NOTES

Reactions of copper(II) and zinc(II) fluoride with hydrazine

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 $CuF_2-N_2H_4$ system. $Cu(N_2H_4)_2Cl_2$ is the only compound known to exist in the systems involving anhydrous copper(II) halides and hydrazine[1]. In the continuation of our work on metal fluoride hydrazine systems[2], we investigated reaction of CuF_2 with anhydrous hydrazine in hope of the formation of a similar fluoride complex.

 CuF_2 was prepared by the fluorination of CuCl at 550°C. The preparation of anhydrous hydrazine, the experimental technique and the methods of analyses were described elsewhere [3]. Copper was determined by EDTA complexometric titration with murexide as indicator [4].

White CuF_2 reacts vigorously in excess of anhydrous hydrazine and gases are evolved simultaneously. A reddish-brown diamagnetic product forms. Two phases could be distinguished under the microscope:

-A red phase, which consists of elemental copper with grain sizes between 1 and 2 μ m.

-A white solid having N₂H₄: F ratio equal to 1.

The white phase is soluble in excess of hydrazine and can consequently be separated from the metal. The chemical analyses and IR spectra show that it is N_2H_3F . The overall stoichiometry is probably represented by the equation:

$$CuF_2 + 4N_2H_4 - \frac{20C}{M_{eff}}Cu + 2N_2H_5F + N_2 + 2NH_3.$$

 NH_3 was detected in the decomposition gases. The same reaction occurs with $CuCl_2$ and anhydrous hydrazine at 80°C in vacuum, but to a much lesser extent [6]. When exposed to open air the mixed product oxidizes to a bluish-green solid. The reaction between CuF_2 and N_2H_4 appears to be extremely sensitive to traces of water in the reactants. To control the reaction, the hydrazine was additionally dried with CuF_2 prior to the reaction.

 $ZnF_{2-}N_{2}H_{4}$ system. Zinc(II) halides form several addition compounds with hydrazine:

(a) $Zn(N_2H_4)_2X_2$ with X=Cl[7], Br[8], I[8] and

(b) $Z_{n}(N_{2}H_{4})_{2}X_{2}'nH_{2}O$ with X=Cl(n=2)[9], Br(n=1)[10], I(n = 2)[10].

To our knowledge the formation of $ZnF_2-N_2H_4$ adducts was not described so far. ZnF_2 does not form compounds with ammonia; but ZnF_2 ·4H₂O, which has a looser lattice, a series of adducts is known: ZnF_2 ·4NH₃·2H₂O, ZnF_2 ·3NH₃·2H₂O and $2ZnF_2$ ·NH₃· 4H₂O[11].

We prepared ZnF_2 by several methods: fluorination of ZnS at 550°C[12], fluorination of $ZnCl_2$ with $N_2H_6F_2$ and F_2 subsequently, hydrofluorination of Zn. Zinc was determined by EDTA complexometric titration with Eriochrom Black T as indicator[13].

When solid ZnF_2 reacted at room temperature with an excess of liquid anhydrous hydrazine, the reaction products formed a protective layer which hindered further reaction. However, when the reaction mixture was stirred in vacuum at 50°C for several days the product was $ZnF_2 \cdot 2N_2H_4$ (Found: 38.5% N_2H_4 , 39.2% Zn and 22.2% F; Calc: 38.24% N_2H_4 , 39.06% Zn and 22.70% F). Zn(N_2H_4)₂ F_2 is stable in vacuum and in dry air, but it hydrolyses in open air, giving hydrazinium(1+) complexes of varying compositions, as indicated by chemical analysis and IR spectroscopy of the hydrolized products. Similar compounds results from the reaction between ZnF_2 and 80% hydrazine hydrate.

The thermal decomposition of $Zn(N_2H_4)_2F_2$ starts in argon at 140°C. Two endothermic (180 and 240°C) and two exothermic peaks (250 and 300°C) were observed in the DTA curve; a residue of ZnF_2 is formed at 340°C.

The IR spectrum of $Zn(N_2H_4)_2F_2$ indicates that hydrazine is bidentate and acts as a bridging ligand. The spectrum has well resolved peaks at: 3220 s, 3136 s, 1638 and 1609 vs, 1248 m, 1220 m, 1188 and 1175 s, 642 and 609 s, 329 m., in cm⁻¹. It is surprising that (NH₂)-wagging as well as (N-N)-stretching frequencies are observed only in the partly reacted product, e.g. $Zn(N_2H_4)F_2$, but they are absent in the spectrum of $Zn(N_2H_4)F_2$; all the other absorptions and their intensities remain unchanged. On the other hand the twisting region of the spectrum exhibits four bands, there is evidence of some hydrogen bonding and (NH₂)stretching vibrations occur at lower wavenumbers as usually. The (Zn-N)-stretching frequency appears at 323 cm⁻¹ while it was observed at 385 and 345 cm⁻¹ with $Zn(N_2H_4)_2Cl_2[14]$, and at 388 cm⁻¹ with $Zn(N_2H_4)_2SQ_4[15]$. The IR spectrum of $Cn(N_2H_4)_2F_2$ is surprisingly similar to the spectrum of $Cn(N_2H_4)_2F_2$, indicating that both compounds might be isostructural with strong secondary bonds between nitrogen and fluoride atoms[16].

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Studies in cyclophosphazenes—VII[†]. On *trans*-2, 4-dichloro-2, 4, 6, 6-tetrakis(dimethylamino)cyclotriphosphazene

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Something of a mystery surrounds *trans*-2, 4-dichloro-2, 4, 6, 6tetrakis(dimethylamino)cyclotriphosphazene (I). Although its presence was not revealed in several early attempts to prepare it,



later work did demonstrate its existence, but no reason for the earlier failures was proposed, nor is any apparent from the description of the experiments.

Specifically, the only tetra-substituted compound isolated by Keat and Shaw[1] from the reaction of hexachlorocyclotriphosphazene with dimethylamine in an 8 molar ratio was cis-2, 4-dichloro-2, 4, 6, 6-tetrakis(dimethylamino)cyclotriphosphazene (II), whose configuration was clearly established by 'HNMR spectroscopy. Likewise only (II), without any trace of (I) was found in the products formed by the reactions of the gem-and of the trans-trisubstituted isomers, 2, 2, 4-trichloro-4, 6, 6-tris (dimethylamino) and trans-2, 4, t-trichloro-2, 4, 6-tris (dimethylamino)-cyclotriphosphazenes respectively. with dimethylamine in a 2 molar ratio[1]. Furthermore, (I) was not detected in the products obtained from the attempted isomerization of (II) to give (I) using either dimethylamine hydrochloride [2] or aluminium chloride [3] as catalysts. All the crudes obtained in the above reactions were subjected to TLC examination to detect (I) but no evidence for its presence was ever found. These results led to the conclusion that the cis-isomer (II) was the thermodynamically favoured one[1].

In later work Green and Sowerby [4] did detect (I) by G. C. and even isolated it, albeit in only ca. 8% yield, from the reaction of hexachlorocyclotriphosphazene with dimethylamine in an 8 molar ratio under exactly the same conditions as employed previously (1). This finding proved that the earlier failure to detect (I) did not stem from its inherent instability. However, it

[†]Part VI: Z. Biran and J. M. E. Goldschmidt, J. C. S. Dalton, 1017 (1979).

left open the question why (I) appeared absent in some experiments, when at least in some of these it was not unreasonable to suppose that it was actually formed. At least two plausible explanations can be suggested. Either (I) was present in the initial reaction product, but absent in the final product because it is relatively more reactive than (II). That is, after its initial formation, (I) subsequently disappeared because it was selectively removed either through decomposition or through further reaction with dimethylamine or water, under the conditions prevailing, leaving the cis-isomer, (II), as the sole product isolated. Or (I) was actually present in the final crude product but was not detected by TLC as applied. As far as the reported failure in attempted isomerizations is concerned three alternative explanations can be suggested. Either (I) was not formed because the equilibrium favours the cis-isomer exclusively, as has been proposed[1], or the isomerization actually did occur and (I) was present at least initially, but for one of the two reasons proposed above, it was not detected. In order to resolve these questions we repeated and extended the above experiments. The results obtained have been discussed briefly elsewhere [5].

RESULTS AND DISCUSSION

Green and Sowerby obtained crystals of (I) from a large scale preparation [4], but copying their experiment on a smaller scale using acetonitrile in which (I) and (II) were produced in roughly equal amounts [6], 'we failed to isolate (I) though its presence in the crude reaction mixture was indicated by G.C. However we succeeded in obtaining a mixture highly enriched in (I) by first precipitating (II) from a solution of the crude mixture in petrol ether (40-60°C). The filtrate was evaporated and the residue then subjected to double sublimation, (0.01 mm Hg/40°C). The sublimate was shown by G. C. to contain 95% of (I) with the remainder being (II). We did not succeed in purifying this material further.

Using this material parallel qualitative tests of the reactivity of (I) and (II) vis-a-vis dimethylamine and water were performed. These showed that (I) and (II) have substantially equal reactivities.

Isomerization of (I) and (II) to give the other isomer was effected readily employing dimethylamine hydrochloride. In both cases the reaction proceeded rapidly to give an *ca.* 1:1 equilibrium mixture of isomers [7].

Trans-2, 4, 6-trichloro-2, 4, 6-tris(dimethylamino)cyclotriphosphazene was allowed to react with dimethylamine in a 2 molar ratio. G. C. analysis of the product obtained under what were obviously conditions of kinetic control showed that it contained (I) and (II) in an approx. 1:4 ratio.

Finally TLC analysis of (I) and (II) showed that these compounds have equal R_f values under the conditions specified earlier [3].

From all the above experiments it can safely be concluded that (I) was formed in all the reportedly unsuccessful experiments,