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Formation of Polycyanogen in the Solid Phase Reaction of Cyanogen Iodide and Potassium Cyanide

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Abstract

The polymerization reaction between ICN and KCN in the solid phase was studied. It was established that the product of the reaction is a linear polycyanogen, having –CN groups attached to the $-(CN)_x-$ conjugated chain. The presence of different iron complexes changes the amount and quality of the product. In some cases, iron-containing polymers were obtained.

Introduction

It is known that the ring form of polycyanogen (also called 'paracyanogen') can be prepared by heating cyanogen iodide in a closed system [1]. Woolf observed in 1953 [2] that the vapour of ICN reacts with alkali cyanides at room temperature, causing a loss of cyanide content of the alkali cyanides and yielding a black, paracyanogen-like compound. On the basis of these observations, we have investigated in detail the solid phase reaction of ICN and KCN.

Experimental

Cyanogen iodide was prepared by the reaction of NaCN and I_2 [3]. The solid phase reactions between ICN and KCN were carried out in high pressure glass tubes (inner volume *ca.* 8 cm^3; length 140 mm; outer diameter 16 mm; inner diameter 8 mm) closed with heat-proof covers. All manipulations were done under hood, taking necessary precautions because of the possibility of explosion.

A typical experiment was performed as follows: A completely powdered mixture of 0.65 g (0.01 mol) KCN and 1.53 g (0.01 mol) freshly prepared ICN was measured in a pressure-proof glass tube. After closing the tube, the mixture was heated in a water bath at 90 °C for 3 h. Then the tube was cooled and opened carefully. The dark, carbonaceous solid material was powdered and dispersed in 100 cm^3 of water. After filtration, the insoluble residual was washed with water, acetone and diethylether, and dried *in vacuo* at 100 °C over P_2O_5.

The potassium content of the residual compounds was analyzed flame photometrically, after digestion in an HNO_3/H_2O_2 mixture; the iron content was determined spectrophotometrically after digestion in an H_2SO_4/H_2O_2 mixture in the form of iron(III)–thiocyanato complex.

Results

The Reaction between ICN and KCN

Although the mixture of ICN and KCN blackens after several days at room temperature and after several minutes at 60–90 °C, preliminary experiments have shown that significant amounts of a water-insoluble, paracyanogen-like, black compound can be prepared only in a closed tube because of the volatility of ICN and the primary intermediates. Therefore, subsequent experiments were carried out as described in the Experimental section. It was also established that the amount of the water-insoluble product depends on the temperature, the amount of the reagents, the reaction time, and the properties of ICN. The water-insoluble compound was obtained only at 60–90 °C. At these temperatures the reaction starts as an explosion because of the vigorous evolution of gases (mainly C_2N_2, CO_2, and HCN, according to the mass-spectrometric analysis), with colour change and swelling of the mixture. We did not obtain any water-insoluble material when the reaction mixture was heated slowly (in 100–120 min) to 90 °C.

We have investigated the effect of the reaction time on the yield at 90 °C. As can be seen in Table I, the reaction occurs with significant yield (*ca.* 32%) in the first 2–3 min; after 3–8 h the amount of the product does not increase (yield is *ca.* 46%).

The amounts of the initial compounds also have a great effect on the yield. In the case of 0.01 mol KCN and ICN, we obtained the water-insoluble compound with *ca.* 46% yield (based on the total amount

TABLE I. The Effect of Reaction Time on the Yield of Polycyanogen[a]

t (min)	Yield (%)
3	32 ± 3
60	33 ± 4
180	42 ± 6
300	43 ± 6
480	46 ± 6

[a] 0.01 mol ICN + 0.005 mol KCN, $T = 90 \pm 1$ °C.

of CN), while 5×10^{-3} mol KCN and 5×10^{-3} mol ICN gave a product with only 27% yield.

The reaction of ICN and KCN has also been investigated in aprotic solvents (benzene, CCl_4). In both cases, intensive gas evolution and fast precipitation of a light brown, water-soluble material have been observed.

The reproducibility of the experiments depends very much on the properties of ICN. On standing at room temperature for 2–3 weeks or dried with air for several hours, ICN did not give any water-insoluble product, most likely because of its hydrolysis and polymerization [4].

Characterization of the Product

The product formed in the reaction between ICN and KCN is a dark brown or black amorphous material, insoluble in water, slightly soluble in dimethylformamide, and fairly soluble in dimethylsulphoxide, concentrated mineral acids and bases. DMSO dissolves *ca.* 30% of the water-insoluble product; the concentration of the saturated solution is higher than 2.5 mg/cm^3. The conductivity of the solution containing 1.25 mg substance in 1 cm^3 DMSO was found to be 19 μS at room temperature, while the conductivity of the solvent was only 4.7 μS, suggesting a partial or total ionic dissociation in the solution. By the action of 0.1 g of anion exchange resin (Molselect DEAE-25), the dark brown colour of the solution (containing 5 mg product in 4 cm^3 DMSO) changed to pale yellow; that is, the molecule is negatively charged. UV–Vis spectrum of the solution shows an uncharacteristic broad absorption band and decreasing absorbance with increasing wavelength.

There are two maxima in the IR spectrum of the solid sample: a broad band between 1200 and 1800 cm^{-1}, characteristic for the $-(CN)_x-$ conjugated double bond system, and a sharp band at 2170 cm^{-1}, characteristic for the CN groups attached to the conjugated chain.

According to the DTG measurements, the decomposition of the solid sample starts at 240 °C in air, and at 520 °C under N_2. In the latter case the loss of the initial amount of the compound is only *ca.* 85% at 800 °C.

The standard microanalytical methods always gave lower N and C content than had been expected. *Anal.* Found. C, 25; N, 34; H, 2. Calc. C, 46.1; N, 53.9; H, 0%. However, it has been observed by several authors [5, 6] that the standard microanalytical methods are not suitable for the analysis of inorganic polymers containing conjugated double bond systems because of their high stability. The product also contains 0.72 ± 0.03% potassium.

When the product (0.52 g) was treated with aqueous solutions (25 cm^3, 0.4 M) of different transition metal salts, its weight increased and, in the case of several metal salts (e.g. $AgNO_3$, $ZnSO_4$, $CuSO_4$), gas evolution was observed. The polymer treated with $FeCl_3$ solution was found to contain 4.7% of iron.

Reactions in the Presence of Metal Complexes

The effect of several iron complexes on the reaction of ICN and KCN has been studied at ICN:KCN:Fe = 1:1:0.1 mole ratio. It was observed that the initial period of the reactions is less violent than it is in the absence of metal compounds. As is seen in Table II, the yield of the water-insoluble product increased in the presence of iron complexes. In the case of $FeCl_3 \cdot 6H_2O$ and $K_3Fe(CN)_6$, the product also contains iron; a new absorption band appears at 2065 cm^{-1} in its IR spectrum. Although $K_4Fe(CN)_6$ increased the yield, it did not influence the composition and IR spectrum of the product.

TABLE II. The Yield, Iron Content and IR Data of the Product Obtained in the Presence of Different Iron Compounds[a]

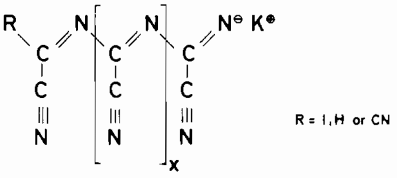
Iron compound	Yield (%)		Fe content (%)		IR (cm^{-1})
	27	46[b]	0	0[b]	1200–1800; 2170
$FeCl_3 \cdot 6H_2O$	40		9.2; 8.4		1200–1800; 2170; 2065
$K_3Fe(CN)_6$		101[b]		5.3[b]	1200–1800; 2170; 2065
$K_4Fe(CN)_6 \cdot 3H_2O$	60		0		1200–1800; 2170

[a] 5×10^{-3} mol ICN + 5×10^{-3} mol KCN + 5×10^{-4} mol iron compound. [b] 10^{-2} mol ICN + 10^{-2} mol KCN + 10^{-3} mol iron compound; $T = 90$ °C, $t = 180$ min.

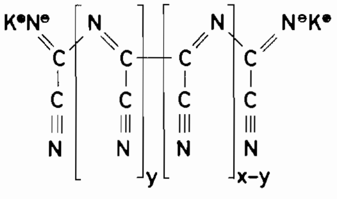
Discussion

It is shown by the experimental results that the product of the solid phase reaction between ICN and KCN, contrary to the assumption of Woolf [2], is not paracyanogen. (Paracyanogen is insoluble in DMSO, and its IR spectrum contains only one broad absorption band at 1400–1700 cm^{-1} [5]). On the basis of chemical nature and IR data, the product obtained by us is very similar to the water-soluble polycyanogen formed in the anionic polymerization of C_2N_2 described by Peska *et al.* [6]. Such a water-soluble compound was obtained when the reaction of ICN and KCN was carried out in CCl_4 or benzene. Peska *et al.* found that the water-soluble polycyanogen has a low polymerization degree (x = 3–6) [6].

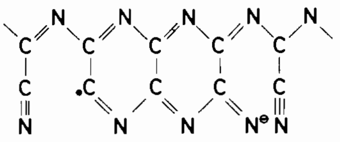
Based on the experimental results and the similarity to the compound obtained by Peska *et al.*, the proposed structure of the product is as follows: The polymer is a linear polycyanogen having –CN groups attached to the –C=N–C=N– conjugated chain. The increase of the conductivity of the DMSO solution and its decolourization by anion exchange resin can be explained by assuming CN^-K^+ ionic groups at the end of the conjugated chain. The following structures are suggested for the polycyanogen:



I



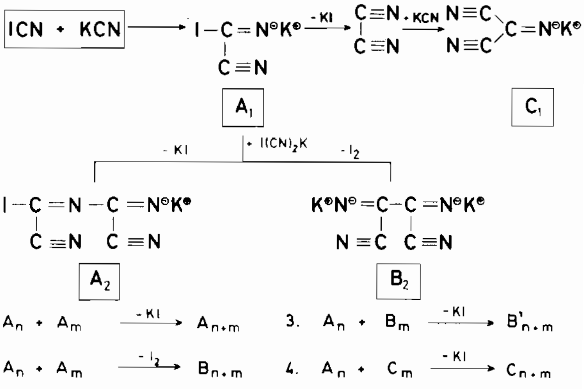
II



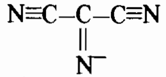
III

We note that there is also a possibility for the formation of cyclic units in both structures (e.g.: **III**).

The proposed mechanism of polymerization reaction can be seen in Scheme 1. The first step is the formation of $I(CN)_2K$ (A_1) from ICN and KCN.



Scheme 1.

(This compound is already known; its adduct with diiminooxalicaciddiethylester can be prepared by the reaction of aqueous KCN and ICN dissolved in ethanol [7].) The reactions of two molecules of $I(CN)_2K$ can give tetracyanogens containing either K and I atoms at the ends of the molecule (A_2) via elimination of KI or only K-atoms at the ends (B_2) via elimination of I_2. The decomposition of $I(CN)_2K$ to cyanogen and KI can proceed simultaneously. Cyanogen may give $K(CN)_3$ (C_1) with KCN. (The formation of $(CN)_3^-$ has also been observed in the interaction of cyanogen and CN^- in aqueous solutions [8]. On the basis of quantum chemical calculations, the possible structure of $(CN)_3^-$ has C_{2v} symmetry:  $N{\equiv}C-\underset{\underset{N^-}{\|}}{C}-C{\equiv}N$ [9]). The intermediates of Type A(A_n) may react:

(a) with molecules of same type (A_m) via elimination of KI or I_2 yielding A_{n+m} or B_{n+m}, respectively;

(b) with molecules of type B(B_m) via elimination of KI giving B'_{n+m}; and

(c) with molecules of type C(C_m) via elimination of KI giving C_{n+m}.

According to this mechanism, only the first process gives active intermediates (which propagate the polymerization); the products of the last three processes can not give any molecules of type A. This means that the average polymerization degree of the product is determined by the relative amount of A_2 formed in the initial period of the reaction, and the relative rate of the first process to that of other three processes. The average polymerization degree and molecular weight of the water-insoluble product were estimated on the basis of its K content. These values are x = 100, $M = 5400$, and x = 200, $M = 11\,000$, based on the structure **I** and **II**, respectively.

The solubility of the polymer and the yield of the water-insoluble fraction are affected by the average polymerization degree, the ionic character of the product and the possible ring structures. As the ionic character increases, the formation of ring structural units **(III)** decreases the solubility of the product in water and DMSO.

Preliminary experiments have shown that it is possible to influence the amount and structure of the product and to obtain polycyanogens containing different metal ions, which may show interesting physical (electric and magnetic) and chemical (redox) properties. Further investigations of the mechanism and the products of the polymerization reaction in the presence of transition metal ions are in progress.

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