PREPARATION AND REACTIONS OF ISOCYANATES OF SULFURIC AND PHOSPHORIC ACID

Professor Dr. Rolf Appel
Institute of Inorganic Chemistry
University of Heidelberg

Abstract

Various syntheses of the disocyanate of sulfuric acid will be described. Its properties and reactions with proton-active materials will be discussed. Reaction with glycols and with diamines leads to the formation of polymeric sulfo-urethanes and sulfo-areas which, however, are only slightly stable towards hydrolysis. Further, a new synthesis of phosphorus oxytrisocyanate will be mentioned.

Organic disocyanates have long served as important starting materials for the preparation of polymers, of which the polyurethanes especially have attained significance in technical fields. Inorganic poly-isocyanates on the other hand were until recent times only seldom described in the literature and relatively little was known about their reactions.

We thus commenced three years ago with a program of research directed primarily towards the preparation of the isocyanates of sulfuric acid for the purpose of studying their poly-addition reactions with lower alcohols and with amines. In this manner, we hoped to gain access to polymeric sulfo-urethanes and sulfo-ureas.

The preparation of sulfuryl disocyanate was accomplished with the assistance of chlorosulfonylisocyanate. This compound can be easily prepared in the reaction between cyanogen chloride and sulfur trioxide according to R. Graf 1:

\[
\text{C}_2\text{CN} + \text{SO}_3 \rightarrow \text{ClSO}_2\text{NCO}
\]

We found that a further convenient procedure consists in the reaction of urea with chlorosulfonic acid. Isocyanic acid then reacts in the sense of a sulfonation to form chlorosulfonylisocyanate:

541

Approved for Public Release
H₂N-CO-NH₂ + Cl₂SO₃H → HNCO + [NH₄]⁺ [ClSO₃]⁻

ClSO₃⁻ [OH⁻ + H⁺] - N=O=C → Cl₂SO₃NCO + HCl↑ + H₂SO₄

Sulfuryldisocyanate could be prepared for the first time in good yield and purity by employing silver cyanate in accordance with

OCNSO₂ Cl⁻ + AgNCO → O₂S(NCO)₂ + AgCl.

Sulfuryldisocyanate is a colourless liquid of low viscosity which boils at 139°C/760 mm and solidifies at -5°C.

This reaction employing the silver salt is, however, too expensive for the preparation of larger quantities of the compound. A further convenient method of synthesis of the disocyanate of sulfuric acid consists of reacting sulfur trioxide with potassium cyanate. This leads to the formation of potassium disulfate together with sulfuryldisocyanate and this latter compound splits off sulfur trioxide upon being heated for longer periods of time at 140°C to yield sulfuryldisocyanate

2 KOCN + 4 SO₃ → K₂S₂O₇ + S₂O₅(NCO)₂

S₂O₅(NCO)₂ → SO₂(NCO)₂ + SO₃

However, the reaction of sulfur trioxide with cyanogen bromide represents the most expeditious method of preparation of SO₃(NCO)₂. In this case, elementary bromine and sulfur dioxide are formed together with sulfuryldisocyanate, whereupon pyrolytic fission can be carried out in the manner just described to produce, as before, sulfur trioxide and the disocyanate of sulfuric acid:

2 BrCN + 3 SO₃ → S₂O₅(KCO)₂ + Br₂ + SO₂

S₂O₅(NCO)₂ → SO₂(NCO)₂ + SO₃

The reactive behaviour of the disocyanate is determined by the two isocyanate groups, which, as would be expected, react with all proton-active materials. With excess water, liberation of CO₂ occurs and sulfamide is formed in quantitative yield:

O₂S(N=O) + 2 H₂O → NH-CO-OH

NH-CO-OH → 2CO₂

O₅S(NH₂)²⁻
If, however, only 1 mole of water in acetonitrile is allowed to act upon the disiocyanate, amidosulfuric acid isocyanate is first formed. This substance is not very stable and it slowly undergoes a head-to-tail polymerization to form a sulfoaryl urea polymer possessing a terminal isocyanate group:

$$\text{OCN-SO}_2\text{-NCO} + \text{H}_2\text{O} \xrightarrow{} \text{HO-CO-NH-SO}_2\text{-NCO}$$

$$\text{H}_2\text{N-SO}_2\text{-NCO} + n \text{H}_2\text{N-SO}_2\text{-NCO} \xrightarrow{\text{H}_2\text{N-SO}_2\text{-}(\text{NH-CO-NH-SO}_2\text{-NCO})_n} \text{NCO}$$

The course of polymerization was measured kinetically and a result for the half life of amidosulfuric acid isocyanate of $T_{25^\circ} = 623$ minutes was found.

In the reaction of sulfoaryl disiocyanate and of amidosulfonic acid isocyanate with alcohols and with amines, a large number of sulfo-urethanes and sulfo-ureas could be prepared. Further details in this respect cannot be included in this report.

The activation of the isocyanate group by the neighbouring SO$_2$-group is so great that both sulfoaryl disiocyanate and amidosulfonic acid isocyanate react with acid amides, although in general these amides are characterized by low proton activity. In this way, the reaction with sulfamide led to the formation of the following compounds:

- **Urea disulfonic acid amide:**
  $$\text{H}_2\text{NSO}_2\text{NH-CO-NH-SO}_2\text{NH}_2$$

- **Sulfoaryl-di-urea sulfoaryl amide:**
  $$\text{H}_2\text{NSO}_2\text{NH-CO-NHSO}_2\text{NH-CO-NHSO}_2\text{NH}_2$$

- **Polysulfoaryl ureas:**
  $$\text{H}_2\text{NSO}_2\text{-}(\text{NH-CO-NHSO}_2\text{-})_n \cdot \text{NH}_2$$

In a similar manner, urea and thio-urea react very readily with both starting compounds. Unfortunately, however, polymers of this type are not very stable. As a result of the numerous SO$_2$ groups with their acidifying influence in the chain, all the compounds just mentioned hydrolyze rather easily.

Further experiments were conducted with the aim of increasing the stability towards hydrolysis by incorporating organic groups in the molecule. By reacting sulfoaryl disiocyanate with ethylene glycol, we were able to obtain polymeric horn-like materials which were readily soluble in dimethylformamide and from which films could be prepared. However, the polymers are not resistant to prolonged treatment with boiling water and hydrolysis occurs in this case also. The course of synthesis is as follows:
... OCN-B-NCO + HO-R-OH + OCN-B-NCO + HO-R-OH ...

-CONH-B-NHCO-O-R-O-CO-NH-B-NH-CO-O-R-O-CO ......

B = SO₂; R = -CH₂-CH₂-

Example: HO-CH₂-CH₂-O-CO-NH-(SO₂-NHCO-O-CH₂-CH₂-O-CO-NH)₃-

-SO₂ NH-CO-O-CH₂-CH₂ OH

M. p. 169°

We hope now to encounter superior properties in the corresponding phosphorus compounds. Phosphorus oxytrichloride will serve as starting material in these studies. This compound can be obtained in the reaction of phosphorus oxytrichloride with monomeric isocyanic acid in the presence of weak bases, although yields are poor.

$$\text{OPCl}_3 + 3 \text{HNO}_2 \rightarrow \text{OP(NCO)}_3 + 3 \text{HCl}$$

Further research will be conducted with dichlorophosphorus oxyisocyanate, OPCl₂(NCO), which can be obtained in good yield from the reaction of phosphorus pentachloride with urethane according to A. V. Kirsanov:

$$\text{PCl}_5 + \text{H}_2\text{N-C-O-C}_2\text{H}_5 \rightarrow \text{Cl}_2\text{P-N=O} + 2 \text{HCl} + \text{C}_2\text{H}_5\text{Cl}$$
