

AMINES, LOWER ALIPHATIC AMINES

1. Introduction

Lower aliphatic amines are derivatives of ammonia with one, two, or all three of the hydrogen atoms replaced by alkyl groups of five carbons or fewer. Amines with higher alkyl groups are known as fatty amines. The names, chemical formulas, molecular weights, CAS Registry Numbers, and common names or abbreviations of commercially important amines are given in Table 1. Amines are toxic,

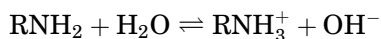
Table 1. **Commercial Lower Aliphatic Amines**

Alkylamine	CAS Registry Number	Molecular Formula	Molecular Weight	Synonym or common abbreviation
Ethylamines				
ethylamine	[75-04-7]	C ₂ H ₇ N	45.08	monomethylamine, aminomethane, MEA
diethylamine	[109-89-7]	C ₄ H ₁₁ N	73.14	<i>N</i> -ethylethanamine, DEA
triethylamine	[121-44-8]	C ₆ H ₁₅ N	101.19	<i>N,N</i> -diethylethanamine, TEA
<i>n</i> -Propylamines				
<i>n</i> -propylamine	[107-10-8]	C ₃ H ₉ N	59.11	mono- <i>n</i> -propylamine, 1-aminopropane, 1-propanamine, MNPA
di- <i>n</i> -propylamine	[142-84-7]	C ₆ H ₁₅ N	101.19	<i>N</i> -propyl-1-propanamine, DNPA
tri- <i>n</i> -propylamine	[102-69-2]	C ₉ H ₂₁ N	143.27	<i>N,N</i> -dipropyl-1-propanamine, TNPA
iso-Propylamines				
isopropylamine	[75-31-0]	C ₃ H ₉ N	59.11	2-aminopropane, 2-propanamine-MIPA
diisopropylamine	[108-18-9]	C ₆ H ₁₅ N	101.19	<i>N</i> -(1-methylethyl)-2-propanamine, DIPA
Alkylamines				
allylamine	[107-11-9]	C ₃ H ₇ N	57.10	monoallylamine, 2-propenamine, 3-aminopropene

Table 1 (Continued)

Alkylamine	CAS Registry Number	Molecular Formula	Molecular Weight	Synonym or common abbreviation
diallylamine	[124-02-7]	C ₆ H ₁₁ N	97.16	<i>N</i> -2-propenyl-2-propenamine, di-2-propenylamine
triallylamine	[102-70-5]	C ₉ H ₁₅ N	137.23	<i>N,N</i> -di-2-propenyl-2-propenamine, tris(2-propenyl)amine
<i>n</i> -Butylamines				
<i>n</i> -butylamine	[109-73-9]	C ₄ H ₁₁ N	73.14	mono- <i>n</i> -butylamine, 1-aminobutane, MNBA
di- <i>n</i> -butylamine	[111-92-2]	C ₈ H ₁₉ N	129.25	<i>N</i> -butyl-1-butanamine, DNBA
tri- <i>n</i> -butylamine	[102-82-9]	C ₁₂ H ₂₇ N	185.36	<i>N,N</i> -dibutyl-1-butanamine, TNBA
Isobutylamines				
isobutylamine	[78-81-9]	C ₄ H ₁₁ N	73.14	monoisobutylamine, 2-methyl-1-propanamine, 1-amino-2-methylpropane, 1-aminobutane, MIBA
diisobutylamine	[110-96-3]	C ₈ H ₁₉ N	129.25	2-methyl- <i>N</i> -(2-methylpropyl)-1-propanamine, DIBA
triisobutylamine	[1116-40-1]	C ₁₂ H ₂₇ N	185.36	2-methyl- <i>N,N</i> -bis(2-methylpropyl)-1-propanamine, TIBA
<i>sec</i> -Butylamine				
<i>sec</i> -butylamine	[13952-84-6]	C ₄ H ₁₁ N	73.14	2-aminobutane, 2-butanamine, 1-methylpropanamine
<i>tert</i> -Butylamine				
<i>tert</i> -butylamine	[75-64-9]	C ₄ H ₁₁ N	73.14	2-methyl-2-propanamine, 2-aminoisobutane, 1,1-dimethylethanamine, trimethylaminomethane
Amylamines				
amylamine		C ₅ H ₁₃ N	87.17	mixture of 1-pentylamine and 2-methyl-1-butylamine
diamylamine		C ₁₀ H ₂₃ N	157.30	mixture of linear and branched isomers
triamylamine		C ₁₅ H ₃₃ N	227.44	mixture of linear and branched isomers
Mixed Amines				
dimethylethylamine	[598-56-1]	C ₄ H ₁₁ N	73.14	<i>N,N</i> -dimethylethanamine, <i>N</i> -ethyl-dimethylamine
dimethyl- <i>n</i> -propylamine	[926-63-6]	C ₅ H ₁₃ N	87.17	<i>N,N</i> -dimethyl-1-propanamine, propyldimethylamine
ethyl- <i>n</i> -butylamine	[13360-63-9]	C ₆ H ₁₅ N	101.19	<i>N</i> -ethyl-1-butanamine, butylethylamine, EBA
dimethyl- <i>n</i> -butylamine	[927-62-8]	C ₆ H ₁₅ N	101.19	<i>N,N</i> -dimethyl-1-butanamine, butyldimethylamine, DMBA

colorless gases or liquids, highly flammable, and have strong odors. Lower-molecular-weight amines are water soluble and are sold as aqueous solutions and in pure form. Amines react with water and acids to form alkylammonium compounds analogous to ammonia. The base strengths in water of the primary, secondary, and tertiary amines and ammonia are essentially the same, as shown by the equilibrium constants. Values of pK_a for some individual amines are given in Table 2.



Primary and secondary amines can also act as very weak acids ($K_a \sim 10^{-33}$). They react with acyl halides, anhydrides, and esters with rates depending on the size of the alkyl group(s). These amines react with carbon disulfide and carbon dioxide, to form alkyl ammonium salts of dithiocarbamic and carbamic acid, respectively. Substituted ureas are obtained upon reaction with isocyanic acid and alkyl or aryl isocyanates. The corresponding thioureas are prepared by reaction with isothiocyanate. Primary amines react with nitrous acid to give highly toxic nitrosamines (see *N-NITROSAMINES*). The lower aliphatic amines are widely used in the manufacture of pharmaceutical, agricultural, textile, rubber, and plastic chemicals.

2. Properties

2.1. Physical Properties. Table 2 lists the physical and chemical properties of the commercially important alkylamines (1–5). Thermodynamic data are available only for the lower alkylamines and are mainly estimates based on a few experimental determinations (6–7). Recently, quantum mechanics-based computational methods have been used to calculate equilibrium constants for amines systems (8–9). This methodology may find practical application as the product selectivities from many manufacturing processes appear to be limited by thermodynamic equilibria.

2.2. Chemical Properties. The chemistry of the lower aliphatic amines is dominated by their basicity and their nucleophilic character, which result from the presence of an unshared pair of electrons on the nitrogen atom. Due to their basicity, amines are often used as neutralization agents or pH adjusters. For example, tertiary amines, such as triethylamine may be used to neutralize inorganic acids liberated during alkylation reactions. The resulting trialkylammonium salt is water-soluble and therefore, is easily separated from the organic phase (10).

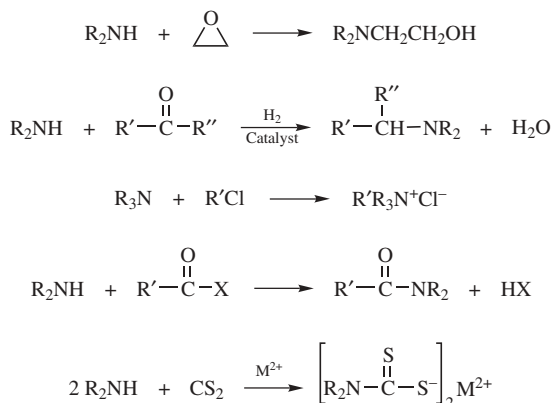
Amines react with a variety of substrates such as epoxides, aldehydes and ketones, alkyl halides, carboxylic acids/halides/esters/anhydrides, and carbon disulfide to produce products used in agricultural, pharmaceutical, textile, polymer, and rubber chemical applications. As shown in the following, respective products of these reactions are amines containing additional functionality (alkanolamines), amines containing additional alkyl groups, quaternary

Table 2. Alkylamine Physical and Chemical Properties

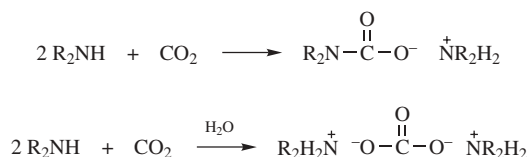
Alkylamine	Mp, °C	Bp, °C	Vapor pressure at 20°C, kPa	Density, gm/ ml at 20°C	Refractive index, 20°C	Water solubility, g/100 g H ₂ O at 20°C	p- <i>K_a</i> at 25°C
Ethylamines							
ethylamine	−81	16.6	116	0.68	1.3663	complete ^a	10.63
diethylamine	−50	55.9	25.9	0.700	1.3864	complete	11.09
triethylamine	−114	88.2	7.2	0.73	1.3980 ²⁵	11.24	10.72
<i>n</i> -Propylamines							
<i>n</i> -propylamine	−83	47.4	33.9	0.72	1.3882	complete	10.57
di- <i>n</i> -propylamine	−47	109.1	2.8	0.74	1.4043	5.30	10.91
tri- <i>n</i> -propylamine	−93	156.9	0.3	0.76	1.4160	0.022	10.66
Isopropylamines							
isopropylamine	−101	32.0	63.7	0.69	1.3771 ²⁵	complete	10.64
diisopropylamine	−96.3	83.0	8	0.72	1.3924	10.32 (30°C)	11.21
Allylamines							
allylamine	−88.2	55–58		0.76	1.4185	complete	9.52
diallylamine	−88	111–112		0.79	1.4405	11.64	9.29
triallylamine		155		0.81 (14°C)	1.4486	0.29	8.31
<i>n</i> -Butylamines							
<i>n</i> -butylamine	−47	77.1	9.6	0.74	1.3992 ²⁵	complete	10.64
di- <i>n</i> -butylamine	−61.9	156.2	0.3	0.76	1.4177	0.57	11.25
tri- <i>n</i> -butylamine	−70	212.6		0.78	1.4283	0.096	
Isobutylamines							
isobutylamine	−84.6	67.6	13.3	0.73	1.3972	complete	10.41
diisobutylamine	−77	140	1.3	0.74	1.4081	0.27	10.65
isobutylamine	<−24	183		0.77	1.4252	tracel	
<i>sec</i> -Butylamine	−72	63	20	0.73	1.3928	complete	10.56
<i>tert</i> -Butylamine	−70.0	44.4		0.69	1.3788	complete	10.68
Amylamines							
amylamine	−55	104		0.75	1.4110		
diamylamine				0.77	1.4258		
triamylamine				0.78	1.4360		
Mixed Amines							
dimethylethylamine	−140	36–38	8.1	0.67	1.3720	complete	
dimethyl- <i>n</i> -propylamine		65		0.71	1.3869		9.25
ethyl- <i>n</i> -butylamine		111	2.4	0.74	1.4050	5.06	10.96
dimethyl- <i>n</i> -butylamine		95		0.72	1.3970	3.52	10.1

^aUnder pressure.

ammonium salts, amides, and dithiocarbamates (11).

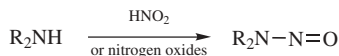


where R, R' = H or alkyl, X = RCO₂, OR, Cl, or OH. Reaction of primary or secondary amines with carbon dioxide produces amine carbamate salts under anhydrous conditions or amine carbonate salts in the presence of water:



The white solid material often observed on the caps of bottles containing amines typically results from amine carbamate formation due to reaction between the amine and carbon dioxide in the air. While tertiary amines do not form carbamates, they can react with carbon dioxide in aqueous solution to produce carbonate salts.

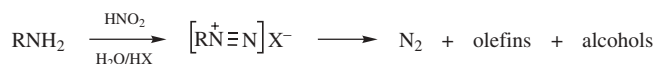
Reaction of secondary amines with nitrous acid or with nitrogen oxides present in air produces nitrosamines (11, 12), which are probable carcinogens. Nitrosamine formation is a concern in several applications that use secondary amines as raw materials. In the rubber industry, use of accelerators made from primary amines or from hindered secondary amines has been investigated as a means of eliminating or reducing formation of nitrosamines (13).



Nitrosamines also can be formed from tertiary amines in the presence of excess nitrous acid. An alkyl group is cleaved from the amine, and the secondary nitrosamine is obtained along with aldehyde or ketone. However, formation of nitrosamines as a result of contact of tertiary amines with nitrogen oxides contained in air is unlikely to occur.

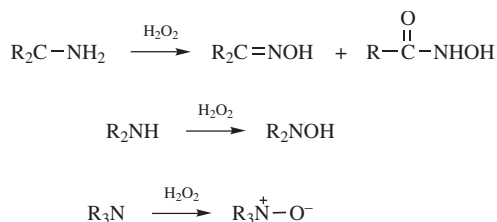


Primary amines do not form nitrosamines. Reaction of primary amines with nitrous acid leads to formation of unstable diazonium salts which decompose to olefins, alcohols (in the presence of water), and nitrogen.



Nitrosamines typically are not formed as by-products during manufacture of amines. Storage and use of secondary amines under a nitrogen atmosphere is an effective method of preventing nitrosamine formation.

Oxidation of amines with hydrogen peroxide or peracids gives a mixture of products from primary amines including hydroxamic acids and oximes, hydroxylamines from secondary amines via amine oxide intermediates, and amine oxides from tertiary amines (12).



Use of other oxidizing agents such as permanganate or manganese dioxide results in removal of hydrogen to give imines, enamines, or nitriles.

Alkylamines are corrosive to copper, copper-containing alloys (brass), aluminum, zinc, zinc alloys, and galvanized surfaces. Aqueous solutions of alkylamines slowly etch glass as a consequence of the basic properties of the amines in water. Carbon or stainless steel vessels and piping have been used satisfactorily for handling alkylamines.

3. Manufacture

Lower aliphatic amines can be prepared by a variety of methods, and from many different types of raw materials. By far the largest commercial applications involve the reaction of alcohol with ammonia to form the corresponding amines. Other methods are employed depending on the particular amine desired, raw material availability, plant economics, and the ability to sell coproducts. The following manufacturing methods are used commercially to produce the lower alkylamines:

Method 1. Alcohol amination: amination of an alcohol over a metal catalyst under reducing conditions or over a solid acid catalyst at high temperature.

Method 2. Reductive alkylation: reaction of an amine or ammonia and hydrogen with an aldehyde or ketone over a hydrogenation catalyst.

Method 3. Ritter reaction: reaction of hydrogen cyanide with an olefin in an acidic medium to produce a primary amine.

Table 3. Manufacturing Data for Aliphatic Amines

Company and Plant Location	Products	Capacity, t/yr	Method
<i>United States Producers</i>			
Air Products and Chemicals, Inc., Pace, Fla. & St. Gabriel, La.	C ₂ -C ₄	137,000	1
Celanese, Bucks, Ala. & Portsmouth, Va.	C ₂ -C ₄	25,500	1,4
Elf Atochem, Riverview, Mich.	C ₂ -C ₄	13,500	1
Sterling Chemicals, Texas City, Tex.	<i>t</i> -butyl	10,000	3
		186,000	
<i>Other American Producers</i>			
Air Products and Chemicals, Inc., Bahia, Brazil	C ₂ -C ₄	41,000	1
Petramin, Iraputo, Mexico	C ₂ -C ₃	3,000	1
		44,000	
<i>West European Producers</i>			
BASF, Antwerp, Belgium & Ludwigshafen, Germany	C ₂ -C ₄ , <i>t</i> -butyl	75,000	1,5
Celanese, Oberhausen, Germany	C ₃ -C ₄	20,000	1,4
Elf Atochem, La Chambre, France	C ₂ -C ₃	25,000	1
		120,000	
<i>Far East</i>			
Mitsubishi Gas Chemical, Niigata, Japan	ethyl	3,000	1
Mitsubishi Rayon, Otake, Japan	<i>t</i> -butyl	2,300	3
Daicel Chemical Industries, Japan	C ₂ -C ₃	12,000	1
Koei Chemical, Sodegaura, Japan	C ₃ -C ₄	2,600	1
Sumitomo Chemical, Niihama, Japan	<i>t</i> -butyl	500	3
Shandong Zibo, P.R.C.	C ₂	3,000	1
Xuanhau, P.R.C.	C ₂	3,000	1
Various, P.R.C.	C ₂ -C ₃	10,000	1
		36,400	
<i>Rest of World</i>			
African Amines, South Africa	C ₂ -C ₃	5,000	1
Alkylamines, Kurkumbh, India	CN	10,000	1
Chemicoplex, Borzesti, Rumania	C ₂ -C ₃	6,000	1
Moravske Chemické, Zavody, Czech.	C ₃ -C ₄	3,300	1
		24,300	

Method 4. Nitrile reduction: reaction of a nitrile with hydrogen over a hydrogenation catalyst.

Method 5. Olefin amination: reaction of an olefin with ammonia.

Method 6. Alkyl halide amination: reaction of ammonia or alkylamine with an alkyl halide.

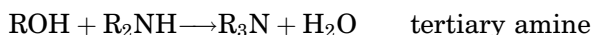
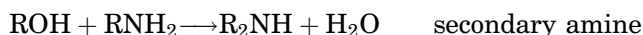
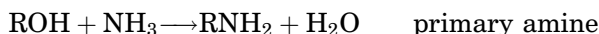
Table 3 gives plant and capacity information for these methods (14).

3.1. Alcohol Amination (Method 1). Amination of alcohols with ammonia typically is conducted over a fixed catalyst bed at elevated temperature and pressure, and produces a mixture of mono-, di-, and tri-alkylamines (15). The reaction section consists of feed systems, vaporizers, and/or preheaters, which pass a liquid or gaseous feed mixture over the catalyst bed in the desired ratio, temperature, and pressure. The amination reaction may be catalyzed either by solid acid catalysts, such as metal oxides and zeolites (16–18) or by supported metal catalysts. Operating conditions for the acid-catalyzed reaction are maintained in the range from 300–500°C and 790–3550 kPa (100–500 psig) at a gas hourly space velocity between 500–1500 vol/vol per hour. The ammonia to alcohol mole ratio varies from 2:1 to 6:1 depending on the amine desired as shown in Figure 1.

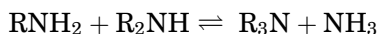
The metal catalysts generally contain cobalt, nickel, copper, chromium, zirconium, or mixtures thereof (19–25). Metal-catalyzed alcohol amination reactions are conducted in the presence of hydrogen to maintain catalyst activity (26). The mole ratio of hydrogen is typically in the range of 1 to 2.5:1 with respect to the alcohol. Operating conditions are maintained in the range of 130–250°C and 790–22,000 kPa (100–3200 psig). Yields are usually in excess of 95%. Most commercial processes employ metal catalysts as increased yields are obtained relative to acid-catalyzed processes. As noted, the acid catalysts require higher reaction temperatures for amination, and side reactions, such as alcohol dehydration (27), are likely to occur.

Alcohol amination reactions are described by a network of two general types of reaction:

1. Sequential substitution reactions, which convert alcohols into a family of primary, secondary, and tertiary amines.



2. Reforming reactions which equilibrate the alkylamines.



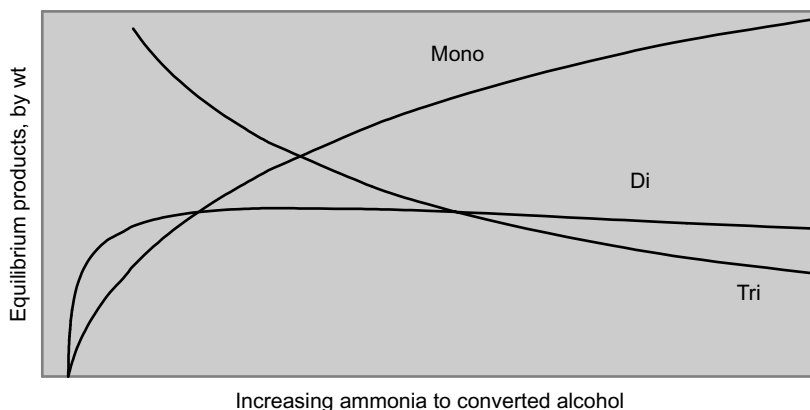


Fig. 1. Alkylamine products vs increasing ammonia.

As the equilibrium product selectivities may not reflect market requirements, process schemes have been developed to increase the flexibility of the process (28) and to selectively produce one or more of the amines (29,30).

Water is a by-product of the amination reactions from alcohols. The mixture of ammonia, water, unconverted alcohol, and amines is continuously separated by distillation. Ammonia, unconverted alcohol, and any amines produced in excess of anticipated sales are recycled to the reactor section. A schematic depicting the typical process flows is presented as Figure 2. Note that the separation requirements vary from process to process depending on the physical properties of the specific alkylamines involved, their product specifications, and the by-products involved. Processing variations might include extractive distillation and/or liquid-liquid separation, particularly for secondary and tertiary amines.

Reforming of the amines produced in excess of anticipated sales may be practiced commercially using both types of catalyst.

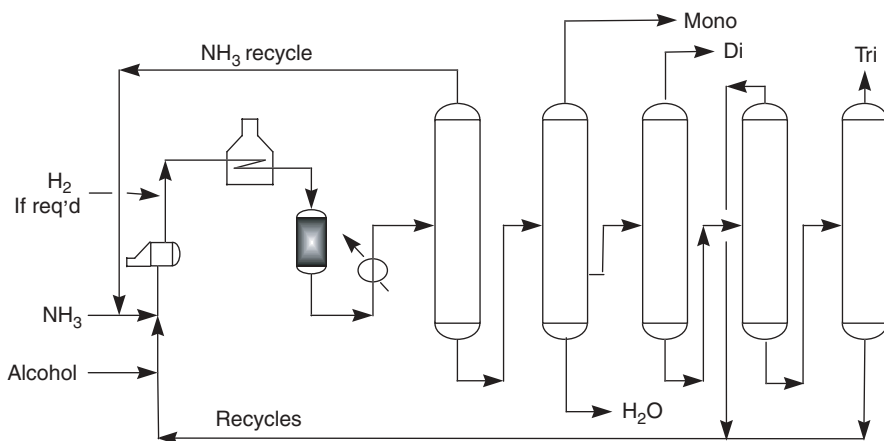
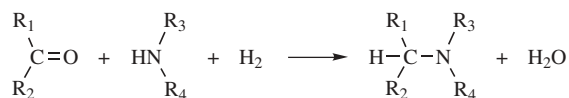


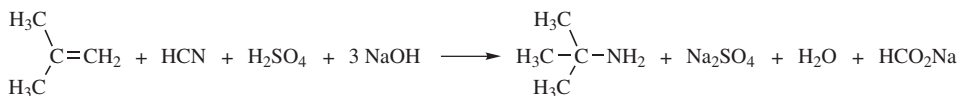
Fig. 2. Generic alkylamines reactor and separation train.

3.2. Reductive Alkylation (Method 2). Ammonia or a primary or secondary amine, hydrogen, and an aldehyde or ketone form aliphatic amines when they react over a hydrogenation catalyst, eg, nickel, cobalt, copper chromite, platinum, or palladium (31). These reactions may be carried out at conditions similar to Method 1 and in similar equipment. Liquid-phase stirred-tank equipment operated either continuous or batch mode is also an option. A larger exothermic heat of reaction limits fixed-bed applications to those with a large excess of ammonia, which acts as a heat sink to restrict the total bed temperature rise. Alternatively, a multistage reactor with interstage cooling or a multitubular reactor with cooling to remove the heat of reaction may be employed, but this increases the cost and operating complexity of the reactor. The heat removal problem is more readily controlled in stirred tank systems with cooling coils or systems that pump the reaction mass through external heat exchangers, eg, loop reactors. Typically these reactions take place at lower temperatures than alcohol amination, and reforming reactions compete less favorably with the reductive alkylation. Consequently, it is quite often possible to control the selectivity to a single product through the judicious choice of catalyst and of the mole ratio of the starting aldehyde or ketone to the amine or ammonia 32, 33. Further it is possible to produce amines with mixed alkyl groups by this method.



R_n = alkyl or H. Operating conditions vary radically depending on the type of equipment selected but typically temperatures used are in the range of 50 to 180°C and pressures of 446–3550 kPa (50–500 psig) are sufficient (34).

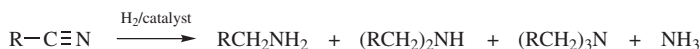
3.3. Ritter Reaction. (Method 3). A small but important class of amines are manufactured by the Ritter reaction (35). These are the amines in which the nitrogen atom is adjacent to a tertiary alkyl group. In the Ritter reaction a substituted olefin such as isobutylene reacts with hydrogen cyanide under acidic conditions. The resulting formamide is then hydrolyzed to the parent primary amine. Typically sulfuric acid is used in this transformation of an olefin to an amine. Stoichiometric quantities of sulfate and formate salts are produced along with the desired amine.



The only low-molecular-weight alkylamine produced by this method commercially is *t*-butylamine.

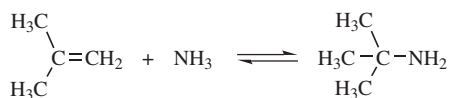
3.4. Nitrile Reduction (Method 4). The reduction of nitriles with hydrogen to simple alkylamines is another technology that is practiced commercially (36,37). As with Method 2, both continuous packed-bed reactor systems designed for removal of the heat of reaction or batch stirred tank or loop reactor systems may be used. Catalysts for this transformation are nickel, cobalt, platinum, palladium, and rhodium. Again the operating conditions vary widely,

depending on the type of equipment; but temperatures and pressures are generally in the range, 50–150°C, and 446–73,900 kPa (50–2000 psig), respectively. Selectivity to primary amine is normally controlled by introducing ammonia as a diluent and nickel or cobalt as catalyst (38). Use of a lithium hydroxide modified Raney cobalt catalyst to favor primary amine formation recently has been described (39)



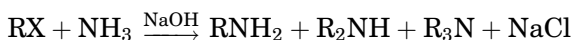
Secondary and tertiary amines are preferentially produced when rhodium or palladium are chosen as catalyst (40). As in Method 2, reforming reactions do not normally compete with the hydrogenation reaction, and high selectivities to the desired product are possible.

3.5. Olefin Amination (Method 5). The most recent technology developed for the production of lower alkylamines is olefin amination (41,42). This zeolite-catalyzed reaction of ammonia with an olefin is practiced in a packed-bed reactor system. *t*-Butylamine currently is the only amine manufactured on a commercial scale via this process (43).



A number of zeolitic materials have been claimed to catalyze this reaction, and reaction temperatures are on the order of 200–350°C with pressures as high as 30000 kPa (4350 psi) reported. Conversion of the olefin to the amine typically is low, and recycle of the unconverted starting materials is necessary to provide an economical process.

3.6. Alkyl Halide Amination (Method 6). The oldest technology for producing amines is the reaction of ammonia with an alkyl halide (11,12). This method is still of commercial importance for the manufacture of allylamines (44) and select mixed alkylamines. Allylamines are not readily made by the other methods mentioned here primarily because either the double bond in the allylamine becomes saturated in methods involving hydrogen or the severe reaction conditions result in cyclization or polymerization by-products (45). Alkyl halide amination occurs under very mild conditions, typically with the addition of aqueous alkali to neutralize the hydrogen halide coproduced by the reaction. As in the Ritter reaction, one mole of salt is produced for every mole of alkyl halide consumed. The resulting waste disposal problem detracts from the general utility of both this method and the Ritter reaction.



4. Shipment and Handling

All the lower alkylamines are classified as either flammable or combustible liquids at normal temperatures and pressure with the exception of

Table 4. **ACGIH Threshold Limit Values**

Alkylamine	TWA, ppm	STEL, ppm
ethylamine	5	15
diethylamine	5	15
triethylamine	1	3
isopropylamine	5	10
diisopropylamine	5	

monoethylamine, which is a flammable gas under these conditions. Anhydrous monoethylamine therefore is shipped under pressure in bulk tank trucks and railcars. Both monoethylamine and monoisopropylamine are available as 70% solutions in water and are shipped in this form as flammable liquids. The liquid amines are available in drums and isocontainers as well as tank trucks and railcars.

The lower alkylamines are toxic and have strong odors. Labeling and packaging of amines must conform with Department of Transportation (DOT) requirements. Amine shipments are regulated by the Coast Guard, the DOT, the International Air Transport Association (IATA), and in some cases, the Drug Enforcement Administration (DEA).

5. Health and Safety Factors

The lower alkylamines all have strong fishy or ammoniacal odors. The American Conference of Governmental Industrial Hygienists has established exposure limits for some of these substances. The values are shown in Table 4 (46). As a general practice, exposure to all alkylamines should be limited, and therefore, they should be handled only in well-ventilated areas. A full face shield with goggles underneath, neoprene, nitrile, or butyl rubber gloves and impervious clothing should be worn when working with alkylamines.

The lower alkylamines are toxic by ingestion, inhalation, and/or skin absorption. Alkylamine vapors in low concentrations can cause lacrimation, conjunctivitis, and corneal edema when absorbed into the tissue of the eye from the atmosphere. Inhalation of vapors may cause irritation in the respiratory tract. Contact of undiluted product with the eyes or skin quickly causes severe irritation and pain and may cause burns, necrosis, and permanent injury. Repeated exposure may result in adverse respiratory, eye, and/or skin effects. If contact with the eyes or skin occurs, the affected area should be washed with water for at least 15 min. If these products are inhaled, the patient should be moved to fresh air and assisted with respiration if required.

6. Economic Aspects, Specifications, and Uses

Table 5 provides a list of major applications for some of the lower alkylamines. As shown in the table, these products are primarily used as intermediates for pesticides, rubber chemicals, and catalysts. Total U.S. consumption of C₂–C₅ amines

Table 5. Products Manufactured Using Alkylamines

Chemical name	CAS Registry Number	Trade Name/Common Name	Use
<i>From Monomethylamine</i>			
2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	[1912-24-9]	Atrazine	herbicide
2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-1,3,5-triazine	[21725-46-2]	Bladex/Cyanazine	herbicide
2-(<i>tert</i> -butylamino)-4-chloro-6-ethylamino-1,3,5-triazine	[5915-41-3]	Terbuthylazine	herbicide
<i>From Diethylamine</i>			
2-diethylaminoethanol	[100-37-8]		corrosion inhibitor
<i>N,N</i> -diethyldithiocarbamate salts			
triethylamine salt	[2391-78-8]		rubber accelerator
diethylamine salt	[1518-58-7]		
sodium salt	[148-18-5]		
zinc salt	[14324-55-1]		
tetraethylthiuram disulfide	[97-77-8]		rubber accelerator
<i>N,N</i> -diethyl- <i>m</i> -toluamide	[134-62-3]	DEET	insect repellent
<i>From Triethylamine</i>			
triethylamine	[121-44-8]		catalyst for foundry molds, phenol-formaldehyde resins; extraction solvent; pH adjuster
diethylhydroxylamine	[3710-84-7]	DEHA	radical scavenger
tetraethylammonium bromide	[71-91-0]		phase transfer catalyst
<i>From Monoisopropylamine</i>			
<i>N</i> -phosphonomethylglycine, monoisopropylamine salt	[38641-94-0]	Roundup/Glyphosate	herbicide
2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	[1912-24-9]	Atrazine	herbicide
dodecylbenzenesulfonate, monoisopropylamine salt	[26264-05-1]		dry-cleaning detergent, fabric finish
<i>From Diisopropylamine</i>			
<i>S</i> -2,3,3-trichloroallyl diisopropylthiocarbamate)	[2303-17-5]	Far-Go/Triallate	herbicide
<i>N,N</i> -diisopropylethylamine	[7087-68-5]	Hünig's Base	proton scavenger, catalyst

Table 5. Products Manufactured Using Alkylamines

Chemical name	CAS Registry Number	Trade Name/Common Name	Use
<i>From Di-n-propylamine</i>			
α,α,α -trifluoro-2,6-dinitro- <i>N,N</i> -dipropyl- <i>p</i> -toluidine	[1582-09-8]	Treflan/Trifluralin	herbicide
<i>From Monobutylamine</i>			
<i>N</i> -butylbenzenesulfonamide	[3622-84-2]		plasticizer
butyl isocyanate	[111-36-4]		intermediate in polyurethane manufacture
<i>From Dibutylamine</i>			
dibutylamine	[111-92-2]		corrosion inhibitor
dibutyldithiocarbamate salts			rubber accelerators
sodium salt	[136-30-1]	NaDBC	
zinc salt	[136-23-2]	ZDBC	
2,3-dihydro-2,2-dimethyl-7-benzofuranyl[(dibutylamino)thio]methylcarbamate	[55285-14-8]	Carbosulfan	insecticide
tetrabutylurea	[4559-86-8]		processing aid
<i>From Tributylamine</i>			
tributylamine	[102-82-9]		catalyst, stabilizer
tetrabutylammonium bromide	[1643-19-2]		phase transfer catalyst
<i>From tert-Butylamine</i>			
<i>N</i> -tert-butyl-2-benzothiazolesulfenamide	[95-31-8]	TBTS	rubber accelerator
2-(tert-butylamino)-4-chloro-6-ethylamino-s-triazine	[5915-41-3]	Terbuthylazine	herbicide
<i>From Diamylamine</i>			
diamyldithiocarbamic acid, zinc salt	[15337-18-5]	ZDAC	rubber accelerator

in 1995 was estimated to be 88,000 mt (47). The percent consumption by carbon chain length and by end use are depicted in Figures 3 and 4. As shown in Figure 3, C₂ and C₃ amines have the greatest market demand of the lower alkylamines. The high demand for C₃ amines is driven by the use of monoisopropylamine in Monsanto's Roundup[®] herbicide. Worldwide manufacturers of alkylamines, their plant locations, and plant capacities are listed in Table 3. The information provided in this table is based on market studies and capacity announcements published in the trade literature (14). Sales specifications (48) and list prices (49) of some alkylamines products are shown in Table 6. Detailed product specifications can be obtained from the manufacturers.

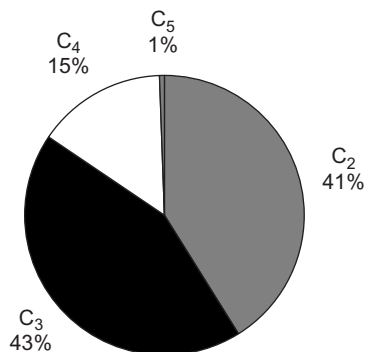


Fig. 3. Percent U.S. consumption of C₂–C₅ alkylamines, 1995.

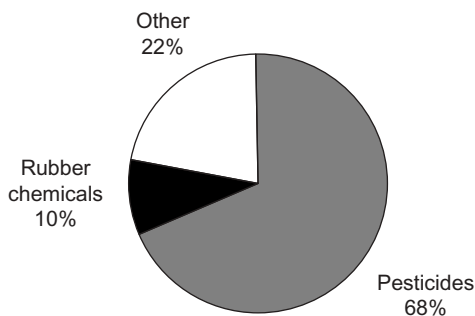


Fig. 4. Percent U.S. consumption of C₂–C₅ alkylamines by end use, 1995.

Table 6. Alkylamines Specifications and Economic Data

Alkylamine	Assay, wt %	Other Amines, wt %	Water, wt %	2000 U.S. price, \$/kg
ethylamine	99.5	0.4	0.1	3.13
ethylamine, 70% solution	70.0–71.0	0.4	balance	3.31
diethylamine	99.2	0.4	0.3	3.22
triethylamine	99.5	0.4	0.1	3.31
<i>n</i> -propylamine	99.0	0.5	0.5	3.02
di- <i>n</i> -propylamine	99.0	0.8	0.2	3.26
tri- <i>n</i> -propylamine	98.5	1.2	0.3	4.17
isopropylamine	99.5	0.4	0.1	2.51
isopropylamine, 70% solution	70.0–72.0	0.3	balance	2.67
diisopropylamine	99.5	0.2	0.1	3.55
<i>n</i> -butylamine	99.5	0.4	0.1	3.42
di- <i>n</i> -butylamine	99.0	0.6	0.2	3.55
tri- <i>n</i> -butylamine	98.0	1.7	0.3	4.14
isobutylamine	99.0	0.5	0.5	8.33
diisobutylamine	98.5	1.3	0.2	2.89

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