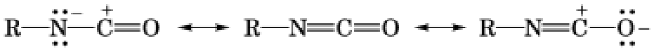
Kirk-Othmer Encyclopedia of Chemical Technology.

ISOCYANATES, ORGANIC

Isocyanates are derivatives of isocyanic acid, HN=C=O, in which alkyl or aryl groups, as well as a host of other substrates, are directly linked to the NCO moiety via the nitrogen atom. Structurally, isocyanates (imides of carbonic acid) are isomeric to cyanates, ROC≡N (nitriles of carbonic acid), and nitrile oxides, RC≡N→O (derivatives of carboxylic acid).

Isocyanates are liquids or solids which are highly reactive and undergo addition reactions across the C=N double bond of the NCO group. Reactions with alcohols, carboxylic acids, and amines have been widely exploited in developing a variety of commercial products. Cycloaddition reactions involving both the C=N and the C=O double bond of the NCO group have been extensively studied and used for product development (1–9).

The basis for the high reactivity of the isocyanates is the low electron density of the central carbon as indicated by the following resonance structures:



$$R-\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{N}}-\overset{+}{C}=O \longleftrightarrow R-N=C=O \longleftrightarrow R-N=\overset{+}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}^{-}$$

Electron withdrawing or donating substituents alter the electrophilic nature of the isocyanate. Thus, whereas *p-N,N*-dimethylaminophenyl isocyanate [16315-59-6] is a rather slow reacting material, sulfonyl or acyl isocyanates are noted to be extremely reactive. The reactivity of isocyanates is also manifested in their tendency to react with themselves to form dimers, trimers, or higher oligomers and polymers. Analytically, isocyanates are readily identifiable through derivatization (urea formation) or via spectroscopy using the strong absorbance between 2300 and 2200 cm^{-1}. Many isocyanates are strong lachrymators (tear-inducing agents). Toxicity data for many of the commercially available isocyanates are discussed herein.

Industrially, isocyanates have become large-volume raw materials for addition polymers, such as polyurethanes, polyureas, and polyisocyanurates. By varying the reactants (isocyanates, polyols, polyamines, and others) for polymer formation, a myriad of products have been developed ranging from flexible and rigid insulation foams to the high modulus automotive exterior parts to high quality coatings and abrasion-resistant elastomers unmatched by any other polymeric material. The most significant mono-, di-, and oligomeric isocyanates, which constitute over 90% of global isocyanate production, are listed in Tables 1, 2, 3.

1. Synthetic Methods

The first synthetic route for isocyanates was reported in 1848 (10, 11). Subsequent efforts by Hofmann, Curtius, and Hentschel pioneered alternative synthetic approaches (12). These efforts highlighted the phosgene–amine approach. Staudinger presented the structural similarities between isocyanates and ketenes and stimulated interest in this class of compounds (13). However, it was not until 1945, when the world was pressed for an

Table 1. Commercially Available Aromatic Isocyanates

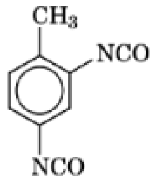
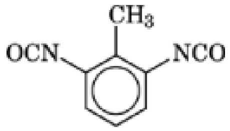
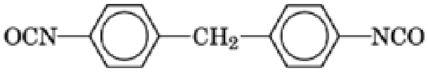
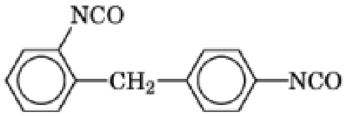
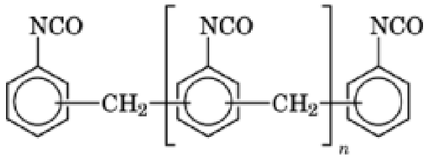
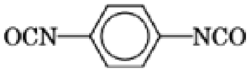
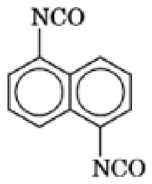
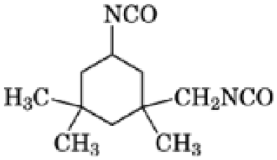
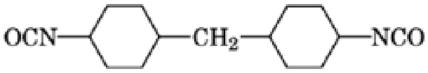
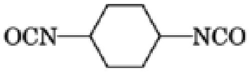
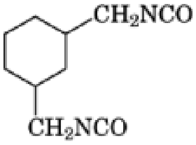
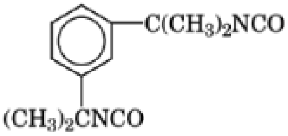
Name	CAS Registry Number	Structure
toluene 2,4-diisocyanate (TDI)	[584-84-9]	
toluene 2,6-diisocyanate (TDI)	[91-08-7]	
4,4′-methylene diphenyl diisocyanate (MDI)	[101-68-8]	
2,4′-methylene diphenyl diisocyanate	[5873-54-1]	
polymeric methylene diphenyl diiso-cyanate (PMDI)	[9016-87-9]	
p-phenylene diisocyanate (PDI)	[935-16-0]	
naphthalene-1,5-diisocyanate (NDI)	[3173-72-6]	

Table 2. Commercially Available Aliphatic Isocyanates

Name	CAS Registry Number	Structure
1,6-hexamethylene diisocyanate (HDI)	[822-06-0]	$OCN(CH_2)_6NCO$
isophorone diisocyanate (IPDI)	[4098-71-9]	
4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI)[a]	[5124-30-1]	
1,4-cyclohexane diisocyanate (CHDI)[a]	[2556-36-7]	
bis(isocyanatomethyl)cyclo-hexane (H_6XDI,DDI)[a]	[38661-72-2]	
tetramethylxylylene diisocyanate (TMXDI)	[2778-42-9]	

[a] Mixture of stereoisomers.

Table 3. Industrially Important Specialty Monoisocyanates

Name	CAS Registry Number
methyl isocyanate (MIC)	[624-83-9]
n-butyl isocyanate (BIC)	[111-36-4]
phenyl isocyanate (PIC)	[103-71-9]
3-chlorophenyl isocyanate	[2909-38-8]
3,4-dichlorophenyl isocyanate	[102-36-3]
p-toluenesulfonyl isocyanate	[4083-64-1]

alternative to natural rubber, that synthetic routes to isocyanates became an area of great importance. Several excellent review articles covering the synthesis and chemistry of isocyanates have been presented (1–9).

1.1. Preparation from Amines

The most common method of preparing isocyanates, even on a commercial scale, involves the reaction of phosgene [75-44-5] and aromatic or aliphatic amine precursors. The initial reaction step, the formation of N-substituted carbamoyl chloride (1), is highly exothermic and is succeeded by hydrogen chloride elimination which takes place at elevated temperatures.

$$R{-}NH_2 \xrightarrow[-HCl]{COCl_2} R{-}NHCOCl \longrightarrow_{-HCl} R{-}N{=}C{=}O$$

(1)

To suppress the formation of side products, primarily ureas and isocyanurates, excess phosgene is employed. In most small-scale batch processes, diluted amine is added gradually to chilled solutions of phosgene followed by venting of excess phosgene. Dehydrohalogenation of the resultant carbamoyl chloride is performed at approximately 80–100°C. Isolation of the desired isocyanate products is achieved by distillation at reduced pressure. The carbamoyl chlorides of certain alkyl isocyanates are stable (or recombine from isocyanate and hydrogen chloride) and distill without decomposing. Because distillation of the crude alkyl isocyanates does not necessarily yield a purified product, alternative synthetic routes are often preferred.

A variation of this method involves the conversion of the amine into the amine hydrochloride prior to treatment with phosgene. This method has the advantage of producing generally cleaner products by retarding the secondary reaction of the free amine with carbamoyl chloride.

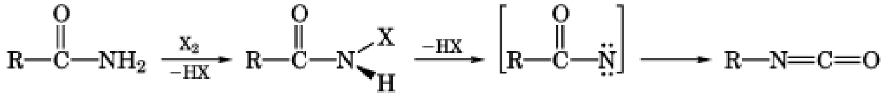
The reaction of isocyanate precursors with reactive groups and phosgene also results in isocyanates. For example, *o*-aminobenzoic acid [118-92-3] and phosgene react to form 2-isocyanatobenzoyl chloride [5100-23-2]. Interestingly, isocyanatophenols have been synthesized from aminophenols, under controlled conditions, without formation of the corresponding chloroformates (14, 15).

Instead of amines, sulfonamides have also been used as starting materials, producing the highly reactive sulfonyl isocyanates, which have found applications in the manufacture of drugs for diabetics and as drying agents (qv) (4, 9, 16).

Oligomers of phosgene, such as diphosgene [503-38-8], $(COCl_2)_2$, have found use in the laboratory preparation of isocyanates. Carbamoyl chlorides, *N,N*-disubstituted ureas, dimethyl- and diphenylcarbonates, and arylsulfonyl isocyanates have also been used to convert amines into urea intermediates, which are subsequently pyrolyzed to yield isocyanates. These methods have found applications for preparation of low boiling point aliphatic isocyanates (2, 9, 17).

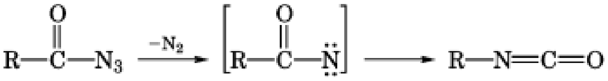
1.2. Preparation from Nitrene Intermediates

A convenient, small-scale method for the conversion of carboxylic acid derivatives into isocyanates involves electron sextet rearrangements, such as the ones described by Hofmann and Curtius (12). For example, treatment of benzamide [55-21-0] with halogens leads to an *N*-haloamide **(2)** which, in the presence of base, forms a nitrene intermediate **(3)**. The nitrene intermediate undergoes rapid rearrangement to yield an isocyanate. Ureas can also be formed in the process if water is present (18, 19).



(2) **(3)**

More convenient is the use of aryl azides which are readily converted into isocyanates upon heating in nonreactive solvents via the loss of nitrogen. The latter method is useful for the synthesis of isocyanates with additional substituents which could not be prepared with phosgene (20).

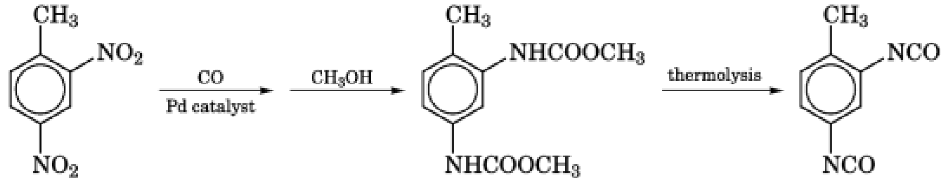


$$R-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{-N_2} \left[R-\overset{O}{\overset{\|}{C}}-\underset{..}{\ddot{N}}\right] \longrightarrow R-N{=}C{=}O$$

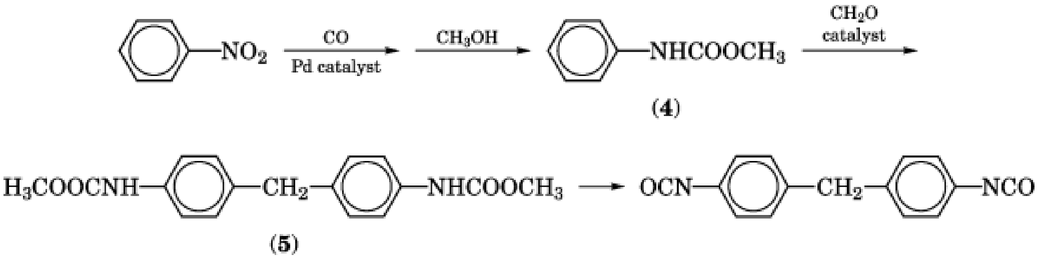
A process for the commercial synthesis of *p*-phenylene diisocyanate using terephthalamide [3010-82-0] as a precursor and involving N-halo intermediates has been studied extensively (21). The synthesis of 1,4-diisocyanatocyclohexane from terephthalic acid [100-21-0] also involves a nitrene intermediate (22).

1.3. Nonphosgene Preparation

The term nonphosgene route is primarily used in conjunction with the conversion of amines (or the corresponding nitro precursor) to isocyanates via the use of carboxylation agents. These multistep approaches are becoming more attractive to the chemical industry as environmental or toxicological restrictions involving chlorine or phosgene are increasingly enforced. For example, 2,4-dinitrotoluene [121-14-27] undergoes reductive carbonylation to form 2,4-toluene diisocyanate (TDI) in the presence of palladium catalysts (23–27). A variation of this process consists in capturing the isocyanate formed with methanol followed by thermolysis of the biscarbamate (26).



Similarly, nitrobenzene, carbon monoxide, and methanol can react sequentially in the presence of noble metal catalysts, to produce methyl *N*-phenylcarbamate [2603-10-3] **(4)**. The phenylcarbamate is subsequently coupled with formaldehyde [50-00-0] to yield the methylenebis(carbamate) **(5)** which is pyrolyzed to yield methylene diphenyl diisocyanate (MDI) (23).



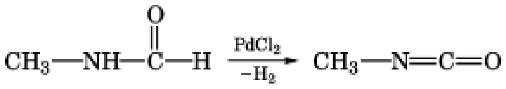
(4)

(5)

Both dimethyl carbonate [616-38-6] and diphenyl carbonate [102-09-0] have been used, in place of carbon monoxide, as reagents for the conversion of amines into isocyanates via this route (28, 29). Alternatively, aniline [62-53-3], toluene diamines (TDA), and methylene dianilines (MDA) have also been used as starting materials in the carbonylations to provide a wide variety of isocyanate monomers.

A simpler nonphosgene process for the manufacture of isocyanates consists of the reaction of amines with carbon dioxide in the presence of an aprotic organic solvent and a nitrogeneous base. The corresponding ammonium carbamate is treated with a dehydrating agent. This concept has been applied to the synthesis of aromatic and aliphatic isocyanates. The process relies on the facile formation of amine–carbon dioxide salts using acid halides such as phosphoryl chloride [10025-87-3] and thionyl chloride [7719-09-7] (30).

More recently, a commercial process has been introduced for the manufacture of methyl isocyanate (MIC) which involves the dehydrogenation of *N*-methylformamide [123-39-7] in the presence of palladium, platinum [7440-06-4], or ruthenium [7440-18-8], at temperatures between 50–300°C (31). Aprotic solvents, such as benzene [71-43-2], xylenes, or toluene [108-88-3], may optionally be used. A variation of this synthesis employs stoichiometric amounts of palladium chloride [7647-10-1], $PdCl_2$.



$$CH_3{-}NH{-}\overset{\overset{O}{\|}}{C}{-}H \xrightarrow[-H_2]{PdCl_2} CH_3{-}N{=}C{=}O$$

Du Pont has reported an alternative catalytic process for the production of MIC starting with methylamine [74-89-5] (32).

$$CH_3NH_2 + CO \longrightarrow CH_3NH\overset{\overset{O}{\|}}{C}H \xrightarrow{O_2} CH_3N{=}C{=}O + H_2O$$

The above processes are only selected examples of a vast number of process options. In the case of carbonylation, the formation of by-products, primarily isocyanate oligomers, allophanates, and carbodiimides, is difficult to control and is found to greatly reduce the yield of the desired isocyanate. Thus a number of nonphosgene processes have been extensively evaluated in pilot-plant operations, but none have been scaled up to commercial production of diisocyanates primarily due to process economics with respect to the existing amine–phosgene route. Key factors preventing large-scale commercialization include the overall reaction rates and the problems associated with catalyst recovery and recycle.

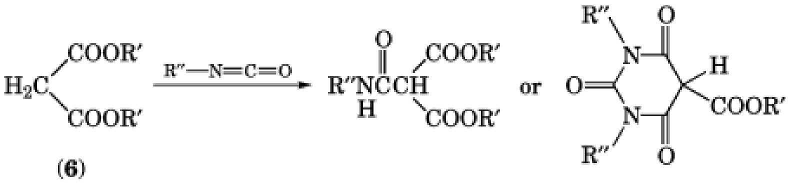
2. Chemical Properties

2.1. Addition Reactions

Isocyanates undergo addition reactions with a wide variety of substrates. Preferred addition occurs across the C=N bond of the NCO moiety. In general, the electron-poor carbon of the isocyanate group serves as the center for attack of isocyanates on electron-rich centers. Electron-withdrawing groups linked to the isocyanate group increase the reactivity of the NCO group. The most commonly used reaction of isocyanates involves their addition to alcohols, amines, and carboxylic acids. Translated to di- or polyfunctional starting materials, these products represent the basis for the diverse group of products generally referred to as polyurethanes.

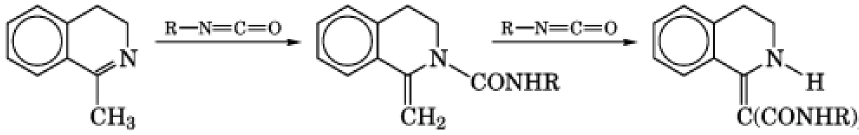
2.2. Insertion Reactions

Isocyanates also may undergo insertion reactions with C—H bonds. Acidic compounds, such as 1,3-dicarbonyl compounds **(6)**, react readily at room temperature to form carboxyamides. At higher temperatures carboxyamides frequently undergo secondary reactions leading to cyclized products (33, 34).



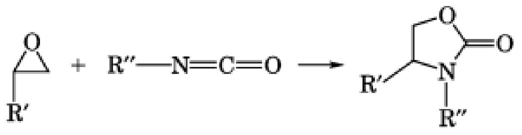
(6)

Another common process involves reaction with C=C or C=N species having adjacent CH_2 or CH_3 groups. Initial attack of the isocyanate is on the electron-rich center of the double bond with subsequent migration and insertion of the CONR group into the CH bond. Suitable reagents include *N*-alkylated acetamidines, 1-methyl dihydroisoquinoline, and 2-methyl-2-oxazoline [1120-64-5] (35).

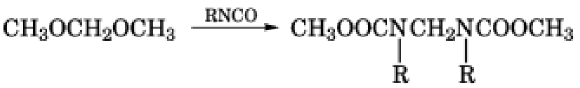


A variety of olefins or aromatic compounds having electron-donating substituents are known to undergo C—H insertion reactions with isocyanates to form amides (36, 37). Many of these reactions are known to involve cyclic intermediates.

Isocyanates insert into RO and RN bonds. Cyclic ethers, such as oxiranes, are known to undergo reactions with isocyanates to form 2-oxazolidinones in high yield (38–40).



Similarly, dimethoxymethane or cyclic acetals react to form carbamates in the presence of catalysts.



$$CH_3OCH_2OCH_3 \xrightarrow{RNCO} CH_3OOC\underset{R}{N}CH_2\underset{R}{N}COOCH_3$$

Tertiary amines have been shown to react with isocyanates in an analogous fashion to form ureas (41–43). Similarly, aziridines (three-membered rings containing nitrogen) are found to react with isocyanates to yield cyclic ureas. Tertiary amines have also been shown to form labile dipolar 1:1 adducts with isocyanates reminiscent of salt formation. In contrast, formaldehyde *N,N*-acetal aminals form insertion products with sulfonyl isocyanates (44, 45).

2.3. Cycloaddition Reactions

Isocyanates undergo cycloadditions across the carbon–nitrogen double bond with a variety of unsaturated substrates. Addition across the C=O bond is less common. The propensity of isocyanates to undergo cyclization reactions has been widely explored for the synthesis of heterocyclic systems. Substrates with C=O, C=N, C=S, and C=C bonds have been found to yield either $2 + 2$, $2 + 2 + 2$, or $2 + 4$ cycloadducts or a variety of secondary reaction products (2).

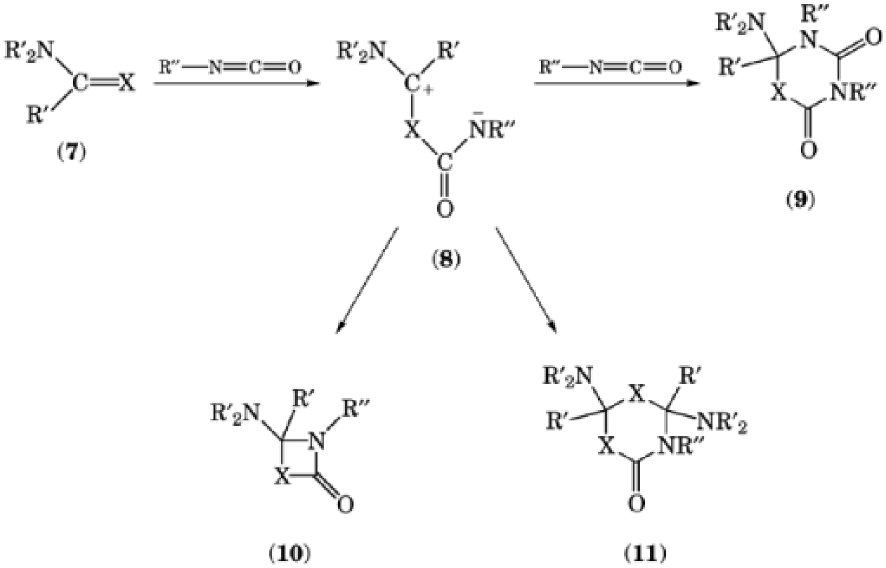
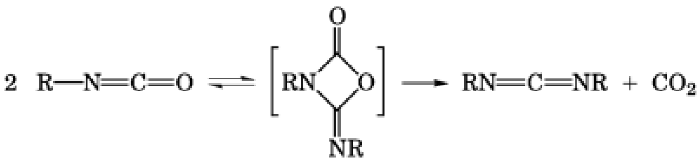


Fig. 1. Cycloaddition reactions of isocyanates: (**7**)$_{X=}$ NR, S, O, or CR_2; (**8**) 1,4-dipolar intermediate; (**9**) 2:1 adduct; (**10**) 1:1 cycloadduct; and (**11**) 1:2 adduct.

Most reactions of this type were found to involve acyclic 1,4-dipolar intermediates which cyclize to four-membered heterocycles or are intercepted by isocyanate or C=X components, such as C=N, C=S, and CR_2, to form a six membered ring. This group of reactions is illustrated in Figure 1. Depending on the nature of the isocyanate and the double-bond system, any of the products shown in Figure 1 can be obtained. Variations in the component ratio or judicious choice of reagents are noted to have pronounced control of product type. Additional reaction details, as well as a description of the multiple transformations involving adjacent substituents, have been summarized (28).

The dimerization and trimerization of isocyanates are special cases of the cycloaddition reaction in that they involve reagents of the same type. The uncatalyzed carbodiimidization of isocyanates likely involves a labile $2 + 2$ cycloadduct **(12)** which liberates carbon dioxide.



(12)

Acyl isocyanates (**13**,X = O, S) have been shown to react as heterodienes in most cycloadduct formations. Notable examples include autodimerization and the addition to imines (46, 47). Unlike aromatic isocyanates, it is not possible to predict the reaction pathway nor the structure of the products which may arise from a given approach or set of reaction conditions.

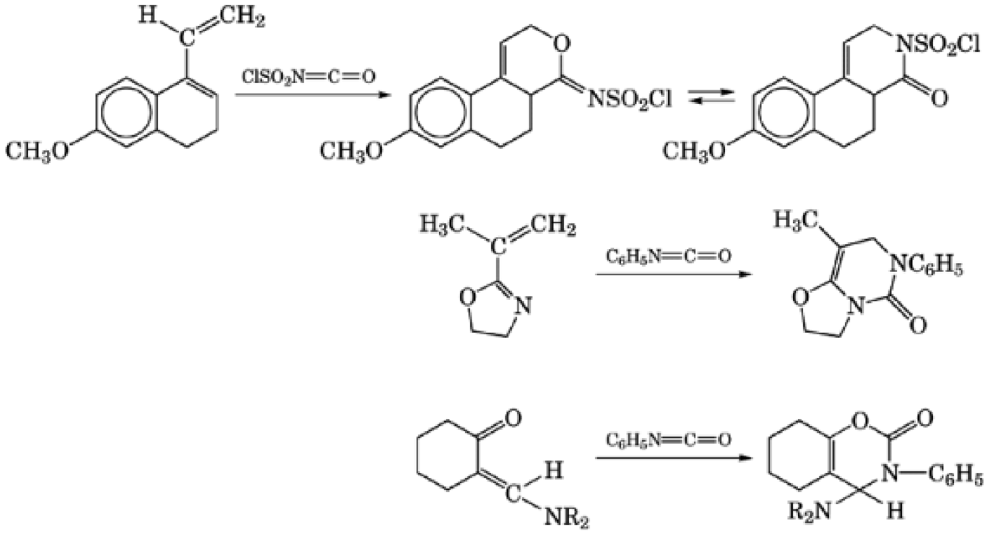
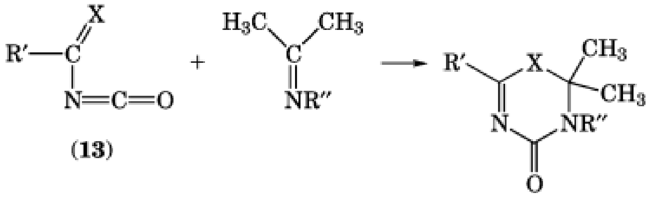


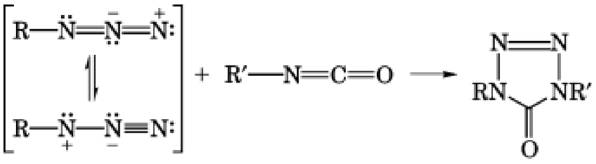
Fig. 2. Diels-Alder-type reactions of aromatic and sulfonyl isocyanates.



(13)

A large number of Diels-Alder-type reactions, involving both aromatic and sulfonyl isocyanates, have been reported. Heterodienes having high electron density are found to add to isocyanates to form six membered heterocycles as shown in Figure 2 (48–50).

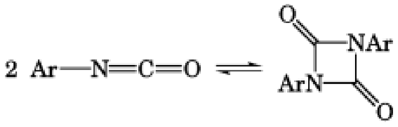
A comprehensive review of reactions of isocyanates and 1,3-dipolar compounds has been previously published (51). The example shown illustrates the reaction of azides and isocyanates to yield tetrazoles (**14**, R = alkyl or aryl, R′ = aryl or sulfonyl) (52, 53).



(14)

2.4. Oligomerization and Polymerization Reactions

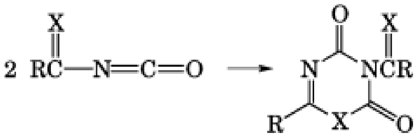
One special feature of isocyanates is their propensity to dimerize and trimerize. Aromatic isocyanates, especially, are known to undergo these reactions in the absence of a catalyst. The dimerization product bears a strong dependency on both the reactivity and structure of the starting isocyanate. For example, aryl isocyanates dimerize, in the presence of phosphorus-based catalysts, by a crosswise addition to the C=N bond of the NCO group to yield a symmetrical dimer **(15)**.



(15)

Slow dimerization is generally noted to occur in some isocyanates during prolonged storage. The tendency for 4,4′-methylene diphenyl diisocyanate to undergo uncatalyzed dimerization is tied to its crystal structure. The molecules of the 4,4′-MDI align in the solid state, with the NCO groups in close proximity, which leads to slow formation of the dimer at room temperature. The structure of the symmetrical MDI dimer has been verified by x-ray analysis (54). It has been reported that substituted benzyl isocyanates form mixtures of both dimers and trimers in high yield when 1,2-dimethylimidazole [1739-84-0] is used as a catalyst (55).

Conversely, acyl isocyanates yield dimers which include the C=X **(16)** moiety (where X = O, S, NR) in the product ring structure (56).



(16)

Reportedly, simple alkyl isocyanates do not dimerize upon standing. They trimerize to isocyanurates under comparable reaction conditions (57). Aliphatic isocyanate dimers can, however, be synthesized via the phosgenation of *N,N′*-disubstituted ureas to yield *N*-(chlorocarbonyl)chloroformamidine intermediates which are subsequently converted by partial hydrolysis and base catalyzed cyclization. This is also the method of choice for the synthesis of 1-alkyl-3-aryl-1,3-diazetidiones (mixed dimers of aromatic and aliphatic isocyanates) (58).

Dimerization is reportedly catalyzed by pyridine [110-86-1] and phosphines. Trialkylphosphines have been shown to catalyze the conversion of dimer into trimer upon prolonged standing (2, 57). Pyridines and other basic catalysts are less selective because the required increase in temperature causes trimerization to compete with dimerization. The gradual conversion of dimer to trimer in the catalyzed dimerization reaction can be explained by the assumption of equilibria between dimer and polar catalyst–dimer intermediates. The polar intermediates react with excess isocyanate to yield trimer. Factors, such as charge stabilization in the polar intermediate and its lifetime or steric requirement, are reported to be important. For these reasons, it is not currently feasible to predict the efficiency of dimer formation given a particular catalyst.

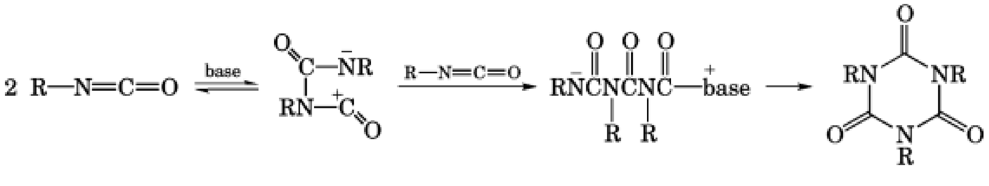
Asymmetric aryl isocyanate dimers, in which the C=O group of one molecule reacts with the C=N group of another, have been postulated as labile intermediates in the formation of carbodiimides **(17)** upon heating isocyanates.

$$2\ \mathrm{R{-}N{=}C{=}O} \rightleftharpoons \mathrm{RN{=}C{=}NR} + \mathrm{CO_2}$$

(17)

Carbodiimide formation is markedly accelerated when phosphine oxides (R_3PO) or phosphates are used as catalysts. Intermediates with P—NR bonds have been postulated as intermediates in these reactions (59, 60).

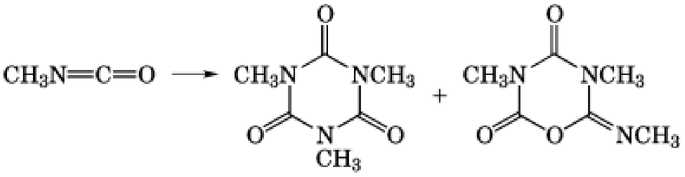
Both alkyl and aryl isocyanates are found to trimerize upon heating or in the presence of catalysts to 1,3,5-trisubstituted hexahydro-*s*-triazinetriones **(18)** (isocyanurates) (57). Only highly substituted isocyanates, such as *tert*-butyl isocyanate [7188-38-7] and *tert*-octyl isocyanate, fail to trimerize under these conditions.



(18)

Commercially, polymeric MDI is trimerized during the manufacture of rigid foam to provide improved thermal stability and flammability performance. Numerous catalysts are known to promote the reaction. Tertiary amines and alkali salts of carboxylic acids are among the most effective. The common step in all catalyzed trimerizations is the activation of the C=N double bond of the isocyanate group. The example **(18)** highlights the alkoxide assisted formation of the cyclic dimer and the importance of the subsequent intermediates. Similar oligomerization steps have been described previously for other catalysts (61).

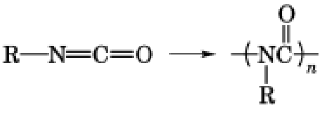
Interestingly, methyl isocyanate is noted to form unusual trimer products in the presence of trialkylphosphine catalysts. Both the expected triazine **(19)** and 3,5-dimethyl-2-methylimino-4,6-dioxohexahydro-1,3,5-oxadiazine **(20)** products are formed (62).



(19) **(20)**

Diisocyanates undergo anionic homopolymerization at subambient temperatures in polar solvents to yield high molecular weight cross-linked isocyanates. This type of polymerization has generally been observed for short-chain, aliphatic diisocyanates which are structurally conducive to an alternating intermolecular and intramolecular propagation mechanism. The thermal homopolymerization of 2,4-toluene diisocyanate [584-84-9] has been reported. The structure of the resultant low molecular weight oligomers has not been established.

Monoisocyanates undergo anionic homopolymerization at subambient temperatures to yield nylon-1 polymers (polyamides) (63).



$$R{-}N{=}C{=}O \longrightarrow \left(\underset{\substack{|\\ R}}{N}\overset{\substack{O\\ \|}}{C} \right)_n$$

Although the crystalline poly(allyl isocyanate) polymers are reported to be stable, many of these polymers depolymerize upon heating to yield monomers and cyclic trimers. The level of temperature sensitivity is a strong function of the length of the side chain. Room temperature depolymerization occurs in polar solvents in the presence of an initiator. Interestingly, the solution properties of poly(alkyl isocyanates) display an unusual degree of chain stiffness which is attributed to their helical configuration (64).

2.5. Addition Polymers

The most commonly referenced reaction of isocyanates involves their addition to polyhydroxyl, polyamine, or polycarboxylic acid compounds to yield addition polymers. Due to the wide diversity of raw material characteristics and the broad range of functionality, polyurethane polymers having a wide range of processing and performance characteristics are available.

The reaction of isocyanates with alcohols to form carbamates is catalyzed by amines and a variety of organometallic compounds.

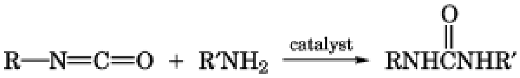
$$\mathrm{R{-}N{=}C{=}O + R'OH \xrightarrow{catalyst} RNH\overset{\overset{\displaystyle O}{\|}}{C}OR'}$$

This simple reaction is the bedrock of the polyurethane industry (see Urethane polymers). Detailed descriptions of the chemistry and process have been published (65–67). Certain carbamates are known to reversibly yield the isocyanate and polyol upon heating. This fact has been commercially used to synthesize a number of blocked isocyanates for elastomer and coating applications.

Similarly, thioalcohols and thiophenols react with isocyanates to form thiocarbamates. Although these reactions are generally found to be much slower than that of the corresponding alcohol, alkoxide catalysts have successfully been used to provide moderate levels of rate enhancement (68).

$$\mathrm{R{-}N{=}C{=}O + R'SH \xrightarrow{catalyst} RNH\overset{\overset{\displaystyle O}{\|}}{C}SR'}$$

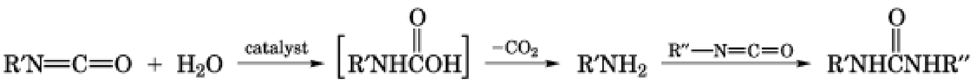
Conversely, the rate of reaction of isocyanates with amines to yield ureas is both rapid and quantitative. Much has been written concerning the reaction



$$\mathrm{R{-}N{=}C{=}O + R'NH_2 \xrightarrow{catalyst} RNH\overset{\overset{\displaystyle O}{\|}}{C}NHR'}$$

kinetics, solvent effects, and catalysis of this reaction (65–67). The rate of reaction is a strong function of the basicity of the amine. Commercially, this relationship has been used to develop a wide variety of sterically hindered or electronically deactivated aromatic diamine chain extenders for reaction injection molding (RIM) and elastomer applications (see Plastics processing) (69).

Industrially, polyurethane flexible foam manufacturers combine a version of the carbamate-forming reaction and the amine–isocyanate reaction to provide both density reduction and elastic modulus increases. The overall scheme involves the reaction of one mole of water with one mole of isocyanate to produce a carbamic acid intermediate. The carbamic acid intermediate spontaneously loses carbon dioxide to yield a primary amine which reacts with a second mole of isocyanate to yield a substituted urea.



$$\mathrm{R'N{=}C{=}O + H_2O \xrightarrow{catalyst} \left[R'NH\overset{\overset{\displaystyle O}{\|}}{C}OH\right] \xrightarrow{-CO_2} R'NH_2 \xrightarrow{R''{-}N{=}C{=}O} R'NH\overset{\overset{\displaystyle O}{\|}}{C}NHR''}$$

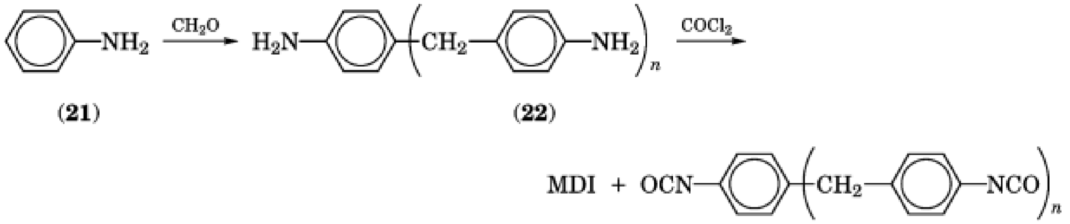
Carboxylic acids react with aryl isocyanates, at elevated temperatures to yield anhydrides. The anhydrides subsequently evolve carbon dioxide to yield amines at elevated temperatures (70–72). The aromatic amines are further converted into amides by reaction with excess anhydride. Ortho diacids, such as phthalic acid [88-99-3], react with aryl isocyanates to yield the corresponding *N*-aryl phthalimides (73). Reactions with carboxylic acids are irreversible and commercially used to prepare polyamides and polyimides, two classes of high performance polymers for high temperature applications where chemical resistance is important. Base catalysis is recommended to reduce the formation of substituted urea by-products (74).

3. Commercial Manufacturing Processes

3.1. Aromatic Isocyanates

A variety of methods are described in the literature for the synthesis of aromatic isocyanates. Only the phosgenation of amines or amine salts is used on a commercial scale (5). Much process refinement has occurred to minimize the formation of disubstituted ureas arising by the reaction of the generated isocyanate with the amine starting material. A listing of the key commercially available isocyanates is presented in Table 1.

For methylene diphenyl diisocyanate (MDI), the initial reaction involves the condensation of aniline [62-53-3] **(21)** with formaldehyde [50-00-0] to yield a mixture of oligomeric amines (**22**, where $n = 1, 2, 3\ldots$). For toluene diisocyanate, amine monomers are prepared by the nitration (qv) of toluene [108-88-3] and subsequent hydrogenation (see Amines by reduction). These materials are converted to the isocyanate, in the majority of the commercial aromatic isocyanate phosgenation processes, using a two-step approach.



(21) **(22)**

In the first step, a solution of amine is mixed with a solution of phosgene. An excess of phosgene is needed to retard by-product formation. The solvents most commonly used in the phosgenation reaction include toluene, xylene, halobenzenes, and decahydronapthalene [91-17-8]. The halobenzenes are preferred because of their polarity. In the second step, the resulting carbamoyl chloride–amine hydrochloride slurry reacts with excess phosgene at temperatures in excess of 100°C to yield the isocyanate. The appearance of a clear solution signals the end of the reaction. Distillation of the solvent followed by fractional crystallization, fractional distillation, or sublimation affords pure isocyanate. Typical process flow sheets for the phosgenation of toluene diamine (TDA) and polymeric methylene dianiline (PMDA), respectively, are shown in Figures 3 and 4.

An excess of phosgene is used during the initial reaction of amine and phosgene to retard the formation of substituted ureas. Ureas are undesirable because they serve as a source for secondary product formation which adversely affects isocyanate stability and performance. By-products, such as biurets **(23)** and triurets **(24)**, are formed via the reaction of the labile hydrogens of the urea with excess isocyanate. Isocyanurates (**25**, R = phenyl, toluyl) may subsequently be formed from the urea oligomers via ring closure.

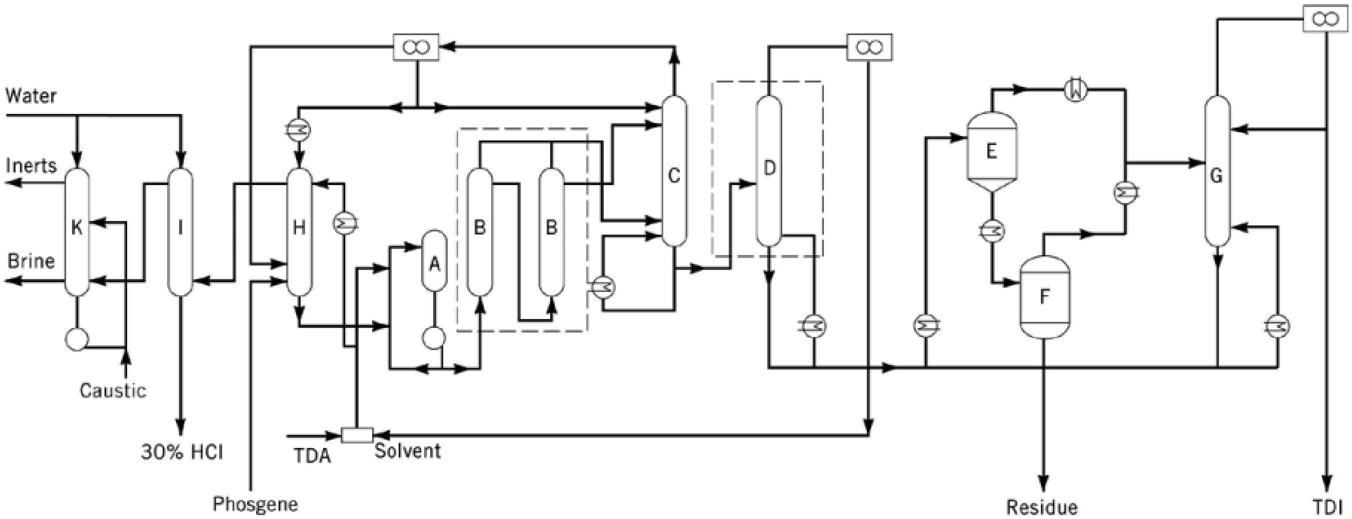


Fig. 3. Schematic of toluene diamine phosgenation process: A, cold phosgenator; B, hot phosgenator; C, wash column; D, solvent distillation; E, preflasher; F, evaporator; G, TDI distillation; H, phosgene removal; I, HCl absorber; and K, phosgene decomposition.

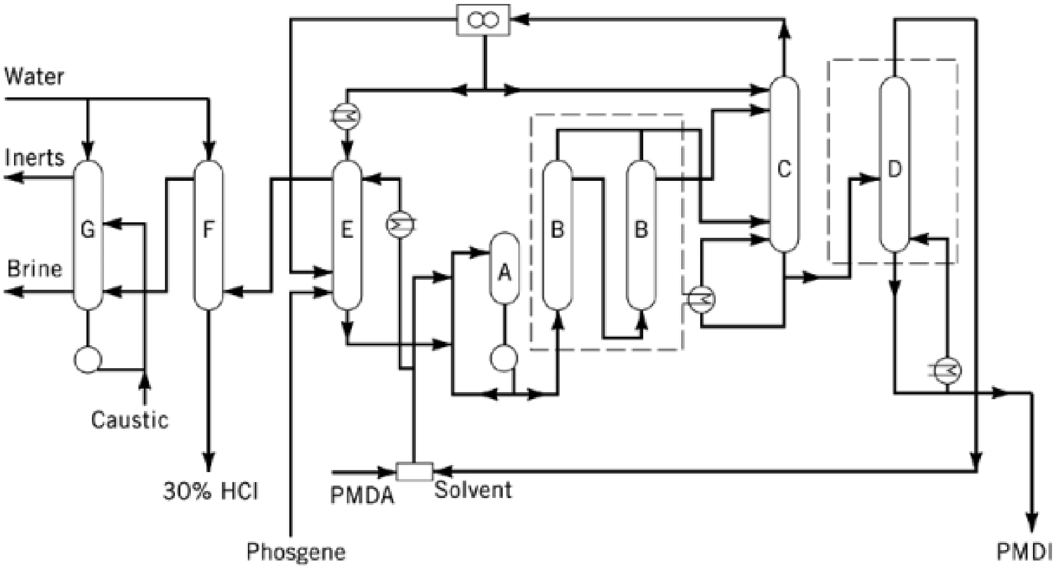
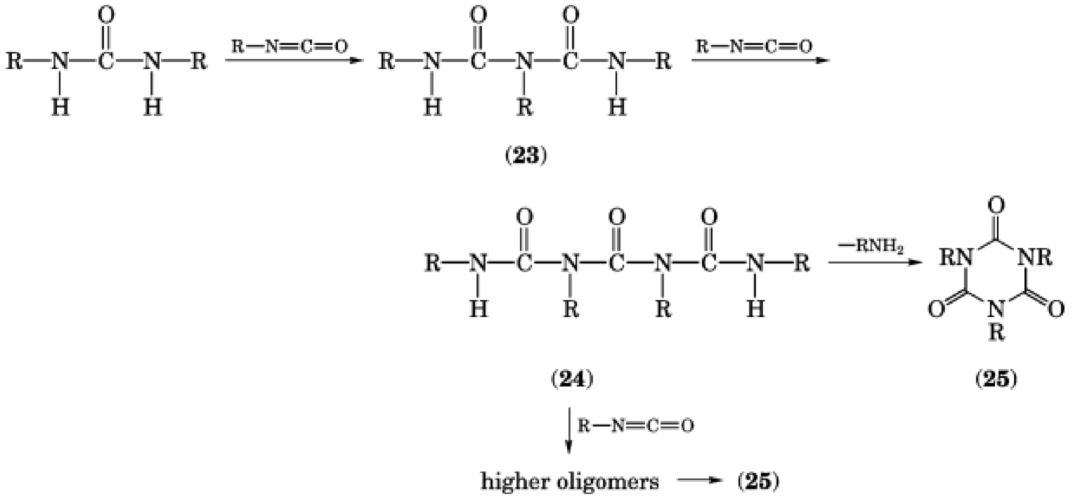


Fig. 4. Schematic of polymeric methylene dianiline phosgenation process: A, cold phosgenator; B, hot phosgenator; C, wash column, D, solvent distillation; E, phosgene removal; F, HCl absorber; and G, phosgene decomposition.



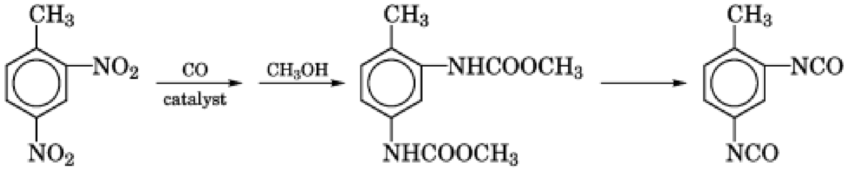
These oligomerization steps result in a continuous increase in viscosity of the desired isocyanate and ultimately cause solidification.

The *in situ* generated disubstituted ureas 5 also react with phosgene to yield thermally unstable allophanoyl chlorides 5 and chloroformamides 5 (75). As shown in Figure 5, the allophanoyl chlorides eliminate hydrogen chloride to form the isocyanate. The chloroformamides, however, yield chloroformamidine-*N*-carbonyl chloride 5, which decomposes to yield both carbodiimides 5 and isocyanide dichlorides 5. The carbodiimides simply contribute to yield loss. The isocyanide dichlorides, although present in small amounts, are a contributor to chlorine-containing impurities which detrimentally affect product performance.

Alternatively, the aromatic amine can first be treated with hydrogen chloride to form a slurry of amine salts, which is subsequently phosgenated. The slurry is processed using a temperature staged reaction sequence. Excess hydrogen chloride and phosgene are vented to retard the formation of isocyanate recombination products. The isocyanate is purified via solvent separation and fractionation. This method has the disadvantage that gaseous phosgene reacts very slowly with the suspended amine salt; thus, high temperatures and pressures are generally needed.

Some of these isocyanates are commercially available in derivatized form, such as biurets and carbodiimides, to provide materials having improved handling or processing characteristics.

Attempts have been made to develop methods for the production of aromatic isocyanates without the use of phosgene. None of these processes is currently in commercial use. Processes based on the reaction of carbon monoxide with aromatic nitro compounds have been examined extensively (23, 27, 76). The reductive carbonylation of 2,4-dinitrotoluene [121-14-2] to toluene 2,4-dialkylcarbamates is reported to occur in high yield at reaction temperatures of 140–180°C under 6900 kPa (1000 psi) of carbon monoxide. The resultant carbamate product distribution is noted to be a strong function of the alcohol used. Mitsui-Toatsu and Arco have disclosed a two-step reductive carbonylation process based on a cost effective selenium catalyst (22, 23). A typical reaction sequence for the production of TDI is as follows.



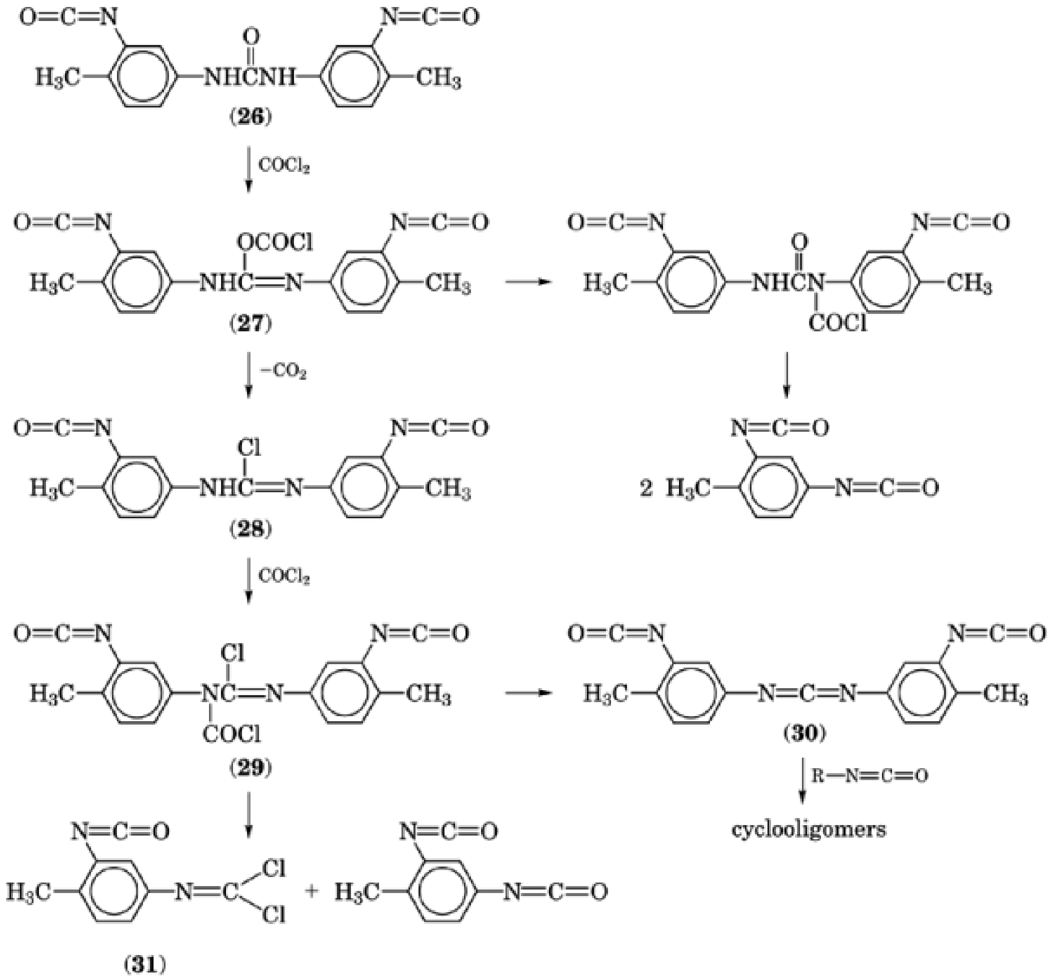
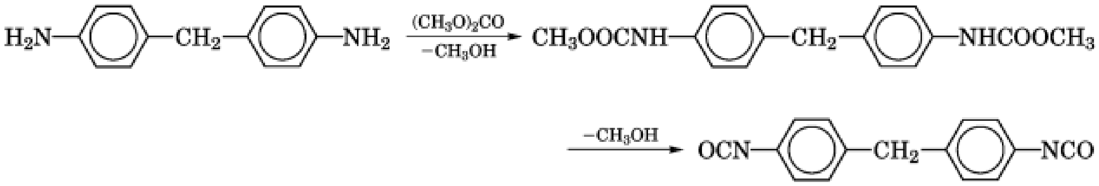


Fig. 5. Reactions of disubstituted ureas.

Two-step approaches based on cocatalysts or alternate catalysts and one-step approaches which circumvent the formation of the biscarbamate intermediates have also been reported (76–81).

Other approaches have explored the reaction of amines with dimethyl carbonate or its precursors (28). A reaction scheme for the production of polymeric MDI is as follows:



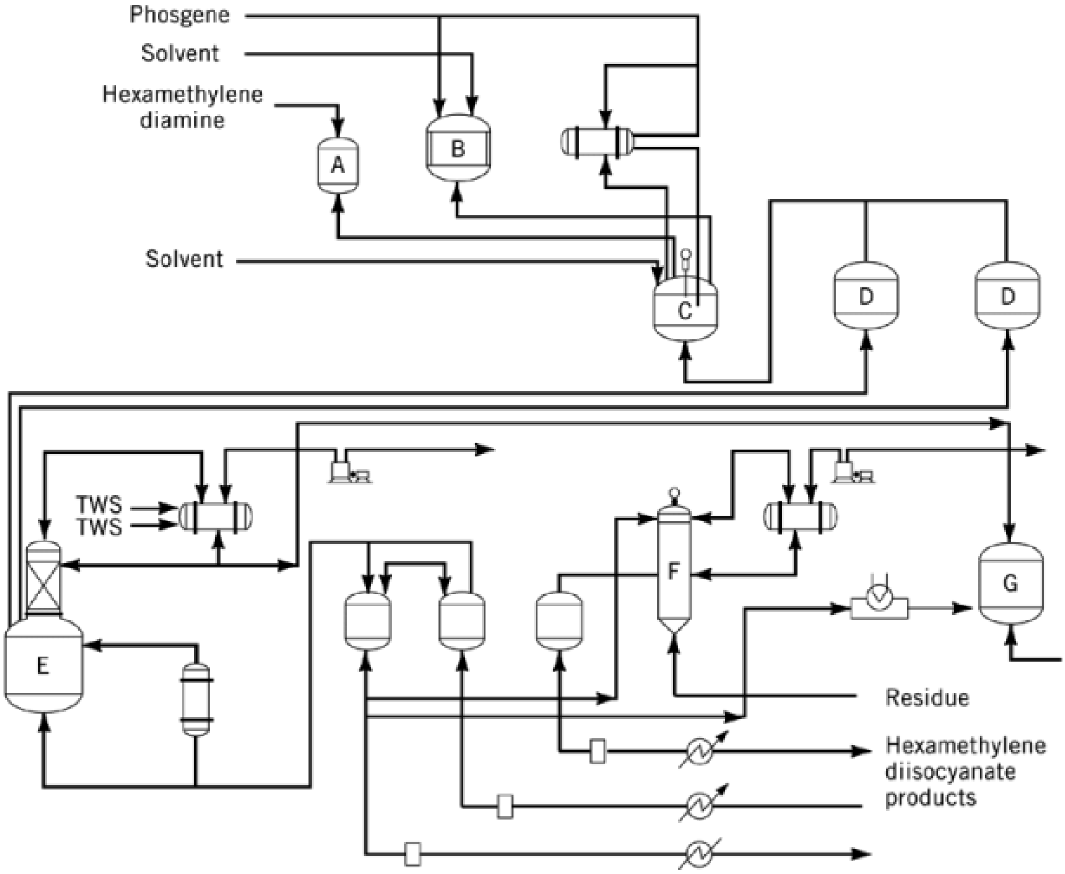


Fig. 6. Schematic of hexamethylene diamine phosgenation process: A, HMDA tanks; B, phosgene solution tanks; C, phosgenation reactor; D, secondary reactors; E, batch still; F, thin-film evaporator; and G, solvent receiver.

This approach is complicated by the fact that the isocyanate is produced via the thermolytic cleavage of the methyl carbamate. Reactions with the unconverted carbamate cannot be prevented. Much effort has been focused on improving the selectivity of the latter step.

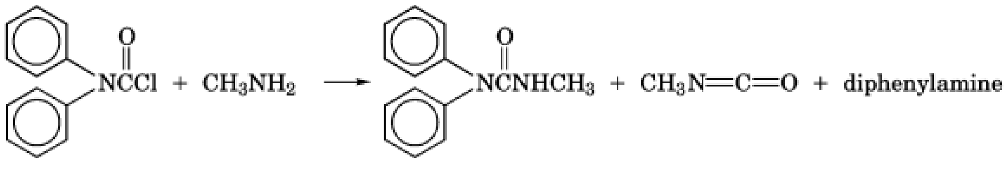
3.2. Aliphatic Isocyanates

Conventional aliphatic isocyanates have historically been manufactured using the hydrogen chloride salt slurry approach. Exceptions to this are the longer chain aliphatics which, due to the increased solubility, have reaction rates conducive to the free amine process (82). In the hydrogen chloride salt approach, a fine slurry of salt reacts with phosgene in an agitated autoclave. The reaction must be carried out at temperatures below 150°C to avoid the formation of chlorinated monoisocyanates as anhydrous hydrogen chloride has been found to displace isocyanate groups. Similar to the aromatic isocyanate processes described, the carbamate salt suspension is treated with phosgene using a series of reactors (9). Typically, the amine salt–phosgene reaction is carried out at a temperature of 30°C for 12–24 hours, then finished using a series of 100°C digestion steps. The resultant isocyanate solution is purified by solvent stripping followed by fractional vacuum distillation. A typical process flow sheet for the phosgenation of hexamethylene diamine [124-09-4] is shown in Figure 6.

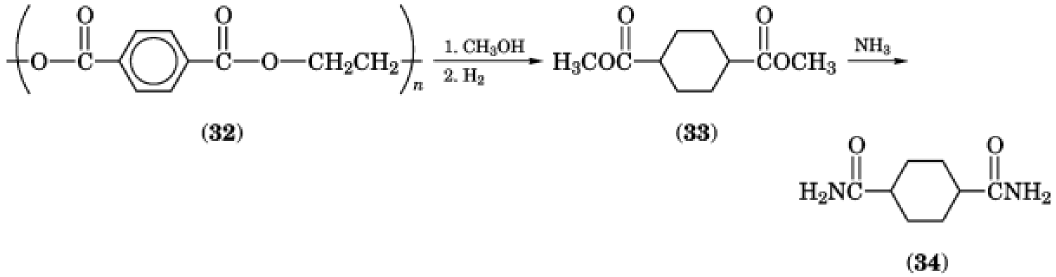
An alternative approach, generally referred to as a two-phase phosgenation, has gained wide scale acceptance for the production of aliphatic isocyanates (82, 83). Typically, a cooled solution of phosgene and amine are mixed in the presence of concentrated sodium hydroxide [1310-73-2]. Reaction rates are very fast and overall product yields exceed 90%. Refinements in the reaction conditions have reduced the by-product formation arising from the reaction of the hydroxide with phosgene to less than 10%. This approach allows for the preparation of isocyanates containing labile groups, such as alkoxy (RO), which would be lost in a traditional high temperature, amine–hydrogen chloride salt phosgenation (39).

Low boiling isocyanates, such as methyl isocyanate [624-83-9], are difficult to prepare via conventional phosgenation due to the fact that the *N*-alkyl carbamoyl chlorides are volatile below their decomposition point. Interestingly, *N*-ethyl carbamoyl chloride decomposes at its boiling point whereas the *N*-propyl carbamoyl chloride is thermolyzed cleanly into isocyanate and hydrogen chloride.

A convenient method for the synthesis of these low boiling materials consists of the reaction of *N,N′*-dimethylurea [96-31-1] with toluene diisocyanate to yield an aliphatic–aromatic urea (84). Alternatively, an appropriate aliphatic–aromatic urea can be prepared by the reaction of diphenylcarbamoyl chloride [83-01-2] with methylamine. Thermolysis of either of the mixed ureas produces methyl isocyanate in high yield (3, 85).

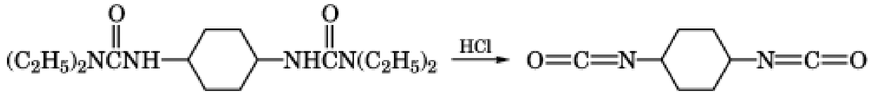


Akzo has been instrumental in developing a new process for the stereospecific synthesis of *trans*-1,4-cyclohexane diisocyanate [7517-76-2] (21). This process, based on the conversion of poly(ethylene terephthalate) [25038-59-9], circumvents the elaborate fractional crystallization procedures required for the existing *p*-phenylenediamine [108-45-2] approaches. The synthesis starts with poly(ethylene terephthalate) (PET) **(32)** or phthalic acid, which is converted to the dimethyl ester and hydrogenated to yield the cyclohexane-based diester **(33)**. Subsequent reaction of the ester with ammonia provides the desired bisamide **(34)**. The synthesis of the amide is the key to the selectivity of this route. Typically, dimethyl 1,4-cyclohexane dicarboxylate [94-60-0] **(33)** is dissolved in a solvent. Ammonia is introduced. Methyl alcohol is removed by cracking and distillation. The desirable trans-amide is noted to precipitate upon prolonged reflux under an ammonia atmosphere.



(32) **(33)** **(34)**

Subsequent chlorination of the amide takes place in a two-phase reaction mixture (a dispersion of diamide in hydrochloric acid) through which a chlorine stream is passed. The temperature of this step must be maintained below 10°C to retard the formation of the product resulting from the Hofmann degradation of amides. Reaction of the *N*,*N*-dichloroamide with diethylamine [109-89-7] in the presence of base yields *trans*-1,4-cyclohexane-bis-1,3-diethylurea **(35)**, which is transformed to the urea hydrochloride and pyrolyzed to yield the diisocyanate **(36)**.



(35) **(36)**

More recently, other nonphosgene routes for the preparation of aliphatic isocyanates have been reported. For example, American Cyanamid has disclosed the reaction of diisopropenylbenzene with HCl and isocyanic acid [75-13-8] to yield tetramethylxylylene diisocyanates (57).

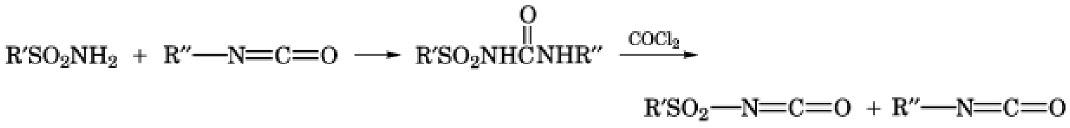
Monsanto has disclosed the use of carbon dioxide–amine complexes which are dehydrated, at low temperatures, with phosphoryl chloride [10025-87-3] or thionyl chloride [7719-09-7], as a viable route to a variety of aliphatic isocyanates. The process relies on the facile formation of the intermediate salt (30).REPLACEVariations of this process, in which phosgene is used as a dehydrating agent, have been reported earlier (84). Table 2 lists commercially available aliphatic isocyanates.

3.3. Specialty Isocyanates

Acyl isocyanates, extensively used in synthetic applications, cannot be directly synthesized from amides and phosgene. Reactions of acid halides with cyanates have been suggested. However, the dominant commercial process utilizes the reaction of carboxamides with oxalyl chloride [79-37-8]. Cyclic intermediates have been observed in these reactions which generally give a high yield of the desired products (86).

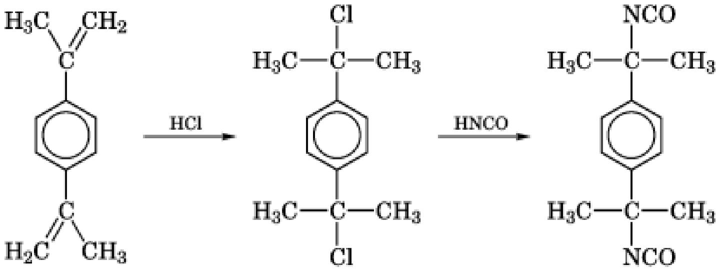
$$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2 + (COCl)_2 \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}N{=}C{=}O$$

Commercially important arenesulfonyl isocyanates are not directly accessible from the corresponding sulfonamides via phosgenation due to lack of reactivity or by-product formation at elevated temperatures. A convenient method for their preparation consists of the reaction of alkyl isocyanates with sulfonamides to produce mixed ureas which, upon phosgenation, yield a mixture of alkyl and arenesulfonyl isocyanates. The desired product can be obtained by simple distillation (16). Optionally, the oxalyl chloride route has been employed for the synthesis of arenesulfonyl isocyanate (87).



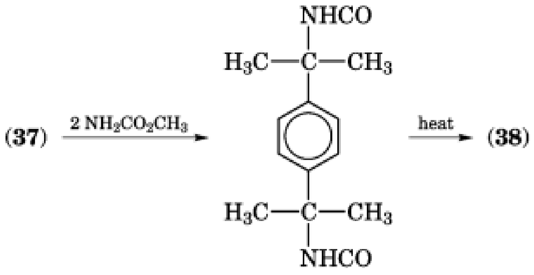
$$R'SO_2NH_2 + R''{-}N{=}C{=}O \longrightarrow R'SO_2NH\overset{O}{\overset{\|}{C}}NHR'' \xrightarrow{COCl_2} R'SO_2{-}N{=}C{=}O + R''{-}N{=}C{=}O$$

Of the many other methods leading to isocyanates, only a few are practical enough in regard to availability of starting materials to be of general applicability. One of the more promising approaches utilizes olefinic substrates which add isocyanic acid in Markovnikov fashion to form alkyl isocyanates (2, 9, 87). This reaction is used to produce 1,4-bis(2-isocyanatoisopropyl)benzene **(38)** from cumene [98-82-8] **(37)** in commercial quantities (22, 57, 88). One approach uses the slow addition of the olefin to an excess of solvent and isocyanic acid in the presence of a catalytic amount of inorganic acid (57, 88). Reaction temperatures are preferably maintained between 25 and 80°C. In the case of a diolefin, such as diisopropenylbenzene, the reaction can be controlled to favor the production of either the mono- or the diisocyanate by controlling the stoichiometry of the isocyanic acid in the reaction mixture. Another approach involves the formation of the dichloro intermediate. The dichloro compound reacts at low temperatures with an excess of isocyanic acid in the presence of a Lewis acid.



(37) **(38)**

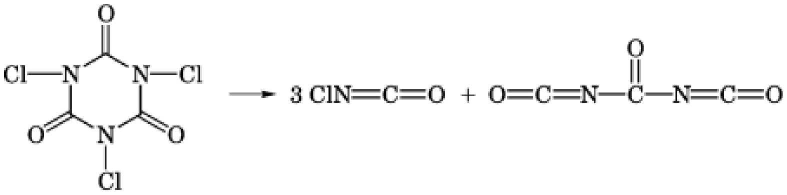
An alternative approach involves the reaction of an alkyl carbamate with a tertiary olefin (89, 90). The resultant carbamates are thermally cracked at temperatures of 150–350°C to yield the isocyanate. The isocyanate is generally purified via distillation.



The exchange of halogen by isocyanato groups has also been suggested as a method of preparing isocyanates from chloro- or bromoalkanes (10). Metal cyanates are the reagents of choice for these exchange reactions which often entail the formation of oligomers of the desired isocyanates. For example, ethyl isocyanate [109-90-0] can be prepared in 90% yield by the reaction of ethyl bromide [74-96-4] with potassium isocyanate (91, 92).REPLACE

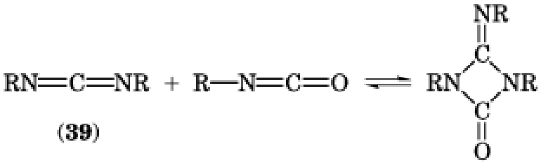
The use of polar solvents, such as *N,N*-dimethylformamide [68-12-2], is noted to result in extensive trimer formation. However, if the isocyanate is trapped using compounds such as alcohols, carboxylic acids, and amines which contain active hydrogen, high yields are obtained (93).

Pyrolysis approaches can also be used to prepare substituted isocyanates which cannot be prepared using other methods. For example, *N,N′,N″*-trichlorocyanuric acid [87-90-1] thermally dissociates to yield chloroisocyanate [13858-09-8] and carbonyl diisocyanate [6498-10-8]. The carbonyl isocyanate is unstable and polymerizes (8, 94). Table 3 lists specialty isocyanates.



3.4. Carbodiimide Formation

Carbodiimide formation has commercial significance in the manufacture of liquid MDI. Heating of MDI in the presence of catalytic amounts of phosphine oxides or alkyl phosphates leads to partial conversion of isocyanate into carbodiimide (95). The carbodiimide **(39)** species reacts with excess isocyanate to form a $2+2$ cycloaddition product. The presence of this product in MDI leads to a melting point depression and thus a mixture which is liquid at room temperature.



4. Analytical Methods

Organic isocyanates are generally characterized with respect to NCO content. A number of spectroscopic and chemical methods for isocyanate determination are available (96).

Isocyanates can be characterized using a strong absorption at $2300-2200\ \mathrm{cm}^{-1}$ in the ir spectrum. The position of the absorbance is influenced by conjugation and neighboring polar groups. This method has been successfully used in both kinetic and post-mortem characterizations of many polyurethane polymers.

Titrations with dibutylamine [111-92-2] can also be used to determine the NCO content of isocyanates and prepolymers. Generally, an excess of amine in a suitable solvent such as chlorobenzene [108-90-7] is added to the sample. The resulting solution is allowed to react and the unreacted amine is back- titrated with dilute hydrochloric acid. For low NCO content levels, a colorimetric method is often used. The isocyanate-containing species is titrated with amine and the unreacted amine is determined using malachite green [569-64-2].

Both vapor-phase chromatography and high performance liquid chromatography, along with nuclear magnetic resonance spectroscopy, have been used for isomer and composition analysis.

5. Health and Safety Factors

Isocyanates are classified as dangerous substances (EEC Guidelines). They are generally labeled toxic and should be handled with care (97). Exposure hazards increase substantially when handling vapors or mists. Isocyanate vapors or mists may be irritating to the nose, throat, and lungs. Even brief exposure may cause irritation, difficult breathing, or coughing. Sensitization may result from excessive exposure. Subsequent exposure to low concentrations has been known to provoke allergic reactions with asthma-type symptoms. Industrially, this is important because MDI-based isocyanates, although having a low vapor pressure, can become airborne during machine flushing and filling procedures. Conversely, toluene diisocyanate (TDI) has a relatively high vapor pressure at ambient temperatures and a vapor density six times that of air. Thus open containers have the potential to yield high concentrations of TDI vapor. Also, many aliphatic isocyanates have high vapor pressures and must, therefore, be handled with special caution. Inhalation of aliphatic isocyanates is reported to retard the growth of laboratory mice (98). A compilation of toxicity information for several of the more common commercial isocyanates is presented in Table 4.

Repeated or prolonged skin contact may cause irritation, blistering, dermatitis, or skin sensitization. Contact with the eye has been reported to cause irritations in testing with rabbits. For these reasons, isocyanates must be handled in well-ventilated areas. Respirators should be worn whenever the possibility of vapor

Table 4. Acute Toxicity of Diisocyanates in Rats

Isocyanate	LC_{50} (rat oral), g/kg	LC_{50} (rat inhalation[a]), ppm	Concentration in air, ppm (STP)
TDI	5,800	110	19.6
MDI	$> 31,600$	370	0.1
IPDI	$> 2,500$	123	0.34
HDI	0.35–1	44–370	
PDI	0.9		
NDI[b]	$> 10,000$		[c]

[a] Aerosol, 4 h.
[b] Naphthalene-1,5-diisocyanate.
[c] Negligible vapor pressure at 50°C.

exposure exists. If inhalation occurs, the affected person should be moved to a well-ventilated area. Chemical goggles should be worn when handling isocyanates. All work areas should be equipped with an eye wash. In the event of eye contact, the eye should be irrigated immediately. The eyes should be held open while flushing with a continuous low pressure stream of water for at least 15 minutes. In the event of direct skin contact, use a safety shower immediately, removing all clothing while washing. In all cases, call a physician immediately.

The most overlooked hazard and contaminant is water (99). Water reacts with isocyanates at room temperature to yield both ureas and large quantities of carbon dioxide. The presence of water or moisture can produce a sufficient amount of CO_2 to overpressurize and rupture containers. As little as 30 mL of water can result in 40 L of carbon dioxide which could result in pressures of up to 300 kPa (40 psi). For these reasons, the use of dry nitrogen atmospheres is recommended during handling. If a plant air system must be used, purification equipment, such as oil traps and drying beds, should be installed between the source and the isocyanate vessel.

Also, the presence of strong bases, even in trace amounts, can promote the formation of isocyanurates or carbodiimides. In the event of gross contamination, the exothermic reaction can sharply increase the temperature of the material. Normally, the trimerization reaction occurs first and furnishes heat for the carbodiimide reaction. The carbodiimide reaction liberates carbon dioxide and forms a hard solid. The liberation of carbon dioxide in a sealed vessel could result in overpressurization and rupture.

Temperature control is important in the handling and storage of isocyanates. Storage at inappropriate temperatures can cause product discoloration, viscosity increases, and dimerization. Handling personnel should consult the technical data sheets for the recommended storage temperature of the specific isocyanate product.

Most commercial isocyanates have a high flash point and are classified as Class IIIB combustible liquids. These materials, however, burn in the presence of an existing fire or heat source in the presence of oxygen. In the event of an isocyanate fire, use a carbon dioxide or dry chemical extinguisher. For fires covering large areas, use of a protein foam or water spray is recommended. Personnel engaged in fighting isocyanate fires must be protected against nitrogen dioxide vapors and isocyanate fumes. Firefighters should wear approved positive pressure, self-contained breathing apparatus and fire-resistant clothing.

6. Economic Aspects and Applications

Since 1971, the overall demand for isocyanates has increased at a compounded rate of 12%. Although this level will not likely be sustained in the future due to the maturation of key application markets, it is probable that additional growth will occur through the year 2000. This trend will likely include a shift in emphasis from TDI to MDI and polymeric MDI-based materials. New growth opportunities in the construction industry, structural

Table 5. 1993 Isocyanate Product Capacities, 10^3 t

Region	TDI	MDI	PMDI	Aliphatic
North America				
BASF	95	12.5	100	
Dow	70	40.5	163.5	
ICI (Rubicon)	32.5	25	150	
Miles	132.5	35	167.5	16
Olin	110			
Total	*485*	*113*	*592.5*	*24.5*
Europe				
ICI		11.5	142.5	
BASF	17.5	29.5	173	pilot
Bayer	206	67.5	298.5	10
Montedipe	121	3.5	88	
Rhône-Poulenc	126.5			5
Dow		39.5	181.5	
Total	*530*	*176.7*	*905*	*27.5*
Pacific				
Korea Fine Chemical	27.5			
Mitsui Toatsu	61		60.5	0.2
Takeda	82.5			0.6
BASF		12.5	30	
Dow Mitsubishi		14	15.5	
Nippon Polyurethanes		20	110	
Sumitomo Bayer		12.5	41	
Sunghua		11.5	27	
Total	*308*	*77.5*	*306*	*3.3*
Latin America				
Pronor	70.5		22	
Bayer	13		22	
Total	*102.5*	*7.5*	*44*	

applications, and growth in the automotive industry exist. Third-world markets are also anticipated to provide growth opportunities.

Globally, BASF, Bayer (Miles in North America), Dow, and ICI historically have been the leading producers of aromatic isocyanates. In North America, Olin is a principal supplier of TDI and aliphatic isocyanates. Rhône-Poulenc and Hoechst are principal suppliers in Europe. A listing of all the principal global suppliers and their respective products and trade names is presented in Tables 5 and 6. A breakdown of isocyanate demand by region is presented in Table 7.

6.1. Aromatic Isocyanates

In North America, aromatic isocyanates are heavily used as monomers for addition and condensation polymers. The principal applications include both flexible and rigid polyurethane foam and noncellular applications, such as coatings, adhesives, elastomers, and fibers.

In the North American flexible foam market, toluene diisocyanate, an 80:20 mixture of the 2,4- and 2,6-isomers, is the monomer of choice due to its low cost and general availability. In both Europe and Japan, MDI blends and prepolymers are finding increased usage. Prepolymers are an adduct or reaction intermediate of a polyol and a monomeric isocyanate. The reaction of the isocyanate and a polyalkylene oxide polyol is the primary reaction which forms the matrix. Density reduction is provided via the *in situ* generation of

Table 6. Trademarks for Global Isocyanate Manufacturers

Manufacturer	Trademark	Region
Akzo	Elate	North America
Bayer	Desmodur	Europe
BASF	Ekanate	North America
BASF	Lupranat	Europe
BASF-Schwarzheide	Systanat	Europe
Cariosa	Cortume	Europe
Dainippon	Sothanate	Pacific
Dainichi Saika	Resamine	Pacific
Dow	Isonate	North America
Dow	Voranate	North America
ICI	Suprasec	Europe
Interchem	Prepol	Europe
Lancro	Quasilan	Europe
Lancro	Isocon	Europe
Miles	Multrathane	North America
Miles	Mondur	North America
Montedison	Tedimon	Europe
Olin	Olin-TDI	North America
Polymer Chemicals	Polidur	Europe
Reichold	Polylite	North America
Rheinchemie	Rhenodur	Europe
Rhône-Poulenc	Scurane	Europe
Rhône-Poulenc	Tolonate	Europe
Rubicon	Rubinate	North America
Shell	Caradate	Europe
Takeda	Takenat	Europe
Thanex	Poronat	Europe
Thiokol	Solithane	North America

Table 7. 1990 Regional Demand for Polyurethane Polymers, 10^3 t

Item	North America[a]	Europe	Pacific
flexible foams furniture/bedding transportation other	940	1127	510
rigid foams appliance building/construction	450	405	177
elastomers[b] automotive RIM footwear	143	111	102
elastomers/coatings/adhesives[c]	234	268	219
other[d]	106	183	148
Total	*1873*	*2094*	*1156*

[a] Includes Latin America.
[b] Includes thermoplastic urethanes and synthetic leather.
[c] Includes paints.
[d] Includes fibers, marine flotation, film, and textiles.

carbon dioxide which arises from the simultaneous water–isocyanate reaction. Optionally, graft copolymers and auxiliary blowing agents can be used. Flexible foams can be produced using either a continuous or molded procedure. The products from the continuous process (buns) are cut to shape for the particular application, while the molded foams are formed to shape during the molding process. The density of the continuous buns is traditionally between $16 - 32\ \mathrm{kg/m^3}\ (1 - 2\ \mathrm{lbs/ft^3})$. Molded foams have densities greater than $32\ \mathrm{kg/m^3}$. Flexible foams find applications as automotive cushions, carpet underlay, furniture, seating, and bedding.

Rigid foams are based primarily on polyfunctional, low molecular weight alcohols and amines. Most global applications conventionally use polymeric isocyanates, TDI, or an undistilled grade of mixed TDI isomers. TDI prepolymers which have hydroxyl and isocyanate groups have been marketed as a low vapor pressure alternative to undistilled TDI. Density reduction is effected via the addition of chlorofluorocarbons, low molecular weight alkanes, or via the *in situ* generation of carbon dioxide. The resultant closed cell foams find applications as insulators in construction, appliance, transportation, pipeline, and tank end uses.

Similarly, polyisocyanurate (PIR) rigid foams are based on PMDI and polyester or polyether polyols (and blends thereof). The cross-link density, aromatic content, cell wall thickness, and polymer distribution are known to have a pronounced effect on the overall performance of the foam. Polyisocyanurate foams are used extensively in industrial applications having service temperature ranges from -200 to 150°C. These foams are known to provide efficient thermal insulation characteristics and structural integrity to a variety of composite applications. Apart from roofing and sheathing, PIR foams are used in garage doors, building panels, and foaming applications. They can also be supplied in the form of boardstock for fabrication into sheets, pipe covering, and other shapes.

Adhesives and coatings formulations utilize both MDI and TDI along with a variety of polyether and polyester polyols. The largest segment of the business is the one-part or moisture-cured approach, which is heavily reliant on prepolymers. Optionally, blocked isocyanate technology may be used to provide systems having an extremely long shelf life. Suitable blocking agents include phenols, diethyl malonate [105-53-3], acetone oxime [127-06-0], and ϵ-caprolactam [105-60-2]. Typical applications include flexible film packaging and wood furniture assembly. Two-part reactive adhesives employ a mixture of pure isocyanates and prepolymers and are primarily used for industrial product assembly and commercial construction.

Elastomers are segmented block copolymers. They employ a mixture of pure MDI-based isocyanates and prepolymers. The hard blocks consist of high melting MDI–glycol units which aggregate via hydrogen bonding to provide a high degree of virtual cross-linking. Suitable glycols include ethylene glycol [107-21-1], butanediols, and hexanediols. The soft block consists of high molecular weight poly(alkylene oxide) polyols. These materials are noted for their resiliency, abrasion resistance, solvent resistance, and the high level of tensile, tear, and elongation performance. Applications include shoe soles, wheels, rollers, belts, gaskets, and thermoplastic polyurethanes. Methylene diphenyl diisocyanate (MDI) is used extensively in the production of Spandex fibers. Spandex is used in foundation garments and swimwear (see Fibers, elastomeric). Typical demand for various applications is presented in Table 7.

6.2. Aliphatic Isocyanates

Aliphatic diisocyanates have traditionally commanded a premium price because the aliphatic amine precursors are more expensive than aromatic diamines. They are most commonly used in applications which support the added cost or where the long-term performance of aromatic isocyanates is unacceptable. Monofunctional aliphatic isocyanates, such as methyl and *n*-butyl isocyanate, are used as intermediates in the production of carbamate-based and urea-based insecticides and fungicides (see Fungicides, agricultural; Insect control technology).

A number of markets have been established for light-stable, aliphatic diisocyanates in the United States. The largest market is in high performance coatings (see Coatings). The largest coatings market is in automotive refinishes. Other coatings include uv-cured coatings for vinyl tile and sheet flooring, electronic circuit boards, powder coatings, and paints. Hydrogenated MDI (H_{12}MDI), *m*-xylylene diisocyanate (XDI), and isophorone diisocyanate [4098-71-9] are currently used in many of these coating applications.

Aliphatic isocyanates have a small but growing market application in thermoplastic polyurethanes (TPU). Medical applications include wound dressings, catheters, implant devices, and blood bags. A security glass system using light-stable TPU as an inner layer is under evaluation for shatterproof automotive windshield applications.

Developments in aliphatic isocyanates include the synthesis of polymeric aliphatic isocyanates and masked or blocked diisocyanates for applications in which volatility or reactivity are of concern. Polymeric aliphatic isocyanates are made by copolymerizing methacrylic acid derivatives, such as 2-isocyanatoethyl methacrylate, and styrene [100-42-5] (100). Blocked isocyanates are prepared via the reaction of the isocyanate with an active hydrogen compound, such as ϵ-caprolactam, phenol [108-95-2], or acetone oxime.

6.3. Specialty Isocyanates

Specialty isocyanates are organic isocyanates having the isocyanate function attached to a carbonyl group or to elements other than carbon. This group is appropriately named because they find use in highly specialized applications. *p*-Toluenesulfonyl isocyanate [4083-64-1] is used as a drying agent for organic solvents. Arenesulfonyl diisocyanates, such as *m*-phenylenedisulfonyl diisocyanate, are used as monomers for base-soluble polymers. Arenesulfonyl monoisocyanates are used as intermediates for pharmaceuticals and herbicides (see Herbicides; Pharmaceuticals).

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