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Edited by **G. A. Melhem**
Arthur D. Little, Inc.
Cambridge, Massachusetts

H. G. Fisher
Union Carbide Corporation
South Charleston, West Virginia

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS
345 East 47th Street, New York, New York 10017

1,3-Butadiene: Thermal Dimerization/Trimerization, Free-Radical Polymerization, and Polymer Decomposition Reactions

Harold G. Fisher
Union Carbide Corporation, P. O. Box 8361, South Charleston, WV 25303

Georges A. Melhem
Arthur D. Little, Inc., 20 Acorn Park, Cambridge, MA 02140

Marc E. Levin
Shell Oil Company, P. O. Box 1380, Houston, TX 77252

Joseph C. Leung
Leung, Inc., 1521 Evergreen Lane, Darien, IL 60561

ABSTRACT

1,3-butadiene monomer undergoes thermally initiated, reversible dimerization/trimerization reactions with essentially the same kinetics in both the gaseous and liquid phases. Kinetics for formation of the dimer and the trimer are available from the open literature. The rate of reaction becomes significant (0.02°C/min = 29°C/day) at temperatures above 70-80°C. Inhibitors (t-butylcatechol, et al.) are used to prevent/minimize free-radical polymerization reactions in the liquid phase and to maintain product quality at ambient or subambient temperatures. These inhibitors do not prevent the dimerization/trimerization reactions.

Unless adequate emergency relief is provided, the adiabatic temperature rise from the dimerization/trimerization reactions can lead to both a free-radical polymerization, initiated by adventitious peroxides, and a thermal decomposition of the resultant polymer to produce residues, volatiles, and noncondensable gases. Temperatures of 600°C and pressures of over 2000 psig are possible. Heat rates of 10,000°C/min and

pressure rise rates of 10,000 psig/min are also possible in unvented/undervented vessels.

Emergency relief devices protecting vessels containing high concentrations of 1,3-butadiene should be reviewed to identify potentially reactive cases. This review is recommended to ensure that current emergency relief system designs are adequate and that equipment is being operated with an adequate margin of safety.

1.0. BACKGROUND

Following an incident involving a butadiene still,[1] thermal stability tests of 1,3-butadiene were conducted using a then standard (but now obsolete) thermal stability apparatus. Mixtures of 1,3-butadiene and several process components were also tested. Unfortunately, the test apparatus had a high thermal inertia (heavy weight process vessel) and high heat losses. Heat rates of 30 to 40°C/min at temperatures of 200 to 340°C and pressures of 1450 to 1800 psig were found to be necessary to initiate an explosive decomposition of 1,3-butadiene. These results are due only to shortcomings of the apparatus and are not an accurate representation of the thermal stability of the chemical under truly adiabatic runaway reaction conditions.

A Material Safety Data Sheet (MSDS)[2] states that explosive decomposition (the above-described reactions) can only occur if the liquid is heated at 30 to 40°C/min at temperatures of 200 to 340°C and pressures of 1450 to 1800 psig. This statement is false and results from inadequacies of the test apparatus in use 27 years ago.

2.0. KINETIC SUMMARY

1,3-butadiene monomer undergoes thermally initiated, exothermic, reversible dimerization/trimerization reactions with essentially the same kinetics in both the gaseous and liquid phases. The forward kinetics are second order, while the reverse kinetics are first order. The dimerization product is predominately 4-vinylcyclohexene (VCH) with some *cis*, *cis*-1,5-cyclooctadiene (COD) and *trans*-1,2-divinylcyclobutane (DVCB) produced. The trimerization product is octahydro diphenyl.

1,3-butadiene readily reacts with oxygen to form polymeric peroxides, which are not very soluble in liquid butadiene and tend to settle to the bottom of a container because of their higher density. These peroxides are explosive and shock-sensitive when concentrated. The addition of antioxidants (t-butylcatechol, et al.) removes free radicals that can cause a rapid, exothermic polymerization. The polymerization inhibitors lose effectiveness at 85–100 °C. Since these inhibitors are nonvolatile, they are only effective in the liquid phase. Nitrogen blanketing is used to exclude oxygen from 1,3-butadiene storage tanks.

1,3-butadiene will undergo a thermal or "adventitious" peroxide-initiated free radical polymerization at higher temperatures to form polybutadiene polymer. At even higher temperatures, the polybutadiene polymer will decompose to form residues, dimers and noncondensable gases such as ethylene and ethane, propylene and propane, butenes and butanes.

3.0. REACTION KINETICS (Dimerization/Trimerization and Reverse Reactions)

A literature review provided kinetics for the forward dimerization/trimerization of 1,3-butadiene and the reverse reactions of the dimers/trimer. In most cases the reaction kinetic constants were measured in the vapor phase at high temperatures. Several of the studies, however, compared reaction kinetics in the vapor phase with those obtained at lower temperatures in the liquid phase. The comparisons are sufficient to indicate reasonable agreement, if not identical kinetics, for both the liquid and vapor phase reactions.

1,3-butadiene produces three dimerization products to include 4-vinylcyclohexene (VCH), 1,5-cyclooctodiene (COD) and 1,2-divinylcyclobutane (DVCB). A comparison of relative reaction rates, stoichiometric information from the literature and NMR values obtained by one of the authors indicate that the production of VCH is the dominant reaction for emergency relief design. The combined production of COD, DVCB and butadiene trimer is low compared to that of VCH.

3.1. Butadiene Dimerization

3.1.1. 4-vinylcyclohexene (VCH) Formation

The predominant product of the dimerization reaction of 1,3-butadiene (BD) is 4-vinylcyclohexene (VCH).[3,4] NMR studies conducted on a sample obtained to support this paper showed a VCH:COD ratio of 19:1. Kinetics for the Diels-Alder dimerization reaction of 1,3-butadiene to form 4-vinylcyclohexene are reported in the open literature.[4-11] An exothermic, second-order kinetic model for the dimerization of BD to form VCH is as follows:[4,6,11]

$$k\ (\text{ft}^3/\text{lb mole hr}) = 5.2917\text{E}{+}11\ \exp(-23690/(1.9872{*}\text{TK}))\ \text{CBD}^2$$

$$\Delta H_R\ (\text{BTU/lb}) = -307.5$$

$$2\text{BD} \rightarrow \text{VCH}$$

where TK (K) is temperature and CBD (lb mole/ft^3) is the concentration of butadiene.

These kinetics reportedly[9] include the formation of COD and DVCB in addition to VCH.

An alternate second-order kinetic model for the dimerization of BD to form VCH is as follows:[7,8,10,11]

$$k\ (\mathrm{ft^3/lb\ mole\ hr}) = 5.1390\mathrm{E}{+}11\ \exp(-24530/(1.9872{*}\mathrm{TK}))\ \mathrm{CBD2}$$

This model is slightly slower than the first model. The two models, however, bracket the data discussed in this paper.

A best estimate second-order kinetic model for the dimerization of BD to form VCH is as follows:

$$k\ (\mathrm{ft^3/lb\ mole\ hr}) = 5.6270\mathrm{E}{+}11\ \exp(-24110/(1.9872{*}\mathrm{TK}))\ \mathrm{CBD}^2$$

The reaction rate from this model is intermediate to the primary and alternate models.

Kinetics for the higher temperature reverse reaction of VCH to form BD are also available.[4,5 8-11]

3.1.2. 1,5-cyclooctodiene (COD) Formation

Kinetics for the dimerization reaction of 1,3-butadiene (BD) to form 1,5-cyclooctodiene (COD) are reported in the open literature.[9] An exothermic, second order kinetic model for the dimerization of BD to form COD is as follows:

$$k\ (\mathrm{ft^3/lb\ mole\ hr}) = 2.5756\mathrm{E}{+}12\ \exp(-28440/(1.9872{*}\mathrm{TK}))\ \mathrm{CBD}^2$$

$$\Delta H_\mathrm{R}\ (\mathrm{BTU/lb}) = {\sim}615$$

$$2\mathrm{BD} \rightarrow \mathrm{COD}$$

where TK (K) is temperature and CBD (lb mole/$\mathrm{ft^3}$) is the concentration of Butadiene

Kinetics for the higher temperature reverse reaction of COD to form BD are also available.[4,9,10]

Kinetics are also available for the reaction of VCH to form COD[9] and the reverse reaction of COD to form VCH.[4,9,10,12]

3.1.3. 1,2-divinylcyclobutane (DVCB) Formation

1,2-divinylcyclobutane is formed by the dimerization of 1,3-butadiene[10] and in turn decomposes to form BD, VCH, and COD.[4,10,13]

3.2. Butadiene Trimerization (Δ3, 3′-octahydro diphenyl)

Kinetics for the reaction of 1,3-butadiene (BD) and 4-vinylcyclohexene (VCH) to form butadiene trimer (Δ3, 3'-octahydro diphenyl) are reported in the open literature.[5] An exothermic, second order kinetic model for the reaction of BD and VCH to form butadiene trimer is as follows:

$$k\ (\text{ft}^3/\text{lb mole hr}) = 7.4959\text{E}{+}15\ \exp(-38000/(1.9872*\text{TK}))\ \text{CBD}*\text{CVCH}$$

$$\Delta H_R\ (\text{BTU/lb}) = \sim 922.5$$

$$\text{BD} + \text{VCH} \rightarrow \text{Butadiene Trimer}$$

where TK (K) is temperature, CBD (lb mole/ft^3) is the concentration of butadiene, and CVCH (lb mole/ft^3) is the concentration of vinylcyclohexene

4.0. POLYMERIZATION INHIBITORS

1,3-butadiene reacts with oxygen or air to form butadiene polyperoxide. This peroxide has the explosive power of TNT and is heat and shock sensitive. The peroxide is only slightly soluble in 1,3-butadiene at high concentrations and forms layers in a process because of its greater density.[14]

Inhibitors such as t-butylcatechol (TBC) are used to prevent/minimize the formation of butadiene peroxide and "popcorn" polymer. These inhibitors react with free radicals to form more stable free radicals, which are then terminated. Oxygen in ppm quantities is required to activate most inhibitors. TBC is consumed as it reacts and must therefore be periodically replaced. The efficiency of free-radical inhibitors varies with temperature. The consumption of inhibitor is adequately described by first order kinetics when sufficient oxygen is present.

Above a certain temperature TBC is rapidly consumed by the generation of free radicals and inhibitor effectiveness is lost. At still higher temperatures the butadiene polyperoxides decompose to produce additional free radicals. The thermally-induced, free-radical polymerization of 1,3-butadiene monomer then occurs.

5.0. "POPCORN" POLYMER FORMATION

1,3-butadiene monomer also forms rubbery "popcorn" polymers caused by polymerization initiators such as free radicals or oxygen. Addition of antioxidants such as t-butylcatechol (TBC) and storage at low temperatures can substantially reduce fouling caused by these polymers. Polymer seeds (free radicals), oxygen, and rust promote the formation of "popcorn" polymers. Butadiene "popcorn" polymer nucleation occurs as a heterogeneous surface reaction. "Popcorn" polymers can grow rapidly and generate tremendous pressure resulting in plugging and/or rupture of pipes and vessels. Rigorous exclusion of oxygen, passivation of metal surfaces, and removal of "popcorn" polymer seeds can mitigate most of the problem.[6,15–17] A recent review has been published.[17]

6.0. REACTION KINETICS (Free-Radical Polymerization)

The dimerization/trimerization reactions of 1,3-butadiene are not affected by the presence or absence of free-radical initiators or polymerization inhibitors. Low temperature storage is required to prevent/limit these reactions.

t-butylcatechol (TBC) inhibitor is used to prevent/limit the thermal and/or "adventitious" peroxide initiated, free-radical polymerization of 1,3-butadiene during storage and low temperature industrial processing. TBC, however, is not an effective inhibitor at the high temperatures resulting from the exothermic dimerization/trimerization reactions. The exothermic, free-radical polymerization of 1,3-butadiene thus occurs in parallel to the dimerization/trimerization reactions at high temperature.

The "adventitious" polybutadiene peroxide catalyzed, free-radical polymerization of 1,3-butadiene monomer is proportional to the square root of the peroxide concentration. This reaction has an activation energy similar to that of the dimerization reaction. A concentration of 1200 ppm active oxygen (one active oxygen atom per molecule of peroxide—about one-half the soluble concentration) is reported to catalyze the free-radical polymerization of 1,3-butadiene at a rate 10–20 times faster than the dimerization reactions. Fortunately, exclusion of oxygen from process vessels minimizes the concentration of polybutadiene peroxide and thus the catalyzed, free-radical polymerization reaction. In the absence of peroxides the free-radical polymerization reaction is insignificant compared to the dimerization reaction.[6]

7.0. REACTION KINETICS (Polymer Decomposition)

Polybutadiene polymer is reported[18] to completely decompose over the temperature range 350–477 °C to produce residue (85.6 wt %; MW = 739), volatiles (9.95 wt %; assumed to be dimers) and lights/noncondensable gas (4.45 wt %; MW ≈ 51).[19] Fifty percent of the polymer decomposes in 30 minutes at approximately 407°C.[20] Using the literature half-life information, we derived exothermic first-order kinetics for the decomposition of polybutadiene polymer as follows:

$$k\ (\text{pph}) = 9.4672\ \text{E+19}\ \exp(-62000/(1.9872{*}\text{TK}))$$

$$\Delta H_{\text{R}}\ (\text{BTU/lb}) = 632.5\ (\text{Ref. } 6)$$

$$\begin{aligned}\text{PBD} = {} & 0.856\ \text{RESIDUE (MW} = 739) + 0.0995\ \text{DIMER (VCH)}\\ & + 0.0445\ \text{LIGHTS/NONCONDENSABLE GAS (MW} \approx 51)\end{aligned}$$

8.0. VALIDATION OF KINETIC MODELS

Experimental data for the thermally initiated reactions of 1,3-butadiene are available from the Accelerating Rate Calorimeter (ARC)[21,22] (Figures 1–4), Vent Sizing Package (VSP2)[23,24] (Figures 5–8), and Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)[25] (Figures 9–12). We used these data to confirm our kinetics, heats of reaction, stoichiometry, physical property, and vapor–liquid models, which were assembled from open literature sources.

The experimental data presented in this paper are primarily the dimerization/trimerization reactions of 1,3-butadiene. The reverse dimerization/trimerization reactions require high temperatures to achieve a substantial rate. Since oxygen was excluded from the reaction mixture, we would not expect the free-radical polymerization reactions of 1,3-butadiene to be significant. Since we therefore expect a low rate of polybutadiene polymer formation, we also expect a minimum pressure effect due to the decomposition reaction of polymer. Each of these expectations is supported by the available data as discussed below.

In many experiments, however, the test vessel ruptured due to the high partial pressure of 1,3-butadiene at the high reaction temperatures or due to using an initial reactant fill ratio which exceeded the volume of the test cell at the critical volume of the reaction mixture (i.e., the test cells become liquid-full and burst due to the hydrostatic pressure caused by liquid expansion). At 25°C the hydrostatic pressure of 1,3-butadiene increases by 98 psi/°C in a liquid-filled vessel due to thermal expansion. The critical volume of 1,3-butadiene is 0.245 g/mL. Vessels with higher fill ratios, which become liquid full below the critical volume, can burst due to hydrostatic pressure.

8.1. Accelerating Rate Calorimeter (ARC) Data

ARC run 4845 was available. A total of 3.5 g (initial 0.55 fill ratio) of uninhibited 1,3-butadiene were charged to a 11.5 mL lightweight, spherical, titanium bomb. Following several heat–wait–search periods to 104°C, the ARC attained a peak heat rate of 10.5°C/min, a peak temperature of 200°C and a peak pressure of 1025 psia. The test was terminated at 200°C.

Our best estimate kinetic model fit the ARC 4845 heat rate versus temperature (Figure 1), pressure rate versus temperature (Figure 2), pressure versus temperature (Figure 3) and temperature versus time (Figure 4) plots quite well.

Note: Inclusion of the 1.5 mL transducer volume and tubing was required to obtain the proper burst pressure.

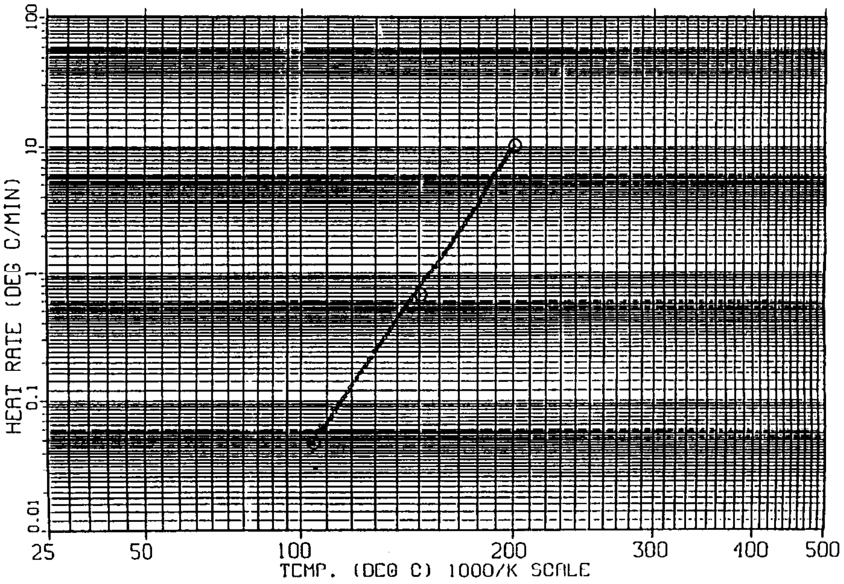

Figure 1. Uninhibited 1,3-butadiene (ARC 4845)

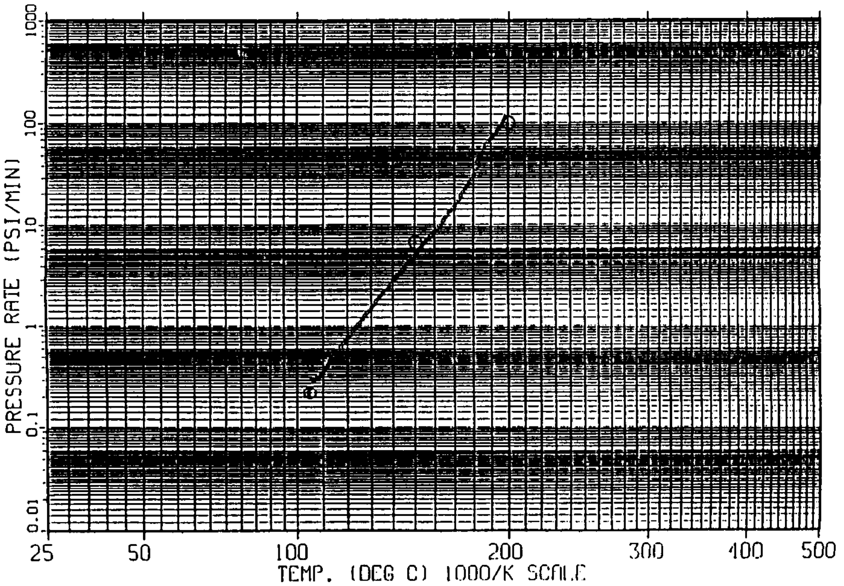

Figure 2. Uninhibited 1,3-butadiene (ARC 4845)

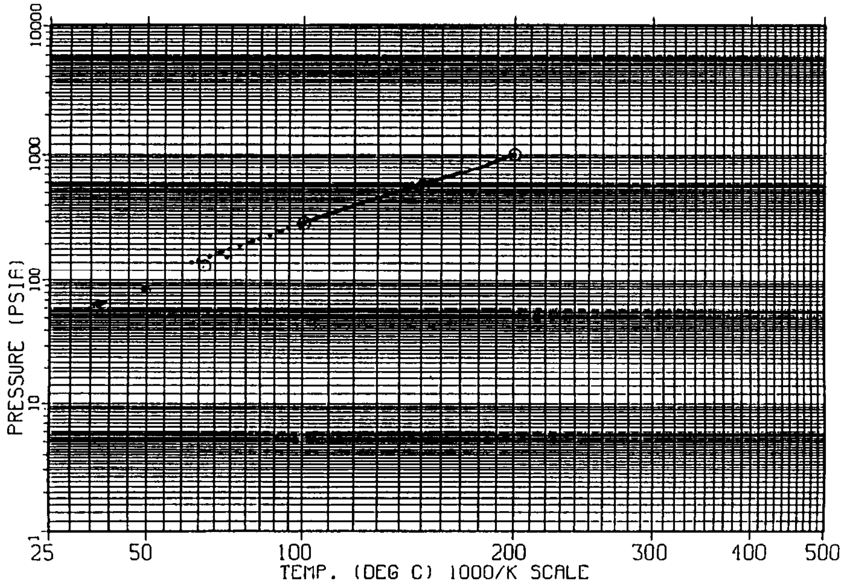

Figure 3. Uninhibited 1,3-butadiene (ARC 4845)

8.2 Vent Sizing Package (VSP2) Data

A total of 62.9 g (0.58 initial fill ratio) of 37.2 wt% 1,3-butadiene and 62.8 wt% of tridecane diluent were charged to an approximate 115 mL cylindrical test cell, which is expected to expand to a volume of approximately 140 mL at rupture. Following a ramped heating period to 120°C, the VSP2 4715 sample appeared to heat by reaction and a positive drift of approximately 0.1°C/min to a temperature of 140°C. The VSP2 then attained a peak heating rate of approximately 6°C/min, a peak pressure of 300 psia and a peak temperature of 295°C. The test cell did not rupture, which allowed a complete check of the kinetic model and the heat of reaction.

The primary kinetic model fit the VSP2 4715 heat rate versus temperature (Figure 4), pressure rate versus temperature (Figure 5), pressure versus temperature (Figure 6), and temperature versus time (Figure 7) plots quite well.

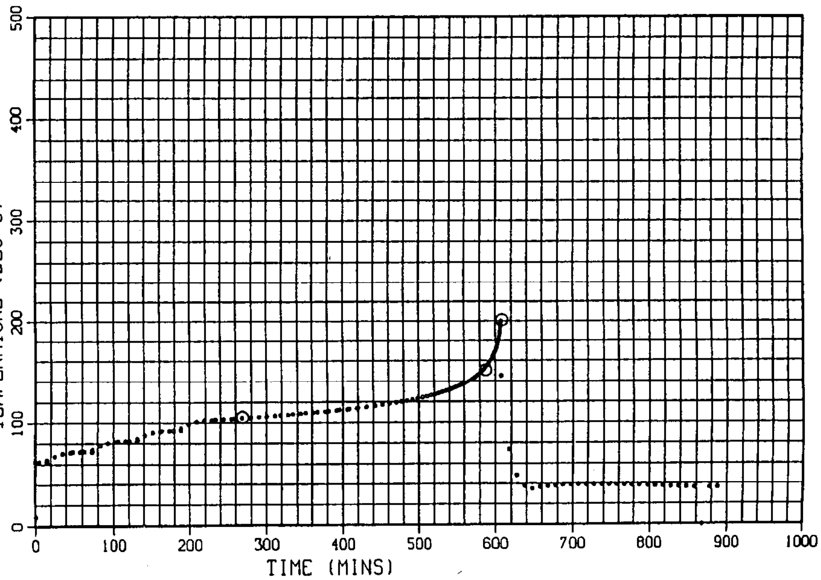

Figure 4. Uninhibited 1,3-butadiene (ARC 4845)

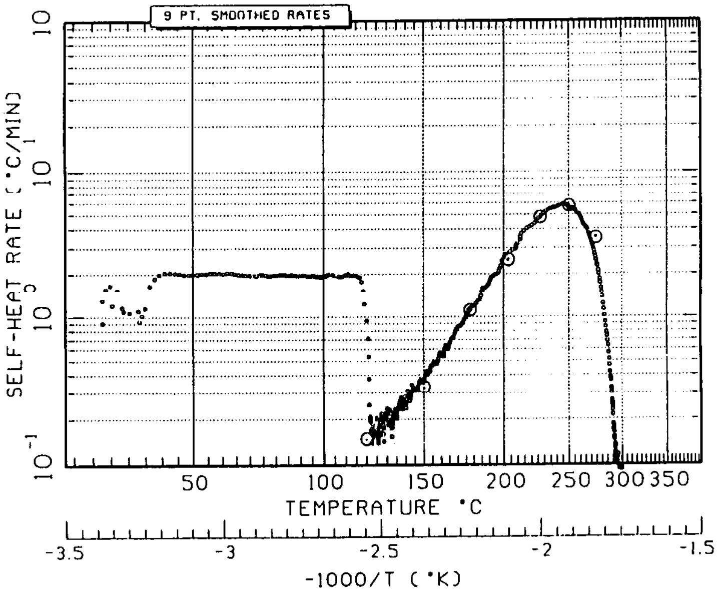

Figure 5. Uninhibited 1,3-butadiene (37.2 wt%) and tridecane (62.8 wt%) (VSP 4715)

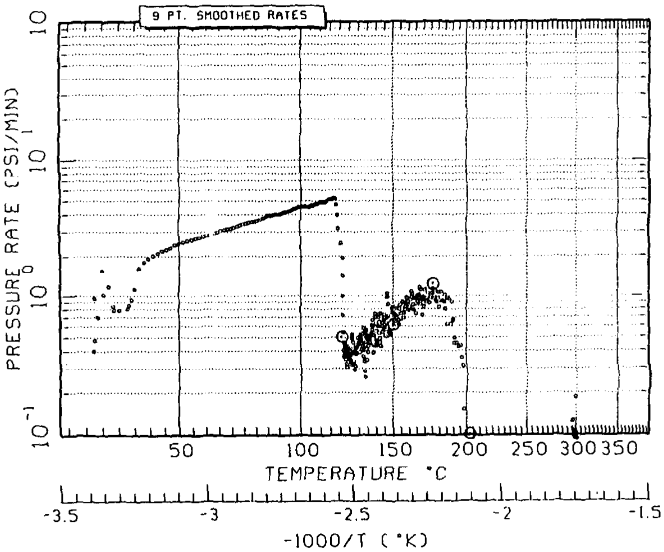

Figure 6. Uninhibited 1,3-butadiene (37.2 wt%) and tridecane (62.8 wt%) (VSP 4715)

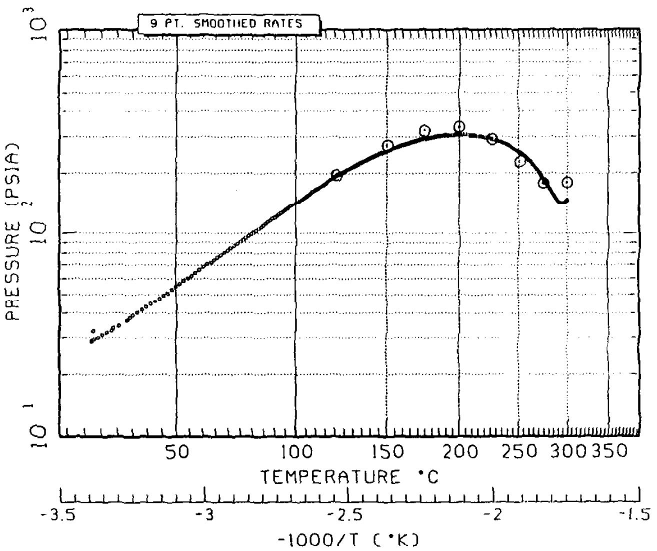

Figure 7. Uninhibited 1,3-butadiene (37.2 wt%) and tridecane (62.8 wt%) (VSP 4715)

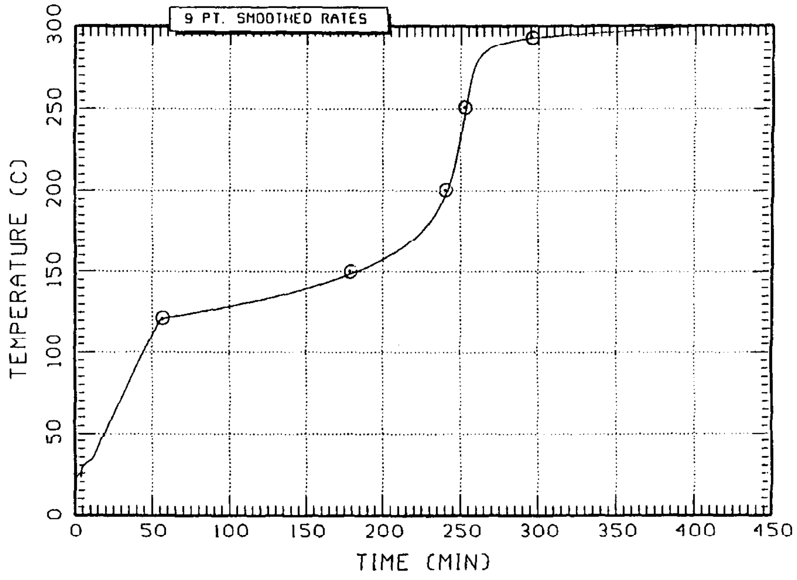

Figure 6. Uninhibited 1,3-butadiene (37.2 wt%) and tridecane (62.8 wt%) (VSP 4715)

8.3. Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) Data

APTAC run 2162 was also available. A total of 32.5 g (initial 0.25 fill ratio) of 1,3-butadiene were charged to a 130 mL spherical, titanium bomb. Following several heat–wait–search periods to 115°C, the APTAC attained a peak heating rate of 835°C/min, a peak temperature of 394°C and a peak pressure of 830 psia. The bomb ruptured.

The upper limit of the heat rate compensation (adiabaticity) of the APTAC instrument is approximately 400 °C/min. The alternate kinetic model exhibits a positive bias on the APTAC 2162 heat rate versus temperature (Figure 9) plot well below this value. The positive bias is also clearly noticeable on the pressure rate versus temperature (Figure 10) plot. The vapor–liquid equilibria model causes an inflection in the pressure versus temperature (Figure 11) plot. This inflection is reflected in both pressure rate increases and decreases, which are clearly not evident on the pressure rate versus temperature (Figure 10) plot. The agreement of the model with the temperature versus time (Figure 12) plot is acceptable.

Note: Inclusion of the 15.72 g weight of the pressure transducer nut and ferrule in addition to the 31.95 g weight of the spherical titanium bomb was required for the model to approximately fit the data.

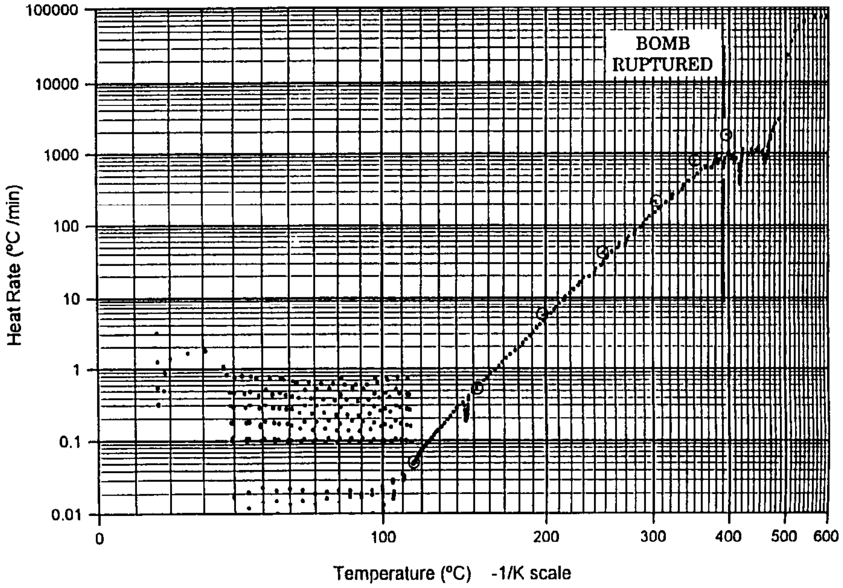

Figure 9. Uninhibited 1,3-butadiene (APTAC 2162)

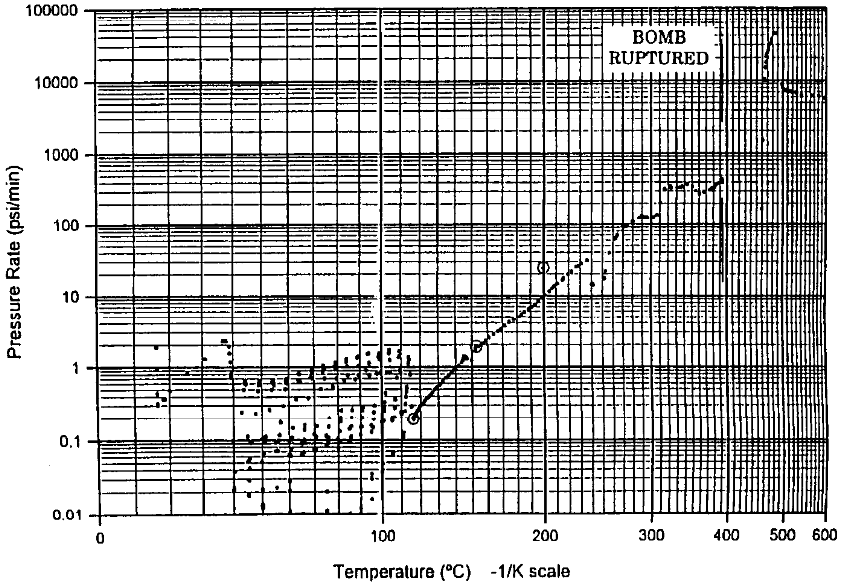

Figure 10. Uninhibited 1,3-butadiene (APTAC 2162)

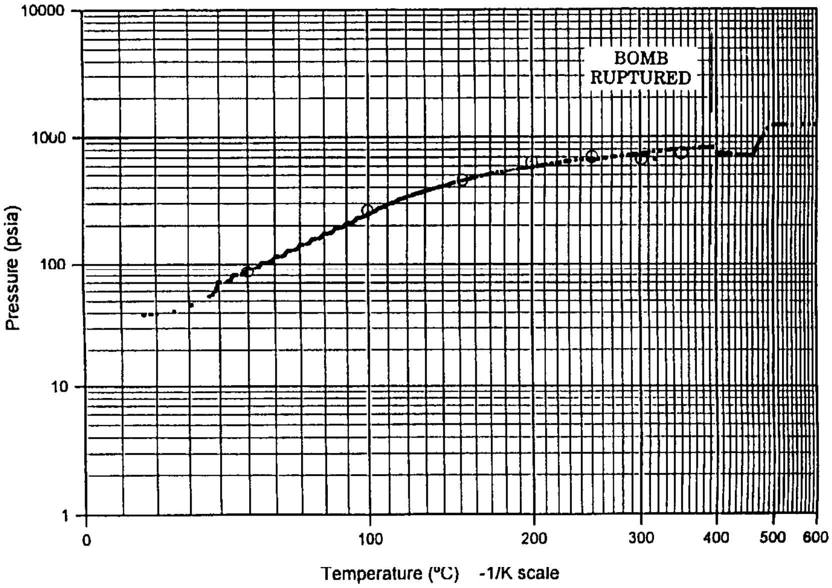

Figure 11. Uninhibited 1,3-butadiene (APTAC 2162)

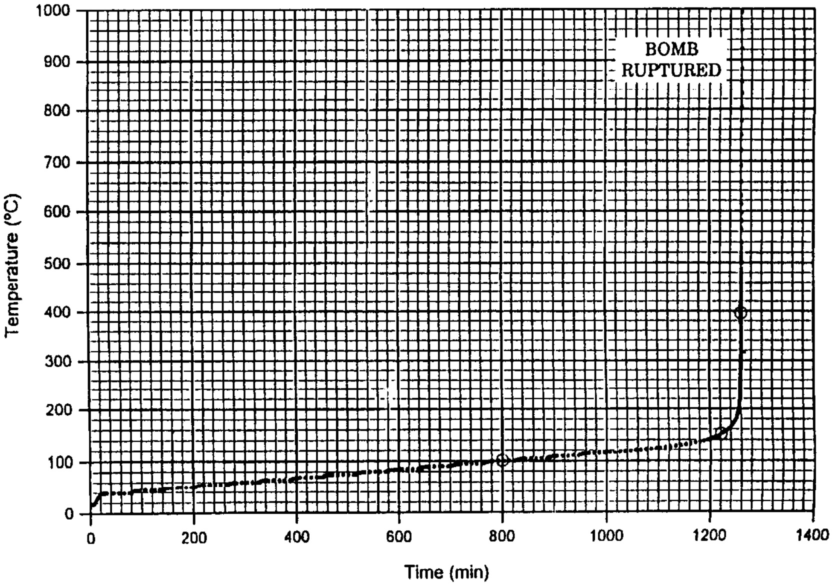

Figure 12. Uninhibited 1,3-butadiene (APTAC 2162)

9.0. CLOSURE

A recent paper[26] contains some of the information discussed in this paper. We chose to concentrate, herein, on the most likely, uncatalyzed, thermally initiated reactions of 1,3-butadiene as a basis for sizing emergency relief devices. The validity and usefulness of our model increases when the relief flow is tempered such as is possible with adequate mlysized emergency relief devices with low set pressures. The reverse dimerization/trimerization reactions become significant at higher temperatures (>300°C) and cause a volatility (pressure) increase. Since the critical pressure and density of 1,3-butadiene are 620 psig and 0.245 g/mL at the critical temperature of 152°C, our model should be valid for emergency relief devices with set pressures at or below 400 psig.

10.0. ACKNOWLEDGMENTS

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11.0. REFERENCES

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