

for chlorinated products

See Lithium bromoacetylide; Lithium chloroacetylide; Sodium bromoacetylide; Lithium trifluoropropynide
See other HALOACETYLENE DERIVATIVES. METAL ACETYLIDES

ETCHEN

I HOPE THIS HELPS.

THERE ARE MANY
REACTIONS WITH CHLORINATED
MATERIALS & CAUSTIC
ATTACHED ARE ONLY
A FEW

GERALD WAGENER

Dichloroacetylene (Dichloroethyne)
[7572-29-4]

C_2Cl_2

$ClC \equiv CCl$

1. Wotiz, J. H. *et al.*, *J. Org. Chem.*, 1961, 26, 1626
2. Ott, E., *Ber.*, 1942, 75, 1517
3. Kirk-Othmer, 1964, Vol. 5, 203-205
4. Siegel, J. *et al.*, *J. Org. Chem.*, 1970, 35, 3199
5. Riemschneider, R. *et al.*, *Ann.*, 1961, 640, 14
6. MCA Case History No. 1989
7. Kende, A. S. *et al.*, *Synthesis*, 1982, 455
8. Kende, A. S. *et al.*, *Tetrahedron Lett.*, 1982, 23, 2369, 2373

Dichloroacetylene is rather endothermic (ΔH_f° (g) +149.4 kJ/mol, 1.57 kJ/g) and a heat-sensitive explosive gas which ignites in contact with air. However, its azeotrope with diethyl ether (55.4% dichloroacetylene) is not explosive and is stable to air [1,2]. It is formed on catalysed contact between acetylene and chlorine, or sodium hypochlorite at low temperature; or by the action of alkali upon polychloro-ethane and -ethylene derivatives, notably trichloroethylene [3]. A safe synthesis has been described [4]. Ignition of a 58 mol% solution in ether on exposure to air of high humidity, and violent explosion of a conc. solution in carbon tetrachloride shortly after exposure to air have been reported. Stirring the ethereal solution with tap water usually caused ignition and explosion [5]. Dichloroacetylene had been collected without incident on 6 previous occasions as a dilute solution. When the cooling system was modified by lowering the temperature in the water separator, liquid chloroacetylene separated there and exploded when a stopcock was turned [6]. A safer low temperature preparation of material free of trichloroethylene has been described [7,8].

See Tetrachloroethylene: Sodium hydroxide

Trichloroethylene: Alkali, or: Epoxides

See also Chlorocycanoacetylene

See other HALOACETYLENE DERIVATIVES

CHLOROETHYLENE WILL
REACT WITH CAUSTIC
AND YIELD HIGH EXOTHERMIC
HEAT OF REACTION BUT
THE MIXTURE MUST BE
HOT BECAUSE OF THE
2 PHASES. MIXING WILL
LOWER THE ONSET TEMP

Chlorodifluoroacetyl hypochlorite
[68674-44-2]

$C_2Cl_2F_2O_2$

$ClCF_2CO.OCl$

Unstable above 22°C and explosive in gas phase at pressures above 27-63 mbar.

See entry ACYL HYPOHALITES (reference 1)

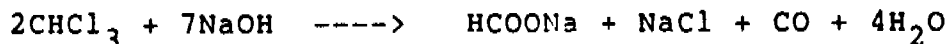
October 22, 1986

Brian Knowles
Per/Tet
Western Division

CHLORINATED ORGANICS AND A STRONG BASE

Brian,

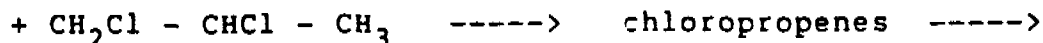
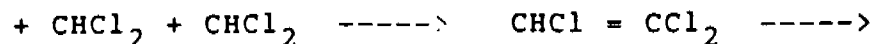
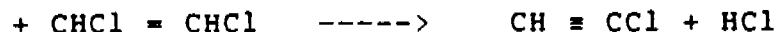
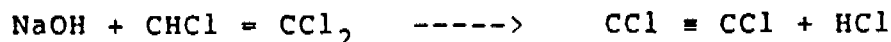
This is a summary of the information I have been able to find on the problem of contacting chlorinated organics with a strong base. All of these reactions have been documented in the past as a reactive chemicals problem.



Heat of Reaction = 30.6 Kcal/mole of NaOH

= 107.1 Kcal/mole of CHCl_3

Explosions were reported in Louisiana and Texas when CH_2Cl_2 containing CHCl_3 was passed through a flake caustic bed and when NaOH was used instead of potash for removing HCl from CHCl_3 .



(Dow MAPP Process)



Emmett Brown
La. AS&TL

db

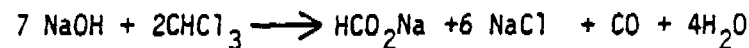
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2. Analyze a sample from every car or truck using a positive identification procedure.
3. Question and investigate anything unusual, i.e., fittings, physical properties, color, etc.
4. Document that identification has been completed before unloading is started.
5. Carry out an audit on a periodic basis to determine that these procedures are followed and their importance understood.

CAUSTIC/CHLOROFORM REACTION

In the January summary of reactive chemicals, an incident was reported in which 500MT of chloroform with a high acidity was being reprocessed by passing it through a pot containing caustic flakes. Several hours later a violent explosion occurred in the caustic pot which blew the 80 pound top about 35 feet.

I hope this incident was not viewed as being due to the high acidity of the chloroform and caustic instead of the well known high energy gas generating reaction between caustic and chloroform.



The ΔH_p for this reaction was calculated to be -30.6 kcal/mole of NaOH or -107.1 kcal/mole of CHCl_3 . Consequently, it is advisable that caustic and chloroform not be brought together at any temperature unless precautions are made to handle both the heat and the large pressure generation. (Texas Division Report TC-1020; 3-17-82)

QUIZ

A drum labeled "Rubinate M," a polymeric isocyanate, ruptured at the bottom and was propelled into the ceiling of a vented hood enclosure. Approximately one hour before the incident, 15 gallons of a waste isocyanate was transferred to the drum which was thought to contain approximately 15 gallons of polymeric isocyanate.

What was a possible cause for this incident and what corrective action would you recommend?

For additional information on the "Safe Handling and Storage of Toluene Diisocyanates" see our product brochure Form No. 109-561-82.

- Remove empty drums to a well-ventilated location or to the out-of-doors.
- Remove all drums and fill with water.
- Allow drums to stand undisturbed for 24 hours.
- All drums should be scrapped. They should be drained and crushed to render them totally unusable.

The drum apparently had been decontaminated with water, which readily reacts with isocyanates to form both an insoluble urea compound and carbon dioxide, our has not been disposed or relabeled in a proper manner and still contained water. Our product literature states isocyanate drums should be decontaminated by the following procedure:

n aug
Doug A. Rausch
Corp S&LP
2030 Willard H. Dow Center
6-0510

Doug Rausch

For address change, new subscriber, extra copies, contact J. [redacted] Corporate Safety & Loss, 2020 Dow Center, The Dow Chemical Company, Midland, MI 48640.

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TRICHLOROETHYLENE
Though usually considered to be non-flammable in use, it has unusually wide flammability limits and can be ignited by a flame or other intense source. The most recent Data Sheet is devoted to all aspects of laboratory use.

Alkali

1. Fabian, F., private comm., 1960
2. *ABCM Quart. Safety Summ.*, 1956, 27, 17
3. Anon., *Jahresber.*, 1978, 70

An emulsion, formed during extraction of a strongly alkaline liquor with trichloroethylene, decomposed with evolution of the spontaneously flammable gas, dichloroacetylene [1]. This reaction could also occur if alkaline metal-stripping preparations were used in conjunction with trichloroethylene degreasing preparations, some of which also contain amines as inhibitors, which could also cause the same reaction [2]. Apparently accidental contact of the solvent with potassium hydroxide solution led to generation of flames in the charging port of a stirred reactor [3].

See also Tetrachloroethylene: Sodium hydroxide

Aluminium

See Aluminium: Halocarbons

Epoxides

Dobinson, B. *et al.*, *Chem. & Ind.*, 1972, 214

1-Chloro-2,3-epoxypropane, the mono- and di-2,3-epoxypropyl ethers of 1,4-butanediol, and 2,2-bis[4(2',3'-epoxypropoxy)phenyl]propane can, in presence of catalytic quantities of halide ions, cause dehydrochlorination of trichloroethylene to dichloroacetylene, which causes minor explosions when the mixture is boiled under reflux. A mechanism is discussed.

See also Alkali, above

Metals

See Aluminium: Halocarbons
Barium: Halocarbons
Beryllium: Halocarbons
Lithium: Halocarbons
Magnesium: Halocarbons
Titanium: Halocarbons

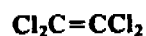
Oxidants

See Perchloric acid: Trichloroethylene
Dinitrogen tetroxide: Halocarbons
Oxygen (Gas): Halocarbons
Oxygen (Liquid): Halocarbons

Water

Brade, C., *Chem. Tech.* (Berlin), 1952, 4, 506-507

Tetrachloroethylene
[127-18-4]



(MCA SD-24, 1971); HCS 1980, 887; RSC Lab. Hazard Data Sheet No. 6, 1982
Aluminium

See Aluminium: Halocarbons

Aluminium, Zinc oxide

Katz, S. *et al.*, *Chem. Abs.*, 1981, 94, 33106

The mixture is burned militarily to produce dense smoke.

Dinitrogen tetroxide

See Dinitrogen tetroxide: Halocarbons

Metals

See Barium: Halocarbons

Lithium: Halocarbons

Sodium hydroxide

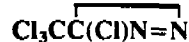
Mitchell, P. R., private comm., 1973

The presence of 0.5% of trichloroethylene as impurity in tetrachloroethylene during unheated drying over solid sodium hydroxide caused generation of dichloroacetylene. After subsequent fractional distillation, the volatile fore-run exploded.

See Dichloroacetylene; also Trichloroethylene: Alkali

See other HALOALKENES

3-Chloro-3-trichloromethyldiazirine
[35295-56-5]



Liu, M. T. H., *Chem. Eng. News*, 1974, 52(36), 3

An ampoule of the compound exploded when scored with a file, indicating high shock-sensitivity.

See other DIAZIRINES

Hexachloroethane
[67-72-1]



HCS 1980, 530