Journal of Fluorine Chemistry, 17 (1981) 187–190

Received: June 24, 1980

ON THE SYNTHESIS AND PROPERTIES OF HYDRAZINIUM(1+) FLUORIDE

P. GLAVIČ and J. SLIVNIK

J. Stefan Institute, E. Kardelj University, Jamova 39, 61000 Ljubljana (Yugoslavia)

SUMMARY

The isolation of N_2H_5F from aqueous solutions is described and compared with the isolation from anhydrous hydrazine. The melting point, solubilities in various solvents and density of N_2H_5F are given.

SYNTHESIS OF N_2H_5F FROM AQUEOUS SOLUTIONS

We isolated N_2H_5F by adding $N_2H_6F_2$ to hot, anhydrous liquid hydrazine and subsequently cooling the solution [1]. Here we describe the synthesis of N_2H_5F from aqueous solution by two different methods: a) by neutralization of hydrazine solutions with hydrofluoric acid and b) by neutralization of hydrazine solutions with solid $N_2H_6F_2$.

80 % hydrazine hydrate and 50 % HF were analytical grade chemicals (Riedel de Häen and Carlo Erba respectively), $N_2H_6F_2$ was prepared by neutralization of these two reagents to pH = 2 [2]. The products were characterized by chemical analysis: hydrazine was titrated potentiometrically with potassium iodate solutions [3] and fluorine was titrated with thorium nitrate solution[4]. X-ray powder diffraction patterns were obtained using Debye-Scherrer 114.6 mm diameter camera. Conductometric measurements were performed in a polyethylene vessel using two 1.5 cm^2 Pt-electrodes mounted on a Teflon frame using a Teflon coated magnetic stirrer.

The neutralization reaction was carried out in a polyethylene beaker held at 0°C by ice-water bath. If the solution obtained was evaporated above room temperature, $N_2H_6F_2$ crystallized out. In order to obtain N_2H_5F we evaporated the solutions under vacuum (10 mPa) or in a vacuum dessicator over solid NaOH at room temperature. At all the mole ratios of HF or 1/2 $N_2H_6F_2$ to N_2H_4 (1:1, 1:2, 1:3) the composition of the product corresponded to N_2H_5F (found: 60.2 % N_2H_4 and 37.4 % F, calculated: 61.56 % N_2H_4 and 36.50 % F). By X-ray diffraction and by conductometric analysis the product was found to contain about 5 % $N_2H_6F_2$. It is interesting to point out that the same product (59.9 % N_2H_4 and 37.8 % F) was obtained from anhydrous hydrazine if the conditions favoured the formation of microcrystalls; large monocrystalls were pure N_2H_5F with 61.0 % N_2H_4 and 36.5 % F.

The synthesis of N_2H_5F is therefore possible from aqueous solutions as well as from anhydrous hydrazine. Fluoride ions can be supplied either by hydrofluoric acid or by solid $N_2H_6F_2$. The synthesis from aqueous solutions is, however, time consuming and yields a product contaminated by small amount of $N_2H_6F_2$. The synthesis in anhydrous hydrazine is faster; using solid $N_2H_6F_2$ we can achieve a 100 % conversion of reagents. Pure N_2H_5F can only be obtained by fractional crystallization from anhydrous hydrazine, the problems being similar to those encountered in the preparation of pure NH_4F.

MELTING POINT OF N_2H_5F

N_2H_5F is hygroscopic, therefore it was handled in a dry box throughout the experiments. The measurements were performed in glass and in polyethylene capillaries. Glass appears to be perfectly suitable material for the purpose. The melting point was determined in a Mettler FP 1 apparatus using a heating rate 0.2°C/min and it was found to be 100.5 ± 0.2°C.

SOLUBILITIES OF N_2H_5F

For the determination of solubility in aqueous solutions we used a polyethylene Landolt's pipette [5] . In contrast to pure N_2H_5F the solution reacts with glass slowly at room temperature and faster at temperatures above 40°C because of hydrolysis. Hydrolysis yields solid, less soluble $N_2H_6F_2$ according to the equation:

$$2\ N_2H_5F\ (aq) \longrightarrow N_2H_4\ (aq) + N_2H_6F_2\ (s).$$

The solubilities of N_2H_5F, which were determined by the content of N_2H_4 in the solution, are given in Table 1. All the solutions were thermostated to ± 0.1°C.

TABLE 1

Solubilities of N_2H_5F in different solvents at 20 and 40°C

Solvent	Solubility of N_2H_5F in g/100 g of solution at	
	20°C	40°C
Water	58.4 ± 1.2	76.1 ± 1.4
53 % hydrazine	24.7 ± 1.2	30.7 ± 1.5
100 % hydrazine	5.2 ± 0.5	16.8 ± 1.7
CH_3OH	2.6 ± 0.1	3.4 ± 0.05
C_2H_5OH	0.3 ± 0.05	0.4 ±
CCl_4	insoluble	
n-hexane	insoluble	
acetone	reaction	

Glass can be used for the determination of solubilities in anhydrous hydrazine, hydrazine hydrate or organic solvents, the value being determined from the fluoride content of the solution.

The solubility of N_2H_5F is higher in water than in hydrazine; it is considerably higher than the corresponding solubility of $N_2H_6F_2$ (e.g. 8.1 g/100 g of aqueous solution at 20°C)

The highest temperature dependence of sulibility was found in anhydrous hydrazine; this fact was succesfully utilized for the synthesis of large amounts of N_2H_5F.

DENSITY OF N_2H_5F

The density of N_2H_5F was determined picnometrically in n-hexane at 25°C and the average of eight measurements amounted 1.467 ± 0.006 g/cm^3.

ACKNOWLEDGEMENTS

The present work was carried out with the financial support of the Research Community of Slovenia which is gratefully acknowledged. The authors wish to thank Miss B. Sedej for chemical analyses.

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