An Analysis of α-Epichlorohydrin-Water Runaways

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A curiosity began after plotting adiabatic reaction calorimeter (ARC) data from a homework problem placed in a textbook entitled Chemical Process Safety by Daniel A. Crowl and Joseph F. Louvar, 2011. The data were for a 50/50 mixture (by mass) of α — epichlorohydrin and water mixture. Two exotherms appeared. The first exotherm involved hydration and polymerization of α-epichlorohydrin. A second exotherm appears as well related to the decomposition of reactants and products. Modeling exotherm 1 as a direct hydration of α-epichlorohydrin to glycerin and HCl underpredicted the observed exotherm. Thus, what are the mystery reactions involved that released more energy than predicted by simply modeling hydration to glycerin? Authored by Georges Melhem and Enio Kumpinsky of ioMosaic, as well as Joshua Tran and Ronald J. Willey of Northeastern University, the paper reports the answers found to this mystery. A combination of 13 intermediate reactions is proposed.

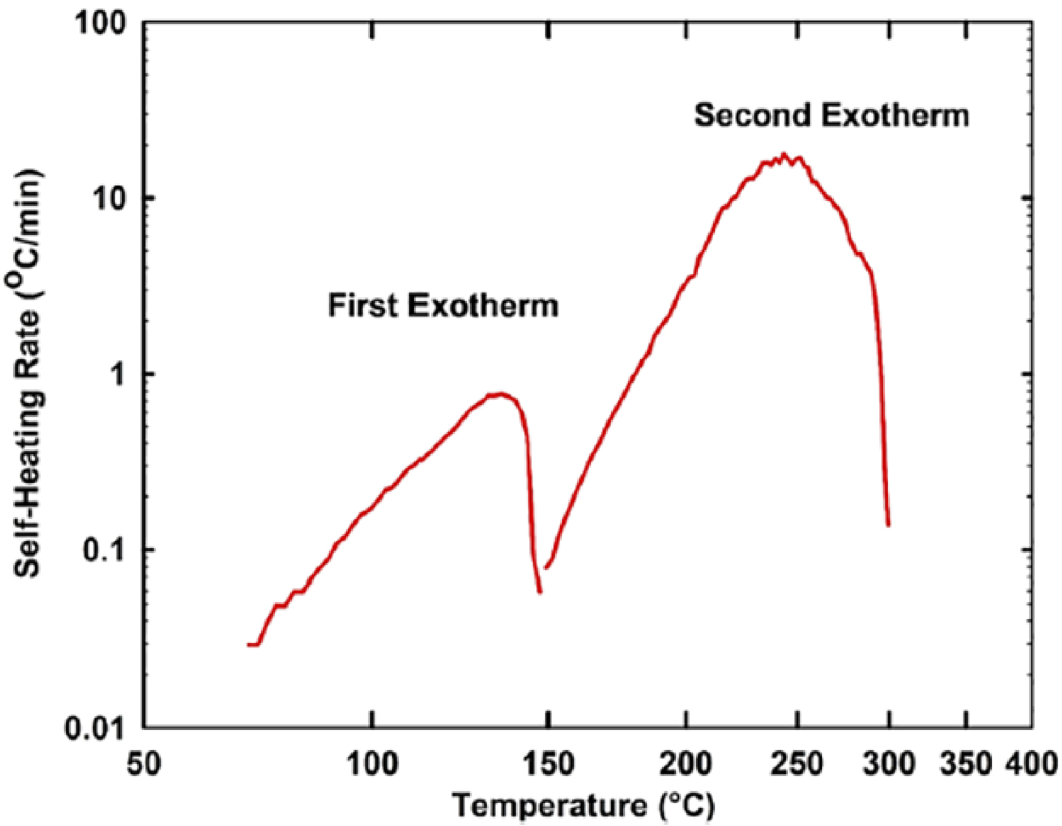
Introduction

Hazards with α-epichlorohydrin include its exothermic reactivity especially if water is present. An Internet search showed a resource that lists 33 chemical accidents with epichlorohydrin (FACTS Hazard Chemical Knowledge Database - Epichlorohydrin). 20 of these accidents were related to chemical transport. 11 involved injuries and 1 involved a fatality. One example of reactivity is reported by the US National Oceanic and Atmospheric Administration NOAA (Epichlorohydrin Incident; Bayport, TX, 2003). On June 26, 2003 washing from an epichlorohydrin tank was transferred to a tank truck. Venting was observed from the tank truck. Upon investigation, significant water was combined with the epichlorohydrin. Self-heating due to an exothermic reaction between epichlorohydrin and water initiated reaching nearly 100 °C. The following paragraph extracted from the article ("Epichlorohydrin Incident; Bayport, TX, 2003) summarizes the hazards.

Epichlorohydrin is a volatile, highly reactive, and toxic chemical (as well as a suspected carcinogen). It is moderately flammable and unstable. While not generally identified as water-reactive, epichlorohydrin will slowly hydrolyze with water, producing heat. In a confined space such as a tank car, the heat could build and enhance the rate of reaction. The by-products formed by such reactions are not expected to be shock sensitive or spontaneously detonate, but the heat formed during the reaction could volatilize enough epichlorohydrin to create a potentially explosive mixture in the presence of an ignition source. Vapors generated would be expected to be heavier than air and may accumulate near the source. Worker safety near the site should be thoroughly evaluated. Clearly, epichlorohydrin is a dangerous chemical.

More insight into the reactivity of epichlorohydrin and water is found in data provided in a homework problem in a textbook (Crowl and Louvar, 2011). Two exotherms can occur – hydrolysis followed by decomposition. The data were obtained from an adiabatic reaction calorimeter (ARC) experiment completed within Dow Chemical during the late 1980 s. Tabulated data provided to the student were time, temperature, temperature rise rate, pressure, and pressure rise rate for an ARC experiment using a 4 g total of a 50:50 mixture (by mass) of α-epichlorohydrin and water placed inside a 9.1 ml stainless steel test cell. The resultant ARC self-heating rate versus temperature plot is shown in Fig. 1. Fig. 1 shows the two exotherms, the first peaking at 154 °C and reaching a pressure of 92.6 psia at this point, the second exotherm peaking at 250 °C and reaching a pressure of 640 psia. The runaways finished by 300 °C with a final pressure of 1840 psia. The problem statement requested the determination of the onset temperature, the final temperature of each exotherm, as well as the activation energy and pre-exponential constant for the first exotherm using a first-order reaction model.

Figure 1: Self-heating rate vs. temperature, °C for a 50:50 α-epichlorohydrin/water mixture ARC test (from Crowl and Louvar (2011), p. 423)



In his process-safety class on reactivity, Professor Wiley used this problem to introduce students to a software program that models reactions completed in an ARC. The specific program, called SuperChems™, is a development by a former student Georges Melhem, now President of ioMosaic, Inc. SuperChems offers a large chemical database and has the capability to add interaction parameters for mixtures. This feature allows users to match experimental calorimetric pressure/temperature data accurately. Willey, working with previous classes, modelled the first runaway in SuperChems as shown as Reaction 1.

α-Epichlorohydrin + 2 Water -→ Glycerin + HCl

The findings, compared to the experimental results, delivered an exotherm that was less severe and peaked earlier for the first exotherm shown in Fig. 1. The heat released given by the reaction shown in Reaction 1 is not high enough to match the results shown in the first exotherm of Fig. 1. Discussing this poor model fit with Georges Melhem initiated an experimental and modeling program led by scientists and engineers associated with ioMosaic. The goal was to understand the underlying reactions involved in epichlorohydrin/water runaway chemistries. These findings are summarized in the **full paper**, published in the April 2023 iChemE Process Safety and Environmental Protection (PSEP) Journal.

Methods

Materials were purchased from Sigma Aldrich or similar chemical suppliers using ACS chemical grade or better. Thirteen separate data acquisition runs, using mixtures shown in Table 1 were completed. Run 2 C is the repeat of the information provided for the problem statement (2 g of epichlorohydrin and 2 g of water in a 9.1 cc ARC bomb). Fig. 2 provides molecular formulas and structures for some of the reactants and suspected intermediates investigated in the study. Mixtures were formulated to help decouple the reaction mechanisms involved. A Netzsch Instruments adiabatic reaction calorimeter was used. The test cell was selected based on the potential overpressure. Those runs of lower pressure build-up used titanium, while stainless steel, Inconel 600, or Hastelloy C were used on runs that resulted in high final pressure. Heat-Wait-Search routines were set up, and exothermic action was monitored. When an exotherm was detected, the instrument then switched to adiabatic mode acquiring time, temperature, and pressure.

Read the Paper

Learn the findings and results of the analysis of α-epichlorohydrin-water runaways, published in the IChemE April 2023 Process Safety and Environmental Protection (PSEP) Journal.

Fire and Explosion

Read this incident report for important lessons learned from this November 7, 1990, runaway reaction at a waste oil recovery factory in Japan during vacuum distillation of ECH waste, leading to a fire and explosion.