JJ
Gretchen
Don
Sharon

Some of us are moving to Trichlor as a parts cleaner — some reactive chem info

Craig

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cc: Joan Pennington
Jack Gathers
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REACTIVITY STUDY, CHLOROFORM AND CAUSTIC

In response to your Dec 19,1988 letter to Joan Pennington requesting help in petitioning the Coast Guard to take the steps necessary to add chloroform to their "incompatibility" registry we feel that there is sufficient reactivity information in the open literature and within Dow to support your position. Attached is documentation which I feel will help support your position when dealing with the Coast Guard. Of course, you will need to get approval from the appropriate Dow departments to release this information. I have consulted with our chlorinated solvents research folks, Emmett Brown and Roger Bowlin, and they are in agreement with this information.

With regards to your statement that trichloroethylene has a similar reactivity with caustic, this is not entirely correct. Sodium hydroxide actually dehydrochlorinates the trichloroethylene thereby producing spontaneously explosive and flammable chloroacetylenes and in addition if ionic halides are present (which probably will be) the explosive dichloroacteylene can also be produced. These specific types of reactions are not possible with chloroform however even though the chemistry is different the severity of the reactivity hazards (generation of heat and pressure) do necessitate deeming it incompatible. The supporting documentation is listed below.

The reaction of sodium hydroxide and chloroform is listed throughout the literature and is consistent with the discussion listed on page 343 of March's "Advanced Organic Chemistry, 2nd edition)". Chloroform undergoes an alpha elimination reaction whereby a proton is given up to produce the unstable trichloromethyl anion CCL3 which decomposes by losing a chloride to form the very unstable and reactive dichlorocarbene--CCL2 which is then hydrolyzed to formic acid and carbon monoxide. Due to the presence of caustic the formic acid is converted to sodium formate. This reaction is very exothermic and high pressures can result from production of CO. Sodium chloride and water are also byproducts. This chemistry is consistent with the following work done in Texas.

The attached Dow CRI report TC-1020 describes adiabatic runaway device experiments which were done to simulate plant conditions that initiated reactive chemicals incidents at Chlorinated Methanes plant in Louisiana and Sarnia. Operators at these plants noticed that upon passing methylene chloride through a caustic filter, that as the chloroform concentration increased, the filter pots glowed cherry-red. The reaction of interest proceeds as follows:

$$7\ NaOH + 2\ CHCl_3 \text{-----} > HCOONa + 6\ NaCl + CO + 4\ H_2O$$

Heat of reaction calculated as -107.1 kcal/mole $CHCl_3$

The experiments consisted of first adding flake caustic to the Parr bomb and then adding methylene chloride. The mixture was heated to 50 deg C and then chloroform was added. No definite reaction was seen at after 24 hrs and then the temp was increased to 100 deg C. At this time the above reaction proceeded at a significant rate and had to be stopped due to excessive pressure generation. The experiment was repeated at 100 deg C with only half the chloroform. The experimental value for the heat of reaction was found to be -40 kcal/mole of CHCL3 which is lower than expected probably due to the reaction not going to completion.

The conclusion drawn from this experiment was that the considerable pressure and heat generated by this reaction makes it especially dangerous. Even though no reaction was seen at 50 deg C the recommendation was that caustic and chloroform should not be brought together at any temperature unless precautions are taken to handle the heat and pressure which is generated.

ARC data produced in the LAD Reactive Chemicals Lab in 1982 is consistent with results reported in the above ARD experiments. The attached ARC reports (LARC #135 and #136) represent ARC experiments done with chloroform and 50% caustic and 100% caustic respectively. In LARC #135 1 part 50% caustic and 1 part chloroform were added to a light Hastelloy-C bomb and run from 30 deg C to 425 deg C with a heat step temperature of 10 deg C. Two exotherms were seen--the first exotherm started at 101 deg C and ended at 305 deg C with a max heat rate of 88 deg C/min and a max pressure of 2958 psia. The second exotherm started at 314 deg C and ended at 331 deg C.

LARC #136 represents a run made by adding 1 part 100%caustic to 1 part chloroform into a heavy Hastelloy-C bomb. Experimental conditions were similar to the previous experiment with exception of the end temperature which was 300 deg C. The reaction proceeded almost immediately with the first exotherm beginning at 32 deg C and ending at 162 deg C with a max heat rate of 56 deg C/min and a max pressure of 929 psia. The second exotherm started at 234 deg C and ended at 263 deg C with a max heat rate of 0.241 deg C/min and a max pressure of 2509 psia.

The conclusion from these ARC experiments is that that a highly exothermic and pressure producing reaction occurs almost immediately as 100% caustic and chloroform are brought together at 30 deg C. It appears that elevated temperatures are required for chloroform and 50% caustic to react (experimental ARC value was found to be 101 deg C) however different conditions could affect this substantially. As stated above in the ARD experiment the conclusion is the same --- chloroform and caustic should not be brought together at any temperature unless precautions are made to handle the heat and pressure which will be generated.

In my estimation this information should suffice as proper documentation to support your petition to the Coast Guard. If I can be of further assistance or if you feel a meeting would be appropriate you may contact me at 1828.

Gerald Wagener

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