THE CHEMISTRY OF THE ORGANIC ISOCYANATES

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I. INTRODUCTION

During the period 1885–1900 a considerable store of information regarding the fundamental properties of isocyanates was discovered. However, it was not until some forty years later that the practical uses of these compounds were realized. Within the last eight years the industrial applications of isocyanates have progressed from almost zero to the point at which a study of such compounds is of major interest, particularly in the field of polymers. Evidence for this growth is found in the patent literature of recent years and in the reports of German industry.

Recently a brief review of the methods of preparation of the isocyanates and of their reactions with active hydrogen compounds has appeared (76), together with a more comprehensive discussion of the industrial uses of these compounds (77). This article has been written so that an exhaustive study of the preparations and reactions of the isocyanates may be readily available. In addition, a few illustrative applications of these compounds have been given.

II. METHODS OF PREPARATION

A great number of methods of preparation of isocyanates are reported in the literature. These can conveniently be classed according to the reaction involved. The most common method involves the reaction between an amine or its salt and phosgene. Curtius, Hofmann, or Lossen rearrangements and double decomposition reactions have also been widely used. In addition, a variety of miscellaneous methods will be mentioned.

A. Phosgene reactions

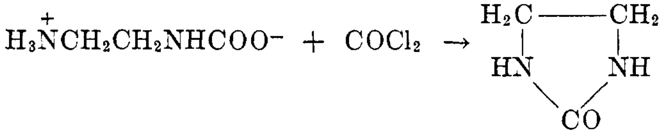
Hentschel, in 1884, showed that an isocyanate could be obtained from the reaction between phosgene and the salt of a primary amine (46). This reaction was modified by Gattermann and Schmidt, who claimed an almost quantitative yield of methyl isocyanate by their procedure (39). They treated molten methylamine hydrochloride with phosgene at 250°C. and obtained methylcarbamyl chloride, which was decomposed by heating with lime.

$$CH_3NH_2 \cdot HCl + COCl_2 \rightarrow CH_3NHCOCl + 2HCl$$
$$2CH_3NHCOCl + 2CaO \rightarrow 2CH_3NCO + CaCl_2 + Ca(OH)_2$$

In later years several modifications of this reaction have been developed. High-boiling isocyanates can be prepared more readily by a reaction between a slurry of the amine hydrochloride in a suitable solvent and phosgene. Solvents such as ethyl acetate (90), toluene (103), and *o*-dichlorobenzene (24) have been used to advantage. Yields are usually good. For example, *p*-nitrophenyl isocyanate has been prepared in 85–95 per cent yield by this method (90). The use of the carbamate salt was found to be superior to the use of the hydrochloride for the preparation of hexamethylene diisocyanate (24), probably because it is more soluble in the medium used than is the hydrochloride.

$$H_2N(CH_2)_6NH_2 + CO_2 \rightarrow H_3\overset{+}{N}(CH_2)_6NHCOO^- \xrightarrow{2COCl_2} OCN(CH_2)_6NCO + 4HCl + CO_2$$

The lower-molecular-weight diisocyanates, such as ethylene and tetramethylene diisocyanate, have not been made successfully by this method, because of intramolecular urea formation.



A more complete discussion of the liquid-phase phosgenation reactions has been given by Pinner (76).

A gas-phase reaction between an amine and phosgene at 180–400°C., in the presence of a catalyst such as bleached clay impregnated with barium chloride, zinc chloride, or sodium bisulfate, was used in Germany (69). Yields as high as 80 per cent were claimed for isocyanates containing as many as seven carbon atoms per molecule. The method was not found to be satisfactory for isocyanates of very high boiling points or for diisocyanates.

At about the same time a similar reaction procedure was developed in this country, with somewhat more promising results. Slocombe and Hardy (92) found that isocyanates could be prepared very rapidly and in good yields, using a vapor-phase process. No catalyst was necessary. The amine vapor and phosgene were mixed efficiently at about 275°C. and the products cooled. The carbamyl chloride corresponding to the amine used was isolated. The higher-boiling isocyanates were obtained by refluxing the carbamyl chloride in benzene or toluene solution. The low-boiling isocyanates were obtained by treating the carbamyl chloride with a tertiary amine. Yields were consistently high for the isocyanates of nine or fewer carbon atoms per molecule, usually 75–86 per cent.

It has been shown that the isocyanate itself was the product of the reaction at 275°C. (85). However, the carbamyl chloride was isolated because the isocyanate, when passed through a cold condenser, combined with an equivalent amount of hydrogen chloride.

$$\mathrm{RNH_2 + COCl_2 \xrightarrow{275°C.} RNCO + 2HCl}$$

$$\mathrm{RNCO + HCl \xrightarrow{25°C.} RNHCOCl}$$

When condensation was effected at 115°C., as was done for phenyl isocyanate, no carbamyl chloride was formed. In addition, methyl isocyanate was obtained directly by causing the hydrogen chloride to react preferentially with pyridine at 115°C.

The only side reaction of any significance in the phosgene processes is the formation of the corresponding disubstituted urea by the reaction of isocyanate with free amine.

$$\mathrm{RNCO + RNH_2 \rightarrow RNHCONHR}$$

This is almost eliminated by the use of the amine salt rather than free amine in the liquid-phase reactions, or by efficient mixing and a slight excess of phosgene in the vapor-phase process.

Urea formation is not always detrimental, however. A process used in Germany for the preparation of phenyl isocyanate consisted in the treatment of *sym*-diphenylurea with phosgene at 150°C., in a high-boiling solvent such as chlorinated naphthalene (59). Yields of 70–80 per cent were claimed.

$$\mathrm{C_6H_5NHCONHC_6H_5 + COCl_2 \xrightarrow{150°C.} 2C_6H_5NCO + 2HCl}$$

The preparation of acyl isocyanates from amides and phosgene has also been reported (104).

$$\mathrm{RCONH_2 + COCl_2 \rightarrow RCONHCOCl}$$

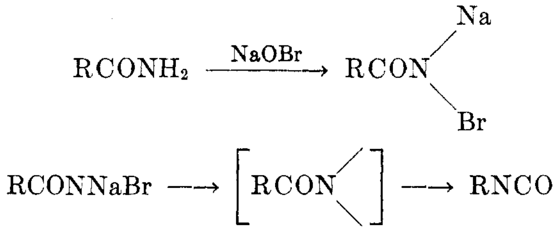
$$\mathrm{RCONHCOCl + CaO \rightarrow RCONCO}$$

B. Curtius, Hofmann, Lossen rearrangements

The method other than the phosgene reaction which has been used most is the Curtius rearrangement of an acid azide in a neutral solvent.

The method was first developed to a considerable extent by Schroeter (88), who prepared several isocyanates by treating an acid chloride with sodium azide and warming the resulting product in benzene solution. Curtius (19, 21) has used the method for the preparation of substituted ethylene diisocyanates. However, he prepared the diazide by treating substituted succinic hydrazides with nitrous acid. Yields from the reaction are usually good, as in the case of undecyl isocyanate, which was obtained in 81–86 per cent yield (2). A complete survey of such preparations reported in the literature is given by Smith (96).

The Hofmann rearrangement of amides is useful only for those isocyanates which do not react readily with water, since an aqueous medium is required.



$$RCONH_2 \xrightarrow{NaOBr} RCON\begin{matrix}Na\\ Br\end{matrix}$$

$$RCONNaBr \longrightarrow \left[RCON\begin{matrix}/\\ \backslash\end{matrix}\right] \longrightarrow RNCO$$

Pyman (78) has given a discussion of the limitations and scope of this reaction, as well as numerous examples. More recent results are given in the papers of Montagne and Guilmart (70) and of Cagniant and Buu-Hoï (15).

The Lossen rearrangement of hydroxamic acids has not been used frequently.

$$RCONHOH \rightarrow RNCO + H_2O$$

The chemistry of the hydroxamic acids and the nature of the Lossen rearrangement have been reviewed recently by Yale (110). In addition, the preparation of aliphatic diisocyanates by this method is described in recent patents (18, 26).

C. Double decomposition reactions

The reaction between organic halides or sulfates and salts of cyanic acid was one of the first methods used for the preparation of isocyanates. Wurtz (108), in 1849, prepared alkyl isocyanates by this method.

$$R_2SO_4 + KCNO \rightarrow RNCO$$

Slotta and Lorenz (93) expressed the opinion that the reaction between the alkyl sulfate and potassium cyanate was the best method for the synthesis of methyl or ethyl isocyanate. Yields as high as 95 per cent were reported. In addition, acyl isocyanates may be prepared in this way, using acid chlorides (48).

$$RCOCl + AgCNO \rightarrow RCONCO$$

D. Miscellaneous preparations

A great variety of other methods has been used for the synthesis of isocyanates. In general, however, they were used only rarely, and are less practical than the reactions described above. The more important of them are given below.

N-Substituted carbamates may be decomposed to give the isocyanate from which the carbamate was derived. This is usually done by heating the carbamate at temperatures ranging from 135°C. to 500°C. (89), or by distilling the carbamate from phosphorus pentoxide (50, 105). Treatment with phosgene at 200°C. has also been described (73), but in the aromatic series this method seems to be specific for *N*-phenylcarbamates (17).

$$RNHCOOR' \xrightarrow{P_2O_5} RNCO$$

$$C_6H_5NHCOOR \xrightarrow{COCl_2} C_6H_5NCO$$

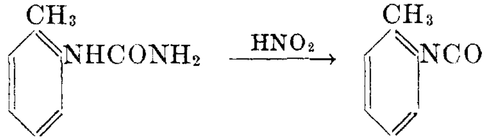
Diazonium chlorides, when treated with potassium cyanate in the presence of copper, are converted to isocyanates (38).

$$ArN_2Cl + KCNO \xrightarrow{Cu} ArNCO$$

Degner and von Pechmann (25) reported that the reaction between diazomethane and nitrourea produced methyl isocyanate.

$$\begin{aligned} H_2NCONHNO_2 + 3CH_2N_2 &\rightarrow [HNCO + H_2NNO_2 + 3CH_2N_2] \\ &\rightarrow CH_3NCO + (CH_3)_2NNO_2 \end{aligned}$$

o-Tolylurea in the presence of nitrous acid is converted to the isocyanate (45).

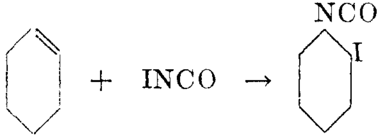


Either isocyanides (40) or isothiocyanates (61) may be oxidized with mercuric oxide to give the isocyanate.

$$RNC + HgO \rightarrow RNCO$$

$$RNCS + HgO \rightarrow RNCO$$

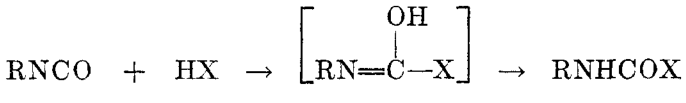
It has also been observed that olefins add iodoisocyanate almost quantitatively at −80°C. (7). The reaction may be used to characterize olefins, since crystalline ureas may easily be prepared.



III. REACTIONS OF ISOCYANATES

A. Active hydrogen compounds

The most characteristic reactions of isocyanates are those which involve compounds containing an active hydrogen.



$$RNCO + HX \rightarrow \left[RN{=}\overset{\displaystyle OH}{\overset{|}{C}}{-}X \right] \rightarrow RNHCOX$$

Generally the reaction proceeds readily at ordinary temperatures or, after moderate heating, without the use of catalysts. However, it is reported that a compound such as cobalt naphthenate and tertiary amines will accelerate the reaction (7, 82).

Isocyanates are hydrolyzed by water with varying degrees of rapidity. Some —for example, octadecyl isocyanate—can be emulsified and will be stable as such for as much as a day. Others are hydrolyzed more readily, with the formation of disubstituted ureas (107, 108).

$$\mathrm{RNCO + H_2O \rightarrow RNHCOOH \rightarrow RNH_2 + CO_2}$$

$$\mathrm{RNH_2 + RNCO \rightarrow RNHCONHR}$$

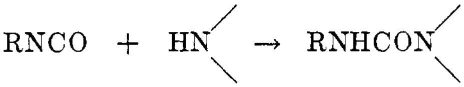
When alkali is used, however, urea formation is decreased considerably and the primary amine is the principal product (109). In general, isocyanates are extremely hygroscopic, and it is this affinity for water, together with subsequent urea formation, which makes handling and storage difficult. Extreme care must be used in drying all equipment used in handling the isocyanates.

Reaction with halogen acids leads to the formation of a carbamyl halide.

$$\mathrm{RNCO + HX \rightarrow RNHCOX}$$

Such a reaction has been observed with hydrogen fluoride (13), hydrogen chloride (47, 63), and hydrogen bromide (37). The carbamyl halides are stable at room temperature, but tend to dissociate into isocyanate and hydrogen halide in the range of 90–100°C. (13, 63, 85).

Practically all compounds containing a hydrogen atom attached to a nitrogen atom will react with isocyanates.



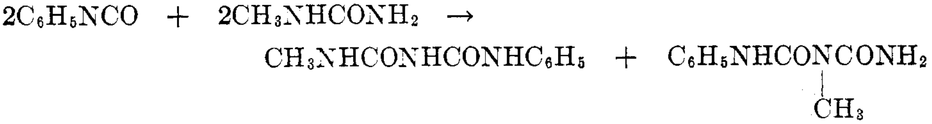
Amines react to give substituted ureas (87), amides give acyl ureas (14), while ureas give biurets (60, 62).

$$\mathrm{RNCO + R_2'NH \rightarrow RNHCONR_2'}$$

$$\mathrm{RNCO + R'CONH_2 \rightarrow RNHCONHCOR'}$$

$$\mathrm{RNCO + H_2NCONH_2 \rightarrow RNHCONHCONH_2}$$

Biltz and Beck (5) have observed that reaction between phenyl isocyanate and methylurea gives two isomeric products.



$$\mathrm{2C_6H_5NCO + 2CH_3NHCONH_2 \rightarrow CH_3NHCONHCONHC_6H_5 + C_6H_5NHCO\underset{\displaystyle CH_3}{\underset{|}{N}}CONH_2}$$

Hydroxylamine reacts with 2 moles of phenyl isocyanate (35).

$$\mathrm{2C_6H_5NCO + H_2NOH \rightarrow C_6H_5NHCONHOCONHC_6H_5}$$

However, if the isocyanate is added dropwise to a large excess of cold hydroxylamine, the urea is formed (35).

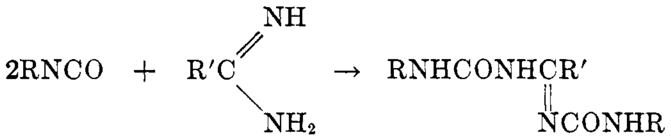
$$\mathrm{C_6H_5NCO + H_2NOH \rightarrow C_6H_5NHCONHOH}$$

In contrast, however, benzohydroxamic acid is reported to give preferential cleavage of the O—H bond (66).

$$\mathrm{RNCO + C_6H_5CONHOH \rightarrow C_6H_5CONHOCONHR}$$

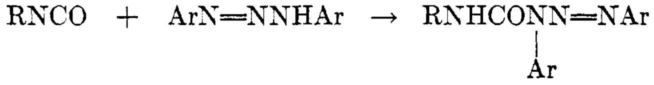
Other nitrogen compounds, such as hydrazines (20), amidines (75), nitramines (87), and diazoamino (43) compounds, behave as expected.

$$\text{RNCO} + \text{H}_2\text{NNHR} \rightarrow \text{RNHCONHNHR}$$



$$2\text{RNCO} + \text{R'C}(=\text{NH})\text{NH}_2 \rightarrow \text{RNHCONHC}(\text{R'})=\text{NCONHR}$$

$$\text{RNCO} + \text{R'NHNO}_2 \rightarrow \text{RNHCON(R')NO}_2$$



$$\text{RNCO} + \text{ArN}=\text{NNHAr} \rightarrow \text{RNHCON(Ar)N}=\text{NAr}$$

Besides the expected product, Caldwell and coworkers (16) have observed that treatment of the phenylhydrazone of acetone with 2 moles of phenyl isocyanate in benzene produces α,β-di(phenylcarbamyl)phenylhydrazine.

$$2(\text{CH}_3)_2\text{C}=\text{NNHC}_6\text{H}_5 + 3\text{C}_6\text{H}_5\text{NCO} \rightarrow (\text{CH}_3)_2\text{C}=\text{NN}(\text{C}_6\text{H}_5)\text{CONHC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{N}(\text{CONHC}_6\text{H}_5)\text{NHCONHC}_6\text{H}_5$$

Reaction with a secondary amine affords a convenient method of analysis (34, 98). An isocyanate may be titrated stoichiometrically with di-*n*-butylamine with good accuracy and reproducibility.

Reaction with amino and amido groups of proteins may account for any toxic effects of the isocyanates. Reports from Germany concerning toxicity are contradictory. However, during the course of several years' experience with isocyanates in this laboratory, only one minor skin irritation of a temporary nature has been observed. When reasonable care in handling was observed, no difficulties were encountered. Some isocyanates are lachrymators, however. This property apparently varies with the vapor pressure of the isocyanate. For example, *m*-tolylene diisocyanate is not a bad lachrymator, while phenyl isocyanate is.

Similarly, compounds containing hydrogen atoms attached to oxygen react with isocyanates. All types of alcohols—primary, secondary, tertiary, and polyhydric—react to give carbamates (44, 56).

$$\text{RNCO} + \text{R'OH} \rightarrow \text{RNHCOOR'}$$

One exception is triphenylcarbinol, which gives no reaction (56). Phenols, including polyhydric phenols, react, especially in the presence of aluminum chloride (65).

It has been observed in this laboratory that tertiary alcohols may be dehydrated by heating with isocyanates (91).

$$2\text{C}_6\text{H}_5\text{NCO} + (\text{CH}_3)_3\text{COH} \rightarrow (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{C}_6\text{H}_5\text{NHCONHC}_6\text{H}_5$$

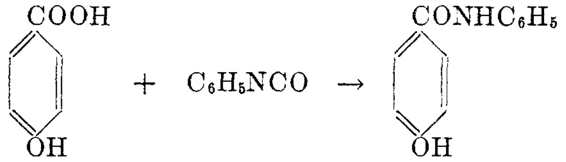
Acids, such as acetic acid, react to give mixed anhydrides, which readily decompose to amides (28, 71).

$$\begin{aligned} RNCO + CH_3COOH &\rightarrow RNHCOOCOCH_3 \\ &\rightarrow RNHCOCH_3 + CH_3COOCOCH_3 + CO_2 + (RNH)_2CO \end{aligned}$$

The hydroxyl group of a hydroxy acid is sometimes more reactive than the carboxyl group, as illustrated by the reaction of β-hydroxyisobutyric acid (10).

$$RNCO + HOCH_2CH(CH_3)COOH \rightarrow RNHCOOCH_2CH(CH_3)COOH$$

However, Humnicki (54) has reported that *o*-, *m*-, and *p*-hydroxybenzoic acids give the amide exclusively.

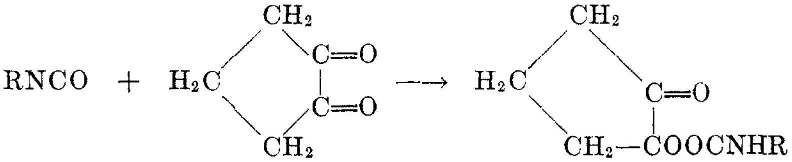


In general, sulfur compounds behave in the same manner as their oxygen analogues.

Compounds which are capable of enolizing are reactive toward isocyanates. For instance, nitromethane (67), malonic ester (29), acetoacetic ester (67), and similar compounds give the typical reaction in the presence of sodium.

$$RNCO + NaCH(COOC_2H_5)_2 \rightarrow RNHCOCH(COOC_2H_5)_2$$

O-Acylation occurs in the case of 1,2-cyclopentadione (27).



A few other reactions of isocyanates are known. A Friedel–Crafts reaction has been observed with aluminum chloride (64).

$$RNCO + ArH \xrightarrow{AlCl_3} RNHCOAr$$

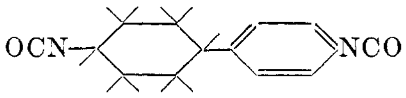
A consideration of the relative reactivity of active hydrogen compounds toward isocyanates indicates that amines react much faster than alcohols, which in turn react faster than water. An example of such a sequence is found in the reaction between ethanolamine and 1 mole of phenyl isocyanate, in which a urea is formed rather than a carbamate (57).

$$C_6H_5NCO + H_2NCH_2CH_2OH \rightarrow C_6H_5NHCONHCH_2CH_2OH$$

Davis and Farnum (23) have studied the relative rates of reaction of phenyl isocyanate with several alcohols in benzene at 26°C. It was found that all primary alcohols investigated reacted at about the same rate. Secondary alcohols reacted about 0.3 as fast as the primary, while tertiary alcohols reacted about 0.005 as fast as the primary. Davis and Ebersole (22) extended the investigation to amines. In ether, at 0°C., primary aliphatic amines reacted about nine times as fast as ammonia, whereas aniline reacted only about one-half as fast as ammonia.

Apparently the basicity of the atom to which the active hydrogen is bound, as well as steric factors, influences greatly the rate of reaction with the isocyanates.

Some recent work in Germany has shown that the isocyanates themselves vary in reactivity. The rate of reaction of aromatic isocyanates with alcohols is decreased greatly by the presence of bulky groups in the ortho position. It was also found that secondary aliphatic and alicyclic isocyanates are much less reactive toward alcohols than are aromatic or benzyl isocyanates. Primary aliphatics fall in between these two classes. This difference has been used to advantage in such compounds as 4,4′-diisocyanatohexahydrobiphenyl.

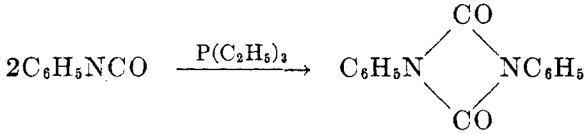


In this compound the isocyanate group attached to the aromatic nucleus is much more reactive than the other. This difference can be used to advantage, since under mild conditions the isocyanate group on the aromatic ring is reactive. After this initial reaction is completed the isocyanate group on the cyclohexyl ring is still available for reactions under more drastic conditions (6).

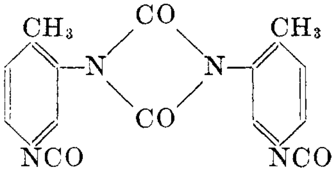
Many of the normal reactions of isocyanates with active hydrogen compounds may be reversed by heating. For example, carbamates may be decomposed to give the isocyanate and alcohol, as described in the section on methods of preparation (6, 17, 50, 73, 80, 89, 105). Carbamyl chlorides and fluorides, as well as certain ureas, may be decomposed similarly (6).

B. Polymerization

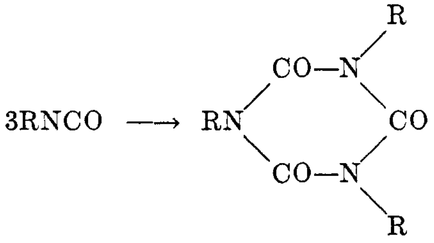
A second general type of reaction of the isocyanates is polymerization. Several catalysts have been used to bring about varying degrees of polymerization. In the presence of triethylphosphine most aromatic isocyanates dimerize, presumably to a compound of the structure shown (8, 36, 51, 52).



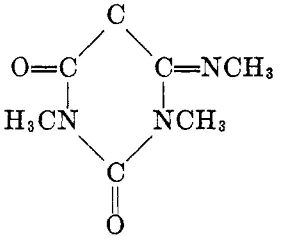
Heating phenyl isocyanate with pyridine also results in dimer formation (79, 97). It has been reported that 2,4-tolylene diisocyanate slowly formed a dimer on standing (6).



Ethyl isocyanate, on the other hand, gives a trimer when brought into contact with triethylphosphine (51). Other catalysts which have been used to induce the trimerization of either aromatic or aliphatic isocyanates are calcium acetate (36), potassium acetate (53), sodium formate (53), sodium carbonate (53), sodium methoxide (67), triethylamine (49), and oxalic acid (3). Peroxides and Friedel–Crafts catalysts are also effective in bringing about polymerization (6). The generally accepted structure for the trimer is that of a trisubstituted cyanuric acid.

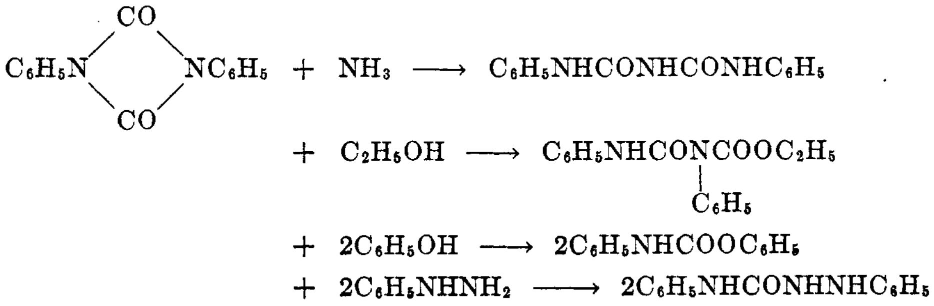


Slotta and Tschesche (94) have reported that a different type of trimer is formed from methyl isocyanate when triethylphosphine is the catalyst. They assigned it the structure of 3,5-dimethyl-2-methylimino-4,6-diketo-1,3,5-trioxdiazine.



Little or no definite information is available on high-molecular-weight polymers of the isocyanates.

The aromatic isocyanates can be regenerated from their dimers by heating (101), although heating to a higher temperature (250°C.) reportedly gives the trimer (101). Phenyl isocyanate dimer reacts with ammonia to give ω-diphenylbiuret (52), with alcohol to give ethyl *N*,*N*′-diphenylallophanate (36), with phenol to give phenyl carbanilate (52), and with phenylhydrazine to give 1,4-diphenylsemicarbazide (30).



C. Other reactions

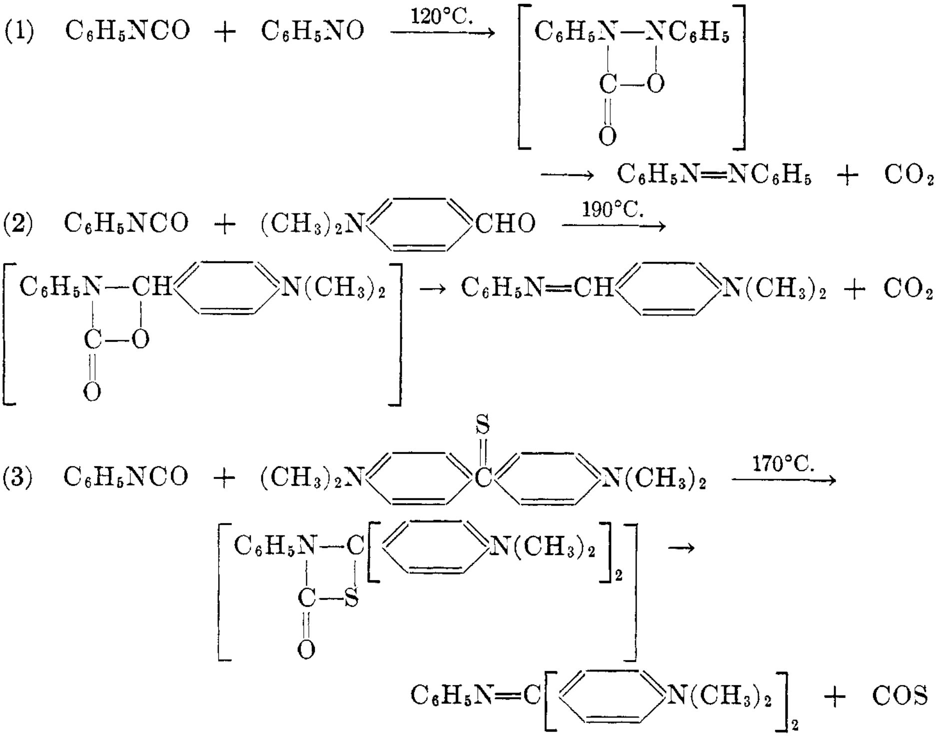
Known reactions of isocyanates not involving active hydrogens or polymerization are few. Slotta and Tschesche (95) reported that methyl isocyanate did not condense with carbon oxysulfide, carbon disulfide, phenyl isothiocyanate, acetonitrile, nitromethane, quinone, acetylene, ethylene, or amylene under the influence of triethylphosphine. With aldehydes, aldoketenes, carbon suboxide, and cyanic acid in the presence of triethylphosphine, only polymers of these substances and the trimer of methyl isocyanate were obtained. No condensation occurred with either dimethylketene or diphenylketene. Treatment with diazomethane gave an insoluble, amorphous substance which could not be identified.

Staudinger (100) has found that dimethylketene will react with phenyl, α-naphthyl, and *p*-nitrophenyl isocyanates to give amorphous substances of molecular weight 3000–6000. He has confirmed that dimethylketene does not react with methyl isocyanate; *p*-anisyl isocyanate is also unreactive. Trimethylamine served as a catalyst in all of his experiments.

Staudinger (99) has attempted to compare isocyanates with ketenes in certain of their reactions.

$$R{-}CH{=}C{=}O \qquad R{-}N{=}C{=}O$$

Unlike ketenes, however, isocyanates do not form four-membered rings at low temperatures with reactive unsaturated compounds, such as nitrosobenzene. However, at higher temperatures compounds are formed which he considers to be degradation products of the additive compounds.



Reactions of isocyanates with active hydrogen compounds are analogous to the corresponding reactions of ketenes.

The isocyanates vary in their reactions when heated. Phenyl isocyanate, on long heating under pressure, gives carbodiphenylimide (101).

$$2C_6H_5NCO \xrightarrow{\text{heat}} C_6H_5N{=}C{=}NC_6H_5 + CO_2$$

tert-Butyl isocyanate, when heated to 180°C., gives isobutylene and cyanuric acid (11). However, the most common reaction is polymerization.

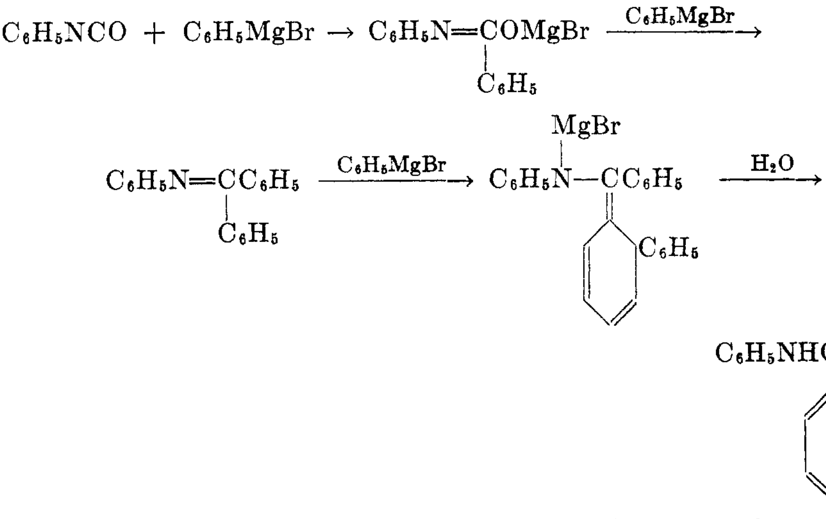
Another general reaction of isocyanates is amide formation upon treatment with a Grignard reagent (9).

$$RNCO + R'MgX \xrightarrow{H_2O} RNHCOR'$$

Entemann and Johnson (31) have shown that the reactivity of the isocyanate group toward a Grignard reagent is less than that of the acetyl group, but greater than that of the fluoroformyl group.

$$CH_3CO\text{—} > \text{—}NCO > \text{—}COF$$

In contrast to the expected amide, however, Gilman (42) obtained a 45 per cent yield of *o*-phenylbenzohydrylaniline from the reaction between phenyl isocyanate and an excess of phenylmagnesium bromide. The proposed reaction sequence was that shown below.

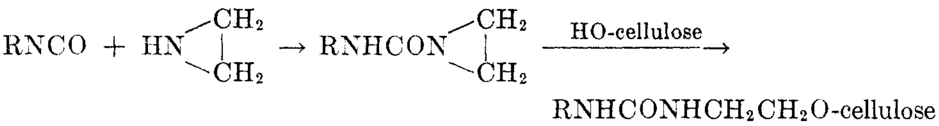


The remaining known reactions of isocyanates are few. Phenyl isocyanate on treatment with chlorine or bromine gives a dichloride or dibromide (44), while phosphorus pentachloride converts it to a chloride which can be reduced with zinc dust to methylaniline (44). Phosphorus pentasulfide converts phenyl isocyanate to phenyl isothiocyanate (68). Reduction with hydrogen and nickel at 190°C. produces methylaniline, carbanilide, aniline, methane, and carbon dioxide (83).

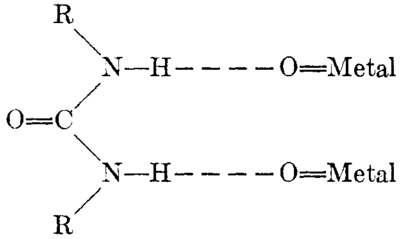
IV. USES OF ISOCYANATES

The principal industrial uses of isocyanates have been in the field of polymers. Copolymers have been prepared from diisocyanates and bifunctional compounds such as glycols (55, 58, 81, 86, 103), diamines (12), and dicarboxylic acid amides (4). Such polymers, especially the polyurethans, have been reported to be harder than nylon, to absorb water less readily, to be unreactive (58). Terpolymers have been made from isocyanates, ethylenimine, and carbon disulfide (32).

Modification of polymers by isocyanate treatment has been the object of much interest. One important example is the foaming of alkyd resins by isocyanates. Such resins, which contain an excess of carboxyl groups, react with diisocyanates at low temperatures with the evolution of carbon dioxide. The gas which is formed causes the plastic to foam and fill the enclosing container and to adhere to the walls of the container (55). Treatment of cellulose with the urea formed from octadecyl isocyanate and ethylenimine renders the cellulose water-repellent. It has been proposed that the reaction proceeds in this manner (72, 73).



Another very important use of isocyanates is in the manufacture of adhesives for bonding rubber to foreign objects, such as rayon or metal. The Germans were very successful in the use of a triisocyanate, tri(*p*-isocyanatophenyl)methane, in such adhesives. Bayer has suggested that the rubber-to-metal adhesion may be due to the presence of a film of moisture and oxide on the metal surface. The water would produce ureide bridges between two isocyanate groups, and such bridges could then form complexes with the metal oxide films. This would account for adhesion to the metal interface. Adhesion to the rubber interface was thought to be due to solubility of the isocyanate in rubber and to secondary valence forces (6).



Many other industrial uses of isocyanates, such as varnish treatment, tanning of leather, paper treatment, and production of electrical insulators, are named in the patent literature.

Outside the field of polymers the uses of isocyanates are few, but show promise of growing rapidly. For example, isopropyl *N*-phenylcarbamate, which appears to be a specific killer of weedy grasses (1), is receiving much attention. Antiallergic substances have been made from isocyanates and proteins containing histamine (33). Carbamates are also of interest in cancer study.

A fairly comprehensive review of the industrial uses of isocyanates has been given recently by Pinner (77).

One other significant use for specific isocyanates is the identification of organic compounds. β-Naphthyl isocyanate is a good reagent for the preparation of crystalline derivatives of most phenols (84), while *p*-nitrophenyl isocyanate is a good reagent for alcohols and amines (102). *p*-Triphenylmethylphenyl and 2-fluorenyl isocyanates have also been recommended for alcohols (106). In addition, Grignard reagents, and consequently alkyl and aryl halides, can conveniently be identified by treatment with 2-naphthyl isocyanate to give the corresponding amide (41).

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