

7.4 – Bromine Derivatives of Cyanuric Acid

Various bromine derivatives of cyanuric acid have been prepared and characterized. These include: partially and fully brominated derivatives of di- and trichloroisocyanuric acids, and sodium dichloroisocyanurate. In addition, partially brominated derivatives of the double salts of trichloroisocyanuric acid and potassium dichloroisocyanurate are possible. The bromine derivatives have lower solubilities than the chlorinated analogs. None of these compounds have been commercially developed.

Introduction

Chloroisocyanurates were first produced commercially in the late 1950s. Although bromine derivatives were patented in the late 1950s and mid 1960s (Paterson 1959 and 1964), they were never commercialized. However, two chloroisocyanurate–sodium bromide mixtures have been marketed, i.e., trichloroisocyanuric acid (Trichlor) tablets (Brom–O–Rings) containing about 4% sodium bromide (initially marketed in the 1980s), and a blend of sodium dichloroisocyanurate (Dichlor) and sodium bromide marketed in 1990s. Bromoisocyanurates are formed in swimming pools and spas by reaction of available bromine (formed by reaction of bromide ion with available chlorine) with cyanuric acid.

An actual bromine compound, bromochlorodimethylhydantoin, was initially

patented in the late 1950s (Paterson 1957, 1959, 1967) and was later commercialized and is used primarily for spa sanitation. Dibromodimethylhydantoin was introduced in 2002.

Structural Formulas

Structural Formulas – The following structural formula represents the various haloisocyanuric acids and its salts, where the substituents X, Y, Z can be H, Cl, or Br; in addition X can be Na or K in metallic derivatives.

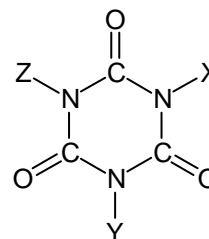


Table 1 illustrates some possible compounds for the above general structure, where Cy represents the six-membered triazine ring including the attached oxygen atoms, i.e., the triisocyanurate anion $C_3N_3O_3^{3-}$. Mixed halogenated derivatives are also possible.

Dihaloisocyanuric Acids

Dichloroisocyanuric acid (~71% av. Cl, HCl_2Cy ; where Cy is the tri-isocyanurate anion $(NCO)_3^{3-}$) is not an item of commerce but is an intermediate in the preparation of sodium dichloroisocyanurate (Dichlor). Bromine derivatives are known (see Table 2) and their prepara-

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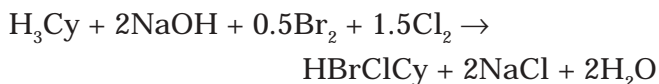
Shorthand Formula	X	Y	Z
HCl ₂ Cy	H	Cl	Cl
HBr ₂ Cy	H	Br	Br
Cl ₃ Cy	Cl	Cl	Cl
Br ₃ Cy	Br	Br	Br
NaCl ₂ Cy	Na	Cl	Cl
NaBr ₂ Cy	Na	Br	Br
KCl ₂ Cy	K	Cl	Cl
KBr ₂ Cy	K	Br	Br

Chlorine Compounds	Bromine Derivatives
HCl ₂ Cy	HBrClCy, HBr ₂ Cy
Cl ₃ Cy	BrCl ₂ Cy, Br ₂ Cly, Br ₃ Cy
NaCl ₂ Cy	NaBrClCy, NaBr ₂ Cy
KCl ₂ Cy	KBrClCy, KBr ₂ Cy
HCl ₂ Cy•NaCl ₂ Cy	HCl ₂ Cy•NaBrClCy*, HCl ₂ Cy•NaBr ₂ Cy*
Cl ₃ Cy•KCl ₂ Cy	Cl ₃ Cy•KBrClCy*, Cl ₃ Cy•KBr ₂ Cy*
Cl ₃ Cy•4KCl ₂ Cy	Cl ₃ Cy•4KBr ₂ Cy*, BrCl ₂ Cy•4KBrClCy*

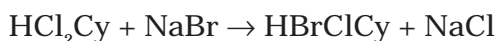
*Examples of potential derivatives.

tion is described below.

Bromochlorisocyanuric Acid – This compound (HBrClCy) was prepared by treating *in situ* formed disodium cyanurate in aqueous media with bromine and chlorine in a 1:1 mol ratio while maintaining the pH at 5 according to the following reaction (Paterson 1964a):



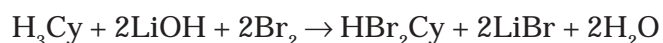
The crystalline product was isolated by filtration, water washing, and drying. This compound also can be prepared by treating an aqueous slurry of dichloroisocyanuric acid with sodium bromide.



The product was isolated as described above.

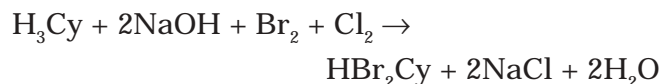
Dibromoisocyanuric Acid – This compound (HBr₂Cy) has been prepared by adding a two-fold excess of bromine to an aqueous solution

of *in situ* formed dilithium cyanurate (Gottardi 1967a). The stoichiometric reaction is:

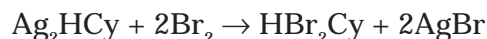


The cooled reaction mixture was stirred for a 24-hour period to allow the reaction to go to completion. The crystalline suspension was filtered, washed with bromine water, and dried under vacuum. The resulting product (88% yield; mp 307-309° C) had the theoretical bromine content.

The preparation of HBr₂Cy in aqueous media also has been reported using a 1:1 mixture of bromine and chlorine (Paterson 1964b):



High purity HBr₂Cy also can be prepared by reaction of powdered disilver cyanurate with bromine vapor at 150°C (Gottardi 1967b).

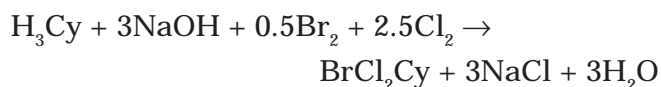


The crude product was washed a number of times with acetone, the clear filtrate evaporated under vacuum at 20°C, and the residue dried further under vacuum at 100°C. The resulting product (74% yield, mp 307-309° C) had 99% of the theoretical bromine content.

Trihaloisocyanuric Acids

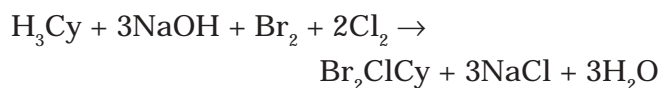
Trichloroisocyanuric acid (Trichlor, ~90% av. Cl) is produced on a commercial scale primarily for use in swimming pool applications. Bromine derivatives are known (see Table 2) and their preparation is described below.

Bromodichloroisocyanuric Acid – Bromodichloroisocyanuric acid (BrCl₂Cy) was prepared by treating a slurry of cyanuric acid with sodium hydroxide and bromine and chlorine while maintaining the pH below 7 according to the following reaction (Paterson 1964a and b):



The crystalline product was isolated as described above. This compound can also be prepared by reaction of trichloroisocyanuric acid with aqueous sodium bromide (Paterson 1959).

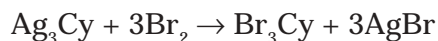
Dibromochloroisocyanuric Acid – This compound (Br₂ClCy) can be prepared as above by adjusting the stoichiometry as shown below.



The crystalline product was isolated as described

above. This compound can also be prepared by reaction of trichloroisocyanuric acid with aqueous sodium bromide.

Tribromoisocyanuric Acid – The attempted preparation of this compound (Br₃Cy) in aqueous media does not produce a pure product. However, it can be prepared by reacting powdered trisilver cyanurate with bromine vapor at 130°C (Gottardi 1996b).



The reaction mixture was washed a number of times with 1:2 acetone/CCl₄ and the clear filtrate concentrated under vacuum at 10°C. The crystallized product was filtered, washed with CCl₄, and dried under vacuum at 100°C. The product (yield 74%, mp 320-325 °C) had the theoretical bromine content.

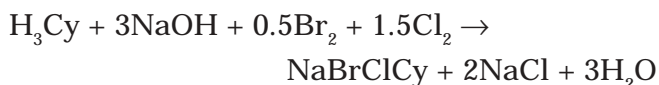
Sodium Dihaloisocyanurates

Sodium dichloroisocyanurate (Dichlor) is produced on a commercial scale as an anhydrous (62% av. Cl) and hydrated (56% av. Cl) product for use in swimming pool and spa disinfection and in dishwasher applications. The potassium salt was produced commercially in the past but is no longer an item of commerce. Bromine derivatives of these two compounds are known (see Table 2) and their preparation is described below.

Sodium Bromochloroisocyanurate – Sodium bromochloroisocyanurate (NaBrClCy) was prepared by treating a slurry of cyanuric acid with sodium hydroxide, bromine, and chlorine while maintaining the pH at 7 according to the following stoichiometry (Paterson 1964a):

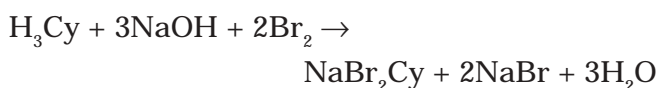
Table 3. Reaction of Trichloroisocyanuric Acid with Sodium and Potassium Halides*			
Reactant	Product	Reactant	Product
NaF	No Reaction	KF	Cl ₃ Cy•KCl ₂ Cy
NaCl	NaCl ₂ Cy	KCl	Cl ₃ Cy•4KCl ₂ Cy
NaBr	BrCl ₂ Cy	KBr	Cl ₃ Cy•2KBrClCy

*Wojtowicz 1975.



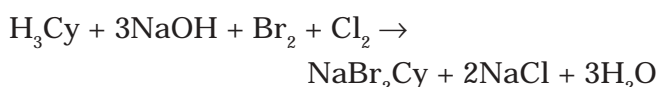
The product was isolated as described above. The potassium salt (KBrCl₂Cy) can be prepared by substituting KOH for NaOH. Sodium or potassium bromochloroisocyanurate can also be prepared by reaction of sodium or potassium dichloroisocyanurate with sodium bromide.

Sodium Dibromoisocyanurate – The preparation of this compound in aqueous media does not produce a pure product. The desired reaction using bromine is:



Reaction of an aqueous solution of *in situ* formed trisodium cyanurate with bromine in a 1:3 molar ratio produced a crystalline slurry which was filtered (Gottardi 1967a). The recovered crystals were washed with bromine water and dried under vacuum to give a crude product in ~88% yield, which based on its bromine content was a mixture containing 88% sodium dibromoisocyanurate and 12% sodium monobromoisocyanurate.

Although use of a mixture of bromine and chlorine can improve bromine utilization, it still would not result in a pure product.



Potassium Dibromoisocyanurate – This compound can be prepared similarly to the sodium salt. Reaction of an aqueous solution of *in situ* formed tripotassium cyanurate with bromine in a 1:3 molar ratio gave a crude product in ~95% yield, which based on its bromine content consisted of 70% potassium dibromoisocyanurate and 30% potassium monobromoisocyanurate (Gottardi 1967a).

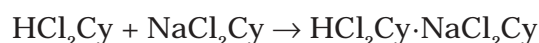
Haloisocyanurate Double Salts

Trihaloisocyanuric Acid–Dihaloisocya-

nurates – Trichloroisocyanuric acid forms two double salts with potassium dichloroisocyanurate: Cl₃Cy•KCl₂Cy and Cl₃Cy•4KCl₂Cy (Nelson 1967). The latter compound was once produced on a commercial scale for use in dishwasher applications. It can be prepared by reaction of trichloroisocyanuric acid dissolved in acetone with aqueous potassium dichloroisocyanurate (Symes 1966) or by reaction of trichloroisocyanuric acid with aqueous potassium chloride, bicarbonate, or carbonate (Wojtowicz 1975a, b, and c). The 1:1 double salt Cl₃Cy•KCl₂Cy can also be prepared by reaction of trichloroisocyanuric acid with potassium fluoride (see Table 3).

Various bromine-containing derivatives of these double salts are possible (see Table 2). Potential routes to bromine derivatives involve reaction of trihaloisocyanuric acid with a dihaloisocyanurate or reaction of the above chlorine double salts with sodium or potassium bromide under appropriate conditions. For example, treatment of the 1:4 double salt with sodium bromide can form BrCl₂Cy•4KBrCl₂Cy.

Dihaloisocyanuric acid–Dihaloisocyanurates – Like trichloroisocyanuric acid, dichloroisocyanuric acid should form double salts with alkali dichloroisocyanurates. For example, the 1:1 double salt of dichloroisocyanuric acid with sodium dichloroisocyanurate can be prepared by heating an equimolar mixture of the two compounds in the presence of a small amount of water.



Potassium and bromine derivatives of this double salt are possible (see Table 2).

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