23H_2O$: Zr, 39.3%) was separated by filtration, washed with dry carbon tetrachloride and dried *in vacuo*. The infrared spectrum shows bands at 3450–3300(s), 1605(s), 1150(w) and 910(m) cm^{-1}. Thermal gravimetric analysis data showed the following cumulative mass losses: 133 °C, 8.4%; 193 °C, 23.4%; 400 °C, 38.0% and 921 °C, 44.2%.

(b) Long reaction time

Zirconium oxide chloride hydrate (5.0 g) and thionyl chloride (50 ml) were protected from the atmosphere by a calcium chloride guard tube and stirred for 48 h, after which time all the zirconium oxide chloride had gone into solution. The thionyl chloride was removed by rotary evaporation under reduced pressure to yield an off-white solid which was finally dried *in vacuo* (5.1 g). This product evolved thionyl chloride on contact with the atmosphere.

(c) Long reaction time in vacuo

Thionyl chloride (300 ml) was distilled onto zirconium oxide chloride hydrate (25 g) *in vacuo* using a conventional vacuum line. The mixture was allowed to warm to room temperature, stirred and the evolved gases collected in a suitable storage bulb. The evolved gases were shown, by infrared spectroscopic analysis, to consist of sulphur dioxide, hydrogen chloride, and thionyl chloride.

The solution of 'zirconium oxide chloride' in thionyl chloride was reduced to ~50 cm^3 by distilling off, *in vacuo*, ~250 cm^3 of thionyl chloride at room temperature to leave a suspension of a white solid in thionyl chloride. This white solid was separated by filtration under nitrogen using a Schlenk tube to yield a white crystalline product (Yield 22.0 g. *Anal.*

0020-1693/87/$3.50

Found: Zr, 23.6; Cl, 60.1. Calc. for $ZrCl_4 \cdot SOCl_2$: Zr 25.9; Cl, 60.4%). Infrared spectroscopic analysis shows bands at 3320(w, br), 3180(w, br), 1598(w), 1239(w, sh), and 1125(m, br) cm^{-1}.

Thermal gravimetric analysis in a nitrogen atmosphere showed the following cumulative mass losses: ambient to 91 °C, 31%; to 246 °C, 81.5%; to 646 °C, 90%, no further loss was observed to 950 °C. A similar experiment carried out in an argon atmosphere showed the following cumulative mass losses: ambient to 101 °C, 30%; to 263 °C, 95%; >600 °C, 97.5%. Differential thermal analysis shows two broad endotherms at 107 and 341 °C.

A sample (3.0 g) of the white crystalline product was treated with dry diethylether to leave a white solid (Yield 3.1 g. Found: Zr, 23.4; Cl, 36.9. Calc. for $ZrCl_4 \cdot 2(C_2H_5)_2O$: Zr, 23.9; Cl, 37.2%). Infrared spectroscopic analysis shows no trace of bands at 1239 and 1125 cm^{-1}.

Solution Spectra

Zirconium oxide chloride (3.45 g, 0.0107 mol) was added to thionyl chloride (100 cm^3) and stirred for 72 h. Infrared spectroscopic analysis of this solution using 0.5 mm path length cell showed the following bands 2800(m), 1335(m), 1140(s). The Raman spectrum of the same solution exhibited bands at 1138(w) and 375(v, w).

The Reaction of Zirconium Tetrachloride with Thionyl Chloride

Zirconium tetrachloride (15 g) is dissolved *in vacuo* in thionyl chloride (150 ml). A precipitate slowly forms and is removed by filtration to yield a small amount of a white crystalline solid. Thionyl chloride (~150 ml) is removed from the filtrate *in vacuo* and the resultant precipitate separated by filtration to yield a white crystalline solid (Yield 15.2 g. *Anal.* Found: Zr, 24.66; Cl, 60.28. Calc. for $ZrCl_4SOCl_2$: Zr, 25.92; Cl, 60.43%). Infrared spectroscopic analysis reveals bands at: 1238(w) and 1132(s, br). Thermal gravimetric analysis in a nitrogen atmosphere showed the following cumulative mass losses: ambient to 118 °C, 31.8%; to 248 °C, 79.5%, to 517 °C, 84.5%, no further loss was observed to 950 °C. In an argon atmosphere the following cumulative mass losses were observed: ambient to 120 °C, 33.0%; to 270 °C, 92%; to >400 °C, 96%. Differential thermal analysis shows two broad endotherms at 120 and 341 °C.

Discussion

Zirconium oxide chloride reacts with thionyl chloride in two distinct stages. The initial reaction, with obvious rapid elimination of sulphur dioxide and hydrogen chloride, leaves a white solid having the composition $ZrOCl_2 \cdot 3H_2O$ in which the basic tetrameric structure of zirconium oxide chloride [9] is retained but incorporating only two coordinated molecules of water per zirconium atom, *i.e.* $[Zr_4(OH)_8(H_2O)_8]Cl_8$, instead of four as in zirconium oxide chloride octahydrate. Thermal gravimetric analysis of this product is consistent with this formulation and agrees with the work of Powers and Gray [2]. In zirconium oxide chloride two of the four coordinated water molecules have longer (and hence weaker) zirconium to oxygen bonds than the other two. It is presumed therefore that during the first stage of this reaction these two water molecules are removed together with interstitial water.

The second stage of the reaction takes place with a much slower evolution of sulphur dioxide and hydrogen chloride and finally results in complete dissolution of zirconium oxide chloride trihydrate. This solution exhibits infrared spectroscopic bands due to the presence of dissolved hydrogen chloride and sulphur dioxide together with an additional strong band at 1140 cm^{-1} which is attributed to the S=O stretch of coordinated thionyl chloride, a shift to lower frequency of 90 cm^{-1} from free thionyl chloride. The Raman spectrum shows weak bands at 1138 and 375 cm^{-1}, the latter being attributed to Zr–Cl bonds.

The white crystalline solid isolated from this solution has the stoichiometry $ZrCl_4 \cdot SOCl_2$ and is very moisture sensitive. This stoichiometry is confirmed by thermal gravimetric analysis in both nitrogen and argon; in nitrogen a mass loss of 31.0% at 91 °C is observed and in argon a mass loss of 30.0% at 101 °C is seen. These values compare favourably with a theoretical mass loss of 33.8% for the loss of thionyl chloride from the adduct $ZrCl_4 \cdot SOCl_2$. A similar adduct prepared directly from zirconium tetrachloride exhibits comparable mass loss data, *i.e.* 31.8% at 118 °C (in N_2) and 33.0% at 120 °C (in Ar). As the temperature is increased further extensive mass losses are observed in both cases, corresponding to volatilisation of zirconium tetrachloride. A slightly greater residue is observed in a nitrogen atmosphere which may be attributed to the formation of a nitride or oxide nitride. The small residue obtained in an argon atmosphere is no doubt due to the formation of ZrO_2 due to water pickup on transfer of the adduct to the instrument. The most significant spectroscopic features of this adduct are a broad band at 1125 cm^{-1}, attributed to the S=O bond of thionyl chloride coordinated to zirconium via oxygen, together with a small but sharp band at 1239 cm^{-1}. Both bands disappear when the product is treated with diethylether to yield a solid product $ZrCl_4 \cdot 2(C_2H_5)_2O$. The band at 1239 cm^{-1} is attributed to a more weakly bound molecule of thionyl chloride since a band in this region (1233 cm^{-1}) has been observed when thionyl chloride is bound to the hexachlorozirconate ion [10]. The adduct formed directly from zirconium tetrachloride and thionyl chloride shows similar although not identical spectroscopic properties, namely bands at 1238 and 1132 cm^{-1}. The latter, which differs from that of the zirconium oxide chloride derived adduct may be due to structural differences. Zirconium tetrachloride is known to exist as a dimer in the vapour phase; the existence of such dimers in thionyl chloride therefore seems likely and consequently isolation of the dimer solvate $Zr_2Cl_8 \cdot 2SOCl_2$ may be expected. By contrast during the course of the breakdown of the zirconium oxide chloride tetramer the $Zr(OH)_2Zr$ bridge bonds will be broken and the OH groups replaced by chlorine. During the course of such a process the intermediate species will always be totally solvated hence preventing the formation of chloride bridges.

References

1 B. Beden and I. Guillaume, *C. R. Acad. Sci. Paris, 269,* 1629 (1969).
2 D. A. Powers and H. B. Gray, *Inorg. Chem., 12,* 2721 (1973).
3 S. Inouc, H. Aki and Z. Hagiwana, *J. Inorg. Nucl. Chem., 37,* 929 (1975).
4 A. V. Shlykov, L. S. Bychikhina and E. S. Pagrebnaya, *Russ. J. Inorg. Chem., 20,* 1801 (1975).
5 L. N. Komissarova, V. E. Plyushchev and I. N. Kremenskaya, *Russ. J. Inorg. Chem., 5,* 281 (1960).
6 C. J. Hardy, B. O. Field and D. Scargill, *J. Inorg. Nucl. Chem., 28,* 2408 (1966).
7 R. C. Paul, S. L. Chadha and S. K. Vasisht, *J. Less-Common Met., 16,* 288 (1968).
8 S. V. Elenson and K. I. Petrov, 'The Analytical Chemistry of Zirconium and Hafnium', Ann Arbor-Humphrey Science, London, 1969, pp. 58–60.
9 T. C. W. Mak, *Can. J. Chem., 46,* 3493 (1968).
10 C. Stables and H. Sutcliffe, unpublished work.