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## **Theoretical and Experimental Techniques for the Evaluation of Reactive Chemical Hazards**

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### **ABSTRACT**

Evaluation of reactive chemical hazards is critical for the design and operation of safer chemical plant processes. Much effort is needed for experimental techniques to measure thermal reactivity of chemical systems. Studying all the various reaction pathways experimentally however is very expensive. Therefore, it is essential to employ simplified screening tools to reduce the number of experiments and to identify the most energetic pathways.

A systematic approach will be presented for the evaluation of reactive chemical hazards. This approach is based on a combination of numerical computational methods and experimental thermal analysis techniques. Numerical computational methods will be used to predict reaction stoichiometries, thermodynamics, and kinetics, which will help to exclude thermodynamically infeasible and non-hazardous reaction pathways. The experimental techniques will be used to evaluate the most energetic systems for more accurate thermodynamic and kinetics parameters or to replace failed numerical methods.

# Theoretical and Experimental Methods for the Evaluation of Reactive Chemical Hazards

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## Abstract

Evaluation of reactive chemical hazards is critical for the design and operation of safer chemical plant processes. Much effort is needed for experimental techniques to measure thermal reactivity of chemical systems. Studying all the various reaction pathways experimentally however is very expensive. Therefore, it is essential to employ simplified screening tools to reduce the number of experiments and to identify the most energetic pathways.

A systematic approach will be presented for the evaluation of reactive chemical hazards. This approach is based on a combination of numerical computational methods and experimental thermal analysis techniques. Numerical computational methods are used to predict reaction stoichiometries, thermodynamics, and kinetics, which will help to exclude thermodynamically infeasible and non-hazardous reaction pathways. The experimental techniques are used to evaluate the most energetic systems for more accurate thermodynamic and kinetics parameters or to replace inadequate numerical methods. This approach employing theoretical and experimental analyses was used to evaluate the decomposition reaction of di-tert-butyl peroxide (DTBP) in toluene. The results of this analysis was compared to literature data for this system.

## Introduction

Thermal stability of reactive system, intermediates, and products is of a significant interest to the chemical industry. The engineering design of equipment to prevent, control, or withstand runaway reactions is of great concern from a safety point of view, and many procedures have been suggested for categorizing reactive chemicals. Since the needs for an assessment procedure varies from one industry to another, much effort has addressed this issue from a specific case or a specific chemical point of view. Therefore, a generalized approach should be based on an understanding of the stoichiometry, thermodynamics, and kinetics of the reactive system and should require minimum time and inexpensive procedures.

In this paper a systematic approach of evaluating reactive systems is presented. This approach is a combination of theoretical and experimental levels of evaluation to identify reaction stoichiometries and estimate thermodynamic and kinetic parameters of potentially hazardous reactions. This approach employing theoretical and experimental analyses was used to evaluate the decomposition reaction of di-tert-butyl peroxide (DTBP) in toluene system. Computational quantum chemistry methods were used to

investigate the possible reaction stoichiometry and heat of reaction. At the same time, screening analysis testing using RSST™ was performed.

## **Systematic Approach**

An evaluation of chemical reactivity must be based on essential information, which includes process operating conditions, process chemistry mechanisms, conditions under which chemical reactive hazards can appear, and parameters for quantifying reactive chemical hazards.

Defining these conditions and parameters will help to simulate the chemical process for optimum safe and economical operating conditions. Evaluating this information is not an easy task. Laboratory testing has been the traditional approach to evaluate chemical reactivity. This approach is practical for simple systems, but may not be applicable for more complex systems. Because of the large number of chemical compounds and different reaction scenarios, evaluation can be very expensive and time consuming. Moreover, in case of a complex reactive system, experimental procedures will provide an overall evaluation of system thermodynamics and kinetics data but will not explain reaction stoichiometry. In fact, system analysis is required beyond laboratory measurements.

Discussed in this paper is a systematic approach to chemical reactivity characterization that consists of three levels, as shown in Figure 1. In each level, the reactive system is evaluated to understand the reaction chemistry, identify the possibility of thermal exothermal activity, and quantify the reactive chemical hazards. The three evaluation levels are:

1. screening evaluation
2. computation evaluation
3. experimental analysis

In the screening evaluation level, reactants, products, and operating conditions are identified. Literature and databases are searched for relevant data for the various substances in the chemical system. Relevant data include physical and chemical properties, thermodynamics, kinetics, incidents, and case studies.

In the second level, possible reaction pathways are proposed and their feasibility is evaluated based on available information or on predicted properties using numerical techniques such as computational quantum chemistry, statistical thermodynamics, and transition state theory. The non-feasible and non-hazardous reaction pathways are excluded and the remaining ones are tested in the third level of evaluation.

The third level includes experimental analysis. Two types of experimental analysis are performed; screening analysis, which may be performed in parallel with the theoretical computational approach level, and the more advanced level of experimental analysis, which will be done, based on the information from both theoretical and screening experimental evaluations. This way of addressing the problem will help in focusing the advanced experimental analysis on the most hazardous reactions. In each of the three evaluation levels, predicting or calculating stoichiometric, thermodynamic, and kinetic

parameters are the main objectives, and many reaction stoichiometries are thereby excluded from the need for expensive experimental analysis.

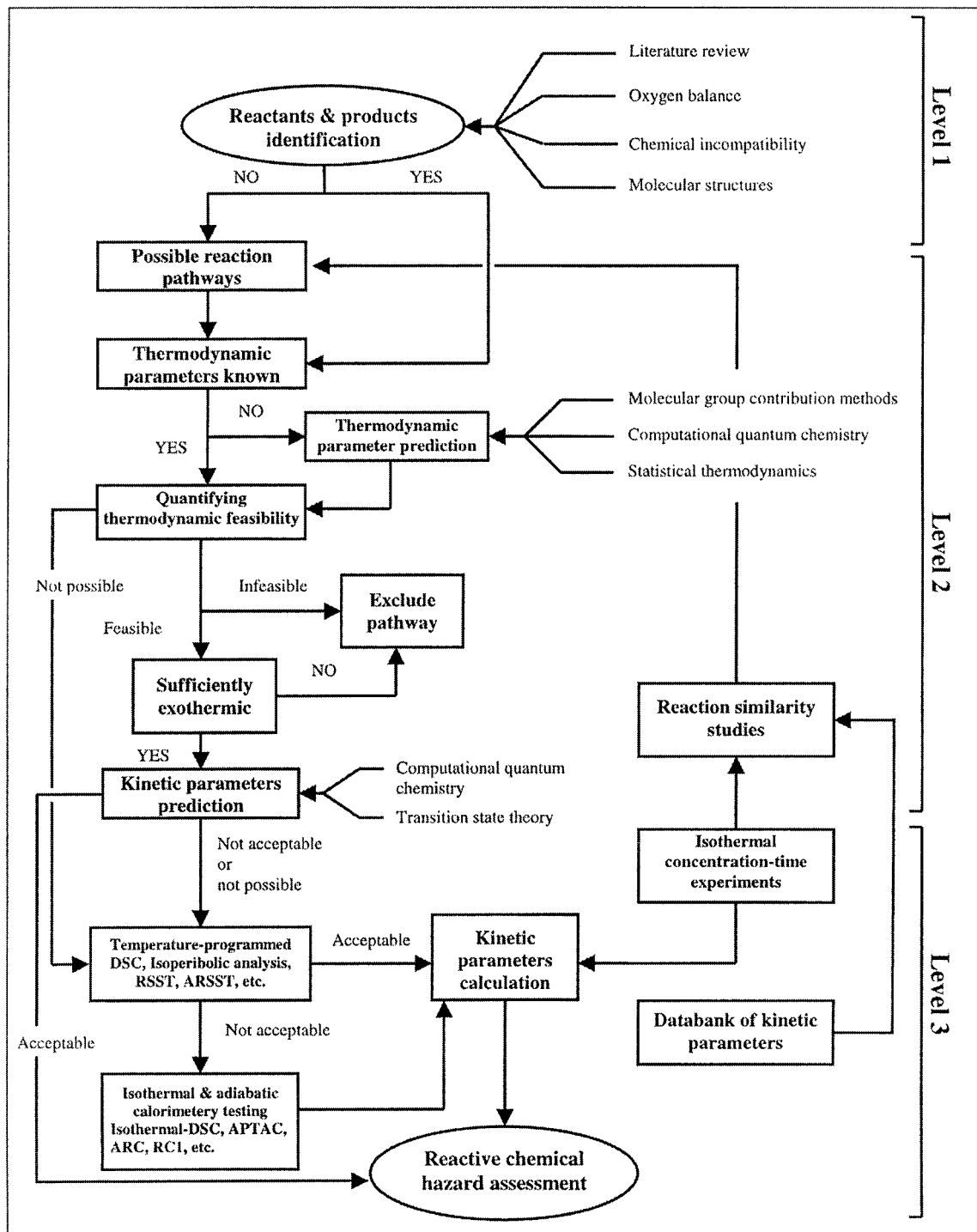


Figure 1. Systematic approach to reactive chemical hazard assessment

## Computation Models

Maintaining the safe operation limits for any chemical process is a primary goal of reactive chemical hazard evaluation. Simulating the dynamic behavior of the process ideally will lead to a determination of safe operating conditions. But process simulating is often not possible because of insufficient information. This information includes possible reaction stoichiometries, thermodynamic parameters, and kinetics of the primary and secondary reactions. However such information is not usually available in the literature or in databanks, especially, for less common and new systems.

To evaluate the potential of reactive chemical hazards, process parameters must be estimated. An experimental approach, in which the possible exothermic reactions are reproduced in the laboratory, could be taken. However, starting with this approach alone, without additional screening steps was found to be time consuming and expensive, due to the large number of possible reaction pathways, even for relatively simple systems. Also, highly unexpected exothermic secondary reactions may dictate the magnitude and time scales of heat releases during a runaway and increase the difficulty of interpreting the data from currently used experimental techniques [Bruneton et al. 1998].

In this approach, a computational screening tier is proposed to accompany the experimental screening analysis. Identification of the stoichiometries of the reactions that drive thermal instability is a major factor to understanding safety issues of a reactive system. Also, identification of the various possible stoichiometries is the first step to start this computational screening tier.

In most reactive systems, primary reactants and products are known, but products of the secondary reactions are not known. Initially, a set of possible reaction stoichiometries must be proposed. The basis of this step may vary depending on the system. Available information of similar systems may be used to build this set of possible stoichiometries. Experimental information about the products formed and the subsequent chemistry is another basis for building this set of possible stoichiometries.

The main objective of this computational screening tier is to exclude (eliminate) any thermodynamically infeasible or non-hazardous pathways and to evaluate the reactive chemical hazards for the remaining reactions through the estimated stoichiometries, thermodynamic, and kinetic parameters of the reaction system. Once the reactants and products are identified or proposed, missing thermodynamic parameters can be estimated using the numerical methods such as molecular group contribution methods or statistical thermodynamics combined with computational quantum chemistry methods.

Molecular contribution methods are theoretical techniques, which use bond and group contributions in known chemical structures to estimate thermodynamic parameters (e.g., Gibbs free energy, heat of formation and heat of reaction) of the system.

Many different group contribution methods are available; however, the method of Benson [1970], which is used in the CHETAH program [ASTM 1998], is the most widely acceptable one. Molecular group contribution methods are preliminary screening tools to detect sufficiently unstable molecules. Sometimes these tools are not able to predict the thermodynamics of certain molecules, because some groups are not implemented in these methods [Bruneton et al. 1997]. In fact, these methods are based on correlations obtained

from a large number of experimental values of thermodynamic properties for common molecules. Occasionally, these methods are unable to differentiate between the various molecular configurations such as isomers and lead to large deviations in the calculated enthalpies. In such cases, implementation of computational quantum chemistry is the next step for the evaluation of system thermodynamics.

Computational quantum chemistry is based on molecular quantum theory when the motion and distribution of electrons is described in terms of electron probability distributions or molecular orbitals [Bruneton et al. 1997]. Numerical techniques have been developed to perform the quantum chemistry calculations. Among the most known techniques are Density Functional Theory (DFT), Hartree-Fock (HF), and semi-empirical parameter techniques. The fundamental quantum chemistry methods, which are also called ab-initio methods, are coupling with statistical thermodynamics to estimate thermodynamic properties, such as enthalpy and entropy of formation of the reactants and products, enthalpy and entropy of the reaction, Gibbs free energy of the ideal gas reaction, and Gibbs free energy of mixing of the reaction.

Predicting thermodynamic information will help in excluding infeasible reactions (pathways) and non-hazardous molecules of the proposed stoichiometries. The amount of energy released in any exothermic reaction is not the only key issue in evaluating the hazard of reactive chemicals, although it is essential. The energetic reactions will be carried to a more advanced evaluation, and the rate (kinetics) at which this energy can be released is the most critical issue. But evaluating the kinetics (activation energy, rate constant) of the reaction system can be challenging or infeasible in case of a complex system of reaction pathways.

A second step of numerical calculations is proposed. Combining computational quantum chemistry (ab-initio methods) with Transition State Theory (TST) calculations is an approach to evaluate reactive system kinetics. Utilizing ab-initio and TST calculations depends on identifying the stoichiometry of the reactions, and then identifying the elementary steps involved in these reactions. The GAUSSIAN 98 [Frisch et al. 1998] package is a commercial software application of ab-initio calculations. More theory and practice concerning this package is found in [Hinchliffe 1994]. Unfortunately, applying TST calculations for predicting kinetics may not be sufficient for some complex systems, but coupling the predicted thermodynamic parameters with experimental screening analysis and concentration-time experimental data is another approach to estimate the kinetics of a reactive system.

At the end of this theoretical reactive system evaluation we conclude that the ability to predict accurate kinetics depends partly on the predicted stoichiometry of the system, which was performed at the beginning and throughout this computational tier. The most exothermic reactions can be further investigated by means of the experimental analysis tier.

## **Experimental Methods**

Most of the safety and thermal reaction risk estimations are based on the exact characterization of a reaction system, including knowledge of the reaction stoichiometry, thermodynamic, and kinetic parameters.

An exact determination of the reaction parameters by traditional means requires extensive and time-consuming laboratory investigations, which may not be cost efficient for many specialty chemicals or immediately applicable to large-scale production purposes due to the variability in raw materials and operating conditions [Maria & Heinzle 1998]. However, as shown in the previous section, the results using the theoretical computational thermodynamics and kinetics approaches are very dependent on the initial assumptions and process conditions used in the evaluation process. Incorrect assumptions may result in the hazards of the system being greatly over or underestimated. As a result, the parameter prediction process is not sufficient for the most energetic reactions within the system.

In such case, where the theoretical approach is indicating a potential for exothermal activity, a more thorough investigation is required for more exact parameter determinations. Up to this point, theoretical computational methods helped to exclude non-hazardous reaction pathways, indicating exothermal reactions, and predicting reliable stoichiometric, thermodynamic, and kinetic parameters. Such knowledge will help to guide the experimental investigations.

For a single reaction, sufficiently accurate estimates of the thermodynamic and kinetic parameters can be achieved by using calorimetric methods [Maria & Heinzle 1998]. However, for more complex reacting system (more than one reaction), calorimetric methods will provide overall measurements of thermodynamic and kinetic parameters without an explanation of reaction stoichiometries. Hence, meaningful interpretation of the experimental results based on reaction stoichiometry might be impossible. The previous theoretical approach of reaction stoichiometry and parameters prediction should be performed to develop an approximate model for the reaction mechanism. A reaction mechanism may also be obtained by isothermal time-concentration experiments through a direct measurement of species concentrations and kinetic parameters. Understanding the reacting systems chemistry is essential for reactivity evaluation. For instance, to predict the pressure behavior, one must start with the reaction stoichiometry to see if reaction is leading to gaseous products [Leung et al. 1986]. Therefore, a major effort to identify reaction stoichiometry is required by various theoretical approaches, as shown in the previous section, coupled with an experimental approach, as discussed below.

Experimental techniques for chemical reactivity evaluations produce data of varying quality. Mainly, there are four common techniques including temperature-programmed differential scanning calorimeter (DSC), isoperibolic, isothermal, and adiabatic analysis.

In this approach these techniques are divided into two levels of screening and advanced analysis techniques. The screening level includes temperature-programmed DSC and isoperibolic analysis, while the advanced level includes isothermal and adiabatic analysis techniques.

Temperature-programmed DSC is an appropriate beginning for an experimental analysis of a reactive system. In the theoretical part, we may predict a reaction model, but not predict the thermodynamics of this reaction(s), or perhaps be uncertain that the predicted values are accurate enough for reactive chemical assessment. Temperature-programmed DSC, especially the closed cell design, is a screening technique for estimating the energy potential (heat of reaction) of system by measuring heat flux, and hence evaluating the

adiabatic temperature increase. If this adiabatic temperature increase is not major, and if the system temperature is not above its boiling point, the potential hazard of this system may be excluded. Otherwise, another screening test is to be performed to find the range of temperatures within which the system is considered active for unexpected or unwanted reactions. Isothermic experiments will give more accurate estimate of the temperature range of reactivity. This estimate will indicate the range of temperatures that should be avoided during chemical processes to eliminate unwanted exothermic reactions. In case the unwanted exothermic reaction initiation temperature is close to or overlapping with the process operating temperature, a more detailed investigation is required.

A more advanced investigation will introduce the thermokinetics approach. On the screening level, knowledge of kinetic parameters was not necessary for reactive chemical evaluation, but in complex systems with many reactions in overlapping temperature ranges, this more elaborate approach is required. This advanced thermokinetics analysis level will help to meet three objectives:

- a. estimation by measurement of the thermodynamic parameters of the overall reactive system in a more accurate way
- b. estimation by measurement of the kinetic parameters of the overall reactive system
- c. minimizing the scale-up error factors by using testing conditions that are closer to process operating conditions

Although kinetic parameter estimation in these methods is for the overall reactive system, the theoretical approach in predicting the stoichiometry of various pathways can help to reduce the system to simpler and more important reactions for further studies.

Isothermal and adiabatic analyses are two techniques used in very advanced thermal analysis. Isothermal analysis can provide the most accurate heat production rates by maintaining the reaction mixture at constant temperature while measuring the heat flux as a function of time. On the other hand, adiabatic analysis is favored, particularly for large reacting masses. In the real plant situations of thermal runaway, neither the process cooling system, nor the reaction container will be able to dissipate the huge released amount of energy. The increasing reactant mass temperature will increase the rate of reaction exponentially, leading to more heat production while nearly adiabatic conditions are maintained.

The data obtained in either the isothermal or adiabatic analysis are then used to calculate the thermodynamic and kinetics parameters of the system. Several sophisticated instrumental designs of isothermal and adiabatic reaction calorimeters with advanced features are available. Calculating times to runaway and to maximum rate reactions are possible with this level of thermal analysis data. A detailed discussion of these methods is available in Gygax [1990].

Up to this point, only temperature-time experimental data were used to evaluate reactive chemical hazards. At the beginning of our presentation to this systematic approach, we mentioned the knowledge of reaction stoichiometry for a sufficient understanding of our experimental data. However, accurate determinations of kinetic parameters for complex reactive systems may not be possible without isothermal concentration-time experimental data. As shown in Figure 1, experimental concentration-time data will help to characterize reaction stoichiometry and hence verify the proposed pathways. Isothermal



concentration-time experimental data can be coupled to experimental thermal analysis data or simulated from other similar systems for which the kinetics parameters are known or available in databanks. These simulated systems may help initially to predict the reaction pathways, and hence to increase confidence in the analysis.

## Reactive System Evaluation

Thermal decomposition of di-tert-butyl peroxide (DTBP) is one of the most extensively studied kinetic systems. Its simple first order kinetic behavior and the importance of DTBP applications in process chemistry were the two main reasons for investigating this system to test our chemical reactivity characterization approach.

Reviewing some of the previous studies on DTBP thermal decomposition [Raley et al. 1948] [Murawski et al. 1951] [Williams et al. 1956] [Huyser & Bredewey 1964] [Baker et al. 1965] [Molyneux 1966] [Shaw & Pritchard 1968], we have proposed possible reaction stoichiometries as an initial step for an evaluation using this systematic approach. Although the possible reaction pathways are many, the information in the literature can help to select the most probable scenarios, as shown in Figure 2. The published results of stoichiometries, thermodynamics and kinetics of this system will be compared to results using this evaluation approach.

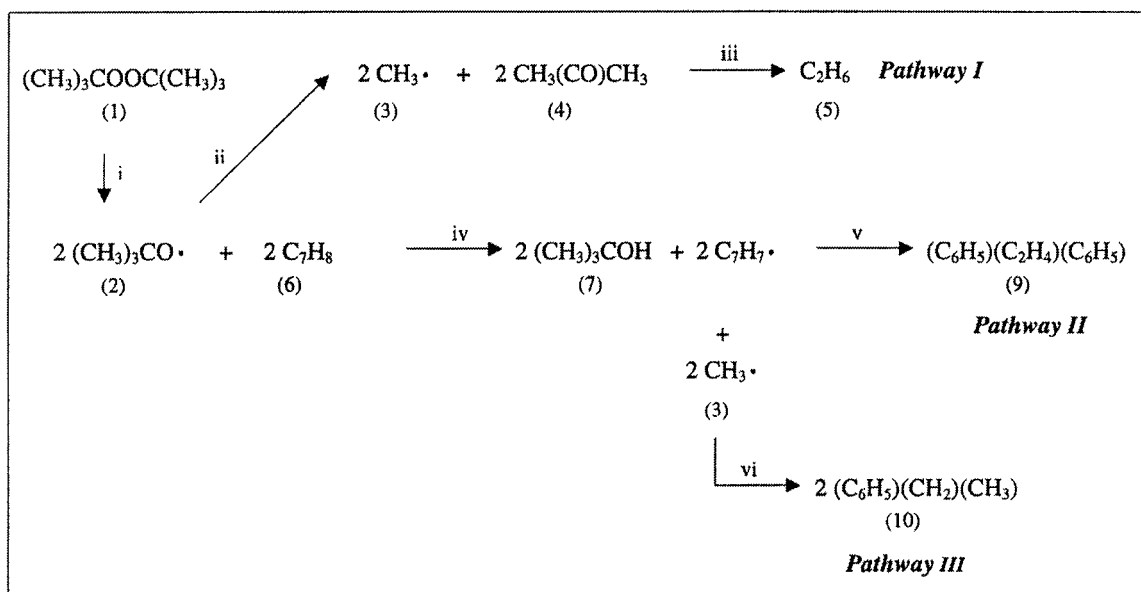


Figure 2. Proposed reaction stoichiometries of DTBP decomposition in toluene

Following a review of the literature, the first step is to run an experimental screening for the presence of thermal hazards. A solution of DTBP in toluene was tested using a Reaction System Screening Tool (RSST™) by Fauske & Associates [Fauske et al. 1989]. Exothermal reactivity was recognized from this testing, but a stoichiometric explanation could not be based on this testing only. To corroborate this behavior, reaction stoichiometry analysis was performed.

Computation quantum chemistry methods for each molecule in Figure 2 for these different pathways permit estimations of the enthalpy of formation and the ideal absolute entropy. Applying these results, we calculate the enthalpy of reaction ( $\Delta H_r$ ) and the Gibbs free energy of reaction ( $\Delta G_r$ ) of each proposed reaction in the ideal gas phase. From these calculations, we focus on the thermodynamically feasible reactions ( $\Delta G_r < 0$ ) and the most exothermic stoichiometries. In this study, the following levels of computational quantum chemistry calculations were performed to determine an efficient method of computation for this system: Semi-empirical (AM1), Hartree-Fock (HF), Density Functional Theory (DFT) B3LYP, and Gaussian-2 (G2).

AM1 is a semi-empirical method, which employs an approximate form of Schrödinger equation with appropriate parameters derived from experimental data for the type of chemical system under investigation [Foresman & Frisch 1996]. The HF method is a simple and inexpensive level of calculations since some exchange correlation effects between electrons are ignored [Bruneton et al. 1997]. In this study, HF was used with the 6-31G\*(d) basis set for both geometry optimization and frequency calculations.

The DFT states that the ground state energy of a system of electrons is a function of the electron charge and correlation effects using functionals, which include terms for exchange and correlation energy that depend on the electron density and density gradient. The B3LYP level of theory was used for this method with the 6-31G\*(d) basis set for both optimization and frequency calculations. The G2 theory is a composite procedure that applies HF/6-31G\*(d) for optimizing structures and computes energy using MP4/6-311G\*(d,p).

These calculations been applied to the ten molecules in our system as shown in Figure 2 to estimate the Gibbs free energies and enthalpies of formation. Then, the Gibbs free energy ( $\Delta G_r$ ) for the six reactions in the system was calculated. A scaling factor of 0.8929 for HF/6-31G\*(d) and of 0.9613 for B3LYP/6-31G\*(d) were applied to reduce a known systematic error in calculated frequencies [Foresman & Frisch 1996]. A summary of the results is shown in Table 1. These Gibbs free energies of reaction ( $\Delta G_r$ ) represent the ideal gas phase. The solvent and mixture interaction contributions are usually small when compared to the ideal gas contribution and is significant only when the solvent has particularly strong affinities with solutes [Bruneton et al. 1997].

Based on these results, we found that all the proposed reactions are thermodynamically feasible ( $\Delta G_r < 0$ ), however, we can predict that pathway I products will be probably the main products of DTBP decomposition. Formation of free radicals  $(\text{CH}_3)_3\text{CO}\cdot$  reaction (i) will be the rate-determining step of this decomposition, and then free radicals  $(\text{CH}_3)_3\text{CO}\cdot$  will proceed through reactions (ii) and (iv). Because reaction (ii) has a lower Gibbs free energy than reaction (iv) and assuming similar reaction rates, the ratio of free radicals  $(\text{CH}_3)_3\text{CO}\cdot$  that will react to form molecules (3) and (4) is expected to be higher than the ratio which will react with solvent molecule (6) according to reaction (iv) to form molecules (7), (8), and (9). Based on this expectation, pathway III product (10) will form in a very small amount since its formation is directly dependent on the occurrence of pathway II.

These expectations are in agreement with the findings of Milas and Surgenor [1949], that acetone (4) and ethane (5) are the only products of DTBP decomposition in the gas phase

at 250°C. In a different study, Murawski et al. [1951] showed that pathway I is the main pathway of the decomposition reaction of DTBP, although some of the methyl free radicals (3) may react with the acetone. Rust et al. [1948] found that no more than 5 to 10 percent of the methyl free radicals (3) will react with acetone, and the majority will follow reaction (ii) stoichiometry.

Table 1. Summary of Gibbs free energy of reaction calculations using three levels of theory

| Reaction | Gibbs free energy of reaction ( $\Delta G_r$ ), (kcal/mol) |              |                 |
|----------|--|--------------|-----------------|
|          | AM1  | HF/6-31G*(d) | B3LYP/6-31G*(d) |
| I        | -5.52  | -2.64        | -24.10          |
| Ii       | -14.55   | -21.87       | -27.96          |
| Iii      | -60.51   | -48.85       | -77.42          |
| Iv       | -19.48   | -4.78        | -12.97          |
| V        | -43.04   | -44.72       | -72.07          |
| Vi       | -51.81   | -47.28       | -75.29          |

According to this analysis, an estimation of enthalpy of reaction could be calculated based on the pathway I scenario using the computational methods and the Benson group contribution method from the CHETAH program. Summary of the results is presented in Table 2.

Table 2. Summary of heat of reaction calculations using five levels of theory for the pathway I

| Level of theory                  | Heat of reaction, ( $\Delta H_r$ )<br>(kcal/mol) | Reference of method   |
|----------------------------------|--|-----------------------|
| AM1                              | -70.88   | Dewar & Thiel (1977)  |
| HF/6-31G*(d)                     | -57.15   | Roothan (1951)        |
| B3LYP/6-31G*(d)                  | -47.93   | Becke (1993)          |
| G2                               | -47.03   | Curtiss et al. (1991) |
| Benson group contribution method | -42.15   | Benson (1970)         |

In our calculations of enthalpy of reaction, the heats of vaporization of DTBP and toluene were not included. The heats of vaporization of DTBP and toluene at 25°C are 9.49 and 9.16 kcal/mol, respectively [Yaws 1999]. Although these values do not represent the actual values since temperature, pressure, and composition are changing throughout the reaction. Not including these values in our calculation will yield an estimated heat of reaction for DTBP alone that is higher than the measured value of DTBP with toluene. Therefore, each measured ( $\Delta H_r$ ) reported here is for DTBP with toluene and includes the heats of vaporization.

As the results in Tables 1 and 2 show, the calculation method selection is a major factor in determining the quality of the calculated values. AM1 and HF/6-31G\*(d) are known to be of lower quality and less expensive (CPU wise) methods, however B3LYP/6-31G\*(d) and G2 are known as a higher quality and more expensive methods.

As shown in Table 2, the Benson group contribution method provided a value of  $\Delta H_r$  which differs by about 4 – 5 kcal/mol from the values calculated using G2 and B3LYP/6-31G\*(d), which are assumed to be more acceptable for this evaluation. However, AM1 and HF/6-31G\*(d) results deviated by about -23 and -10 kcal/mol, respectively.

Based on this systematic approach of reactivity evaluation, the stoichiometry of DTBP decomposition as estimated using the computational level is to be verified using experimental analysis, which was performed on the screening level and in parallel with the computational analysis of this system.

Experimental screening analysis using RSST™ was performed for 30%, 50%, and 60% solutions of DTBP on toluene with nitrogen backup pressure of about 250 psig to reduce liquid boiloff before decomposition. A temperature ramping rate of 1°C/min was applied for samples masses of 8.032 to 9.565 g placed in the cell with a thermal inertia ( $\phi$ -factor) of about 1.048, which was kept under constant stirring during the experiments. An example of temperature and pressure profiles during the DTBP decomposition is shown in Figure 3. A summary of the experimental data is presented in Table 3 for the tested samples.

Heat of decomposition reaction of DTBP in toluene is calculated by Equation (1):

$$\Delta H_r = \frac{\phi C_{vs} (T_{\max} - T_o)}{x} \quad (1)$$

where,  $\phi$ : thermal inertia factor ( $\phi$ -factor) =  $\frac{(m_s C_{vs}) + (m_c C_c)}{(m_s C_{vs})}$

$T_{\max}$ : maximum temperature due to decomposition reaction, °C

$T_o$ : onset temperature at which exothermic decomposition is first detected, °C

$m_s$ : sample solution mass, g

$x$ : fraction of reactant in the sample solution

$m_c$ : mass of testing cell, g

$C_{vs}$ : heat capacity of sample solution, kcal/g-K

$C_c$  : heat capacity of cell, kcal/g-K

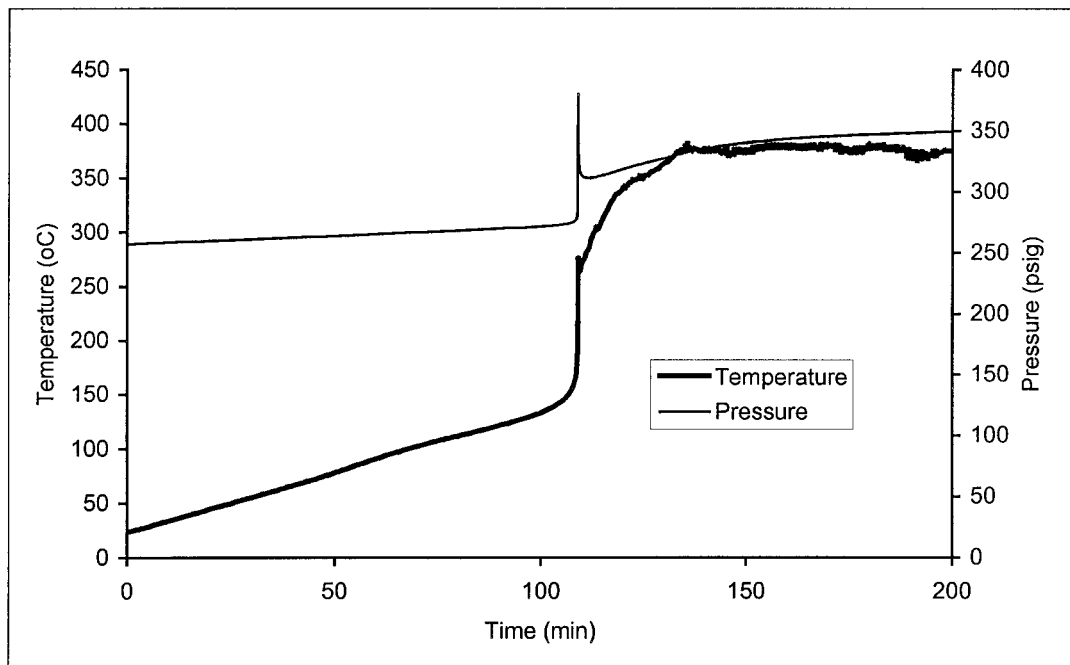


Figure 3. Temperature and pressure profile during DTBP decomposition in toluene

Table 3. RSST™ measured  $T_{\text{onset}}$ ,  $T_{\text{max}}$ , and  $\Delta T_{\text{ad}}$  for DTBP decomposition in toluene

| Sample                        | 30% a  | 30% b  | 30% c  | 50%    | 60% a  | 60% b  |
|-------------------------------|--------|--------|--------|--------|--------|--------|
| Sample mass, (g)              | 8.450  | 9.565  | 8.032  | 9.189  | 8.744  | 9.273  |
| Cell mass, (g)                | 1.383  | 1.510  | 1.535  | 1.431  | 1.233  | 1.249  |
| Solution $C_v$ , (cal/g-K)    | 0.5657 | 0.5492 | 0.5496 | 0.6873 | 0.7916 | 0.7921 |
| $\phi$ -factor                | 1.0579 | 1.0575 | 1.0695 | 1.0453 | 1.0356 | 1.0340 |
| $T_{\text{onset}}$ , (°C)     | 130    | 111    | 105    | 124    | 133    | 125    |
| $T_{\text{max}}$ , (°C)       | 248    | 237    | 240    | 328    | 374    | 376    |
| $\Delta T_{\text{ad}}$ , (°C) | 118    | 126    | 135    | 204    | 241    | 251    |

Heat capacity of the sample solution,  $C_{vs}$ , was estimated at an average temperature between  $T_o$  and  $T_{\text{max}}$  considering the proportion of DTBP and toluene in each sample and based on the correlations in Yaws [1999]. In such case we are assuming that the change

in average heat capacity during the decomposition reaction is negligible. In fact, heat capacity estimation is one of the main sources of uncertainty in the estimated heat of reaction.

Assuming that this reaction can be represented by a first order kinetic equation, then the reaction rate constant,  $k$ , can be calculated from Equation (2):

$$k = \frac{\left(\frac{dT}{dt}\right) - (\text{RSST}^{\text{TM}} \text{ temperature ramping rate})}{(T_{\text{max}} - T)} \quad (2)$$

where  $(dT/dt)$  is the sample heating rate.

Since the reaction rate is related to the temperature through the Arrhenius expression:

$$k = A \exp\left(\frac{-E_A}{RT}\right) \quad (3)$$

where  $A$  is frequency parameter,  $R$  is gas constant, and  $E_A$  is the activation energy. Substituting the experimental value of  $k$  from Equation (2) into (3) will result in Equation (4):

$$\log(k) = \log(A) - \frac{E_A}{2.303 R T} \quad (4)$$

which is used to estimate the Arrhenius parameters of activation energy and frequency factor. Figure 4 shows  $\log(k)$  vs.  $(1/T)$  plot for the thermal decomposition of 60% DTBP sample in toluene. Table 4 summarizes the heats of reaction and Arrhenius parameters determined from the RSST<sup>TM</sup> data, and Table 5 shows some of the reported values measured using various techniques.

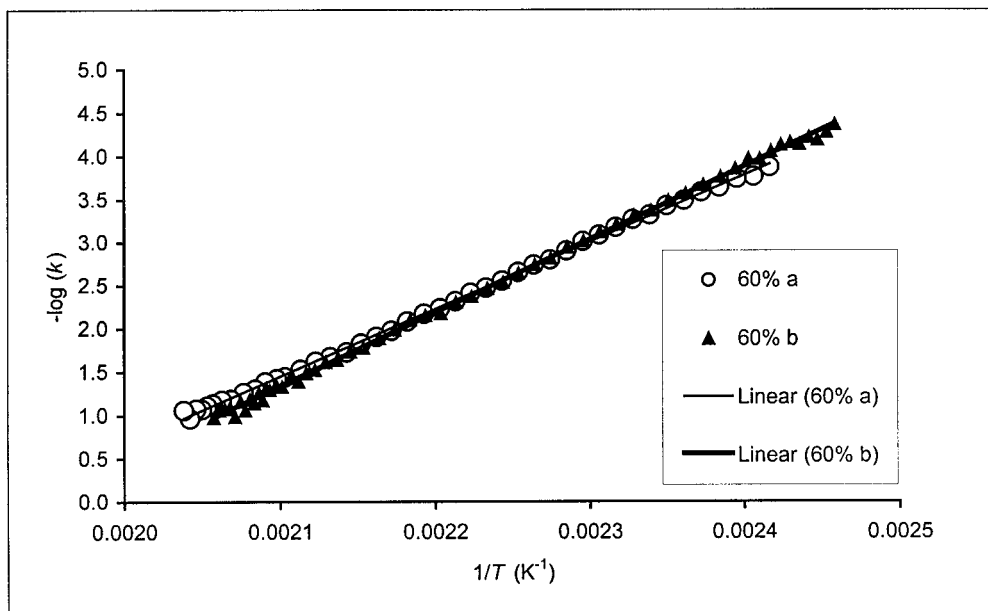


Figure 4. First order kinetic rate data from DTBP decomposition

The Arrhenius parameters show an acceptable agreement with published data, considering that RSST™ is a screening tool, yet the results are comparable to those found through isothermal time-concentration studies or through thermal analysis using the Accelerated Rate Calorimeter (ARC) or other low thermal inertia apparatus. Heat of reaction values at 60% concentration justifies the assumption made during the theoretical evaluation that pathway I is dominant in the DTBP decomposition.

The value of  $\Delta H_r$  in Table 4 decreased as the DTBP concentration decreased, and this could be because of energy losses due to sample vaporization or to the surroundings. These energy losses are more significant in the lower concentration samples, since reducing the concentration of the reactant reduces the total generated energy, while the heat transfer surface (testing cell) was kept constant. Therefore, the fractional energy losses in the lower concentration samples are higher than that of higher concentration samples. According to that, we believe that the 60% DTBP samples are more representatives compared to other samples and with respect to the theoretical calculated values.

Table 4. RSST™ measured heat of reaction and Arrhenius parameters for DTBP decomposition in toluene

| Sample                      | $\Delta H_r$ , (kcal/mol) | $E_a$ , (kcal/mol) | Log ( $A$ ), (sec <sup>-1</sup> ) |
|-----------------------------|---------------------------|--------------------|-----------------------------------|
| 30% a                       | -34.42                    | 38.17              | 16.42                             |
| 30% b                       | -35.67                    | 42.09              | 18.22                             |
| 30% c                       | -38.68                    | 38.63              | 16.67                             |
| 50%                         | -42.86                    | 35.99              | 15.15                             |
| 60% a                       | -48.15                    | 35.61              | 14.89                             |
| 60% b                       | -50.10                    | 38.86              | 16.49                             |
| Average                     | -----                     | 38.23 ± 2.34       | 16.31 ± 1.20                      |
| Relative Standard Deviation | -----                     | ± 6.12%            | ± 7.35%                           |

In the computational quantum chemistry analysis we assumed that the solvent effects are negligible. To justify this assumption, toluene was replaced with benzene as a solvent, and another set of samples was tested. Results, presented in Table 6, indicate that for 30%, 50%, and 60% DTBP solution in benzene,  $\Delta H_r$  values and Arrhenius parameters are within the range of DTBP in toluene solutions, showing acceptable agreement with the assumption has been made in the theoretical calculation level.

Table 5. Heat of reaction and Arrhenius parameters for DTBP decomposition

| Sample concentration | $\Delta H_r$ (kcal/mol) | $E_A$ (kcal/mol) | $\log(A)$ (sec <sup>-1</sup> ) | Experiment                      | Reference             |
|----------------------|-------------------------|------------------|--------------------------------|---------------------------------|-----------------------|
| 25% in toluene       | -42.4                   | 37.71            | 15.95                          | Low $\phi$ factor apparatus     | Leung et al. 1986     |
| 30% in toluene       | -41                     | 37.944           | 16.21                          | ARC                             | Tou & Whiting 1981    |
| 60% in toluene       | -45 to -49              | 37.80 $\pm$ 1.1  | 16.15 $\pm$ 0.61               | ARC                             | Tou & Whiting 1981    |
| Pure                 | ----                    | 37.83 $\pm$ 0.32 | 15.82 $\pm$ 0.11               | Isothermal static system        | Shaw & Pritchard 1968 |
| Pure                 | ----                    | 37.20            | 15.62                          | Average of 11 different studies | Molyneux 1966         |

Table 6. Summary  $\Delta H_r$ ,  $E_A$ , and  $\log(A)$  of DTBP decomposition in benzene

| Sample concentration | $\Delta H_r$ , (kcal/mol) | $E_A$ , (kcal/mol) | $\log(A)$ , (sec <sup>-1</sup> ) |
|----------------------|---------------------------|--------------------|----------------------------------|
| 30%                  | -34.35                    | -31.50             | 13.05                            |
| 50%                  | -40.27                    | -37.21             | 15.85                            |
| 60%                  | -47.27                    | -31.75             | 13.13                            |

## Conclusions

A systematic approach of evaluating reactive chemical hazards was presented. In this approach a combination of computational quantum chemistry methods and experimental analysis results in better understanding of reaction stoichiometry and better estimations of thermodynamics and kinetics of reactive systems. Performing computation quantum chemistry together with screening experimental analysis at the early stages of system evaluation will focus the research on the most possible and most hazardous reaction stoichiometry and hence reducing the need of intensive detailed experimental analysis. More detailed and advanced experimental analyses may be still required for more complex systems.

This approach was applied in the evaluation of di-tert-butyl peroxide decomposition reaction in toluene. Computational quantum chemistry was applied at different levels of theory to predict the most probable reaction stoichiometry, and the heat of reaction of the



most possible pathway was calculated. Screening tests using RSST™ were performed and the heat of reaction was estimated showing an acceptable agreement with the theoretical calculation, and hence corroborating the proposed reaction stoichiometry. Also, Arrhenius parameters were estimated through this screening tool showing a good agreement with literature values calculated using more advanced experimental techniques.

In general, this approach of evaluating chemical reactivity can be applied to different systems. The degree of success in applying this approach will depend on the system complicacy and on the appropriate level of theory to predict its thermochemistry data.

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