

Evaluation of 1,3-butadiene dimerization and secondary reactions in the presence and absence of oxygen

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Abstract

Thermal stability evaluation of exothermic chemical reactions is of great importance to the safer design and operation of chemical processes. Dominant reaction stoichiometries and their thermochemistry parameters are key elements in the evaluation process. Identification of significant reaction pathways under possible process conditions will lead to an understanding of the overall thermodynamic and kinetic behavior.

The kinetics of 1,3-butadiene (BD) is an excellent example of conjugated dienes that undergo addition reactions. At elevated temperatures, 1,3-butadiene monomers can dimerize exothermally, and as temperature increases, secondary exothermic reactions will take place. The very high temperature and pressure rates that these reactions can attain may lead to a reaction runaway or even a thermal explosion. BD is a vapor at ambient conditions, usually stored as a pressurized liquid, and is a carcinogen, so the experimental evaluation is potentially difficult and hazardous.

In this paper, the thermal stability of BD is evaluated. Dimerization and other secondary reactions are investigated by experimental thermal analysis using an automatic pressure adiabatic calorimeter (APTACTM), by theoretical computational quantum chemistry methods, and empirical thermodynamic-energy correlations. A theoretical approach is conducted to predict some of the BD reaction behavior. Results are compared to other literature data obtained using different experimental methods.

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1. Introduction

1,3-butadiene's inherent tendency to react with a large number of chemicals, to dimerize and polymerize, and its cancer-causing behavior requires that specific handling, storage, and shipping procedures need to be followed [1]. 1,3-Butadiene reactivity has led to many incidents (eight incidents from 1994–1999) [2].

The effective evaluation of the reactivity hazards associated with 1,3-butadiene manufacturing, transporting, and handling stems in part from the ability to predict reaction mechanisms under various scenarios and to quantify the relevant thermodynamic and kinetic parameters.

Experimental calorimetry and analysis of the data is a traditional technique for evaluating reactivity hazards. Various calorimeters are available for researchers. However, few of these calorimeters are suitable to test pressurized liquids and toxic substances such as 1,3-butadiene. The special considerations and testing procedures make the experimental analysis quite expensive.

In this paper, polymerization of inhibited 1,3-butadiene in the presence and absence of oxygen was evaluated for its thermal reactivity and runaway behavior using theoretical computational models and thermal analysis techniques. The automated pressure tracking adiabatic calorimeter (APTACTM) was used for overall thermodynamic and kinetic parameters measurements. At the same time, a theoretical evaluation was conducted to predict plausible hazardous reaction pathways. Thermo-kinetic parameters for these pathways are calculated and compared with experimental results and with literature values.

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2. Butadiene reactivity hazards

Butadiene is known for its strong tendency to react through numerous exothermic pathways of which the most significant non-catalytic pathways are dimerization, polymerization, and decomposition.

Several researchers have studied the dimerization of butadiene under various conditions [3–6]. The general conclusion derived from these investigations is that dimerization is a homogeneous bimolecular reaction, not catalyzed by oxygen, unaffected by anti-oxidants, and with the same kinetics in the liquid and gaseous phases.

The thermally initiated dimerization reaction is difficult to prevent except by lowering the butadiene storage temperature. Since the reaction rate increases about nine fold for every 20 °C increase in temperature, care must be taken to maintain butadiene at a low temperature [7].

Also, 1,3-butadiene reacts readily with oxygen to form polymeric, impact sensitive, peroxides, which are not very soluble in liquid 1,3-butadiene and tend to settle at the bottom of the container because of their higher density. Therefore, it is imperative to exclude any source of oxygen from butadiene. Oxygen or peroxides may initiate long-chain polymerization reactions to form a variety of polymers. Some of these polymers are known as popcorn polymers, which are hard, opaque, and porous and have been reported to ignite spontaneously on exposure to air [7]. Popcorn polymers can grow exponentially [8], particularly in the presence of seeds, or oxygen, and rust. They have been known to generate tremendous pressure resulting in sudden rupture or plugging of containers, distillation towers, and pipes [9].

It is reported that rigorous exclusion of oxygen from the system, metal surface passivation, and removal of popcorn polymer seeds can mitigate most of these problems [8]. Addition of antioxidants such as *t*-butylcatechol (TBC) or butylated hydroxy toluene (BHT) removes free radicals that are known to initiate rapid exothermic polymerizations. However, the high boiling points of many of these materials render them effective primarily in the liquid phase leaving the gaseous phase more vulnerable to reaction initiation.

3. Results and discussion

The accumulated experimental data underscores the fact that 1,3-butadiene reactions are complex and follow many pathways. In this article, the reactions of 1,3-butadiene, in the presence and absence of oxygen, were investigated using theoretical computational models and experimental adiabatic calorimetry. The focus of this study was on the dimerization and polymerization reaction pathways.

3.1. Dimerization of butadiene

Butadiene dimerization follows the Diels–Alder reaction. They are generally thermally reversible and can proceed in

both the gas and liquid phases. The reactions are exothermic and follow second-order kinetics (first-order with respect to each reactant). Three possible mechanisms have been proposed for the Diels–Alder reactions: a concerted mechanism, a two-step mechanism, and an asynchronous two-stage mechanism [10]. The concerted mechanism suggests that the butadiene monomers will dimerize directly to the final product through an activated transition state barrier. However, the two-step mechanism suggests the formation of various diradicals as the first step followed by the formation of the product as the final step. The asynchronous two-stage mechanism is a combination of the two earlier mechanisms. Years of controversy over which mechanism is most dominant has not reached an end, although it is likely to be an asynchronous two-stage mechanism [11].

Dimerization of butadiene through the Diels–Alder reaction is second-order in the gas phase and in solution [5]. In general the gas phase reactions are fairly clean, but the second-order rate constants do show marked drifts in later stages of a run [5]. In his study, Vaughan [3] demonstrated that only after some 50% butadiene conversion, the deviation from the second-order mechanism is appreciable. Vaughan interpreted the deviations as caused by a secondary reaction of the dimer with unreacted monomer.

In this study, a reaction mechanism (as in Fig. 1) is suggested based on previous work [11–13] to predict a reaction mechanism and calculate thermokinetic parameters.

In this mechanism, *trans*-butadiene (*t*-BD) and *cis*-butadiene (*c*-BD) will dimerize into 4-vinylcyclohexane (VCH), *cis*, *cis*-cycloocta-1,5-diene (COD), *trans*-1,2-divinylcyclobutane (*t*-DVCB), and *cis*-1,2-divinylcyclobutane (*c*-DVCB) dimers. These reactions will take place through the formation of the intermediate octa-1,7-diene-3,6-diyl diradicals (*trans*, *trans*), (*cis*, *trans*), and (*cis*, *cis*). There is a 4.8 kcal/mol rotational barrier between the *t*-BD and *c*-BD isomers [14]. Rapid equilibrium allows reactions to take place with either the *trans* or *cis* forms. In this study, the two 1,3-butadiene isomers were considered for the ab initio thermo-kinetic calculations, however, in the experimental analysis, an overall thermo-kinetics calculations were conducted, which is independent of the isomer rotational barrier.

To investigate the dominant reaction pathway and its thermo-kinetic parameters, computational quantum chemistry (ab initio method) calculations were performed using the complete basis set (CBS) level of theory. The CBS extrapolation models employ asymptotic extrapolation of second-order energy and relatively small basis sets for the higher-order correlation energy [15]. Recently, a new version, CBS-4M, allows calculations of molecular properties with a reasonable degree of accuracy for molecules of relatively high molecular size [16]. All quantum chemistry calculations were performed using the Gaussian 98 program [17]. The calculated Gibbs free energy and enthalpy of reactions are presented in Table 1. The calculated heats of reaction and Gibbs free energies in Table 1 are used for relative comparisons of the various

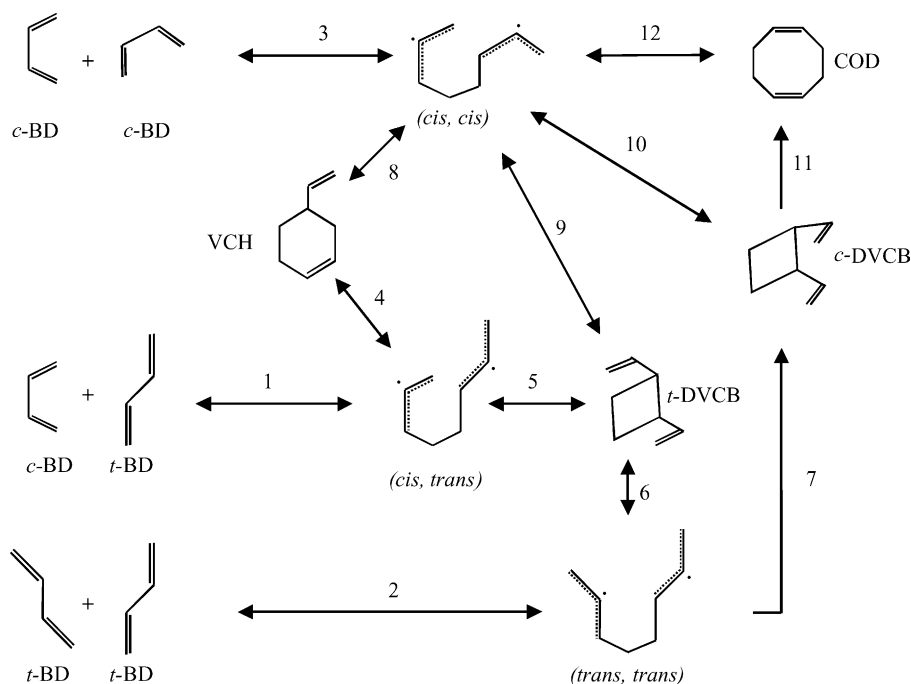


Fig. 1. Proposed reaction pathways of 1,3-butadiene dimerization.

Table 1

Gibbs free energies and heats of reactions of 1,3-butadiene dimerization calculated using the CBS-4M level of theory

Reaction	ΔG_r (kcal/gmol)	ΔH_r (kcal/gmol)
1	-2.2	-12.4
2	42.9	31.0
3	66.7	57.5
4	-27.3	-30.7
5	-3.7	-5.8
6	-45.2	-45.9
7	-43.7	-44.6
8	-99.7	-103.9
9	-76.1	-79.0
10	-74.6	-77.7
11	-14.9	-16.5
12	-89.5	-94.2

proposed reactions and were not used for accurate calculations of the overall dimerization reaction energies. A higher and more complicated level of theory would be necessary to perform more accurate calculations.

Evans and Polanyi [18,19] examined the relationship between the thermodynamics of a reaction and the activation barrier represented by the activation energy E_a . They showed empirically that as a reaction type becomes more exothermic, its activation barrier generally decreases. Evans and Polanyi also noted that in many cases the activation barrier, E_a , for a given reaction is related to the heat of reaction, ΔH_r , by the Polanyi equation:

$$E_a = E_a^0 + \gamma_P \Delta H_r$$

where E_a^0 is the intrinsic barrier of reaction and γ_P is the transfer coefficient, and E_a^0 and γ_P are constants for the same reaction mechanism. Applying the Polanyi equation to determine the dominant pathway is possible for this set of reactions based on activation energy predictions of proposed elementary reaction steps.

Since, Reactions 1, 2, and 3 share the same mechanism, E_a^0 and γ_P values are expected to be the same for the three reactions [20]. It is assumed that the rapid equilibrium between the *cis* and *trans* isomers of 1,3-butadiene at low temperatures will allow all the three reactions (1, 2, and 3) to have, approximately, the same initial reactant concentrations. In this case, the predicted values of heat of reaction were sufficient to show that Reaction 1 is dominant over 2 and 3 since it has the lowest heat of reaction. Therefore, diradical (*cis, trans*) will be the main intermediate. Similarly, Reaction 4 to form VCH and Reaction 5 to form *t*-DVCB are proceeding with the same mechanism, however, Reaction 4 has a much lower heat of reaction, which suggests that it will have a lower activation barrier and that is more dominant. For the (*cis, cis*) intermediate, Reactions 8, 9, 10, and 12 compete and Reaction 8 to form VCH is expected to have the lowest activation energy barrier. According to this analysis, the butadiene dimerization main pathway could be the formation of VCH through the (*cis, trans*) intermediate and to a lesser extent through the (*cis, cis*) intermediate. This reaction pathway to form VCH has a heat of reaction of -43.1 kcal/mol. In fact, this conclusion is in an agreement with other researcher findings that VCH is the main product of the butadiene dimerization reaction [3–6,21–23].

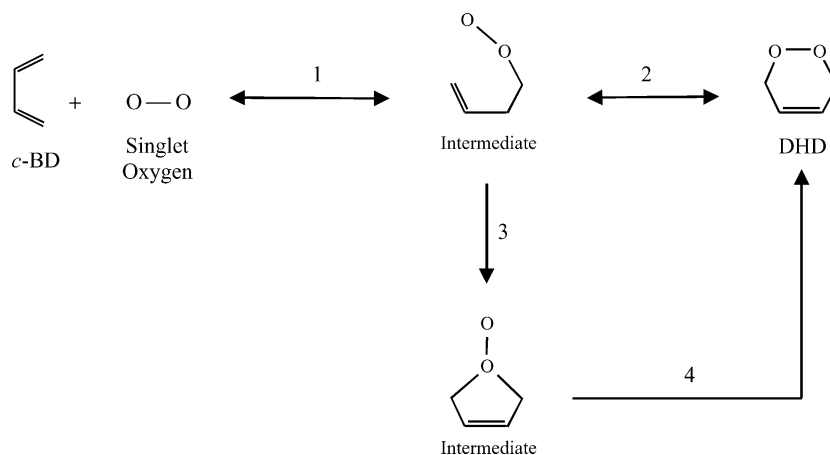


Fig. 2. Proposed reaction pathways of 1,3-butadiene with singlet oxygen to form 3,6-dihydro-1,2-dioxin (DHD).

Table 2

Gibbs free energies and heats of reactions of 1,3-butadiene with singlet oxygen reactions calculated using the CBS-4M level of theory

Reaction	ΔG_r (kcal/gmol)	ΔH_r (kcal/gmol)	Comment
1	-1.8	-12.5	Forward reaction
2	-50.0	-51.1	Forward reaction
3	-29.4	-28.8	
4	-20.6	-22.3	

Table 3

Heats of reaction for butadiene polymerization propagation steps using HF/6-31g(d) level of theory

Reaction	ΔH_r (kcal/gmol)
Isotactic 1,2-addition	-97.6
Syndiotactic 1,2-addition	-88.1
<i>Cis</i> -1,4-addition	-79.3
<i>Trans</i> -1,4-addition	-84.7

3.2. Polymerization of butadiene

In the presence of peroxide or any free radical initiator, butadiene will start to polymerize with itself. However, in the presence of air, oxygen will help to form a free radical that will ultimately initiate the butadiene polymerization reaction. In this article, the reaction of butadiene with singlet oxygen is discussed. This reaction will lead to the formation of 3,6-dihydro-1,2-dioxin (DHD), which is a highly reactive peroxide that may initiate the polymerization of the butadiene. Possible reaction pathways leading to the formation of DHD are suggested based on previous research and are illustrated in Fig. 2 [8,24]. CBS-4M quantum computational level of theory was used to predict reaction thermodynamic parameters as presented in Table 2.

Applying the same concepts of reaction pathway predictions on BD reactions with oxygen as in Fig. 2 suggests that DHD will be formed through Reactions 1 and 2 dominantly. Reaction 3 is expected to have a higher activation barrier than that of Reaction 2. The values of Polanyi equation parameters were obtained from literature [20] based on the reaction mechanism.

When comparing the dimerization Reaction 1 and the peroxide formation Reaction 1, it is noticed that they have almost the same heat of reaction (-12.41 and -12.52, respectively), which may indicate that they have very similar activation barriers. However, when the following reactions in every pathway are compared, it was found that the peroxide formation reactions generally have lower activation barriers and hence may have dominance over the dimerization reactions. This

peroxide reaction dominance will increase the chances of polymerization reaction initiation and therefore increase the reactivity hazards potential [25].

Polymerization of butadiene can proceed via isotactic 1,2-, syndiotactic 1,2-, *cis*-1,4-, and *trans*-1,4-additions. More information about these polymer geometries is available in the literature [7]. Heats of reaction for the polymerization propagation steps were calculated using the Hartree-Fock, HF/6-31g(d), level of theory [26] and are presented in Table 3. This level of theory is acceptable for relative comparison of reaction energy. A higher level of theory is required to pursue more accurate values. It is obvious that the energy release associated with the polymerization reactions exceeds those of the dimerization reaction and is therefore more favorable. Due to the higher heat of reaction, the reactivity hazards of butadiene can therefore be predicted to be more significant in the presence of air or any other free radical initiator.

3.3. Experimental calorimetric analysis

Adiabatic experimental analysis using the APTACTM was performed for the thermal polymerization of 1,3-butadiene monomer in the absence and presence of oxygen. This system was investigated by other researchers using adiabatic calorimetry [25,27].

The butadiene monomer was transferred to the APTACTM from a 500 ml compressed cylinder. The tested butadiene monomer was inhibited with 100 ppm of TBC. This inhibitor is not expected to affect the dimerization reaction (in absence of air) although it may delay the polymerization reactions

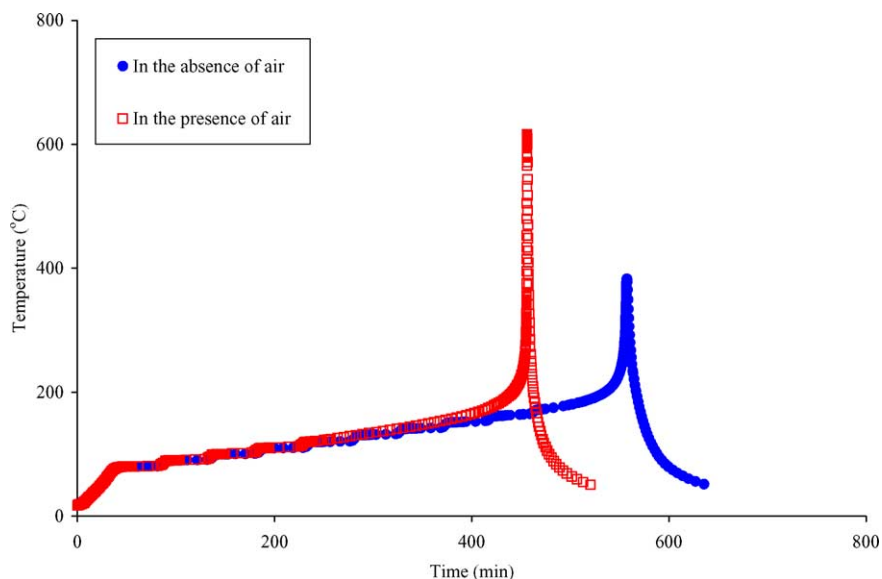


Fig. 3. 1,3-Butadiene reaction temperature profile in the presence and absence of oxygen.

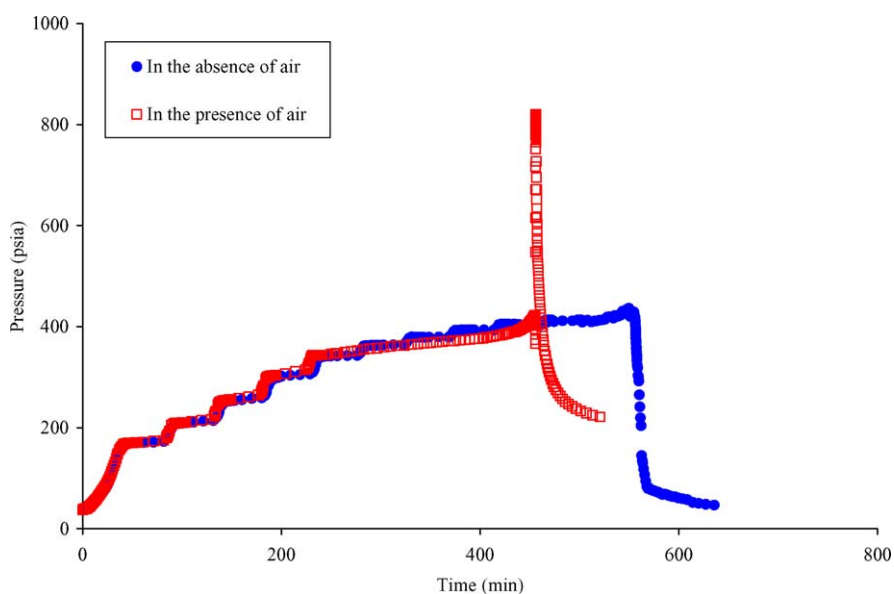


Fig. 4. 1,3-Butadiene reaction pressure profile in the presence and absence of oxygen.

(in presence of air). Sample weights ranged from 10 to 13 g and 130 ml APTACTM test cells of titanium and stainless steel were used in these testing. The combination of test cell and sample resulted in thermal inertia factors, ϕ -factor, ranging from 1.2–1.4. Heat-wait-search mode of operation was applied with a heating rate of 2.0 °C/min. Although the APTACTM is capable of measuring reaction thresholds as low as 0.02 °C/min, however, in this work, a threshold value of 0.1 °C/min was used to measure the reaction onset temperature. This threshold was applied to provide a more consistent and stable temperature readings.

The overall heat of reaction was calculated, and first- and second-order kinetics were assumed to fit the polymerization reaction temperature–time data. Typical temperature and

pressure profiles are presented in Figs. 3 and 4, respectively. A summary of the results is presented in Table 4. It is clearly indicated from the pressure and temperature profiles and calculated reaction and activation energies that butadiene reaction without oxygen (dimerization) is considered less hazardous than that with oxygen (polymerization).

Activation energies also indicate that the overall activation barrier of the dimerization reaction is higher than that of the polymerization path. These findings are in agreement with the early theoretically predicted behavior. The differences between the predicted and measured values of heats of reaction are due, in part, to the thermal effects of butadiene vaporization. The heat capacity of the butadiene sample was estimated at the onset temperature of the reaction for both

Table 4

Measured overall heat of reaction and activation energy of butadiene using the APTACTM

Reaction	ΔH_r (kcal/gmol)	Second-order E_a (kcal/gmol)	First-order E_a (kcal/gmol)
1,3-butadiene without oxygen	-14.1 ± 1.5	28.3 ± 1.3	24.3 ± 0.7
1,3-butadiene with oxygen	-24.4 ± 4.2	20.1 ± 2.1	18.5 ± 1.8

liquid and vapor phases assuming ideal gas conditions and using correlations available in the literature [28]. Therefore, the heat capacity estimation is a main source of uncertainty in the measured overall heat of reaction because of continuous temperature and composition changes during the experiment.

The main cause of such differences between experimental and calculated heats of reaction is due to the level of theory used to predict reactions thermochemistry. Applying higher level of theory, as the CBS-4M with the dimerization reactions, resulted in an acceptable heat of reaction (-43.1 kcal/mol) when compared to the experimental value (-14.1 kcal/mol) and the associated thermal and physical effects. However, applying a lower level of theory, as the HF/6-21g(d), to calculate the heat of reaction of butadiene polymerization (-79.3 to -97.6 kcal/mol) resulted in significant differences with those measured values (-24.4 kcal/mol). However, the general trend of dominance of polymerization reactions over dimerization reactions is still possible with relatively lower level theory calculations.

4. Conclusions

Successful qualitative theoretical predictions of 1,3-butadiene dimerization and polymerization reaction pathways were possible through the application of quantum chemistry calculations and thermodynamic-energy correlations. Theoretical calculations were found to overestimate the thermo-kinetic parameters of the system due to other physical and thermal effects associated with the experimental data. However, theoretical calculations still can predict dominant pathways

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