



Molecular simulation studies on chemical reactivity of methylcyclopentadiene

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ABSTRACT

Molecular simulations are important to predict thermodynamic values for reactive chemicals especially when sufficient experimental data are not available. Methylcyclopentadiene (MCP) is an example of a highly reactive and hazardous compound in the chemical process industry. In this work, chemical reactivity of 2-methylcyclopentadiene, including isomerization, dimerization, and oxidation reactions, is investigated in detail by theoretical computational chemistry methods and empirical thermodynamic–energy correlation. On the basis of molecular simulations, an average value of -15.2 kcal/mol for overall heat of dimerization and -45.6 kcal/mol for overall heat of oxidation were obtained in gaseous phase at 298 K and 1 atm. These molecular simulation studies can provide guidance for the design of safer chemical processes, safer handling of MCP, and also provide useful information for an investigation of the T2 Laboratories explosion on December 19, 2007, in Florida.

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1. Introduction

Appropriate assessment of reactive hazards has been a significant concern in the chemical process industry [1]. The U.S. Chemical Safety and Hazard Investigation Board (CSB) reported that there were 167 reactive chemical incidents between 1980 and 2001, which resulted in an average of five fatalities annually [2]. The lack of accurate knowledge about the chemistry of reactants, intermediates, and products has been one of major causes of these incidents [3]. Therefore, to prevent similar incidents, it is urgent to recognize chemical reactivity and thermal runaway reactions of hazardous materials for safe operation of a chemical process facility [4].

Methylcyclopentadiene (MCP), C_6H_8 , has recently been involved in a serious industrial incident which occurred on December 19, 2007, in Florida [5]. The explosion destroyed a T2 laboratory and led to four fatalities and multiple injuries. T2 Laboratories is a small company with about a dozen employees, who were making methylcyclopentadienyl manganese tricarbonyl (MMT). MMT is an additive used to boost gasoline octane rating and is marketed as Ecotane by T2 Laboratories and is sold in about 70 nations. The process chemistry of manufacturing MMT is summarized in Fig. 1 from a U.S. Patent [6]. Among the chemical process, the first step is carried out at $110^\circ C$ in diglyme, which is a common solvent in

organic synthesis [7]. This reaction is considered to be very hazardous in a batch reactor process, because more than half a ton of metallic sodium reacts with MCP, and release hydrogen gas as a byproduct. Preliminary findings conducted by CSB indicate that large amounts of thermal energies led to a runaway reaction and caused a high-pressure reactor vessel to rupture [8].

It is well known that chemical reactivity information can be obtained from the literature sources or by using calorimetric techniques in the laboratory. However, for reactive materials with insufficient experimental data, such as MCP, estimation methods are of prime importance. Molecular simulation has been used to provide a unique and reliable approach for prediction of reactive hazards, such as hydroxylamine, NH_2OH [9]. MCP is an example of a highly reactive, hazardous, and poorly characterized compound in industry. It is reported that MCP is usually stored below $-20^\circ C$, or in very diluted alcoholic solution [10]. Dimerization is measurable above $0^\circ C$ and normally completes within 2–3 h at $60^\circ C$ [10]. Since MCP is not commercially available (only methylcyclopentadiene dimer 93% can be purchased from Sigma–Aldrich Co.), the experimental evaluation of its calorimetric data is extremely difficult.

Reaction pathways, thermodynamic properties and kinetic parameters are important parts of chemical reactivity characterization [11,12]. Hazardous reactions of MCP include ring expansion, decomposition, isomerization, dimerization, polymerization and oxidation. The pyrolysis of MCP has been examined in two shock tubes with a variety of techniques by Ikeda et al. [13]. High temperature shock tube results on the decomposition demonstrated that

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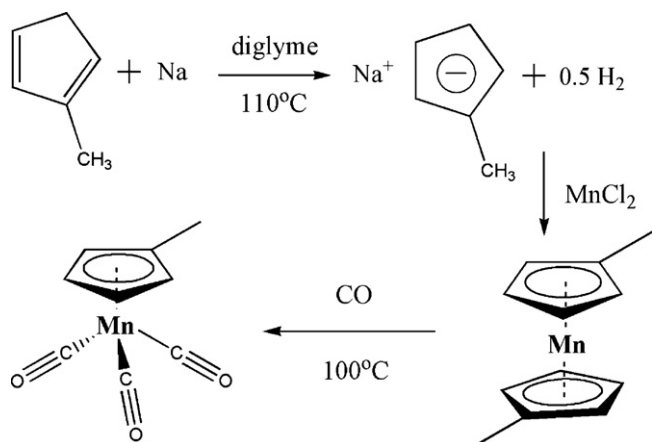


Fig. 1. Summary of the process chemistry of manufacturing MMT.

a large number of higher aromatics were produced. Five-member ring expansion in MCP is a transition from aliphatic to aromatic compounds, which has been theoretically investigated by Dubnikova and Lifshitz [14].

In this work, the chemical reactivity, especially the heat of reaction and isomerization, dimerization and oxidation reactions of MCP was thoroughly analyzed using the molecular simulation approach. The mechanisms of isomerization are elucidated using Transition State Theory (TST). The theoretical computational methods were used to predict plausible hazardous reaction pathways and their heats of reactions. Identification of the dominant reaction pathways will lead to a better understanding of the thermodynamic and kinetic characterization of MCP.

2. Theoretical methods

Density functional and *ab initio* computations for the gaseous phase at 298 K and 1 atm were performed using the Gaussian-03 program package [15,16]. A variety of theoretical methods, Austin Model 1 (AM1) [17], Hartree–Fock (HF) [18], second-order Møller–Plesset perturbation theory (MP2) [19] and Becke 3 Lee, Yang, and Parr density functional theory (B3LYP) [20,21] were used for geometry optimizations and frequency calculations. Employed also were Pople-style basis sets [22,23], 6–31G(d), including polarization functions for angular flexibility to represent regions of high electron density among bonded atoms [24].

One way to calculate enthalpies of reaction is to calculate heats of formation, and take the appropriate sums and difference. However, the heat of reactions can be obtained also by simply taking the difference of the sum of these values for the reactants and the products, because the Gaussian program provides the sum of electronic and thermal enthalpies [25]. The same method can be used to calculate Gibbs free energies of reactions. Since the number of atoms of each element is the same on both sides of the reaction and all of the atomic information cancel out, only molecular data are needed.

Frequency calculations at several levels of theory were performed to obtain zero-point energies and frequencies for all species in the reaction pathways without symmetry restrictions. Each calculated structure was characterized as either a local minimum with no imaginary frequency or a transition state with only one imaginary frequency. Vibrational analysis was also at the same level of theory to characterize the optimized structures as local minima or transition states. The QST2 method was used to search and optimize the transition state structures. The calculation of intrinsic reaction path (IRC) was also conducted to follow the reaction pathways and

used to check whether a transition state connects two minima of interest on the potential energy surface [26].

3. Results and discussion

3.1. Isomerization reaction

As a product of thermal cracking of petroleum hydrocarbons, MCP has three isomers depending upon the location of the methyl group with respect to the sp^3 carbon in the molecule (Fig. 2). All three isomers are optimized using AM1, HF, MP2, and B3LYP, with the same basis set, 6–31G(d). All of the total energies and relative energies including the zero-point energy (ZPE) correction are summarized in Table 1. As can be seen, these theoretical methods give the consistent results that the lowest energy isomer is 2-MCP.

The mechanisms of sigmatropic rearrangements have been systematized by the Woodward–Hoffmann rules of orbital symmetry, and concerning the nature of the [1,5] rearrangement also has been reported by Spangler [27,28]. Particularly, the [1,5] sigmatropic hydrogen shifts in the heterocycles have been examined using *ab initio* calculations [29]. It would be interesting to know the isomerization mechanism and rates in the three isomers of MCP. In this case, the isomerization reactions from 2-MCP to 1-MCP, and also from 1-MCP to 5-MCP can be described in a sigmatropic [1,5] hydrogen shift mechanism, as shown in Fig. 2. The reaction coordinate involves a substantial H-atom motion as the carbon–carbon double bonds rearrange.

A transition state is defined as the geometry that has a zero derivative of energy and a positive second derivative of energy with respect to movement of the nuclear coordinates for all but one geometric movement, which has a negative curvature. The energy of the transition state structure must be calculated to determine the activation energy and the reaction rate. In this work, we use the QST2 method to calculate the configuration and the energies of the transition states of two isomerization reactions. The transition structures, TS1 and TS2 as shown in Fig. 2, are obtained and each have only one imaginary frequency (-1227.29 cm^{-1} for TS1, -1263.93 cm^{-1} for TS2). The energy barrier of the 2-MCP to 1-MCP isomerization is 27.98 kcal/mol at the B3LYP level of the theory, whereas the barrier for isomerization of 1-MCP to 5-MCP is 24.05 kcal/mol. The activation energy difference can be explained by the relatively small endothermicity of the 2-MCP to 1-MCP isomerization compared to the 1-MCP to 5-MCP isomerization. The values of activation energy are consistent with the experimental results reported by McLean et al. [30]. Therefore, the reaction rate constant k can be calculated based on Transition State Theory using

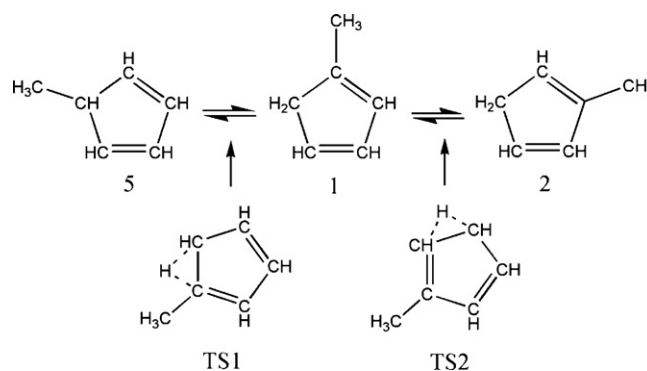


Fig. 2. Isomerization mechanism of three MCP isomers with two transition states (TS1 and TS2).

Table 1Total energies (E : au) and relative energies (ΔE : kcal/mol) including zero-point energy (ZPE) correction of three isomers.

Isomers	HF		MP2		B3LYP		AM1	
	E	ΔE	E	ΔE	E	ΔE	E	ΔE
2	-231.7137	0.00	-231.7135	0.00	-233.3030	0.00	0.1680	0.00
1	-231.7134	0.25	-231.7131	0.26	-233.3028	0.15	0.1684	0.24
5	-231.7077	3.78	-231.7073	3.91	-233.2958	4.51	0.1755	4.46

Note: The same basis set, 6-31G(d) is used in this work.

Eq. (1):

$$k = \frac{k_B T}{h} e^{-\Delta E_a / RT} \quad (1)$$

where k_B is Boltzmann's factor, h is Planck's constant, ΔE_a is the activation energy, T is the absolute temperature and R is the gas constant. Both k_{5-1} and k_{1-2} are estimated to be $1.42 \times 10^{-5} \text{ s}^{-1}$, $1.86 \times 10^{-8} \text{ s}^{-1}$, respectively, at 298 K and 1 atm.

The equilibrium constant K_a is defined by the relation

$$K_a = e^{-\Delta G_i^\circ / RT} \quad (2)$$

when the reaction system reaches equilibrium, K_a can be calculated according to Eq. (2) for the chemical equilibrium among the three isomers. Therefore, the molar ratio (or ratio of concentration) of three isomers can be estimated to be 0.61:0.39:0.0006, for 2-MCP, 1-MCP, 5-MCP respectively, at 298 K and 1 atm.

3.2. Dimerization reaction

From the results of Section 3.1, because more than 60% of isomers are 2-MCP under the chemical equilibrium condition, 2-MCP is selected as the starting material in the following reactions. Dimerizations of 2-MCP follows the Diels–Alder reaction, which has been studied in great detail both theoretically [31] and experimentally [32]. Three possible mechanisms have been proposed by Woodward and Katz for the Diels–Alder reactions: a concerted mechanism, a two-step mechanism, and an asynchronous two-stage mechanism [33]. The concerted mechanism suggests that the reactants 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 previous mechanisms. Several semi-empirical and *ab initio* theoretical studies of Diels–Alder cycloadditions have been conducted: some studies have shown that *ab initio* SCF methods favor a concerted mechanism [34], while semi-empirical approaches favor steps involving biradicals [35]. Diels–Alder dimerizations of a series of substituted cyclopentadienes have been studied by Froese et al. [36], but the dimerization reaction has not been investigated. In this work, the two-step mechanism is proposed, as shown in Fig. 3. There are 12 reactions with three different reaction pathways and 9 final products. To determine the dominant reaction pathways and their thermo-kinetic parameters, computational quantum chemistry calculations were performed using three different levels of theory. The resulting heats of reaction and Gibbs free energies are summarized in Table 2.

To simplify the procedure of predicting the kinetics of elementary reactions, a linear thermodynamic-energy correlation, the Evans–Polanyi equation [37], is commonly used to estimate activation barriers from heats of reactions:

$$E_a = E_a^0 + \gamma_P \Delta H_r \quad (3)$$

where E_a^0 is the intrinsic activation barrier, γ_P is the positive transfer coefficient, and ΔH_r is the heat of reaction. This equation indicates

that as a reaction type becomes more exothermic, its activation barrier decreases. Hence, it is possible to apply Eq. (3) to identify the dominant pathways based on activation energy predictions of proposed elementary reactions. 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. All three theoretical methods (AM1, HF and B3LYP) give the same results which are sufficient to conclude that reactions 1 and 2 are dominant over 3 since they have the lower heats of reaction. Therefore, diradicals I-1 and I-2 will be the main intermediates. Similarly, reactions 4–6 proceed with the same mechanism, however, reaction 4 has much lower heat of reaction (-10.4 kcal/mol) than reactions 5 and 6 (-2.1 kcal/mol and 9.9 kcal/mol, respectively), which is expected to have lower activation barrier and therefore is more dominant. Also, among reactions 7, 8 and 9, reaction 7 is expected to be more dominant.

On the basis of this analysis, the main dimerization reaction pathways are through intermediate I-1 and I-2, to form product P-1-1 (dimerization 1) and P-2-1 (dimerization 2). The optimized molecular structures of these main final products are shown in Fig. 4. Previous experiment using a gas chromatography to separate the mixture of dimers indicated that P-1-1 and P-2-1 are the major compositions, which is consistent with the simulation result [38]. As for the overall heats of reactions, B3LYP level calculations yield -12.75 kcal/mol and -12.41 kcal/mol, for dimerization 1 and dimerization 2, respectively.

3.3. Oxidation reaction

Singlet ($^1 \Delta_g$) oxygen addition to unsaturated and aromatic compounds, which involves the formation of organic peroxides and hydroperoxides, plays an important role in chemical processes, which can directly initiate a chain of radical reactions [39]. 1,4-Cycloaddition of oxygen to a system containing two conjugated double bonds results in the formation of the 1,4-peroxides. Two different mechanisms were suggested for 1,4-oxygen addition: a stepwise mechanism involving a linear biradical intermediate, and a single-step mechanism with a symmetric transition structure with significant charge transfer from the organic donor to oxygen. The first mechanism involving linear biradical intermediates seems to be reasonable. Although there is no direct experimental evidence to support this mechanism, it is possible, because the intermediates have been observed in the reaction of singlet oxygen with 2,4-hexadiene [40]. In this paper, possible reaction pathways are suggested based on the first mechanism and are illustrated in Fig. 5. The reactions will lead to the formation of highly reactive peroxide, which may initiate the polymerization of MCP. The quantum computational level of theory was used to predict the reaction thermodynamic values presented in Table 3.

According to the results of the calculations, the oxidation reaction is significantly exothermic. The reaction involves the formation of intermediates, in which the oxygen molecule is attached to one of the terminal carbon atoms. Applying the same concepts of reaction pathway predictions on reactions with oxygen as in Fig. 5 suggests that the organic peroxide will be formed. Compared to dimerization reactions, it is found that the peroxide formation reactions

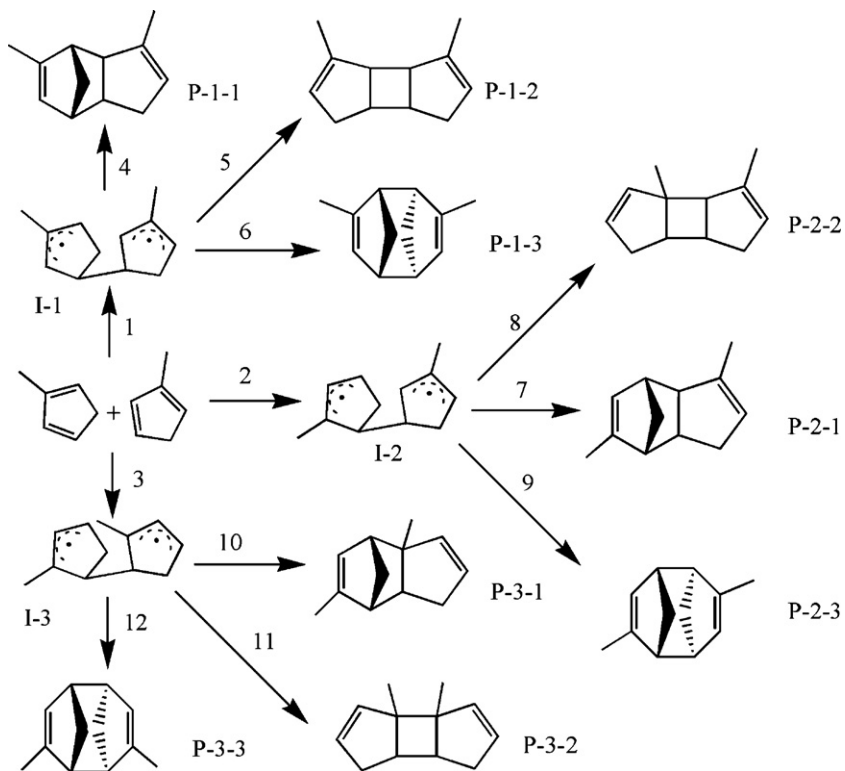


Fig. 3. Two-step mechanism of dimerization reactions.

Table 2

Heats of reactions (ΔH_r) and Gibbs free energies (ΔG_r) of dimerization reactions of 2-MCP calculated using three levels of theory.

Reactions	AM1		HF		B3LYP	
	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r
1	-14.26	-4.08	-4.37	4.56	-2.36	2.25
2	-14.17	-2.32	-4.34	5.69	-3.12	2.38
3	-13.09	0.61	-3.03	8.07	2.71	5.48
4	-4.75	-0.91	-9.57	-6.29	-10.40	-2.32
5	34.29	39.54	-0.39	5.52	-2.10	2.97
6	7.61	14.10	14.24	21.33	9.90	16.31
7	-4.84	-0.81	-9.33	-7.14	-9.29	-4.41
8	38.28	42.02	0.84	8.77	-0.35	5.38
9	7.58	12.39	11.56	16.56	9.61	15.10
10	1.32	3.99	-6.30	0.94	-4.63	2.38
11	50.57	53.79	45.62	50.37	35.29	43.18
12	6.44	9.41	12.90	17.82	18.67	23.63

Note: The same basis set, 6-31G(d) is used, and the unit is kcal/mol.

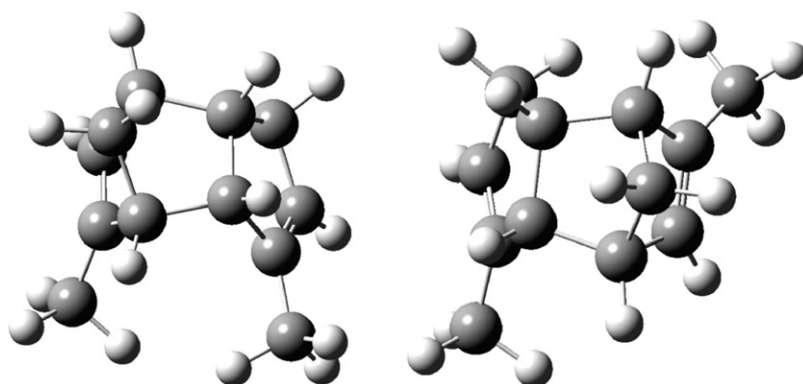


Fig. 4. Molecular structures of two major products in dimerization reactions.

Table 3Heats of reactions (ΔH_r) and Gibbs free energies (ΔG_r) of oxidation reactions of 2-MCP calculated using three levels of theory.

Reactions	HF		MP2		B3LYP	
	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r
1	-41.82	-32.93	-11.54	-8.58	-23.47	-14.25
2	-41.79	-33.84	-10.92	-7.95	-22.70	-13.75
3	-0.32	3.33	-33.67	-24.07	-25.98	-22.76
4	-0.35	4.24	-34.30	-24.70	-26.75	-23.25

Note: The same basis set, 6-31G(d) is used, and the unit is kcal/mol.

generally have lower activation barriers (higher heat of reaction is released) and hence may be dominant. Heat of these peroxide reactions is calculated to be -45.57 kcal/mol using the B3LYP level theory. The reactivity hazard of MCP is predicted to be more significant in the presence of air or any other free radical initiator, because the energy release associated with the oxidation reactions exceeds those of the dimerization reactions.

3.4. Comparison of different methods

The heat of reaction for gaseous MCP was calculated under standard conditions at several levels of theories, including HF, B3LYP, MP2, and AM1. AM1 is a semi-empirical method and is convenient to do within the Gaussian program. The most important advantage of AM1 is its small CPU time, even for relative large molecules. Therefore, it is recommended that AM1 method should be used at the beginning of the modeling work to identify the possible reaction pathways. This method is used for relative comparisons of the various proposed reactions but usually not for accurate calculations of the overall reaction energies.

Hartree–Fock is the lowest level *ab initio* theory employed here. Since HF method does not include a full treatment of electron correlation, it is not accurate to optimize the structure of radicals or diradicals in the reaction pathways. However, the overall heat of reaction calculated with the Hartree–Fock model can still provide good results, because only reactants and products must be optimized. In order to obtain more accurate values of heat of reaction, higher level theory, such as the MP2 model, is also used in this work. The density functional methods, although not truly *ab initio*, include electron correlation at only a moderate increase in computing cost by using functions of electron density. B3LYP is expected to yield better results than the HF or AM1 methods. The overall reaction enthalpies and Gibbs free energies including two dimerizations and an oxidation reaction are summarized in Table 4. As for overall reaction heats in two dimerization reactions, HF and B3LYP methods are close with -12 to -13 kcal/mol. All three methods (HF,

MP2, and B3LYP) provide consistent results for the overall heat of oxidation, ~ -45 kcal/mol.

In order to save CPU time and obtain acceptable heat of reaction values, 6-31G(d) is a practical choice. It should be noted that the same basis set is used throughout this work, because an objective was to compare different theoretical methods.

3.5. Investigation of the T2 Laboratories explosion

As it was mentioned by CSB in its investigation on the T2 Laboratories explosion, excessive reactor pressure and temperature led to a runaway chemical reaction and an explosion. Part of the reactor vessel ruptured and injuries occurred 750 ft from the reactor's location with debris found a mile from the blast. The CSB team may conduct reactive chemistry testing to analyze the chemical hazards leading to the reactor failure. But this testing and analysis could take more than a year to result in a published review. Molecular simulation, however, is a quick and reliable approach to estimate this incident. Here, the available information was used to find the possible causes and reduce the likelihood of such accidents. Based on the process chemistry analysis and a molecular simulation approach, some potential causes of the T2 Laboratories explosion incident are identified as follows:

1. The first step of the chemical process includes the mixing of reactive materials (MCP) with metallic sodium and generates hydrogen gas, which will cause a pressure increase in the reactor. Hydrogen gas is very easy to be ignited because of its low minimum ignition energy, a high flame speed, and a wide range of flammability. Also vapors from MCP can ignite at 80°C according to safety warnings for the chemical solution.
2. MCP is highly reactive and will dimerize even at 0°C as mentioned previously. From the molecular simulation results, the dimerization reaction is thermodynamic feasible and exothermic ($\Delta H_r \approx -15$ kcal/mol) at 298 K and 1 atm. Exothermic reactions generate heat, which causes the temperature in the vessel to rise. If the thermal energy is not efficiently dissipated to the surroundings, it will finally lead to an unexpected runaway reaction.
3. Molecular simulation results also indicate that the oxidation reaction is more favorable than dimerization reactions in the presence of air. Large amounts of reaction heat ($\Delta H_r \approx -46$ kcal/mol) will be released, and peroxide intermediates will be produced. The peroxides will increase the chance of polymerization reaction initiation and therefore increase the reactivity hazards.

The molecular simulation approach could provide some guidance for the safer chemical processes and safer handling of MCP. For example, since both dimerization reactions and oxidation reactions are quite exothermic, it is especially important to control the local temperature and pressure inside the reactor for the reactions with MCP involved, and efficiently dissipated the thermal energies to the surroundings. Organic peroxides, which can be produced

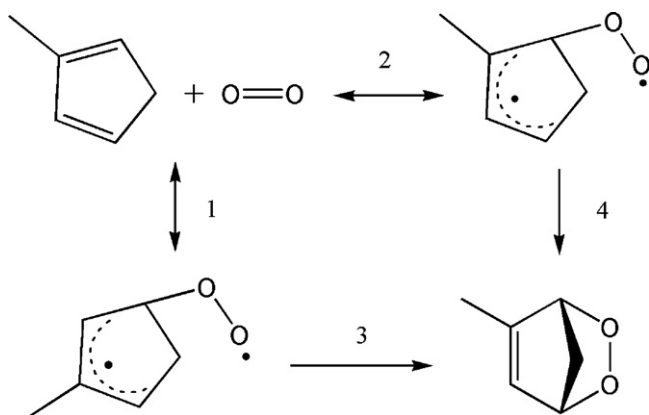


Fig. 5. Proposed reaction pathways of oxidation reactions.

Table 4
Summary of calculated overall reaction heats (ΔH_r) and Gibbs free energies (ΔG_r) of three dominant reactions.

Methods	Dimerization 1		Dimerization 2		Oxidation	
	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r
AM1	-19.00	-4.99	-19.01	-3.13	—	—
HF	-13.94	-1.73	-13.67	-1.45	-42.14	-29.60
MP2	—	—	—	—	-45.21	-32.65
B3LYP	-12.75	-2.32	-12.41	-2.16	-49.45	-37.00
Average	-15.23	-3.01	-15.03	-2.25	-45.57	-33.08

Note: For dimerizations, AM1, HF and B3LYP methods are used, and for oxidation, HF, MP2 and B3LYP methods are used. The same basis set, 6-31G(d) is used, and the unit is kcal/mol.

by oxidation reactions, will also initiate polymerization reactions. Therefore, MCP should be handled or fed to the reactor very carefully under nitrogen atmosphere. Another concern is the possibility of changing the chemical process. Roesky and coworkers reported an improved synthesis of sodium cyclopentadiene directly by the reaction of dicyclopentadiene with metallic sodium [41]. From the molecular simulation results, the dimers of MCP are much more stable than its monomers. Therefore, it might explore the dimers as the starting material and synthesize MCP, which will be used *in situ* for the next reaction.

4. Conclusions

Molecular simulations were performed to investigate the chemical reactivity of MCP. It is possible to predict qualitatively the dominant reaction pathways of dimerization and oxidation through the application of quantum chemistry calculations and thermodynamic-energy correlation. Both the dimerization and oxidation reactions are quite exothermic. However, exposure of MCP to air is extremely dangerous due to the relatively high value of the oxidation reaction heat. Theoretical methods provide an understanding of reactive hazards at the molecular level and also guide strategies for safer handling of hazardous materials such as MCP. The results reported here could provide the support to the investigation of the T2 Laboratories explosion on December 19, 2007, in Florida.

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References

- [1] L. Bretherick, Reactive Chemical Hazards: An Overview, Proceedings of the International Symposium on Preventing Major Chemical Accidents, AIChE, New York, 1987.
- [2] Improving Reactive Hazard Management, U.S. Chemical Safety and Hazard Investigation Board Hazard Investigation, Washington, D.C., 2002.
- [3] J.A. Barton, P.F. Nolan, Incidents in the chemical industry due to thermal-runaway chemical reactions, IChemE Symp. Ser. 115 (1989) 3–18.
- [4] S.R. Saraf, W.J. Rogers, M.S. Mannan, Using screening test data to recognize reactive chemical hazards, J. Hazard. Mater. 104 (2003) 255–267.
- [5] CSB Deploys to Fatal Jacksonville, Florida Explosion. Available from: <http://www.csb.gov/index.cfm?folder=news_releases&page=news&NEWS_ID=403>.
- [6] F.J. Wu, B.C. Berris, D.R. Bell, Process for making methylcyclopentadienyl manganese tricarbonyl compounds, U.S. Patent 07/464, (1990) 312.
- [7] F.A. Cotton, H. Chao, C.A. Murillo, Q. Wang, A trimetal chain cocooned by two heptadentate polypyridylamide ligands, Dalton Trans. (2006) 5416–5422.
- [8] J. Johnson, Florida explosion investigation yields preliminary results, Chem. Eng. News 86 (2) (2008) 11.
- [9] S.R. Saraf, W.J. Rogers, M.S. Mannan, M.B. Hall, L.M. Thomson, Theoretical thermochemistry: ab initio heat of formation for hydroxylamine, J. Phys. Chem. A 107 (2003) 1077–1081.
- [10] S.M. Csicsery, Methylcyclopentadiene isomers, J. Org. Chem. 25 (1960) 518–521.
- [11] S.R. Saraf, W.J. Rogers, M.S. Mannan, Classifying reactive chemicals, Chem. Eng. Prog. 100 (2004) 34–37.
- [12] T. Ando, Y. Fujimoto, S. Morisaki, Analysis of differential scanning calorimetric data for reactive chemicals, J. Hazard. Mater. 28 (1991) 251–280.
- [13] E. Ikeda, R.S. Tranter, J.H. Kiefer, R.D. Kern, H.J. Singh, Q. Zhang, The pyrolysis of methylcyclopentadiene, Proc. Combust. Inst. 28 (2000) 1725–1732.
- [14] F. Dubnikova, A. Lifshitz, Ring expansion in methylcyclopentadiene radicals, J. Phys. Chem. A 106 (2002) 8173–8183.
- [15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C. 02, Gaussian, Inc., Wallingford, CT, 2004.
- [16] R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W.L. Hovell, R. Gilliland, GaussView, Version 3.09, Semichem, Inc., Shawnee Mission, KS, 2003.
- [17] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model, J. Am. Chem. Soc. 107 (1985) 3902–3909.
- [18] W.J. Hehre, L. Radom, P.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.
- [19] M.H. Gordon, J.A. Pople, M.J. Frisch, MP2 energy evaluation by direct methods, Chem. Phys. Lett. 153 (1988) 503–506.
- [20] A.D. Becke, Density-functional thermochemistry. 3. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.
- [21] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789.
- [22] W.J. Hehre, R. Ditchfield, J.A. Pople, Self-consistent molecular-orbital methods. 12. Future extensions of Gaussian-type basis sets for use in molecular-orbital studies of organic-molecules, J. Chem. Phys. 56 (1972) 2257–2261.
- [23] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, Self-consistent molecular-orbital methods. 20. Basis set for correlated wave-functions, J. Chem. Phys. 72 (1980) 650–654.
- [24] M.J. Frisch, J.A. Pople, J.S. Binkley, Self-consistent molecular-orbital methods. 25. Supplementary functions for Gaussian-basis sets, J. Chem. Phys. 80 (1984) 3265–3269.
- [25] J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd edition, Gaussian, Inc., Wallingford CT, 1996.
- [26] C. Gonzalez, H.B. Schlegel, Reaction path following in mass-weighted internal coordinates, J. Phys. Chem. 94 (1990) 5523–5527.
- [27] R.B. Woodward, R. Hoffmann, The conservation of orbital symmetry, Angew. Chem. Int. Ed. 8 (1969) 781–853.
- [28] C.W. Spangler, Thermal [1, j] sigmatropic rearrangements, Chem. Rev. 76 (1976) 187–217.
- [29] S.M. Bachrach, Theoretical studies of the [1,5] sigmatropic hydrogen shift in cyclopentadiene, pyrrole, and phosphole, J. Org. Chem. 58 (1993) 5414–5421.
- [30] S. McLean, C.J. Webster, R.J.D. Rutherford, Kinetic isotope effect for the thermally induced migration of hydrogen in cyclopentadienes, Can. J. Chem. 47 (1969) 1555–1559.
- [31] O. Diels, K. Alder, Synthesis in the hydro-aromatic tier, Justus Liebigs Ann. Chem. 460 (1928) 98–122.
- [32] J. Sauer, R. Sustmann, Mechanistic aspects of Diels–Alder reactions: a critical survey, Angew. Chem. Int. Ed. 19 (1980) 779–807.
- [33] R.B. Woodward, T.J. Katz, The mechanism of the Diels–Alder reactions, Tetrahedron 5 (1959) 70–89.

- [34] J.J. Gajewski, K.B. Peterson, J.R. Kagel, Transition-state structure variation in the Diels–Alder reaction from secondary deuterium kinetic isotope effects: the reaction of a nearly symmetrical diene and dienophile is nearly synchronous, *J. Am. Chem. Soc.* 109 (1987) 5545–5546.
- [35] J.W. McIver Jr., Structure of transition states, are they symmetric, *Acc. Chem. Res.* 7 (1974) 72–77.
- [36] R.D.J. Froese, M.G. Organ, J.D. Goddard, T.D.P. Stack, B.M. Trost, Theoretical and experimental studies of the Diels–Alder dimerizations of substituted cyclopentadienes, *J. Am. Chem. Soc.* 117 (1995) 10931–10938.
- [37] R.I. Masel, *Chemical Kinetics and Catalysis*, John Wiley & Sons, Inc., New York, 2001.
- [38] M.A. Diez, M.D. Guillen, C.G. Blanco, J. Bermejo, Chromatographic study of methylcyclopentadiene dimers and iso-dimers and determination of their boiling points, *J. Chromatogr.* 508 (1990) 363–374.
- [39] E.A. Lissi, M. Encinas, E. Lemp, M.A. Rubio, Singlet oxygen O₂ bimolecular processes. Solvent and compartmentalization effects, *Chem. Rev.* 93 (1993) 699–723.
- [40] K. Gollnick, A. Griesbeck, [4 + 2]-Cycloaddition of singlet oxygen to conjugated acyclic hexadienes-evidence of singlet oxygen induced cis-reversible trans-isomerization, *Tetrahedron Lett.* 24 (1983) 3303–3306.
- [41] T.K. Panda, M.T. Gamer, P.W. Roesky, An improved synthesis of sodium and potassium cyclopentadienide, *Organometallics* 22 (2003) 877–878.