Formation of $[S(CN)_2]_n$ in the Solid Phase Reaction of ICN and KSCN

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We recently published a method to prepare polycyanogen, $(CN)_n$, from ICN and KCN in a solid phase reaction [1]. Now we report here that the solid phase reaction of ICN and KSCN yields $[S(CN)_2]_n$, which is a co-polymer of CN and SCN.

Preparation of the Polymer

Heating of the mixture of ICN and KSCN (1:1 mole ratio) in a closed tube yields a brown product from which a cocoa-brown amorphous material can be obtained after washing with water, acetone, chloroform and diethylether. On the basis of experiments carried out at different temperatures (70 and 90 °C) and reaction times (1, 3, 5 and 9 h), it was established that the highest yield can be obtained in the reaction at 90 °C for 5 h. Accordingly, the preparation of the polymer was performed as follows. A finely powdered mixture of 0.97 g (0.01 mol) KSCN and 1.53 g (0.01 mol) freshly prepared ICN [2] was measured into a pressure-proof glass tube [1]. After closing the tube, the mixture was heated in a water bath at 90 °C for 5 h. Then the tube was cooled and opened carefully. The dark, solid material was powdered and dispersed in 100 cm^3 of water. After filtration, the insoluble residue was washed with 10 cm^3 of water, acetone, chloroform and diethylether, and dried *in vacuo* at 100 °C over P_2O_5. Yield: 0.4–0.5 g (47–59%), cocoa-brown, amorphous powder.

Characterization of the Product

The product is insoluble in common organic solvents, slightly soluble in concentrated bases, nitric acid, hydrochloric acid, and pyridine, and fairly soluble in concentrated sulphuric acid, dimethyl formamide and dimethyl sulphoxide. It can be precipitated from its solutions by water or acetone.

Similarly to $(CN)_n$ [1], the standard microanalytical methods gave lower S, C, and N content than had been expected for $[S(CN)_2]_n$. *Anal.* Found: C, 23.27; N, 29.54; S, 29.49. Calc.: C, 28.56; N, 33.31; S, 38.13%. The N content of the polymer was also determined by the Kjehldahl method, after a strong digestion [3] of the sample. The obtained value (31.17%) is near the calculated one. The product also contains about 0.3% of potassium, according to the flame photometric analyses.

There is a strong maximum in the IR spectrum of the solid sample at 2180 cm^{-1} characteristic of CN groups attached to a conjugated chain [1]. The weak maxima at 2050 and 2070 cm^{-1} indicate the presence of thiocyanate and isothiocyanate groups in the molecule [4]. The broad absorption band between 1000 and 1700 cm^{-1} is a consequence of the conjugated $-(C{=}N)_n-$ chain.

According to the DTG measurements, the decomposition of the solid sample starts at 200–210 °C (weight loss *ca.* 32%). The first, endothermic process is followed by an exothermic process at 600–850 °C (weight loss *ca.* 50%). The loss of the initial amount of the compound is only *ca.* 85% at 850 °C.

Like polycyanogen [1], $[S(CN)_2]_n$ also absorbs different metal ions (Cd^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Ag^{+}) from their aqueous solutions (0.1–0.4 M). In the case of $AgNO_3$ solution a slight gas evolution was observed. The polymer treated with $FeCl_3$ solution was found to contain 0.63% of iron.

Contrary to the reaction of ICN and KCN [1], the yield of the solid phase reaction of ICN with KSCN was not influenced by added metal salts (*e.g.* $FeCl_3$, $ZnSO_4$). However, the colour of the product changed from brown to greenish-brown and greyish-brown, respectively. The polymer prepared in the presence of $FeCl_3 \cdot 6H_2O$ contains 2.8% of iron.

The product of the solid phase reaction between ICN and KSCN can be separated into two fractions by extraction with DMSO. DMSO dissolves about 42% of the product, the concentration of the saturated solution is about 20 mg/cm^3. UV–Vis spectrum of the diluted solution shows a shoulder at about 370 nm. The conductivity of the solution containing 18 mg substance in 1 cm^3 DMSO was found to be 68 μS at room temperature, while the conductivity of the solvent was only 4.77 μS, suggesting a partial or total ionic dissociation in solution. Adding 0.1 g anion exchange resin (Molselect DEAE-25) the brown colour of the solution (4 cm^3) changed to pale yellow; that is the molecule is negatively charged. The K content of the DMSO-soluble fraction is greater (0.4%) than that of the non-extracted material. Presumably potassium ions are attached to the negatively charged groups at the ends of the polymer chain, as in the case of polycyanogen [1], so the average molecular weights are about 13 000, 15 300, and 9800 for the product of the solid phase reaction,

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the DMSO-insoluble, and the DMSO-soluble fractions, respectively. The small difference in the average molecular weights indicates that the insolubility is due to mainly structural differences.

The reaction of ICN and KSCN has also been investigated in benzene and CCl_4. In both cases a brownish yellow material has been obtained, fairly soluble in water and acetone.

Conclusion

The product obtained in the solid phase reaction between ICN and KSCN is a chain polymer with a composition of $[S(CN)_2]_n$. The polymer chain contains –S–C=N– and –C=N– units, and –SCN and –CN groups are attached to the carbon atoms in the chain. Most likely there are $-C{=}N^{-}K^{+}$ ionic groups at the ends of the molecules. We note that there are also possibilities for the formation of cyclic units in the chains and cross-linkings between the chains causing insolubility.

This polymer is essentially different from the polymer observed in the thermal decomposition of CuSN [5]. The latter is yellow and its IR spectrum contains only one broad absorption band between 1100 and 1400 cm^{-1}.

References

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