Group Contribution Method 를 이용한 MEKPO 분해반응의 위험성예측

김용하, 유미정, 한의진, 김구회*, 윤인섭
서울대학교 응용화학부, 서울대학교 화학공정신기술연구소*

Hazard Prediction of MEKPO Decomposition Reaction Using Group Contribution Method

Yong Ha Kim, Mi Jung Ryu, Euijin Han, Ku Hwoi Kim, En Sup Yoon
School of Chemical Engineering, Seoul National University
Institute of Chemical Processes, Seoul National University*

Introduction

With the view to the risk analysis and safety management of these kinds of materials, it is important to predict thermal hazards of new materials. Methyl ethyl ketone peroxide (MEKPO), one of the hazardous peroxide compounds, has been being the causal material of many tremendous accidents in the chemical process industries. Adiabatic temperature rise (ΔT_{ad}) can be a good index of thermal hazards since it represents potential of violent decomposition process. Thermodynamic properties that are indispensable to obtain ΔT_{ad}, are conventionally obtained from experiments [1]. But these experiments can be hazardous as well as it requires many times and costs. Computer aided prediction using group contribution method, therefore, can be a good alternative. It can be readily applied to materials of which properties are unknown.

In this study, computer aided group contribution method was used to obtain values of the enthalpy and Gibbs free energy of MEKPO decomposition processes. Feasibilities of each decomposition reaction set were studied, and then ΔT_{ad} for feasible decomposition processes was obtained with $\Delta_r H$ and C_p from group contribution method.

Computer Aided Assessment with Group Contribution Method

Group contribution method has accuracy, simpleness and wide-distribution at a time. The property of a chemical is a function of structurally dependent parameters, which are determined by summing the number frequency of each functional group occurring in the molecule times its contributions [2, 3]. Group contribution method by Joback can divide the functional group more easily than other group contribution methods and express a lot of materials. Groups of distinctions are consisted of non-ring, ring, halogen, oxygen, nitrogen and sulfur groups. In these properties standard state enthalpy of formation, standard state Gibbs energy and polynomial coefficients for standard heat capacity are necessary. Equations of the three properties are as follows;

$$\Delta H_f^\circ = 68.29 + \sum_k N_k(\Delta HF_k) \tag{1}$$

$$\Delta G_f^\circ = 53.88 + \sum_k N_k(\Delta GF_k) \tag{2}$$

$$C_p^\circ = \left[\sum_k N_k(C_{pAk}) - 37.93\right] + \left[\sum_k N_k(C_{pBk}) + 0.21\right]T + \left[\sum_k N_k(C_{pCk}) - 3.91E(-4)\right]T^2 + \left[\sum_k N_k(C_{pDk}) - 2.06E(-7)\right]T^3 \tag{3}$$

where N_k is the number of groups of type k in the molecule, F_k is the contribution for the group labeled k to the specified property, f, and T is the temperature in Kelvins.

Methyl Ethyl Ketone (MEKPO)

Methyl ethyl ketone peroxide (MEKPO) is the typical sort of highly reactive chemical. It is used as a catalyst for the room temperature curing of unsaturated polyester resins and an initiator for polymerization reactions. MEKPO is manufactured in the oxidation process of methyl ethyl ketone (MEK) with hydrogen peroxide (H_2O_2) [4].

Procedure of MEKPO process has three steps. The first step is an oxidation process of MEK. The second step is a decomposition reaction of hydrogen peroxide (H_2O_2). And the third step is decomposition of MEKPO.

The first step is only a desired reaction, but the second and third are undesired side reactions. Decomposition reactions of H_2O_2 and MEKPO are sensitively affected by temperature. The major decomposition products from MEKPO are carbon dioxide (CO_2), water (H_2O), acetic acid($C_2H_4O_2$), formic acid(CH_2O_2) and MEK (C_4H_8O). The reactant (H_2O_2) and product (MEKPO) are so sensitive that they can explode with thermal decomposition at a rise of temperature. The thermal decomposition of MEKPO proceeds from runaway reaction under circumstances which competent temperature controls are absented. The reactant (H_2O_2) and product (MEKPO) are decomposed subsequently.

In general, MEKPO exists as a mixture of seven different types as followings: 10 wt% $C_4H_{10}O_4$, 45 wt% $C_8H_{18}O_6$, 12 wt% $C_{12}H_{26}O_8$, 5 wt% $C_{16}H_{34}O_{10}$, 2 wt% $C_{20}H_{42}O_{12}$, 1 wt% $C_{24}H_{50}O_{14}$ and 25 wt% $C_{12}H_{24}O_6$(cyclic trimer) [5]. Due to the complex structure, some of them have higher potential of reactive hazard and thermal sensitivity. And various types of them can lead to parallel decomposition reaction.

Case Study

In order to assess the risk of the runaway reaction in the MEKPO Process, the adiabatic temperature rise by following has to be calculated [1];

$$\Delta T_{ad} = \frac{\Delta H_r}{mC_p} \tag{4}$$

where ΔH_r is heat of reaction, m is reactant substance mass, and C_p is specific heat of reaction mixture. The ΔH_r and C_p can be calculated from the enthalpy of formation, ΔH_f for each component. But the thermodynamic properties of MEKPO were unknown, so group contribution method was used. And then the 3 steps reaction mechanisms for the MEKPO process are presented and ΔH_r, ΔG_r and Cp of the mixtures for each reaction are evaluated. The 3 steps are oxidation of MEK, decomposition of hydrogen peroxide (H_2O_2) and decomposition of the MEKPO. As a result, the adiabatic temperature rise was predicted and compared with the reference data [4].

Results

The feasible reaction pathways of MEKPO decomposition process were obtained. At first, all the possible reaction mechanisms are obtained considering that possible products from MEKPO decomposition process are carbon dioxide (CO_2), water (H_2O), acetic acid ($C_2H_4O_2$), formic acid (CH_2O_2) and MEK (C_4H_8O) for each formulas of MEKPO. Secondly, Gibbs free energies of each reaction mechanism are evaluated to ascertain feasibilities of each reaction. The followings are most feasible mechanisms for each formula of MEKPO, and each values of heat of reaction and adiabatic temperature rise are shown in Table 1 and the result of study is shown in Table 2.

$$C_4H_{10}O_4 \rightarrow \frac{8}{5}H_2O + \frac{3}{5}CO_2 + \frac{1}{5}CH_2O_2 + \frac{4}{5}C_4H_8O \tag{5}$$

$$C_8H_{18}O_6 \rightarrow H_2O + 2C_2H_4O_2 + C_4H_8O \tag{6}$$

$$C_{12}H_{26}O_8 \rightarrow H_2O + \frac{8}{3}C_2H_4O_2 + \frac{5}{3}C_4H_8O \tag{7}$$

$$C_{16}H_{34}O_{10} \rightarrow 2H_2O + CO_2 + \frac{3}{2}C_2H_4O_2 + 3C_4H_8O \tag{8}$$

$$C_{20}H_{42}O_{12} \rightarrow H_2O + 4C_2H_4O_2 + 3C_4H_8O \tag{9}$$

$$C_{24}H_{50}O_{14} \rightarrow 3H_2O + 2CO_2 + C_2H_4O_2 + 5C_4H_8O \tag{10}$$

$$C_{12}H_{24}O_6 \rightarrow 2C_2H_4O_2 + 2C_4H_8O \tag{11}$$

Conclusion

Conclusively, it was proved that essential thermodynamic properties are obtained easily and they are reliable, so potentially more hazardous decomposition pathways could be distinguished by the feasibility of process and ΔT_{ad} from this study.

Acknowledgement

Brain Korea 21 Project of Ministry of Education & Human Resource Development has been

supporting this study.

References

1. Mannan, M. S., W. J. Rogers and A. Aldeeb, "A Systematic Approach to Reactive Chemicals Analysis", *Proc. HAZARDS XVI*, Manchester, U.K., 41-58 (2001).

2. Joback, K. G., *A Unified Approach to Physical Property Estimation Using Multivariate Statistical Techniques*, S.M. Thesis, MIT, Cambridge, 1984.

3. Poling, B. E., J. M. Prausnitz, J. P. O'Connell, *The Properties of Gases and Liquids*, 5^{th} *ed.,* McGraw-Hill Co., New York, 2001.

4. Liaw, H. J., C. C. Yur, Y. F. Lin, "A mathematical model for predicting thermal hazard data", *Journal of Loss Prevention in the Process Industries*, **13**, 499-507 (2000).

5. Milas, N. A., A. Golubovic, "Studies in Organic Peroxides. XXV. Preparation, Separation and Identification of Peroxides Derived from Methyl Ethyl Ketone and Hydrogen Peroxide", *Journal of the American Chemical Society*, **81**, 5824-26 (1959).

Table 1. Heat of Reaction and Adiabatic Temperature Rise for Feasible Reactions in Step 3.

Number of Equation	ΔH_r [kJ/gmol]	ΔT_{ad} [K]
(5)	-256.66	2153
(6)	-335.25	1791
(7)	-428.57	1819
(8)	-562.84	2114
(9)	-615.20	1919
(10)	-790.43	2344
(11)	-305.07	1365

Table 2. Heat of Reaction and Adiabatic Temperature Rise

Hydrogen Peroxide	Thermal Inertia	ΔH_r [kJ/gmol]		ΔT_{ad} [K]	
		Data from this study	Reference data	Data from this study	Reference data
100% MEKPO	Φ = 1.0	-333.91	NA	1972.0	NA
50% MEKPO	Φ = 1.0	-166.96	NA	986.0	NA
	Φ = 4.2	-39.75	NA	235.0	219.1
25% MEKPO	Φ = 1.0	-83.48	NA	493.0	NA
	Φ = 2.9	-28.78	NA	170.0	187.9

(NA: Not Available)