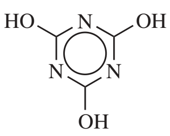
CYANURIC AND ISOCYANURIC ACIDS

1. Introduction

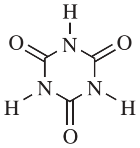
Cyanuric acid [108-80-5] is a white crystalline solid, which was discovered by Scheele in 1776 but did not achieve commercial importance until the late 1950s, primarily via its derivatives. The chemistry of cyanuric acid is diversified because of multiple reaction sites leading to a number of useful products, eg, chloroisocynaurates and organoisocyanurates. In addition, the thermal dissociation product of cyanuric acid, isocyanic acid, is very useful in organic synthesis and in other applications, eg, diesel engine pollution control.

2. Structure

Cyanuric acid is a heterocyclic compound containing a 1,3,5 triazine ring that exists in two isomeric foms, ie, enol and keto tautomers, which can be considered as cyclic trimers of cyanic (HOCN) and isocyanic acid (HNCO), respectively.



enol
cyanuric acid



keto
isocyanuric acid

Infrared (ir), Raman, and ultraviolet (uv) spectroscopic, and X-ray crystallographic data suggests that the keto (iso) form prevails in the solid state and in neutral or acidic solutions (1–3). In alkaline solution, the anion formed is that of the enol tautomer. Through common usage, both forms are collectively called cyanuric acid (CA). The following line formulas for cyanuric acid are used in the article: $H_3(NCO)_3$ or H_3Cy, where $(NCO)_3$ and Cy represent the triisocyanurate anion (Cy can also represent a mixed isocyanurate/cyanurate anion such as that in sodium dichloroisocyanurate).

3. Nomenclature

The trihydroxy form is variously designated cyanuric acid, *s*-triazine-2,4,6-triol or 2,4,6-trihydroxy-*s*-triazine. The trioxo structure, or *s*-triazine-2,4,6(1*H*,3*H*,5*H*)-trione is the basis for the isocyanuric acid nomenclature. The triazine-based system is preferred in the scientific literature and is used by government regulatory agencies; however, the less cumbersome (iso)cyanurate designations persist in commerce.

4. Properties

4.1. Acidic Dissociation Constants.

Cyanuric acid is a titrable weak acid: $pK_{a1} = 6.88$, $pK_{a2} = 11.40$, $pK_{a3} = 13.5$ (4). The temperature dependent equation for K_{a1} (T in kelvin) is given by $\log K_{a1} = -31.08 + 0.154T - 2.441 \times 10^{-4}T^2$ (5). The pH of a saturated aqueous solution of pure CA at room temperature is ~4.8.

4.2. Solubility.

Solubility of CA in water is only 0.2% at 25°C but increases to 2.6% at 90°C and 10.0% at 150°C (6). In aqueous alkali (eg, NH_4OH, NaOH, KOH) solubility increases due to salt formation. The solubility in 96% H_2SO_4 at 25°C is 14.1%. Cyanuric acid is only slightly soluble (~0.1%) at room temperature in common organic solvents such as acetone, benzene, diethyl ether, ethanol, and hexane (7). Solubility is significant in basic nitrogen compounds (eg, dimethylformamide 7.2%) or unusual solvents such as DMSO (17.4%). By contrast with CA, its chlorinated derivatives TCCA and DCCA are readily soluble in polar organic solvents (eg, ketones, nitriles, and esters) (8).

4.3. Hydrates.

In aqueous media CA forms a dihydrate, which crystallizes as colorless monoclinic prisms that effloresce in dry air (9). The transition temperature from dihydrate to anhydrous CA is ~57°C (10). The densities of anhydrous CA and CA dihydrate at 25°C are 1.75 and 1.66 g/mL, respectively (8).

4.4. Sublimation/Dissociation. Cyanuric acid, $H_3(NCO)_3$, is an odorless, white, infusible, crystalline solid that does not melt up to 330°C. At higher temperatures it sublimes and dissociates to isocyanic acid (HNCO) [75-13-8].

$$H_3(NCO)_3(s) \rightleftharpoons H_3(NCO)_3(g) \rightleftharpoons 3\ HNCO(g)$$

The equilibrium constants for dissociation of CA in the gas phase are 0.02 and 0.76 MPa^2 (1.9 and 74.3 atm^2) at 365 and 434°C, respectively (11). Below 350°C, isocyanic acid tends to polymerize, whereas above 350°C it can form by depolymerization of CA.

Isocyanic acid formed by thermal depolymerization of CA can be condensed at low temperature and employed in synthesis (12,13). Isocyanic acid is also formed in good yield by reaction of NaOCN with stearic or oxalic acid (14). It polymerizes at room temperature to a mixture of cyclic trimer $(HNCO)_3$ and linear polymer $(HNCO)_x$, cyamelide [462-02-2] (15). Cyamelide is converted to CA by heating at 200–250°C (8).

The possible formation of dicyanic acid from HNCO has been studied in the gas, liquid, and solid phases by NMR and MS (14).

4.5. Vapor Pressure. The vapor pressure of CA at 167–200°C is given by $\log P\ (\text{kPa}) = 5552/T + 11.54$ (T in kelvin) (16). Over the 295–360°C range the vapor pressure is given by: $\log P\ (\text{kPa}) = 6740/\text{T} + 13.38$ (11).

4.6. Spectral Data. Spectroscopic data are available (1–3). Proton nuclear magnetic resonance (^{1}H nmr) is of limited usefulness because of proton exchange and CAs symmetry and low solubility. Nuclear quadrupole resonance measurements (^{14}N) have been reported (17).

4.7. Thermodynamic Data. Thermodynamic values for CA are (18): ΔH_f° −690.8, −660.2 (19) kJ mol^{-1}, ΔH_{comb} 918.4 kJ mol^{-1}, $\Delta H_{subl}{}^{25°C}$ 133.6 kJ mol^{-1} (20) $C_p{}^{25°C}$ 132.9 kJ mol^{-1} K^{-1} (20), and ΔH_{neut} (NaOH) 1st H 28.2, 2nd H 17.2 kJ mol^{-1}.

5. Chemistry

Cyanuric acid is a cyclic triimide, and undergoes reactions at N, O, or C, eg, salt formation, hydrolytic and oxidative ring cleavage, *C*-halogenation, *N*-halogenation, and alkylation. Reaction at nitrogen produces isocyanurates $R_3(NCO)_3$, whereas reaction at oxygen forms cyanurates $(RO)_3(NC)_3$. Mixed derivatives are possible, as in the case of the sodium salt of dichloroisocyanuric acid. Virtually all of the organo derivatives of CA are produced by reactions characteristic of a cyclic imide, wherein isocyanurate nitrogen (frequently as the anion) nucleophilically attacks a positively polarized carbon of the second reactant. See Ref. 21 for a review of cyclic imide chemistry.

Although numerous mono-, di-, and trisubstituted organic derivatives of cyanuric and isocyanuric acids appear in the literature, many are not accessible via cyanuric acid. Cyanuric chloride 2,4,6-trichloro-*s*-triazine [108-77-0], is generally employed as the intermediate to most cyanurates. Trisubstituted isocyanurates can also be produced by trimerization of either aliphatic or aromatic isocyanates with appropriate catalysts (22) (see ISOCYANATES, ORGANIC). Alkylation of CA generally produces trisubstituted isocyanurates even when a deliberate attempt is made to produce mono- or disubstituted derivatives. There are exceptions, as in the production of mono(2-aminoethyl) isocyanurate [18503-66-7] in nearly quantitative yield by reaction of CA and aziridine in DMF (23).

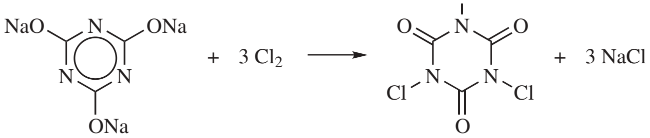
5.1. Hydrolysis. Compared to its precursor (HNCO), CA is unusually stable to hydrolysis. It is only slowly hydrolyzed by hot aqueous alkali and virtually inert to acidic hydrolysis. Indeed, CA can be heated under pressure in sulfuric acid solution at 200°C with minimal decomposition.

5.2. Oxidation. Although the triazine ring of cyanuric acid is stable to oxidizers such as peroxydisulfate, it can be cleaved by alkaline hypochlorite: $2\ H_3(NCO)_3 + 9\ ClO^- \rightarrow 3\ N_2 + 6\ CO_2 + 9\ Cl^- + 3\ H_2O$ (24). Chloroisocyanurates are similarly decomposed by alkaline hypochlorite (8).

Although CA is stable to ozone, it can be oxidized by ozone and uv-ozone under hydrothermal-supercritical conditions (25) and by $O_3{-}H_2O_2$ (26). In addition, CA can be oxidized by sulfate ion radicals generated by laser photolysis (27).

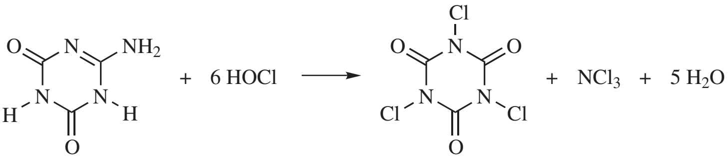
5.3. Salt Formation. Although much weaker than the parent compound isocyanic acid ($pK_a = 3.7$), CA is sufficiently acidic to form salts. Many inorganic and organic salts of CA have been reported (18). Lead and zinc cyanurates are useful as corrosion inhibitors (28). The 1:1 adduct melamine cyanurate [37640-57-6] is prepared by reaction of melamine with CA in aqueous media and has achieved commercial importance (29).

5.4. Chloroisocyanurates. The kinetics of *N*-chlorination of CA in basic media have been studied by stopflow spectrophotometry (30). The *N*-chloro derivatives are the most important commercial products derived from CA. Trichloroisocyanuric acid [87-90-1] (Cl_3Cy TCCA) or 1,3,5-trichloro-*s*-triazine-2,4,6−1*H*,3*H*,5*H*)-trione, is produced commercially in >90% yield by chlorination of aqueous trisodium cyanurate, prepared from CA and NaOH in a 1:3 molar ratio (31):



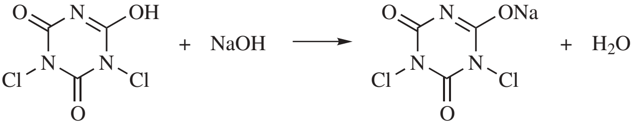
Another commercial process is based on reaction of HOCl and chlorine with monosodium cyanurate (32). TCCA also can be formed by reaction of preformed or *in situ* generated HOCl with CA slurry (33) or by reaction of dichlorine monoxide with finely powdered CA (34). Small amounts of ammelide and ammeline present in commercial CA are converted to TCCA by HOCl or Cl_2O; the exocyclic amino groups are converted to unstable $-NCl_2$, which is cleaved by HOCl forming a carbonyl group and NCl_3 (35,36). By contrast, reaction of melamine with excess HOCl produces hexachloromelamine which is realtively stable to

HOCl (8). The reaction with ammelide is shown below.



Dichloroisocyanuric acid [2782-57-2] (HCl_2Cy DCCA) or 1,3-dichloro-*s*-triazine-2,4,6(1*H*,3*H*,5*H*)-trione is produced commercially in >90% yield by chlorination of disodium cyanurate, prepared by reaction of CA and caustic in a 1:2 molar ratio (31). It also can be prepared by reaction of CA with TCCA (37), HOCl (33), or Cl_2O (34). Drying fine crystalline TCCA needles isolated from concentrated aqueous NaCl also forms DCCA (38). Monochloroisocyanuric acid cannot be isolated from aqueous media because of rapid disproportionation to DCCA and CA.

DCCA is a fairly strong acid ($pK_a = 3.75$), much stronger than CA, and salts are readily prepared by neutralization with aqueous base (39):

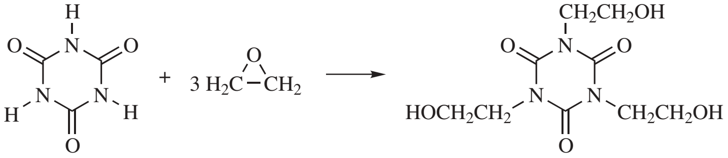


Only the monosodium [2893-78-9] and monopotassium [2244-21-5] salts of DCCA have achieved commercial significance. Sodium dichloroisocyanurate ($NaCl_2Cy$ SDCC) forms a mono $NaCl_2Cy \cdot H_2O$ (SDCC · H) [52671-45-1] (8) and a dihydrate $NaCl_2Cy \cdot 2H_2O$ (SDCC · 2H) [51580-86-0] (40). Both the anhydrous salt and its dihydrate are items of commerce. SDCC also can be prepared by reaction of TCCA with trisodium cyanurate [3047-33-4] (41). Other routes to SDCC include reaction of a moistened powdered mixture of TCCA, CA, and $NaHCO_3$ (42), reaction of crude CA with NaOCl (43), and reaction of NaH_2Cy with HOCl (44) or Cl_2O (45). Reaction of TCCA with saturated NaCl solution also forms SDCC: $Cl_3Cy + NaCl \rightarrow NaCl_2Cy + Cl_2$ (46). Other metal chlorides and salts also can be used leading to formation of numerous other metal dichloroisocyanurates (46).

5.5. Chloroisocyanurate Double Salts. Two double salts of potassium dichloroisocyanurate KCl_2Cy (PDCC) and TCCA are known, ie, $Cl_3Cy \cdot KCl_2Cy$ [30622-37-8] and $Cl_3Cy \cdot 4KCl_2Cy$ [306 22-37-8]. The latter has been produced commercially. It can be prepared by reaction of TCCA dissolved in acetone with aqueous PDCC (47), by reaction of TCCA with saturated KCl solution (46), or by reaction of CA with KOCl (48). A number of mixed metal dichloroisocyanurate double salts have been prepared (49). Other double salts also are possible, including those containng DCCA as well as bromoisocyanurates (8). Some properties of CA and chloroisocyanurates are given in Reference 50.

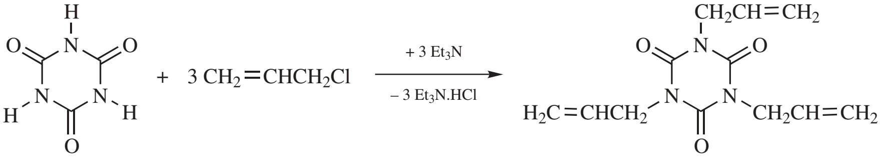
5.6. Bromoisocyanurates. Bromo and bromochloro derivatives of CA include HBrClCy [889325-49-2], HBr_2Cy [15114-43-9], NaBrClCy [20367-88-8], $NaBr_2Cy$ [15114-43-8], KBr_2Cy [15114-46-2], $BrCl_2Cy$ [89696-38-8], Br_2ClCy, and Br_3Cy [17497-85-7] (51–54) (see CHLORAMINES AND BROMAMINES). Various bromo and bromochloro containing double salts also are possible (8).

5.7. Reaction with Epoxides. Cyanuric acid and ethylene oxide react nearly quantitatively at 100°C forming the commercial product tris(2-hydroxyethyl)isocyanurate [839-90-7] (THEIC) (55–59).



Propylene oxide yields the hydroxypropyl analogue (55,56). CA and alkylene oxides react at ~200°C in inert solvent to give *N*-hydroxyalkyloxazolidones in ~70% yield (60). THEIC also can be prepared via *in situ* ethylene oxide formation by reaction of CA and 2-chloroethanol in aqueous caustic (59). THEIC can react further via its hydroxyl functionality to form esters, ethers, urethanes, phosphites, etc (61). Heating THEIC under vacuum yields 2-oxazolidone (7). Reaction of CA with epichlorohydrin in alkaline dioxane solution gives tris(3-chloro-2-hydroxypropyl)isocyanurate [7423-53-2] (62) (see CHLOROHYDRINS). This material can be converted into the commercial product, tris(2,3-epoxypropyl)isocyanurate [2451-62-9] (triglycidyl isocyanurate) by dehydrohalogenation with alkali (62). Reaction of CA with glycidol [556-52-5] yields tris(2,3-dihydroxypropyl)isocyanurate (63).

5.8. Reaction with Organo Halides. The commercial product triallyl isocyanurate [1025-15-6] (TAIC) is formed in 82% yield by action of CA on allyl chloride at 130°C in the presence of triethylamine (56,64).



A mixed allyl- and hydroxyethyl-substituted isocyanurate is obtainable by reacting alkaline CA with a mixture of 2-chloroethanol and allyl chloride (65). Various di- and trisubstitiuted isocyanurates (or cyanurates) can be prepared from CA and the appropriate organohalide using bases such as triethylamine, NaOH, or AgOH as acid acceptors (7,56,64,66,67–69). The choice of base can influence the type of product obtained. For example, reaction of CA with methyl iodide in the presence of AgOH yields trimethyl cyanurate, whereas in the presence NaOH, trimethyl isocyanurate [827-16-7] is obtained. Similarly, reaction of CA with acetyl chloride in the presence of AgOH forms triacetyl cyanurate. Reaction of CA with pentabromobenzyl bromide yields tris(pentabromobenzyl)isocyanurate in 75% yield. The product melts >340°C and has potential use as a flame retardant additve for engineering plastics (70).

5.9. Reaction with Carbonyl Compounds. Cyanuric acid readily dissolves in aqueous formaldehyde forming tris(hydroxymethyl)isocyanurate

[10471-40-6] (18), which in turn reacts with acetic anhydride to yield tris(acetoxymethyl)isocyanurate [54635-07-3], either thionyl chloride or phosphorus pentachloride to give tris(chloromethyl)isocyanurate [63579-00-0], and phenyl isocyanate in pyridine to yield tris(*N*-phenylcarbamoxymethyl)isocyanurate [21253-39-4] in 87% yield (71). Reaction of CA with paraformaldehyde and 2,6-dicyclohexylphenol yields tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate (72).

5.10. Addition to Aliphatic Double Bonds. Cyanuric acid adds to acrylonitrile in alkaline dimethylformamide at 130°C forming bis(2-cyanoethyl)- [2904-27-0] and tris(2-cyanoethyl) [2904-28-1] isocyanurates (56). Acidic hydrolysis forms the corresponding carboxyethyl derivatives, whereas, hydrogenation in the presence of ammonia produces bis- [69455-19-2] and mono-3-aminopropyl [69455-20-5] isocyanurates (56). Addition of CA to acrolein produces tris(3-oxopropyl)isocyanurate, useful as a crosslinking agent for coatings and plastics (58). Ketene in acetone reacts with alkaline CA to give triacetyl cyanurate [13483-16-4] in high yield rather than the isocyanurate (73). Cyanuric acid adds to *N*-substituted maleimides forming trisubstituted isocyanurates that can be hydrolyzed, forming carboxylic acid and secondary amine functionalities (57).

5.11. Other CA Reactions. Trimethyl isocyanurate [827-16-7] can be synthesized in 60% yield by the reaction of CA with dimethyl sulfate in alkaline medium (7) or with diazomethane (74), and in essentially quantitative yield by thermal rearrangement of trimethyl cyanurate [877-89-4]. Isomerization of alkyl cyanurates to the corresponding isocyanurates is frequently observed (18,75). Cyanuric acid reacts with bicyclic amide acetals forming triols, useful for preparation of polyurethanes (76). Reaction of tris(tributylstannyl)isocyanurate with acetyl chloride yields triacetylisocyanurate [35843-57-3] (77).

5.12. Organometallic Derivatives. Organogermanium, organosilicon, and organotin substituted isocyanurates have been prepared by reaction of CA with the appropriate reagent containing a reactive chlorine or hydroxyl: $[(C_2H_5)_3Ge]_3Cy$, $[(CH_3)_3Si]_3Cy$, $[(CH_3)_3SiNH]_3Cy$, $[(C_4H_9)_3Sn]_3Cy$ [752-58-9], and $[(C_6H_5)_3Sn]_3Cy$ [752-74-9] (78–80).

5.13. Reactions Involving Dissociation of CA. Isocyanic acid produced by thermal dissociation of CA has many useful synthetic applications.

Isocyanates. Isocyanic acid adds to double and triple bonds of unsaturated compounds such as alkenes, alkynes, diazo, and carbonyl forming isocyanates (81). HNCO also has been used to prepare acyl isocyanates, isocyanatosilanes, and organophosphorus isocyanates (82).

Ring Formation. Addition reactions of HNCO across carbon–nitrogen double bonds exhibit a tendency toward cyclization, eg, azines can form bitriazoles, Schiff bases can form either four- or six-member rings, and ketenes can give six-member rings.

Reaction with Alcohols. HNCO reacts with alcohols forming carbamates and allophonates.

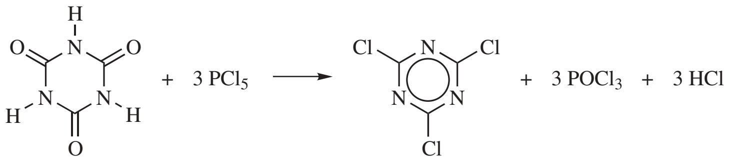
Reaction with Carboxylic Acids. Carboxylic acids yield amides on reaction with HNCO. Heating CA with high boiling fatty acids at 250°C gives high yields of the corresponding nitriles (83).

Reaction with Amines. Primary and secondary amines react with HNCO forming ureas.

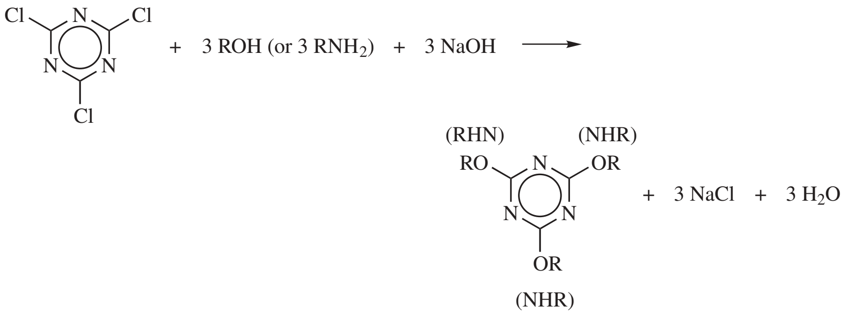
Reaction with Inorganic Compounds. Reaction of HNCO with hydrogen halides gives carbamyl halides. Cyanuric acid and ammonia react under pressure and catalysis at 350–400°C to produce melamine [108-78-1] (84). Carbohydrazide is produced in 71% yield by refluxing a mixture of CA and hydrazine hydrate (85). Heating a mixture of CA and boric acid >200°C produces hexagonal boron nitride, useful in electronic applications (86). Metal cyanates are obtained by treating CA with alkali metal carbonates at 350–550°C in an atmosphere of carbon dioxide (87). Metal cyanides are obtained by reducing HNCO to HCN with C or CO followed by reaction with alkali metal hydroxides (88).

5.14. Triazine Chemistry via Cyanuric Chloride.

Conversion of CA into cyanuric chloride [108-77-0] $(ClCN)_3$ by PCl_5 is an example of reaction at carbon (89).



Cyanuric chloride as an imidoyl chloride reacts as an acid chloride, unlike chloroisocyanurates. It is a convenient precursor to alkyl or aryl cyanurates by reaction with alcohols or phenols, or to substituted melamines by reaction with amines; alkaline conditions are employed in both cases and yields are generally high.



Cyanuric chloride reacts with sodium sulfide to form trithio(iso)cyanuric acid [638-16-4] (18). Reaction of cyanuric chloride with 1, 2 or 3 mol of ammonia followed by hydrolysis yields mono-, di-, and triaminotriazines, eg, ammelide, ammeline, and melamine. For a review of cyanuric chloride chemistry, see Ref. 90.

6. Preparation

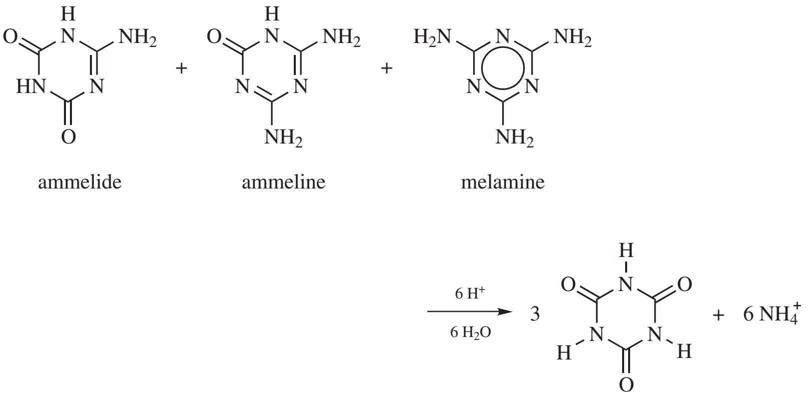
6.1. Pyrolysis of Urea.

On a commercial scale, CA is produced by pyrolysis of urea [57-13-6]. When urea (mp 132.7°C) is heated at ~250°C for 1 h, it is converted to crude CA with evolution of ammonia.

$$3\ H_2NCONH_2 \longrightarrow H_3(NCO)_3 + 3\ NH_3 \qquad \Delta H = \sim 172\ \text{kJ mol}^{-1}$$

The molten urea thickens and eventually solidifies. The initial decomposition reaction of urea is dissociation into isocyanic acid and ammonia. The latter two compounds recombine forming an equilibrium amount of ammonium cyanate. Biuret [108-19-0] ($H_2NCONHCONH_2$), mp 192°C, is an intermediate during the pyrolysis; some triuret [556-99-0] ($H_2NCONHCONHCONH_2$), mp 233°C, may also form. These intermediates form by successive reactions of urea with isocyanic acid. Urea cyanurate [69455-21-6] and possibly biuret cyanurate (91) are formed initially. Cyanuric acid can form by trimerization of HNCO and by cyclization of triuret. Other intermediates include cyanamide (H_2NCN) [420-04-2] and guanidine [$H_2NC({=}NH)NH_2$] [113-00-8] which form by ammination of isocyanic acid and urea, respectively. Other analogous compounds also may form by ammination of biuret and triuret. These intermediates result in formation of aminotriazine by-products, primarily ammelide [645-93-2], some ammeline [645-92-1], and minor amounts of melamine [108-78-1]. Water is formed on ammination of urea and its intermediates resulting in hydrolysis of some urea to NH_3 and CO_2, reducing yield. Mechanisms for urea pyrolysis have been proposed (92–94).

6.2. Crude CA Purification. The crude product containing aminotriazines can be purified by digestion with acids (eg, hydrochloric, nitric, or sulfuric); this hydrolyzes the acyclic impurities to carbon dioxide and ammonia and the aminotriazines to CA and ammonia (95).



Other options for the purification of CA include: dissolution in hot water, aqueous ammonia, aqueous formaldehyde, or hot dimethylformamide followed by filtration to remove most of the impurities. The CA is recoverable by cooling the aqueous solution (96), acidifying the ammonium hydroxide solution (97), or cooling the dimethylformamide solution with further precipitation of CA by addition of carbon tetrachloride (98). Sodium hydroxide addition precipitates monosodium cyanurate from the formaldehyde solution (99).

6.3. By-product Reduction. By-product formation can be reduced by use of a stripping gas or vacuum to facilitate removal of ammonia (8,100); however, sublimation of urea becomes excessive if the pressure is too low. Addition of ammonium salts (eg, F^-, Br^-, Cl^-, NO_3^-, or SO_4^{2-}) (8,101–103), acids, or pyrolysis of preformed urea salts, eg, urea hydrochloride [506-89-8], sulfate, or nitrate

[124-47-0] (104,105) significantly reduces aminotriazine formation. However, these alternatives can present potential corrosion problems. Pyrolysis of urea cyanurate also provides a higher assay product. Although pyrolysis of the urea derivatives, biuret and triuret, give less aminotriazines due to reduced ammonia evolution, these materials are not readily available on a commercial scale and in addition would be too expensive.

6.4. Pyrolysis in Organic Solvents.

Aminotriazine formation can be reduced to an acceptable level (<1%), thus eliminating the need for acid digestion, by pyrolysis of urea in certain high boiling solvents. Numerous solvents are disclosed in the patent literature. Some of these solvents (eg, hydrocarbon oils, aromatics, and chlorinated organics) do not dissolve urea and therefore still produce a crude product. Some solvents react with urea forming intermediates, eg, in alcohols, carbamates and allophanates are formed that decompose to CA. These intermediates can produce undesirable by-products, eg, olefins and organic carbonates. Since all organic solvents undergo some oxidation and discoloration yielding discolored product that requires further purification, exclusion of air is crucial. Chemical and physical solvent losses can render a process uneconomical. Desirable solvents are good solvents for urea, poor solvents for CA, high boiling, and stable to pyrolysis intermediates, ammonia, oxygen, and heat. Although no perfect solvent has been identified, some solvents, eg, dinitriles (106) pyrrolidinones (107,108), and sulfones (109) largely meet these requirements.

6.5. Other Routes to CA.

High purity CA may be produced by thermal decomposition of carbamyl chloride (or allophanic chlorides) produced by the high temperature reaction of ammonia and phosgene (110), hydrolysis of cyanuric chloride (13), or acid digestion of aminotriazines, eg, melamine (111). These methods are not commercially viable due primarily to high raw materials costs and/or unwanted by-product formation. However, the conversion of by-product or waste cyanuric chloride or aminotriazines to CA on a break-even or near break-even basis may be economic as a pollution control measure.

Cyanuric acid of variable purity can also be prepared from gaseous isocyanic acid (HNCO) [75-13-8] produced by (*1*) volatilization of urea (8,112), (*2*) by oxidation of HCN over a silver catalyst (113,114), and (*3*) by reaction of H_2, CO, and NO (60–75% yield) over palladium or iridium catalysts at 280–450°C (8,115).

7. Manufacture

The majority of the cyanuric acid produced commercially is made via pyrolysis of urea [57-13-6] in directly or indirectly fired stainless steel rotary kilns. Small amounts of CA are produced by pyrolysis of urea in stirred batch or continuous reactors, over molten tin, or in sulfolane.

7.1. Kiln Pyrolysis of Urea.

The feed to the kiln, either urea melt or aqueous solution, is sprayed onto a moving bed of crude CA pebbles. The kiln slopes slightly downward to facilitate transport of the crude CA toward the spill area at the end of the kiln. The kiln operates under slight vacuum allowing air to be drawn into the kiln to avoid explosive concentrations of ammonia

(15–27 mol%). Concentrations of urea, CA, intermediates, and by-products vary along the length of the kiln. The average product temperaure is ~250°C. The crude product exiting the kiln after a residence time of ~1 h consisting of 2–20 mm pebbles, typically contains ~20% aminotriazines. About 75% of the crude CA is recycled to the front of the kiln. The gases from the kiln consisting of air, ammonia, CO_2, urea, CA, and probably HNCO and cyanamide are scrubbed in aqueous urea and the resultant solution containing small amounts of biuret, CA, and aminotriazines is recycled to the urea feed to the kiln.

7.2. Operational Problems. Since conversion of urea to CA is endothermic and goes through a plastic stage, heat, and mass transport are important process considerations. In the later stages of pyrolysis, heat transfer becomes poor and care must be exercised to prevent the reaction mass from being heated ~300°C since yields are lowered by decomposition of the product. Other problems are agglomeration and adhesion of the reaction products to the wall of the kiln. Agglomeration impedes conversion and adhesion results in a higher level (20–30%) of aminotriazines due to overheating. Agglomeration and adhesion during kiln pyrolysis of urea can be diminished by low heat rates and peripheral speeds (116), sufficiently high wall temperatures (116,117), radiant heating (118), multiple urea injection ports (116), use of heat transfer fluids (117), recycling 60–90% of the crude CA to the urea feed to the kilns (116), and prior formation of urea cyanurate (119).

7.3. Acid Digestion. Purified CA (>99% assay) is produced by digesting the ground crude product in 15–20% sulfuric acid. The digestion can be carried out at atmospheric pressure or above (95,116). The digested CA slurry is filtered and washed to remove ammonium bisulfate and residual sulfuric acid. A small portion of the filter cake (~10%) is dried conventionally at temperatures up to 200°C, granulated, and packaged for merchant sales. The remainder of the CA filter cake, which contains a small amount of water, is converted to *N*-chloroisocyanurates.

7.4. Pollution Control. The ammonia by-product from digestion is typically trapped as NH_4HSO_4, which can represent a significant water pollution burden. Indeed, many patents dealing with the manufacture of CA seek alternatives to aminotriazine formation and subsequent hydrolysis. When nitric acid is employed in crude CA purification, NH_4NO_3 is formed which can be sold as fertilizer, often blended with urea. Gaseous ammonia by-product from the pyrolysis of urea can be recovered or burned and does not represent an exceptional pollution problem.

Other pollution constraints appear in the production of chloroisocyanurates. Biocidally active chlorine in waste streams must be destroyed by hydrogen peroxide or other suitable reagents, and triazine compounds must be reduced in the effluent since they represent a nitrogen pollution load. This is generally achieved by dechlorination and acidification to yield CA, which can be filtered off as is or after conversion to the monosodium salt and recycled (120).

7.5. Pyrolysis Alternatives. Beside continuous horizontal kilns, numerous other methods for dry pyrolysis of urea have been described, eg, use of stirred batch or continuous reactors, ribbon mixers, ball mills, etc (121), heated metal surfaces such as moving belts, screws, rotating drums, etc (122), molten tin or its alloys (123), dielectric (124) and microwave heating (125), and gas (126) and vibrational (127) fluidized beds (with performed urea cyanurate). All of these modifications yield impure CA.

In pyrolysis employing molten tin, a flow of molten urea on the surface is eventually converted to a sheet of crude CA 15–20 mm thick. After reaching the edge of the tin bath, the moving sheet falls into a mill. The resultant powdered crude CA (contaminated with tin metal) is subjected to acid hydrolysis to convert aminotriazines (30–40%) to CA. Tin losses can amount to 15-kg/t product.

7.6. Solvent Processes.

Of the many solvents disclosed, only sulfolane (tetramethylene sulfone) (109) and *N*-cyclohexyl-2-pyrrolidinone (108) have been employed commercially.

Pyrolysis. The process can be carried-out batchwise or continuously. The pyrolysis employing either molten or solid urea feed is typically carried out under reduced pressure, eg, 27–40 kPa (200–300 torr) at temperatures of $\sim$200–250°C. Residence time varies from one to several hours depending on temperature. The ammonia by-product is removed continuously after passing through a solvent condenser and pressure control valve. The reactor produces a slurry of crystalline CA dispersed in the solvent that is saturated with CA and contains small amounts of urea and biuret.

Product Recovery. Product recovery can vary: (*1*) the slurry can be cooled, diluted with methanol, filtered and the CA washed with methanol, the filtrate distilled to remove methanol, the solvent returned to the process, and the CA dried to remove residual methanol; (*2*) the CA slurry can be quenched in water and after hydration of the CA is centrifuged and the CA washed with water; the centrate is distilled to remove water, the solvent returned to the process, and the CA is dried in a flash dryer; (*3*) the slurry can be concentrated in a crystal separator, the CA freed of solvent in a falling film evaporator and the solvent returned to the process; and (*4*) the CA slurry can be filtered by centrifugation, the centrate returned to the pyrolysis vessel and the CA crystals dried under vacuum to remove residual solvent along with small amounts of urea and biuret. The dry off-white or tan CA containing $<1\%$ aminotriazines and traces of occluded solvent can usually be used for the manufacture of chloroisocyanurates.

Product Purification. CA destined for use in other applications may require purification, which can involve recrystallization from water or other treatment.

8. Economic Aspects

8.1. Cyanuric Acid.

Occidental Chemical Corp. and Clearon Corp., in the United States, are the world's largest bulk suppliers of cyanuric acid and chloroisocyanurates. They have a combined CA capacity in excess of 40,000 t/year, 90% of which is converted into chlorinated derivatives. The main foreign producers are in Japan with smaller producers in several European countries, China, Taiwan, and Korea.

8.2. Chloroisocyanurates.

Global capacity for trichloroisocyanuric acid and anhydrous and hydrated sodium dichloroisocyanurate was about

180,000 t in 2000 (128). Most product produced in Japan is exported to the US. The US market is the largest and grew at 5.5%/year from 1996 to 1999. Swimming pool and spa sales represent ~83% of the total U.S. consumption, which is expected to grow at about 3.5%/year from 1999 to 2004.

9. Specifications and Analysis

Cyanuric acid is sold mainly in coarse granular form and is also available in powdered form. Typical composition of commercial product is CA $\geq$99%, ammelide and ammeline $\leq$0.5%, and moisture and volatiles <0.5% (1–4% in some domestic product). Trace amounts of ammonium salts (typically sulfate) are also present.

9.1. Analysis. Various methods are available for analysis of cyanuric acid, its impurities, and derivatives.

Titrimetry. Cyanuric acid can be titrated as a monobasic acid in aqueous media (end point pH ~8.5). However, this method is of limited utility because of interferences by weak acids (eg, acetic acid) and aminotriazine impurities such as ammelide and ammeline. Cyanuric acid dissolved in DMSO–benzene can be titrated potentiometrically with tetrabutylammonium hydroxide in benzene–methanol (129). Although ammelide and ammeline do not interfere, melamine does; biuret interferes slightly. Since crude CA contains only small amounts of biuret and melamine, the error is small. Cyanuric acid in wastewater can be determined by amperometric titration with $Hg(NO_3)_2$ (130). Urea can be determined after hydrolysis to ammonia with urease followed by distillation and titration with acid. Ammonium ion can be determined by basification/distillation/alkalimetry. Available Cl_2 on chloroisocyanurates is determined iodometrically.

Via Melamine Cyanurate. Aqueous solutions of CA can be analyzed by precipitation of melamine cyanurate and quantitated gravimetrically (131), volumetrically (132), or turbidimetrically (133,134). Since ammelide is acidic it also may interfere in this method if present.

Liquid Chromatography. Aqueous solutions of CA (eg, swimming pool water) can be accurately analyzed by hplc (134,135).

Ion Chromatography. Cyanuric acid in swimming pool water and crude cyanuric acid and its by-products (ammelide, ammeline, and melamine) can be determined by ion chromatography (136).

Gas Chromatography. Solid CA samples can be readily analyzed after derivitization with organosilylating agents; this method allows simultaneous determination of CA, ammelide, ammeline, and melamine (8,137).

Spectrophotometry. Solutions of CA and chloroisocyanurates can be analyzed via uv spectrophotometry (4,134). Ammelide and ammeline can be determined by uv spectrophotometry after separation from CA via their acid solubility or by means of a cation exchange resin (138). Biuret can be determined by uv spectrophotometry. Solid cyanuric acid and the chloroisocyanurates can be readily identified via ir (139).

Polarography. Aqueous solutions of CA can also be analyzed by differential pulse polarography (140).

Ion-Selective Electrodes. Ammonium ion in cyanuric acid can be dtermined by means of an ion-selective electrode (141). An isocyanurate ion specific electrode has been used to determine CA in swimming pool water (142).

X-Ray Diffraction. Solid cyanuric acid and the chloroisocyanurates can be readily identified by X-ray diffraction.

10. Health and Safety Factors

10.1. Toxicity. Acute toxicities (LD_{50} g/kg, rats) for CA and chloroisocyanurates are CA >5.0, SDCC 1.67, PDCC 1.22, and TCCA 0.75 (143). A review of toxicological studies on CA and its chlorinated derivatives is given in Ref. 144. These studies show that the compounds are safe for use in swimming pool and spa/hot tub disinfection, sanitizing, and bleaching applications when handled and used as directed.

10.2. Biodegradability. Most uses of chloroisocyanurates are regulated by the EPA under FIFRA. Cyanuric acid (or cyanurate) is ultimately the end product of use of chloroisocyanurates in bleaching, sanitizing, and disinfection applications. Since the *N*-chloro derivatives are biocidal, biodegradation studies have centered on the residual CA, which has been shown to undergo biodegradation under environmental conditions (145).

10.3. Thermal Stability. Cyanuric acid is stable and relatively inert. Chloroisocyanurates also are stable when dry and uncontaminated and kept away from fire or a source of high heat.

11. Uses

11.1. Cyanuric Acid. Cyanuric acid is widely used to stabilize av Cl_2 (from chlorine, hypochlorites, or chloroisocyanurates) against decomposition by sunlight (ie, uv light) in swimming pools. Near-optimal stabilization is achieved with 25–50 ppm CA (146). Recommendations for using CA and chloroisocyanurates in swimming pool disinfection can be found in Ref. 147 (see WATER, TREATMENT OF SWIMMING POOLS).

Cyanuric acid is used on a small scale for reducing nitrogen oxides (NO_x) in stationary diesel engine exhaust gases. It can also be used for NO_x reduction in coal, oil, or gas fired boilers. The CA is heated to sublime it into the exhaust gases where it dissociates to HNCO. The HNCO rapidly reacts with nitrogen oxides, via initial postulated cleavage into NH and CO radicals, forming nitrogen (148). The reaction with NO is

$$2\ HNCO + 2\ NO \rightarrow 2\ N_2 + CO + CO_2 + H_2O$$

Cyanuric acid in the form of the adduct melamine cyanurate is useful as a flame retardant additive in various plastics, eg, polyamide resins and compositions (149) and in acrylonitrile–butadiene–styrene (ABS)-polycarbonate compositions (150). It also is useful as a solid lubricant (151) and in preparation of abrasive slurries (152). Cyanuric acid in combination with other additives can be used as a flame retardant in resins such as polyurethane, polyester, epoxy, vinyl, etc, and in polyurethane foams. (153).

11.2. Chloroisocyanurates. Most of the CA produced commercially is chlorinated to produce TCCA, anhydrous SDCC and its dihydrate (SDCC · 2H). They have become standard ingredients in formulations for scouring powders, household bleaches, institutional and industrial cleansers, automatic dishwasher compounds, and general sanitizers, and most importantly, in swimming pool and spa/hot tub disinfection. The choice of chloroisocyanurate for any particular application depends on the desired combination of solubility, av Cl_2, and pH. SDCC has a much greater water solubility than TCCA (see table below). However, TCCA has the highest av Cl_2 content and dissolves much slower than the salts. This is used to advantage in swimming pool sanitation where TCCA is tableted and dispensed into the water by means of erosion-type feeders, either floating on the surface or in-line with the filtration system. SDCC is usually broadcast into the swimming pool or spa. Compared to hypochlorites, chloroisocyanurates provide better storage stability, ease of handling, and dispensing, solubility, and formulation stability with adjunct ingredients (see Bleaching agents).

Derivative	Calc'd. av Cl_2 %	mp, °C	Aq. solubility,[a] %
Cl_3Cy, TCCA	91.5	249–251	1.2
HCl_2Cy, DCCA	71.7	198	0.7
$NaCl_2Cy$, SDCC	64.5		17.0
$NaCl_2Cy \cdot 2H_2O$, SDCC · 2H	55.4		19.2

[a] At 20°C.

The chloroisocyanurates can be used in the bleaching of cotton, synthetics, and their blends; they do, however, attack proteinaceous fibers, such as silk or wool, presumably via active chlorine reaction with the peptide (amide) linkage. However, chloroisocyanurates can be used as shrink-proofing agents in wool finishing (154) (see Textiles, Wool). The same action of chlorine upon proteins contributes to the effectiveness of chloroisocyanurates in automatic dishwashers.

11.3. Organo(iso)cyanurates. Tris(2-hydroxyethyl)isocyanurate (THEIC) is used as an additive in the production of high performance polyester magnet–wire enamels and in electrical varnishes. THEIC increases adhesion and imparts improved resistance to heat and weather in a variety of resin systems. In addition, the use of THEIC produces a significantly improved combination of mechanical, chemical, and electrical properties. The enamels and varnishes are used in the manufacture of electric motors, television tubes, and transformer coils (61).

Homopolymers of triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC) are brittle and find little application. However, TAC and TAIC can be used as crosslinking agents [eg, with polyethylene, poly(vinyl chloride) and ethylene–propylene systems (155)] and as curing agents. Either TAC or TAIC can be used as comonomer with unsaturated polyester resins (see Polyesters, unsaturated) or other unsaturated monomers including diallyl phthalate, methyl methacrylate, and styrene to form a variety of materials with enhanced properties.

Tris(2,3-epoxypropyl)isocyanurate (ie, triglycidyl isocyanurate) is used as a cross-linking agent for carboxylated polyesters and as curing agent for weather-resistant powder coatings (qv) (156).

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