

SAFETY OF CHLORINATION REACTIONS

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Chlorination reactions are part of various processes in the chemical industry, to manufacture heavy chemicals, specialty chemicals, pesticides and pharmaceuticals, in inorganic and organic chemistry. They are a valuable tool in organic synthesis.

The hazard of processing chlorine involves :

- Gas phase explosion ;
- Runaway reaction or thermal explosion in the condensed phase.

Gas phase explosion hazard with chlorine as an oxidizer is present in gas phase chlorination processes as well as in chlorinations in the condensed phase.

Gas phase chlorination processes are mostly continuous processes operating in the flammable area. Gas phase explosion hazard is related to burner malfunctions.

Where chlorination is made by chlorine injection in the liquid phase, gas phase explosion hazard is related to chlorine evolution in the vapour phase, giving a flammable mixture with the solvent or reaction mixture vapour. Here hazard assessment is achieved by comparing the gas phase composition with the flammable area of the gaseous mixtures. Auto-ignition is also considered because the auto-ignition temperature of gaseous mixtures containing chlorine is close to the ambient temperature.

The relevant flammability data is obtained in a specially designed 20 litre sphere. The main features of this explosion vessel include : Hastelloy C 276 walls, central ignition with spark, hot wire or pyrotechnic ignition source, 200 bar pressure resistance, ambient to 300°C initial temperature, easily opened for frequent cleaning. This apparatus allows precise determination of the flammability limits, autoignition temperature, explosion overpressure, rate of pressure rise and flame speed. A review of flammability data in chlorine is given.

Runaway reaction hazard in chlorination reactions is related to a series of dangerous process situations or process deviations such as :

- Delay in reaction initiation
- Reaction mixture instability
- Production of unstable species like chloramines, nitrogen trichloride, chloro nitroso compounds.
- Demixing or separation of unstable species in case of chlorination made in aqueous solution, because the chlorinated compounds are less soluble in water than the initial reactant.

A full review in runaway reaction hazard in chlorination reactions is given with examples from the literature and from the laboratory.

Keywords : Chlorination reactions, Gas explosion, Runaway reactions

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INTRODUCTION

Quite similar to oxygen, chlorine is used as an oxidizer in a wide range of chemical processes where it is reacted with organic and inorganic compounds to produce chlorinated products or intermediates. A wide range of useful products are obtained such as bleach, metallic chlorides, reactive monomers to manufacture plastics, heat exchange fluids, chlorinated solvents and intermediates in organic synthesis to produce specialty chemicals, pesticides and pharmaceuticals.

Chlorine is involved in a wide range of process situations including gas phase reactions in a burner or on a catalyst, solid/gas reactions in a fluid bed, gas/liquid reactions in a packed column, gas/liquid reactions by injecting chlorine in a liquid phase in a semi-batch process or in a continuous process. The reaction of chlorine takes place without catalyst, in the presence of a catalyst or in photochemical reactions.

Compared to oxygen, chlorine is a more reactive gas because it is processed as a pure gas whereas oxygen is mostly reacted using air. More problems would occur with oxygen if the use of pure oxygen was widespread in the chemical industry.

Compared to pure oxygen, chlorine is even more reactive. The self-ignition temperature of gaseous mixtures of organic vapours with chlorine is much lower than that of their mixtures with oxygen. Natural light can split the chlorine molecule to produce reactive chlorine radicals. Many reactions of chlorine take place near the ambient temperature. The combustion of iron in chlorine can be initiated at temperatures slightly above 100°C.

Chlorine is toxic to man and animals. Many chlorinated compounds are also toxic.

For all the above reasons, the chemical processes where chlorine is involved are submitted to careful safety studies where the specific chemical properties of chlorine are considered

THERMAL EXPLOSION HAZARD IN THE CONDENSED PHASE

Chlorine is a strong oxidizer. Mixtures of chlorine and organic fuels may have a high energy content and are unstable. The thermal instability of condensed phases containing chlorine can appear in various process conditions :

- When chlorine is injected in a liquid reaction mixture, the chlorination reaction may not start immediately allowing chlorine to accumulate in the reaction mixture. The reaction may start suddenly when a large concentration of chlorine is present in the reaction mixture and give a severe runaway reaction producing a large quantity of insoluble HCl. An example of such an induction period in chlorination is mentioned in the literature for the chlorination of ketones in methanol (1). To avoid this type of incident, the reaction onset should be checked before allowing a large concentration of unreacted chlorine to be dissolved in the liquid phase.
- When chlorine is reacted with an organic fuel in a liquid reaction mixture, highly unstable substitution products may be obtained. This process situation is dangerous in two cases :
 - if a high concentration of unstable chlorination product is obtained in the condensed phase

- if a chlorinated liquid phase separates from the bulk liquid phase "by segregation".

The latter situation is frequent in the chlorination of aqueous solutions of organic reactants because the chlorinated products are less soluble in water than the initial reactants.

Examples of this dangerous process situation are the synthesis of alcohol hypochlorites by injecting chlorine in an alkaline aqueous solution of alcohol.

Traugott Sandmeyer described the synthesis of Methyl and Ethyl hypochlorites (2) (3) and suffered severe injuries.

Roland Fort and Leon Denivelle (4) described the synthesis and properties of a series of other alcohol hypochlorites obtained following Sandmeyer's Method.

The oxidation of organic compounds containing Nitrogen in their formula (amines, amides, cyanides) using chlorine, gives unstable chloramines. The very unstable Nitrogen trichloride is finally obtained. NCl_3 is only slightly soluble in water and can separate from aqueous solutions giving a very sensitive dense oil. Liquid NCl_3 can detonate.

NCl_3 can be obtained by chlorination of aqueous solutions containing ammonium ions. NCl_3 compound was first obtained by Pierre Louis Dulong (1785 - 1838) by chlorination of ammonium chloride solutions. Dulong was seriously injured by several explosions of liquid NCl_3 . (5)

At least one accident is known where liquid NCl_3 could separate in a waste-water treatment where bleach was used to oxidize cyanide ions. After an agitation failure, the actuation of a bottom valve triggered the detonation. Direct chlorination would lead to the same dangerous situation.

The chlorination of organic compounds with a N - O bound will leave this chemical bound unaffected. The chlorination of oximes will give chloro oximes or chloronitroso compounds (6) (7) which can demix from aqueous solutions giving an unstable dense oil.

This ends in process situations similar to NCl_3 formation and demixion.

- Accumulation of unstable chlorinated compounds in the bulk liquid phase.

The accumulation of unstable chlorinated products in the bulk liquid phase is most likely when a solvent is used where this product is soluble. The most common example is nevertheless the accumulation of NCl_3 produced by electrolysis of KCl or NaCl salt containing ammonium ions, in a NCl_3 removal process using extraction in carbon tetrachloride. If NCl_3 is not continuously thermally decomposed, high NCl_3 concentrations in the CCl_4 solution are obtained with a potential runaway decomposition hazard.

Such an incident is known in the literature (8). Note that the decomposition kinetics of NCl_3 in CCl_4 solutions is strongly influenced by the wall material.

Recommendations

When chlorine is reacted with organic reactants, specially if nitrogen containing compounds or ammonium ions are present, the possible formation of unstable chlorinated compounds should be considered. Any segregation of a separate phase from the bulk liquid is potentially dangerous and should be investigated carefully. The demixion of an unstable liquid phase may induce a high vapour pressure of the unstable product in the gas phase because the gas phase is in equilibrium with the separated unstable liquid. This problem should be considered.

If no segregation occurs, the process situation is safer, however it is necessary to check for low concentration of unstable chlorinated compounds (NCl₃, Alcohol hypochlorites, others...) in the bulk liquid phase.

GAS PHASE EXPLOSION HAZARD IN CHLORINATION REACTIONS

Gas phase explosion hazard is present when chlorine is mixed with a fuel in the gas phase. The fuel may be hydrogen, a solvent or organic vapour, ammonia, etc.

When chlorine is reacted with a fuel in a burner, as in the manufacture of HCl from Hydrogen and chlorine or in the manufacture of chlorinated solvents from hydrocarbons and chlorine, most incidents occur when the burner is set on-stream, either by lighting the burner with a pilot flame or by preheating the gas and the burner. Of course the gas mixture is in the flammable range and explosions occur due to maloperation.

When chlorine is reacted with a fuel on a catalyst bed, maloperation will result in catalyst burn- out and/or gas phase explosion before or after the catalyst. Here the determination of the fuel gas flammable limits in chlorine are of interest if the feed gas is not in the flammable range in normal process conditions.

When chlorine is injected or bubbled in a liquid phase containing a reactant and/or a solvent, chlorine evolution in the gas phase may produce a flammable mixture with the reactant, product, solvent or reaction mixture vapour. Here inertizing is difficult as in other oxidation processes because the oxidizer is bubbled through the liquid reaction mixture.

As far as possible, it is recommended to keep the gas phase composition outside the flammable range. Various methods are used :

- 1) Lowering the fuel vapour pressure below the Lower Flammability Limit in chlorine by lowering the process temperature.
- 2) Raising the fuel vapour pressure above the Upper Flammability Limit in chlorine by raising the process temperature.
- 3) Inertizing the gas phase by flushing the reactor gas phase with an inert gas such as Nitrogen, CO₂, HCl.

To keep the reactor gas phase below the L.F.L. in chlorine (method 1) is the safer method where only proper temperature control is necessary.

To keep the reactor gas phase above the U.F.L. in chlorine (method 2) may not be quite safe. On start-up the temperature must be set to the process normal value ensuring enough fuel vapour pressure before chlorine injection. If a condenser is used where the fuel vapour pressure is depleted, the gas flow composition may enter the flammable range. Glass condensers are better not used or protected from light.

Inertizing (method 3) is a difficult technique when the chlorine flow evolving from the liquid reaction mixture may change.

If chlorine does not evolve in the gas phase in normal process conditions, an inert gas flush in the reactor gas phase is recommended (see below). If a chlorine flow evolves from the liquid reaction mixture unreacted, enough inert gas flush must be provided in the reactor gas phase to lower the chlorine concentration below the minimum oxidizer concentration (MOC) of the fuel flammable range.

If HCl is released in the gas phase, this gas contributes to the reactor gas phase blanketing. However one should take into account rapid changes in the process conditions, if the wanted chlorination reaction stops due to catalyst depletion or reactant consumption. More unreacted chlorine can be released in the gas phase, the HCl production can disappear. Therefore monitoring of the gas phase chlorine concentration using a chlorine analyser is recommended.

SELF-IGNITION, DEFLAGRATION AND DETONATION IN THE GAS PHASE

Self-ignitions of gaseous mixtures containing chlorine and a fuel, near the ambient temperature, are known. Self-ignitions can turn into severe deflagrations or detonations.

Self-ignition occurs in mixtures with a composition both in the flammable range and outside the previously determined flammable range. This phenomenon can be explained as follows :

- The self-ignition temperature of gaseous mixtures is not a clear-cut limit. It is best represented by an induction period versus temperature relation. Self-ignition will be observed at lower temperature if a longer induction period is allowed.
- Near the self-ignition temperature, the flammable area is enlarged to a wide range of equivalence ratios.
- When long induction periods are necessary, weak ignition sources can initiate the explosion, such as light, wall effects, tar deposits, catalyst deposits on the wall, NCl_3 decomposition flame (5) (9).

A combination of these influences may explain the above mentioned self-ignition phenomenon outside the flammable range.

As an example, the self-ignition of gas phase mixtures of Dioxane and chlorine was thoroughly investigated by F. Battin-Leclerc (10) (11). Dioxane is sometimes mentioned as a solvent for chlorination processes (12) whereas self-ignitions of dioxane + chlorine mixtures is easily obtained near the ambient temperature.

The flammable limits of dioxane + chlorine mixtures were determined in a 4.6 litre explosion vessel together with the explosion overpressures and maximum rates of pressure rise (12).

The explosion overpressures obtained are of the same order of magnitude of that of explosion of gaseous fuel in air but half of the expected thermodynamic explosion overpressures in chlorine.

The gas phase detonation of gaseous mixtures of Dioxane and chlorine was successfully investigated in shock tubes by A. Elaissi (13) (14).

This mixture was shown to be very sensitive to detonation compared to mixtures of fuel in air or oxygen.

The full investigation of this example, chosen for convenience, shows that mixtures of organic fuels with chlorine can exhibit self-ignition followed by deflagration and detonation thus explaining violent explosions observed in the past.

EXPERIMENTAL SET-UP TO STUDY EXPLOSION LIMITS, EXPLOSION CHARACTERISTICS AND SELF-IGNITION OF GASEOUS MIXTURES

A new explosion vessel, a 20 litre sphere, was built to investigate gas phase explosions with special attention for experiments using chlorine as an oxidizer. See fig.1.

This new facility allows the measurement of :

- The flammability limits of gaseous mixtures using various ignition sources : single spark, fusing wire, chemical ignitors.
- The explosion characteristics i.e. explosion overpressure and maximum rate of pressure rise.
- The laminar burning velocity deduced from the pressure-time history of the explosion. (15) The pressure is recorded at a rate of 20,000 Points/s.
- The self-ignition temperature and induction period of gaseous mixtures, down to a few minutes. Sampling is possible to check for gas phase reaction.
- Flash points in chlorine.

The main features of this explosion vessel are :

- Hastelloy C276 walls to lower wall effects i.e. to prevent the reaction of chlorine with fuel before ignition, catalysed by stainless steel.
- The vessel is made of two half-spheres connected through a flange assembly kept tight by clamps.

The upper half-sphere is fixed, the lower half-sphere is movable, using a pneumatic jack, to allow quick opening of the vessel for frequent cleaning. Combustion in chlorine produces soot deposits on the walls, which may promote or prevent ignition of subsequent mixtures. Cleaning after each positive test is necessary to obtain reliable flammable limits in chlorine.

The vessel design pressure is 200 bar, thus allowing initial pressure of 10 to 20 bar according to the expected explosion pressure. The vessel temperature can be set between ambient temperature and 300°C. Mixing is ensured before ignition using a propeller mixer. Central ignition is made using spark, hot wire or a pyrotechnic ignition source.

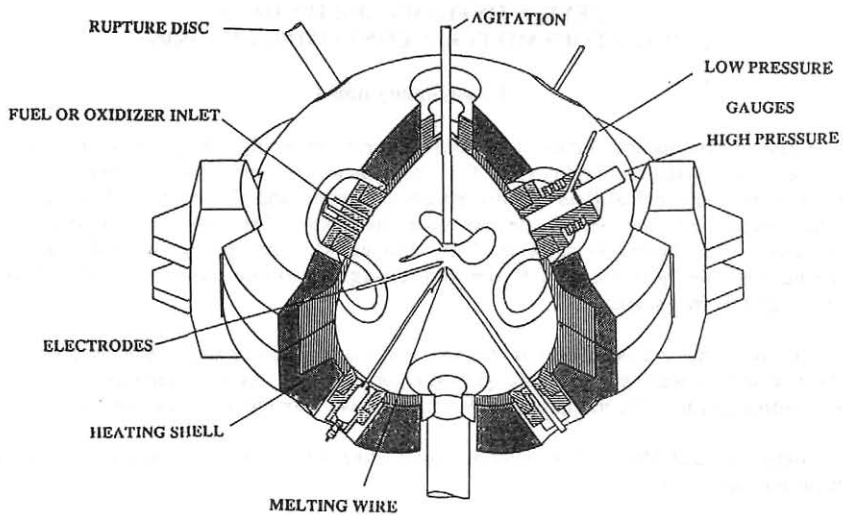


Figure 1 20 LITRE EXPLOSION VESSEL

REVIEW OF FLAMMABILITY DATA OF GASEOUS MIXTURES CONTAINING CHLORINE

Flammability limits

A review of flammability limits of gaseous mixtures containing chlorine was first given by Mal'tseva, Roslovskii and Frolov (16) (17). The experimental set-up used to obtain these data was a double-wall vertical glass cylinder, 80 mm in diameter and 120 mm high. The experiment initial temperature was set by thermostating the vessel. The fuel was introduced after evacuation, and allowed to vaporize. Then chlorine was admitted in the explosion vessel. Mixing was only by molecular diffusion (no stirring). A 10 min waiting time was observed before ignition by a spark.

Our comment on this method is that the wall material is correct, mixing is poor or not effective and the waiting time before ignition is too long and may have allowed the mixture to react before ignition. The results are summarized in table 1 for the reader convenience.

Dokter (18) and Medard (19) published some more data collected in table 2, together with interesting discussions.

Further flammability data obtained either using our 4.6 litre stainless steel cylinder described in Ref (12) (C) or our 20 litre Hastelloy C sphere,(S) are given in table 3.

Miscellaneous data can be found in the literature, like the flammability limits of benzene in chlorine (20) : LFL = 8 % vol, UFL = 52 % vol.

The experimental data is given under atmospheric initial pressure, unless otherwise specified.

Self-ignition temperatures

Data on self-ignition temperature of gaseous mixtures of fuel and chlorine are given by Mal'tseva (17), Dokter (18) and others. A collection of data is given in table 4.

CONCLUSION

Owing to the importance of chemical reactions involving free chlorine in the chemical industry, the collection of experiences and experimental data is of great interest. This should contribute more to process safety than information on less dangerous chemicals or processes. It is surprising that only limited effort or support is devoted to collect safety data on chlorination reactions. The literature on the safety of chlorination reactions is very limited compared to the literature on oxidation reactions using oxygen. The authors hope that their contribution will promote further experimental work in this field. The new 20 litre explosion vessel, specially designed to study the flammability of gaseous mixtures containing chlorine as an oxidizer will allow the obtention of reliable data at a reasonable cost, for a wide range of initial conditions.

Table 1
Flammability limits of gaseous fuels in chlorine.
Data of Mal'tseva (16) (17)

Fuel	Temperature (°C)	LFL % vol	UFL % vol
Hydrocarbons			
CH ₄	20 - 22	5,6	63,0
C ₂ H ₆	20 - 22	4,95	55,4
C ₃ H ₈	20 - 22	4,30	50,0
C ₄ H ₁₀	20 - 22	3,31	49,5
C ₅ H ₁₂	20 - 22	2,42	43
Alcohols			
CH ₃ OH	70	13,8	73,5
C ₂ H ₅ OH	83	5,06	64,1
C ₃ H ₇ OH	102	3,03	51,5
C ₄ H ₉ OH	120	2,53	48,8
C ₅ H ₁₁ OH	143	1,98	37,6
Carboxylic acids			
H COO H	105	27,62	82,0
CH ₃ COO H	122	15,83	56,0
C ₂ H ₅ COO H	145	9,33	50,8
C ₃ H ₇ COO H	170	7,81	49,8
C ₄ H ₉ COO H	190	5,84	48,8
Chloro-alkanes			
CH ₃ Cl	20	10,2	56,0
CH ₂ Cl ₂	50	16,7	52,9
CH Cl ₃	not combustible		
C ₂ H ₅ Cl	20	8,98	49,2
1-2 C ₂ H ₄ Cl ₂	100	16,4	36,8
C ₂ H ₃ Cl ₃	not combustible		
C ₃ H ₇ Cl	60	6,88	41,8
C ₃ H ₆ Cl ₂	100	9,95	35,0
C ₃ H ₅ Cl ₃	not combustible		
C ₄ H ₉ Cl	100	5,42	44,5

NB compositions are in percents by volume. Isomers are not specified. Refer to the original papers.

Table 2
Flammability limits of gaseous fuels in chlorine.
 Data published by Dokter (18) and Medard (19).

Fuel	Temperature (°C)	LFL (% vol)	UFL (% vol)	Ref
H ₂		3,5	89	(18)
CH ₄		5,51	63	(18)
CH ₄	100	3,6	66	(18)
CH ₄	200	0,6		(18)
CH ₃ Cl		10,2	63	(18)
C ₂ H ₆		4,95	58,8	(18)
H ₂		8	86	(19)
CH ₄	20	5,6	70	(19)
CH ₄	100	3,6		(19)
CH ₄	200	0,6		(19)
C ₂ H ₆		6,1	58	(19)
C ₃ H ₈		5	40	(19)
CH ₃ Cl		10	63	(19)
CH ₂ Cl ₂		16	53	(19)

Table 3
Flammability limits of gaseous fuels in chlorine

Fuel	Temperature (°C)	LFL (% vol)	UFL (% vol)	Apparatus
CH ₃ Cl	25	7	65	(C)
C ₃ H ₈	70*	2	60	(S)
C ₃ H ₆ Cl ₂	200**	4,5		(S)
(CH ₃) ₃ C-O-CH ₃	60	2	33	(C)
1-4 Dioxane	80	2,5	41	(C)
CH ₃ COOH	120	5	36	(C)
Acetone	60	4,5	60	(C)
Chlorobenzene	130	7,5	43,5	(S)
Toluene	160	3,5	50	(S)
2 chloro toluene	150	5	45	(C)
α chloro toluene	160	4		(S)
α dichloro toluene	160	6		(S)
α trichloro toluene	160	9		(S)
2 Fluoro toluene	100	4	37	(C)

* Po = 1,7 Atmosphere abs.

** Po = 1,3 Atmosphere abs.

(C) = 4.6 litre cylinder

(S) = 20 litre sphere

Table 4
Auto-ignition temperature of gaseous fuels in chlorine

Fuel	AIT in chlorine (°C)	Author
CH ₄	318	(17)
C ₂ H ₆	280	(17)
dimethyl ether	ambient	(17)
C ₁ -C ₃ carboxylic acids	300 - 320	(17)
C ₄ -C ₇ carboxylic acids	230 - 190	(17)
C ₂ -C ₄ carboxylic anhydrides	290 - 215	(17)
C ₃ -C ₅ ketones	325 - 205	(17)
C ₁ -C ₈ alcohols	225 - 210	(17)
C ₂ -C ₇ aldehydes	110 - 160	(17)
H ₂	207	(18)
CH ₃ Cl	215	(18)
CH ₂ Cl ₂	262	(18)
C ₂ H ₆	205	(18)
C ₃ H ₆	150 - 100	(18)
1,2 C ₃ H ₆ Cl ₂	180	(18)
Dioxane (0,26 ATA)	100	(10 - 11)
chloro benzene	> 165	20 litre sphere
C ₃ H ₈ (1,7 ATA)	165	20 litre sphere
C ₃ H ₆ (1,7 ATA)	60	20 litre sphere

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