

# Exothermic reactions Runway for Non Pressure Reaction of Epoxidation of Butene Diol with hydrogen peroxide

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## ABSTRACT

*Exothermic reactions with runaway potentials are carried out in industry either in continuous or semi-batch mode. Non pressure reaction are controlled reactant is fed to the reactor at predetermined rate continuously irrespective of reaction conditions and it is likely that rate of addition of the controlled reactant is more. This will lead to accumulation of this reactant in the reaction mass which at latter stage will react at faster rate due to higher temperature, leading to runaway reaction. Epoxidation of Butene Diol was carried out by its reaction with hydrogen peroxide. Since theoretical  $\Delta T_{ad}$  for this reaction is 675°C, the reactions were carried out. Butene Diol and water were charged in the flask and hydrogen peroxide was added slowly. The rise in temperature,  $\Delta T$ , was noted and heat of reaction  $Q$ , calculated. The gas chromatograms of butene diol and samples were carried out. Confirm this  $\Delta H_r$  by simple laboratory experiments avoiding loss of heat to reactor or atmosphere. By measuring  $\Delta T_{ad}$  in an apparatus whereby reaction temperature and outside apparatus temperature are maintained in equilibrium. If the theoretical  $\Delta T_{ad}$  is high enough to boil a reactant, dilute the reaction mass with suitable solvent to keep reaction temperature below its boiling point. By removing the heat,  $Q$ , and measuring the same at nearly at constant process temperature.*

**Keywords:-** Exothermic Reaction, Temperature Runway, Non Pressure Reaction, Epoxidation of Butene Diol

## 1. INTRODUCTION

Reactive chemicals are involved in many industrial incidents every year harming people, property, and the environment. Majority of chemical reactions carried out in industry are exothermic in nature. Some reactions require very little activation energy to be initiated. If the reaction is exothermic, the energy initially produced may accelerate a continued reaction and release energy too rapidly to be controlled. The autoclave reactor is a small cylindrical reactor; built to withstand high pressures, used to evaluate the kinetics of high-temperature, high-pressure reactions and the production of small quantities of specialty chemicals. The reactor is typically packed with a supported catalyst, and reactant is added by injection. Pressure in the system is elevated by increasing the temperature of the autoclave. Additional pressure, if needed, can be obtained with the injection of additional gaseous reactant or an inert.

The present work to arrive at reasonably close prediction and prevention of runaway reactions carried out by and within means of MSME chemical units consists of theoretical estimation of  $\Delta H_r$  to predict the runaway nature of reaction and its comparison with practically determined  $\Delta H_r$  and details measures to prevent a potentially runaway reaction. In semi-batch mode reactions carried out in MSME units, one of the reactant is control fed to the reactor over a period and the heat generated is also removed continuously to prevent built up of heat leading to runaway reaction. While studying exothermic reactions for potential runaway, none of the two methods, theoretical estimation or experimental determination of Heat of Reaction,  $\Delta H_r$ , give accurate results as mentioned earlier. Since process design in exothermic reactions is advisable to be carried out with 25 % safety margin, theoretical estimation results within 25 % of actually observed on plant scale should be acceptable. Non pressure reaction are controlled reactant is fed to the reactor at predetermined rate continuously irrespective of reaction conditions and it is likely that rate of addition of the controlled reactant is more than consumption in reaction due to deviation in reaction condition parameters. This will lead to accumulation of this reactant in the reaction mass which at latter stage will react at faster rate due to higher temperature, leading to runaway reaction.

Exothermic reactions with runaway potentials are carried out in industry either in continuous or semi-batch mode. In continuous mode, all reactants are fed to the reactor continuously and the process is equilibrated with intrinsic design to control the flow through the reactor to avoid runaway and the product removed continuously. These type of reactions are carried out in large scale industry and are not within the scope of present study. Reactions carried out in MSME units are usually known and prediction of thermal runaway can be made by evaluating thermal kinetics of the reaction theoretically.

Heat removal capacity of cooling system can be calculated with detailed engineering and cooling system data or with simple experiment.

## **2. ESTIMATION OF ACCUMULATION OF CONTROLLED REACTANT**

The exothermic chemical reactions carried out in industry are semi batch processes wherein one of the reactant is control fed to the reactor over reaction period so as to control heat of reaction in progressive manner that can be removed by cooling system over a period. Here it is important that the rate of reaction, and therefore rate of heat generation is equivalent to rate of addition of controlled reactant. If the rate of addition of controlled reactant is more than the rate of reaction, the excess of controlled reactant will accumulate in reaction mass and at one stage the rate of reaction will increase causing all of this accumulated reactant to react in a very short time. This will result in large heat generation in short time and the existing cooling system will not be able to remove this heat in equivalent time leading to runaway reaction. It is, therefore, important to determine the rate of addition of controlled reactant so that no accumulation of controlled reactant in reaction mass takes place. This can be done in lab experiments by analyzing the reaction mass for controlled reactant. These semi-batch reactions can be classified in two types.

### **2.1. Pressure Reactions**

In this type, the reaction is carried out under pressure in pressure vessel, autoclave, and controlled reactant is also fed under pressure. In this type, if the heat generated is more than removed, pressure in the reactor will increase and will prevent flow of controlled reactant to the reactor preventing accumulation of reactant in the reaction mass. The exotherm due to sudden reaction of accumulated reactant and, therefore, runaway is thus prevented. These reactions are comparatively less prone to runaway, even as pressure hazards are present.

### **2.2. Non-Pressure Reactions**

In this type, the controlled reactant is fed to the reactor at predetermined rate continuously irrespective of reaction conditions and it is likely that rate of addition of the controlled reactant is more than consumption in reaction due to deviation in reaction condition parameters. This will lead to accumulation of this reactant in the reaction mass which at latter stage will react at faster rate due to higher temperature, leading to runaway reaction.

## **2. MATERIAL**

### **2.1 Butene Diol**

Butene Diol C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> which is also known as cis-Butene-1,4-diol is a chemical compound used in the production of endosulfan. It reacts with hexachlorocyclopentadiene to form endosulfan diol. Endosulfan diol then reacts with thionyl chloride to form endosulfan. Its Boiling point is 235 °C and Molar mass is 88.104 g/mol with Density 1.07 and is Solubility ethanol, acetone.

### **2.1. Hydrogen peroxide**

Hydrogen Peroxide is a chemical compound with the formula H<sub>2</sub>O<sub>2</sub>. In its pure form, it is a very pale blue liquid that is slightly more viscous than water. It is used as an oxidizer, bleaching agent, and antiseptic, usually as a dilute solution (3%–6% by weight) in water for consumer use, and in higher concentrations for industrial use. Its Boiling Point is 150.00C and molar mass is 34.017 g/mol.

### **2.2. Equipment**

Epoxidation of butene diol was carried out in a 1 litre 4-neck round bottom flask fitted with stirrer, thermometer in a socket, air condenser and a dropping funnel. The flask was kept in mantle and also covered with asbestos rope to avoid loss of heat to atmosphere. To prevent the loss of heat to atmosphere, next experiment was carried out by carrying out reaction in water bath as shown in Figure no. 1. and adjusting temperature of water bath continuously through dimmerstate to that of reaction inside the flask. This way loss of heat to reaction flask or atmosphere will be negligible.

## **3. METHODOLOGY**

Epoxidation of Butene Diol was carried out by its reaction with hydrogen peroxide. Since theoretical  $\Delta T_{ad}$  for this reaction is 675°C, the reactions were carried out total dilution with water as solvent to keep maximum temperature of reaction below 100°C, the boiling point in reaction. Butene Diol and water were charged in the flask and hydrogen peroxide was added slowly through the dropping funnel under continuous stirring. The rise in temperature,  $\Delta T$ , was noted and heat of reaction  $Q$ , calculated from the formula is  $Q_{cal} = m \cdot C_p \cdot \Delta T$  where,  $M$  is reaction mass in gm,  $C_p$  is specific heat capacity of reaction mass in cal/gm°C and  $\Delta T$  rise in temperature in °C.



**Figure 1** Experimental Setup

#### 4. THEORETICAL ESTIMATION OF $\Delta H_r$

##### From Heats of Formation

Theoretical Estimation of heat of reaction,  $\Delta H_r$ , can also be made from standard heats of formation,  $\Delta H_f$ , of the reactants and products. For a reaction



It will be sum of  $\Delta H_f$  of the products minus sum of  $\Delta H_f$  of the reactants, i.e.

$$\Delta H_r = c\Delta H_f(C) + d\Delta H_f(D) - a\Delta H_f(A) - b\Delta H_f(B) \quad (ii)$$

$\Delta H_f$  for most of the compounds are readily available from various data bases.

We will apply bond energy method for case study of Schiff Base hydrogenation and heat of formation method for case study of Epoxydation of Butene Diol.

#### 5. CASE STUDIES DETERMINATION OF $\Delta H_r$ FOR EPOXIDATION OF BUTENE DIOL

##### 5.1. Charge : Butene Diol : 75 gm.; water : 75 gm.; Catalyst : 7.5 gm. Hydrogen Peroxide : 59 gm diluted to 98 gm. with water.

At initial temperature of 34°C, 50 gm. of the peroxide solution was added in 15 minutes; temperature rose to 50°C and 1<sup>st</sup> sample was drawn for analyzing reaction progress. Balance peroxide solution was added in next 15 minutes, temperature rose to 65°C and 2<sup>nd</sup> sample was drawn. Within next 15 minutes the temperature rose rapidly to 101.7°C with water boiling. The temperature slowly dropped afterwards. Samples drawn after 15 and 30 minutes were analyzed for extent of reaction by gas chromatography.

From the analysis of 1<sup>st</sup> sample, it is seen that whereas the peroxide added was about 50 %, the reaction completed was only 10.73 % suggesting accumulation of about 11.6 gm peroxide (100% basis) till then. Analysis of second sample after 30 minutes showed extent of reaction at about 35 % only even as 100 % addition was complete suggesting accumulation of about 19.2 gm peroxide (100% basis). This accumulated peroxide reacted at faster rate due to high temperature raising temperature beyond 100°C.

##### 5.2. Charge: Butene Diol: 50 gm.; Water:300 gm.; catalyst: 5 gm.

39 gm. Of Hydrogen Peroxide ( 50% ) diluted with water to 156 gm. added slowly over a period of 3 hours through dropping funnel. Initial and Final Reaction Temperature was 32°C and 75.5°C respectively. Difference in temperature rise was 43.5°C. Total Reaction Mass = 511 gm

$$C_p \text{ of reaction mass} = ((50 \times 2 \times 0.239) + (2.62 \times 19.5 \times 0.239) + (441.5 \times 1)) / 511 = 0.934 \text{ cal / gm.}$$

$$\text{Therefore, Experimental } \Delta H_r = 511 \times 0.934 \times 43.5 = 20761 \text{ cal}$$

$$\text{Theoretical } \Delta H_r = 490.65 \times 50 = 24532 \text{ cal}$$

##### 5.3. Charge : Butene Diol : 50 gm.; Water : 200 gm.; Catalyst : 5 gm.

39 gm. Of Hydrogen Peroxide ( 50% ) diluted with water to 156 gm. added slowly over a period of 4.0 hours through dropping funnel. Initial and Final Reaction Temperature was 33°C and 63.5°C respectively. Difference in temperature rise was 30.5°C. Total Reaction Mass is 461 gm

$$C_p \text{ of reaction mass} = ((50 \times 2 \times 0.239) + (2.62 \times 19.5 \times 0.239) + (391.5 \times 1)) / 461 = 0.928 \text{ cal / gm.}$$

$$C_p \text{ Butene Diol} = 2.0 \text{ J/gm; } C_p \text{ Hydrogen Peroxide} = 2.62 \text{ J/gm; } C_p \text{ Water} = 1.0 \text{ cal/gm )}$$

$$\text{Experimental } \Delta H_r = 461 \times 0.928 \times 30.5 = 13048 \text{ cal.}$$

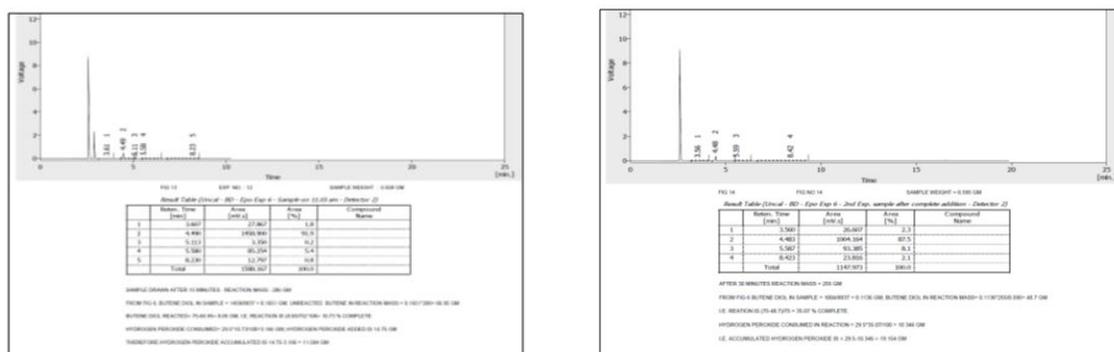
$$\Delta H_r, \text{ theoretical for this reaction is } 490.65 \text{ cal / gm}$$

$$\text{Therefore, Theoretical } \Delta H_r = 490.65 \times 50 = 24532 \text{ cal.}$$

#### 6. RESULTS AND OBSERVATION

**6.1. Charge: Butene Diol : 75 gm.; water : 75 gm.; Catalyst : 7.5 gm. Hydrogen Peroxide : 59 gm. Diluted to 98 gm. with water.**

At initial temperature of 34°C, 50 gm. of the peroxide solution was added in 15 minutes; temperature rose to 50°C and 1<sup>st</sup> sample was drawn for analyzing reaction progress. Balance peroxide solution was added in next 15 minutes, temperature rose to 65°C and 2<sup>nd</sup> sample was drawn. Within next 15 minutes the temperature rose rapidly to 101.7°C with water boiling. The temperature slowly dropped afterwards. Samples drawn after 15 and 30 minutes were analyzed for extent of reaction by gas chromatography. The chromatograms are shown in Figure 2. From the analysis of 1<sup>st</sup> sample, it is seen that whereas the peroxide added was about 50 %, the reaction completed was only 10.73 % suggesting accumulation of about 11.6 gm peroxide (100% basis) till then. Analysis of second sample after 30 minutes showed extent of reaction at about 35 % only even as 100 % addition was complete suggesting accumulation of about 19.2 gm peroxide (100% basis). This accumulated peroxide reacted at faster rate due to high temperature raising temperature beyond 100°C.

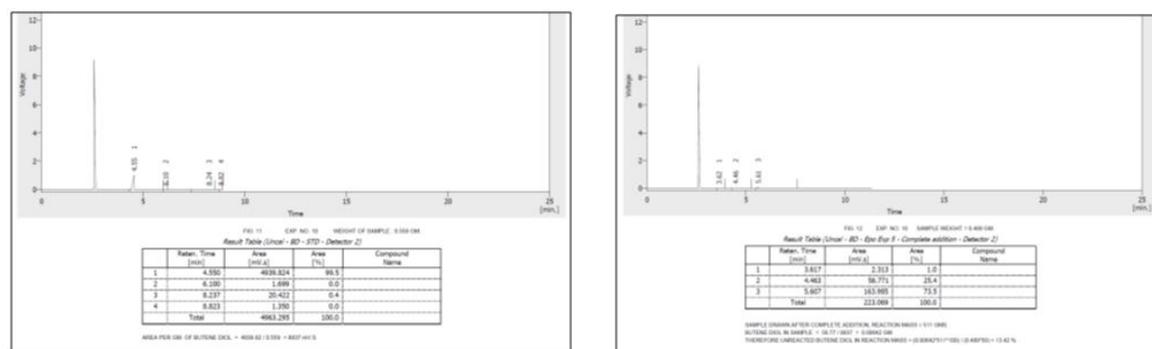


**Figure 2 Results of Gas Chromatography**

**6.2. Charge: Butene Diol: 50 gm.; Water:300 gm.; catalyst: 5 gm.**

The experimental ΔHr is about 85% of the theoretical. This lower experimental ΔHr may be due to loss of heat to atmosphere and /or due to incomplete reaction. To correlate this loss of heat analysis of the product was carried out by Gas Chromatography. Chromatograms of pure Butene Diol and product Epoxydized Butene Diol are shown in Figure 2. The sample was also analyzed for hydrogen peroxide content. From Figure 2, unreacted Butene Diol = 13.42\*50 / 100 = 6.71 gm. out of 50 gm. Or reaction is 100 -(6.71\*100/50) = 86.58 % complete. Theoretical ΔHr, therefore will be 24532\* 86.58/100 = 21240 cal; Experimental ΔHr is 20761 cal. From analysis of hydrogen peroxide content, no peroxide was detected meaning all peroxide was decomposed though not reacted. That means 13.42 % (100-86.58) or 2.62 gm hydrogen peroxide is decomposed but not reacted and the heat of this decomposition will add to ΔHr experimental.

2 H<sub>2</sub>O<sub>2</sub> = 2H<sub>2</sub>O + O<sub>2</sub> Heat of decomposition = 23440 cal / Mole(34 gms) or 690 cal/gm. For 2.62 gms, it will be 2.62\*690 = 1808 cal ΔHr, theoretical, therefore will be 21240 + 1808 = 23048 cal against experimental ΔHr of 20761 cal. The difference in ΔHr experimental and theoretical is 2287 cal i.e. about 9.9 %, which is very reasonable for process design. To study the effect of faster addition of controlled reactant than the rate of reaction and with less diluent water to absorb the reaction heat, next experiment was carried out as below.



**FIGURE 3 Results of Gas Chromatography**

**6.3. Charge : Butene Diol : 50 gm.; Water : 200 gm.; Catalyst : 5 gm.**

The experimentally determined ΔHr is only about 53 % of calculated theoretically. The low value of experimental ΔHr is likely due to loss of heat to mantle and atmosphere. To check the progress of reaction with respect to accumulation of controlled reactant, hydrogen peroxide, samples of reaction mass were drawn after 2,3 and 4 hours of reaction and analyzed for butene diol and hydrogen peroxide contents. Hydrogen peroxide content was determined by iodometric titration.

Sr no.	Reaction period Hour	Reaction mass, gm	Unreacted Butene diol	Unreacted Peroxide
1	2.0	275	46.2%	Not Detected
2	3.0	320	24.1%	Not Detected
3	4.0	360	00.23%	Not Detected
4	5.0	360	00.24%	Not Detected

Table No. 1:- The rate of addition of controlled reactant

From the Table 1, it is seen that the rate of addition of controlled reactant, hydrogen peroxide, is equivalent or lower than the rate of reaction so that there is no accumulation of controlled reactant at any stage. The reaction was complete in 4 hours as analysis after 4 and 5 hours is almost identical.

To prevent the loss of heat to atmosphere, next experiment was carried out by carrying out reaction in water bath as shown in fig. no. and adjusting temperature of water bath continuously through dimmerstat to that of reaction inside the flask. This way loss of heat to reaction flask or atmosphere will be negligible.

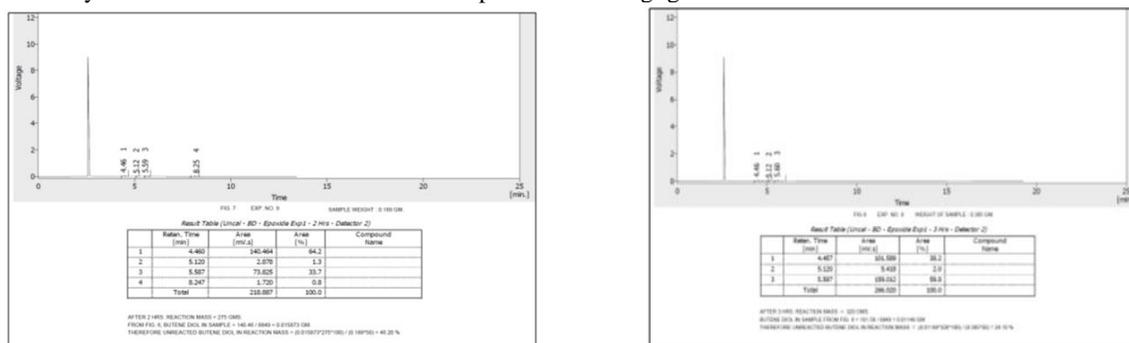


FIGURE 4 Results of Gas Chromatography

**7. CONCLUSION**

To overcome the loss experiment was carried out to maintain the reaction vessel temperature at same level of reaction temperature by external controlled heating of reaction vessel. The ΔHr, experimental was found to be 20761 calories against theoretical ΔHr of 24532 calories. Even as the difference in theoretical and practical ΔHr is within acceptable limits, the reaction was studied in details of extent of reaction and side reactions for better understanding of the difference. From this study, it was found that most of the difference can be accounted for the incomplete predicted reaction and side reaction of hydrogen peroxide decomposition. In case rate of addition of controlled reactant is more than rate of reaction, the accumulation of controlled reactant will occur which can lead to very fast reaction rate at later stage leading to runaway reaction. Assume higher of 1 or 2 as near true ΔHr. escalate this ΔHr by 25 % safety factor. From this escalated ΔHr, find out ΔTad by following equation Potential ΔTad = 1.5 \* ΔHr theoretical / Cp reaction mass. If ΔTad under ‘4’ is greater than 200°C the reaction is predicted Potentially Runaway. This finding can further be supported with simple laboratory experiments within facilities available with MSME units. Unless the experimental results are in wide variation with estimated theoretical ΔHr, the plant reaction process can then be designed with 25 % higher safety margin for ΔHr for efficient heat removal so as to prevent runaway reaction. This method of predicting and preventing a runaway reaction can be easily implemented by MSME units with no requirement of cost preventive calorimetry technique. Further, the method can be followed in house with no concern of technical information leakage.

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