Journal of Fluorine Chemistry, 21 (1982) 393–396

Received: April 27, 1982

NEW SYNTHESES OF PENTAFLUOROTELLURIUM HYPOCHLORITE

Carl J. Schack and Karl O. Christe
Rocketdyne, a Division of Rockwell International
Canoga Park, California 91304 (U.S.A.)

SUMMARY

Chlorination of pentafluoroorthotelluric acid with either chlorine fluorosulfate or chlorine monofluoride furnishes pentafluorotellurium hypochlorite in new, high yield reactions. Additional characterizing data for this useful hypochlorite are presented.

INTRODUCTION

Covalent hypochlorites are reactive compounds which have been successfully employed in numerous synthetic applications [1]. Pentafluorotelluri hypochlorite was reported by Seppelt and Nothe several years ago [2]. Their synthetic procedure involved treatment of the mercury salt of the pentafluoroorthotelluric acid with chlorine monofluoride.

$$Hg(OTeF_5)_2 + 2ClF \longrightarrow HgF_2 + 2TeF_5OCl$$

A quantitative yield was claimed. However, the required mercury salt must be prepared from TeF_5OH and was obtained in only 72% yield [2]. Since the reactions of ClF and $ClOSO_2F$ with either fluorocarbon alcohols [3] or acids [4,5] resulted in good yields of the corresponding hypochlorites, their reaction with TeF_5OH was examined as a possible simple, direct route to TeF_5OCl.

0022-1139/82/0000-0000/$02.75

EXPERIMENTAL

Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel valves and a Heise Bourdon-Tube type gauge. Pentafluoroorthotelluric acid was prepared by the method of Seppelt [2] with slight modification. Chlorine fluorosulfate and chlorine monofluoride were synthesized as reported [6,7]. Sodium fluoride pellets were purchased from Harshaw. Infrared spectra were obtained using 5 cm path length stainless steel cells with AgCl or CsI windows. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å line of an Ar ion laser with the sample in a sealed quartz tube cooled to -100 °C. Mass spectra were measured with an EAI Quad 300 Quadrupole Spectrometer and ^{19}F nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 MHz.

Synthesis of TeF_5OCl Using $ClOSO_2F$

A 30 ml stainless steel cylinder was loaded with TeF_5OH (4.76 mmol) and $ClOSO_2F$ (4.41 mmol) at -196°C. The cylinder was allowed to warm slowly overnight to room temperature where it remained for several hours. Separation of the products was accomplished by fractional condensation through U-traps cooled at -78, -112, and -196°C while keeping the reaction cylinder at -30°C. By-product $HOSO_2F$ was retained in the cylinder and unreacted TeF_5OH (0.44 mmol) was found in the -78° trap. The TeF_5OCl (4.31 mmol) was obtained in the -112°C trap and only traces of unexamined material passed to the -196° trap. Based on the limiting reagent, $ClOSO_2F$, the yield of TeF_5OCl was 97.7%. The identification of the TeF_5OCl was based on its ^{19}F nmr spectrum which agreed with the literature [2] and on its mass, infrared, and Raman spectra. In addition, the reported b.p. of 38°C was verified and the previously unreported vapor pressure temperature correlation was measured, (T°C;P,mm): -46.3, 11; -32.9, 26; -23.3, 45; -14.2, 77; 0.0, 159; 9.2, 236; 20.1, 383. This relation is described by the equation $\log P = 7.8623 - 1548.5/T°K$. The latent heat of vaporization of TeF_5OCl is 7.08 Kcal/mol, and the derived Trouton constant is 22.8 indicating a nonassociated liquid.

Synthesis of TeF_5OCl Using ClF

A 30 ml stainless steel cylinder was loaded with TeF_5OH (2.80 mmol) at -196°C. After warming the cylinder to -78°C, ClF (4.82 mmol) was gradually bled into it, and finally the closed cylinder was allowed to warm to room temperature for a couple of hours. The reaction products were separated by fractional condensation at -78, -95, and -196°C with only a short pumping period. Unreacted ClF (1.96 mmol) contaminated with some $FClO_2$ and Te-F type material passed to the -196°C trap. The higher temperature fractions consisted of TeF_5OCl and HF. By condensing this material into a cylinder containing NaF pellets and allowing it to stand overnight at ambient temperature, the HF was removed by complexing and a subsequent fractionation furnished pure TeF_5OCl (2.58 mmol). Based on the limiting reagent TeF_5OH, the yield of the hypochlorite was 92%.

RESULTS AND DISCUSSION

It was found that either chlorinating agent reacted readily to provide the hypochlorite in high yield (90 + %).

$$TeF_5OH + ClX \longrightarrow TeF_5OCl + HX \ (X{=}F,\ OSO_2F)$$

The observed direct conversion of TeF_5OH to TeF_5OCl makes this an attractive method for synthesizing the hypochlorite. When $ClOSO_2F$ is used as the chlorinating agent, it is necessary to use an excess of TeF_5OH (5-10 mol%) over $ClOSO_2F$ in order to facilitate separation of the TeF_5OCl, which is easy from TeF_5OH but difficult from $ClOSO_2F$. In the case of ClF as the chlorine source, it should be used in excess to consume the TeF_5OH efficiently. However, the by-product HF must be removed from TeF_5OCl by complexing in order to produce pure hypochlorite.

Although most of the observed properties for TeF_5OCl agreed well with those reported [2] some discrepancies were noted. In the infrared spectrum a very strong band at 708 cm^{-1} was listed. In none of our samples was such an absorption observed. The mass spectrum of TeF_5OCl exhibited all the ions previously reported except TeF_4O^+. However, some ions not previously given were observed. These included; TeF_4OCl^+, TeF_3O^+, TeF_2O^+ and $TeFO^+$. Peak intensities due to the various Te and Cl isotopes confirmed these assignments. Investigation of the chemistry of TeF_5OCl is in progress.

ACKNOWLEDGEMENT

The authors gratefully acknowldege support for this work by the U. S. Air Force Office of Scientific Research under Contract F49620-81-C-0020.

REFERENCES

1 C. J. Schack and K. O. Christe, Israel J. Chem., 17 (1978) 20.
2 K. Seppelt and D. Nothe, Inorg. Chem., 12 (1973) 2727.
3 A. Majid and J. M. Shreeve, Inorg. Chem., 13 (1974) 2710.
4 D. D. DesMarteau, J. Am. Chem. Soc., 100 (1978) 340.
5 C. J. Schack and K. O. Christe, J. Fluorine Chem., 12 (1978) 325.
6 C. J. Schack and R. D. Wilson, Syn. Inorg. Metal-Org. Chem., 3 (1973) 393.
7 C. J. Schack and R. D. Wilson, Inorg. Chem., 9 (1970) 311.