Thermal hazard assessment of TMCH mixed with inorganic acids

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Abstract. 1,1-Bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (TMCH) is a typical peroxide with two peroxy groups that may runaway and/or explode due to mixing with inorganic acids, such as HCl, HNO₃, H₂SO₄, or H₃PO₄. In this study, reactivities of TMCH mixed with the above inorganic acids were assessed by differential scanning calorimetry (DSC). Furthermore, data obtained by DSC, such as exothermic onset temperature (T_0), maximum temperature (T_{max}), and heat of decomposition (ΔH_d) could be employed to acquire thermal safety parameters. Moreover, thermal activity monitor III (TAM III) was employed to investigate the thermal hazards while storing or transporting TMCH and TMCH mixed with four types of commonly used inorganic acids, here as HCl, HNO₃, H₂SO₄, or H₃PO₄ under isothermal conditions. Mixing TMCH with those inorganic acids resulted in higher ΔH_d except H₃PO₄, and mixing TMCH with HCl clearly decreased T_0 . Therefore, the phenomena of mixing those incompatible materials with TMCH can be concluded as the worst cases in terms of contamination hazards during storage and transportation of TMCH.

1 Introduction

Most organic peroxides (OPs) can decompose readily even with inadvertent physical impact, while mixing with incompatible materials or being under extreme conditions, such as external fire and the high temperature environment. Furthermore, they will inevitably release a large amount of energies resulting in fire, explosion, or chemical release accidents [1–3]. The peroxy functional group (–O–O–) in OPs' structure, which is intrinsically unstable and thermally reactive, and it readily causes thermal runaway accidents because the peroxy functional group will break while reacting with incompatible materials, for example, acids, bases, metals, and ions. In view of process safety, as well as environment protection, some liquid organic peroxides are intrigue while handling. For instance, it is hardly predict to 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (TMCH), a highly sensitive, exothermic, and unstable material. Accordingly, it must conserve well and proactively design safety protocol during preparation, manufacturing, application, transportation, and storage [4–8]. In addition, TMCH is used in the manufacturing process of styrene or polyethylene and is treated as an initiator of polymerization or cross-linking agent. Furthermore, TMCH can be employed as an activator in the process industries. Consequently, TMCH must be well mastered and stored with caution in order to eliminate any potential thermal hazard which caused by mixing TMCH with other incompatible

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materials during the whole gamut of its process span [9–13]. Historically, there have been incidents related to organic waste solvents that have caused thermal hazard accidents, because the mixtures of organic waste solvent may have further induced a decomposition reaction due to improper disposal and inferior safety management. Decomposition hazards can be coped with through adequate process safety. Process safety not only protects the property from accidents, but also reduces environmental impact because of runaway reaction. OPs will decompose and may contribute to process hazards, thermal runaways, and environmental impacts.

The aim of this study was to appraise the environmental concerns with thermal hazard of TMCH and the thermal decomposition reaction of TMCH mixing with various incompatible substances, such as hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), or phosphoric acid (H₃PO₄). The thermal stability parameters including apparent onset temperature (T_0), heat of decomposition (ΔH_d), and maximum temperature ($T_{\max}$) were reckoned by differential scanning calorimetry (DSC). Furthermore, we used the thermal activity monitor III (TAM III) to calculate time to maximum rate under isothermal conditions (TMR_{iso}), highest or peak heat flow, and reaction time. The apparent activation energy (E_a) for TMCH under different isothermal temperatures (60.0, 70.0, 80.0, and 90.0 °C) were tested by TAM III. Therefore, we can establish inherently safer designs in the storage and transport of TMCH to avoid jeopardizing the system under thermal upsets.

2 Experiments and methods

2.1 Samples

To assess reaction and determine the related parameters of TMCH with four inorganic acids (HCl, HNO₃, H₂SO₄, H₃PO₄), 88.0 mass% of TMCH was procured from the ACE Chemical Corp. in Taoyuan, Taiwan and then stored in a refrigerator at 4.0 °C. Mixing TMCH with the four types of commonly used inorganic acids, HCl, HNO₃, H₂SO₄, and H₃PO₄, whose concentrations of HCl, HNO₃, H₂SO₄, and H₃PO₄ were 37.0, 69.0, 95.0, and 85.0 mass%, respectively. HCl and H₂SO₄ were purchased from the Merck Display Technologies Ltd. in USA and HNO₃ and H₃PO₄ were purchased from the Panreac in USA.

2.2 Differential scanning calorimetry (DSC)

Temperature-programmed screening experiments were performed on a Mettler TA8000 system coupled with a DSC 821° measuring cell [14]. The DSC results show the profiles of heat flow versus temperature that the reference sample and the target sample are heated at the same time. The temperature between the reference sample and the target sample are different because the target sample releases energy during thermal decomposition and it, in turn, resulted in heat generation in the cell. Therefore, the temperature in reference sample's cell and target sample's cell did not sustain equally after heating test. The system of programmable temperature control applied in DSC, which is used to acquire the various heating and cooling rates from 0.01 to 100.0 °C and measure the range of temperature of target sample from −150.0 to 700.0 °C. For a better equilibrium, the heating rate in this study was set at 4.0 °C min^{−1}, and the rising range of temperature was chosen from 30 to 300.0 °C.

2.3 Thermal activity monitor III (TAM III)

Isothermal calorimetry, TAM III, is a delicate thermal sensitivity and elaborate stability detecting equipment. It is easy to operate and only requires few sample quantity during detecting process. Accordingly, TAM III is broadly applied in many areas, such as material science, pharmaceutical science, chemistry, physical chemistry, and life science [15–17]. The liquid in TAM III's thermostat was mineral oil, which is in a reactor with a total volume of 22 liter (L), and the maximum heating rate of TAM III was ±2.0 K h^{−1} for usage of chemical and physical equilibrium. Moreover, the

temperatures were set at 15.0–150.0 °C, and the decomposition of sample was, in turn, detected by TAM III under isothermal conditions. The software of TAM III was furthermore employed to control the thermostat and compute some thermokinetic parameters [18, 19]. The aim of this study was to use TAM III to determine the thermal decomposition reactions of 88.0 mass% TMCH and 88.0 mass% TMCH individually mixed with 6.0 N HCl, 6.0 N HNO₃, 6.0 N H₂SO₄, or 6.0 N H₃PO₄. Here, the amount of the sample in a cell was 100.0 mg TMCH mixing with 10.0 mg HCl, HNO₃, H₂SO₄, or H₃PO₄ at 60.0, 70.0, 80.0, and 90.0 °C.

3 Results and discussion

3.1 Thermal analysis by DSC

The DSC test results were detected by DSC 821° with thermal spectrum analysis including heating and temperature conditions, showing heat release or heat decomposition, starting temperature, or the dynamics calculations. Figure 1 shows the thermal curve of TMCH with or without inorganic acids, and it is one exothermic peak while TMCH decomposing.

Figure 1. DSC thermal curves of heat flow versus temperature for TMCH mixing with HCl, HNO₃, H₂SO₄, and H₃PO₄ decomposition at scanning rate of 4.0 °C min⁻¹.

Table 1. Calorimetric data from the dynamic scanning experiments of TMCH 88.0 mass% and TMCH 88.0 mass% mixed with 6.0 N HCl, HNO₃, H₂SO₄, and H₃PO₄ by DSC.

Samples	Mass/mg	T ₀ /°C	T _{max} /°C	ΔH _d /kJ mol ⁻¹	Total heat of reaction/W g ⁻¹
88.0 mass% TMCH	2.9	120.2	146.6	1112.8	3227.1
88.0 mass% TMCH+ HCl (6.0 N, 1.0 mg)	3.1	52.7	64.3	1646.3	5103.6
88.0 mass% TMCH+HNO ₃ (6.0 N, 1.0 mg)	3.1	115.7	118.4	1720.4	6895.8
88.0 mass% TMCH+H ₂ SO ₄ (6.0 N, 1.0 mg)	2.8	119.0	120.8	1783.1	4992.7
88.0 mass% TMCH+H ₃ PO ₄ (6.0 N, 1.1 mg)	2.9	123.4	146.6	1398.9	4056.9

The results of TMCH with inorganic acids which were used as the contaminants are displayed in Table 1. It caused the T_0 emerged earlier while TMCH mixing with HCl, especially, and not only the T_0 occurred earlier but also it formed a fierce thermal reaction and then causing high temperature when TMCH was mixed with H_2SO_4 . In addition, it revealed that the similar reaction phenomenon between TMCH and TMCH mixed with H_3PO_4 , such as the similar T_0 , but the ΔH_d of TMCH mixed with H_3PO_4 increased significantly. The T_0 was induced to occur earlier as HNO_3 was mixed with TMCH, and it formed a relatively high heat of reaction after the mini-exothermic reaction of the first peak. In conclusion, all of the inorganic acids could alter the original decomposition reaction of TMCH while TMCH is mixing with the inorganic acids.

3.2 Isothermal analysis by TAM III

TAM III was used to evaluate the decomposition reaction of TMCH and the reaction of TMCH mixing with various inorganic acids. Figures 2 to 6 delineate the decomposition of pure TMCH and TMCH mixed with incompatible substances under different isothermal temperatures by TAM III. Figure 2 shows the decomposition of 88.0 mass% TMCH at various temperatures, in which the heat flow was low and not visible when the temperature was at 60.0 °C, whereas the heat flow was high and substantial at 90.0 °C

Table 2. Scanning data of the thermal runaway decomposition at 60.0 °C by TAM III.

Samples	Mass/mg	TMR_{iso}/h	Highest heat flow/ $W\ g^{-1}$
88.0 mass% TMCH	100.1	94.71252	0.00029
88.0 mass% TMCH+ HCl (6.0 N, 10.2 mg)	99.5	1.27623	0.23796
88.0 mass% TMCH+HNO ₃ (6.0 N, 11.8 mg)	100.6	0.41744	0.11802
88.0 mass% TMCH+H ₂ SO ₄ (6.0 N, 10.6 mg)	100.6	18.93276	0.24074
88.0 mass% TMCH+H ₃ PO ₄ (6.0 N, 12.0 mg)	100.2	93.37667	0.00038

Figure 2. TAM III thermal curves of heat flow versus time for 88.0 mass% TMCH decomposition at 60.0, 70.0, 80.0, and 90.0 °C.

When TMCH mixed with 6.0 N HCl, the heat flow was prominent at 60.0 °C, and they were similar at decomposition at 80.0 or 90.0 °C as shown in Fig. 3. We found that there are two exothermic peaks when TMCH mixed with 6.0 N HNO_3 . In addition, Fig. 4 illustrates that the energy generated from first exothermic peak, which forced the second exothermic reaction to appear earlier. Furthermore, the first exothermic peak almost occurred at the same time around 60.0–90.0 °C, but the most high second exothermic peak was at 90.0 °C. Therefore, TMCH mixed

with HNO_3 not only resulted in two exothermic peaks, but also released enormous amount of heats, which may lead to serious thermal hazard. The heat flow was higher at $90.0\text{ }^\circ\text{C}$ when TMCH mixed with 6.0 N HNO_3 , $6.0\text{ N H}_2\text{SO}_4$, or $6.0\text{ N H}_3\text{PO}_4$ as revealed in Figs. 3, 4, 5, and 6. The heat flow of TMCH mixed with H_2SO_4 was higher than TMCH mixed with other inorganic acids. In Fig. 6, there are also two exothermic peaks when TMCH mixed with H_3PO_4 at 80.0 and $90.0\text{ }^\circ\text{C}$. The exothermic peak was similar, but ΔH_d was higher at $90.0\text{ }^\circ\text{C}$ than at $80.0\text{ }^\circ\text{C}$. TMCH mixed with H_3PO_4 could increase the probability of the second thermal hazard to be happened. The thermal stability parameters, such as TMR_{iso} and the maximum heat flow, can be calculated by TAM III. TMR_{iso} is employed to assess the emergency response, and we therefore applied TMR_{iso} in prevention of thermal runaway reactions.

Figure 3. TAM III thermal curves of heat flow versus time for TMCH mixing with 6.0 N HCl decomposition at 60.0 , 70.0 , 80.0 , and $90.0\text{ }^\circ\text{C}$.

Figure 4. TAM III thermal curves of heat flow versus time for TMCH mixing with 6.0 N HNO_3 decomposition at 60.0 , 70.0 , 80.0 , and $90.0\text{ }^\circ\text{C}$.

Figure 5. TAM III thermal curves of heat flow versus time for TMCH mixing with 6.0 N H₂SO₄ decomposition at 60.0, 70.0, 80.0, and 90.0 °C.

Figure 6. TAM III thermal curves of heat flow versus time for TMCH mixing with 6.0 N H₃PO₄ decomposition at 60.0, 70.0, 80.0, and 90.0 °C.

In Tables 2 to 5, the results presented that the TMR_{iso} of TMCH was 94.71252, 28.49707, 3.53645, and 0.58584 h and the TMR_{iso} of TMCH mixing with HCl, at 60.0, 70.0, 80.0, and 90.0 °C were reduced to 1.27623, 0.42682, 0.43239, and 0.46303 h, correspondingly. The results indicated that the TMR_{iso} of TMCH mixing with HNO₃ was 0.41744, 0.42490, 0.50855, 0.46303 h and the TMR_{iso} of TMCH mixing with H₂SO₄ at 60.0–90.0 °C were reduced to 18.93276, 6.60274, 2.66964, 1.23899 h, respectively.

Table 3. Scanning data of the thermal runaway decomposition at 70.0 °C by TAM III.

Samples	Mass/mg	TMR_{iso}/h	Highest heat flow/W g ⁻¹
88.0 mass% TMCH	100.3	28.49707	0.00163
88.0 mass% TMCH+ HCl (6.0 N, 9.5 mg)	99.1	0.42682	0.09202
88.0 mass% TMCH+HNO ₃ (6.0 N, 10.9 mg)	99.7	0.42490	0.08624
88.0 mass% TMCH+H ₂ SO ₄ (6.0 N, 9.5 mg)	100.2	6.60274	0.26238
88.0 mass% TMCH+ H ₃ PO ₄ (6.0 N, 9.0 mg)	99.3	24.29267	0.00174

Table 4. Scanning data of the thermal runaway decomposition at 80.0 °C by TAM III.

Samples	Mass/mg	TMR_{iso}/h	Highest heat flow/W g ⁻¹
88.0 mass% TMCH	101.0	3.53645	0.00557
88.0 mass% TMCH+ HCl (6.0 N, 9.7 mg)	101.2	0.43239	0.12052
88.0 mass% TMCH+HNO ₃ (6.0 N, 10.0 mg)	100.1	0.50855	0.10800
88.0 mass% TMCH+H ₂ SO ₄ (6.0 N, 11.8 mg)	100.2	2.66964	0.21654
88.0 mass% TMCH+ H ₃ PO ₄ (6.0 N, 11.5 mg)	100.6	4.30909	0.00588

Furthermore, the TMR_{iso} of TMCH mixing with H₃PO₄ at 60.0, 70.0, 80.0, and 90.0 °C were reduced to 93.37667, 24.29267, 4.30909, and 1.32272 h. In contrast, as TMCH was mixed with H₂SO₄, whose TMR_{iso} was not visible at 80.0 and 90.0 °C. However, the TMR_{iso} of TMCH was smaller when mixed with HCl, HNO₃, and H₃PO₄. Moreover, the maximum heat flow of TMCH mixed with above inorganic acids was also increased significantly. However, the TMR_{iso} of TMCH mixing with H₃PO₄ was increased due to decomposition mechanisms. The higher maximum heat flow and temperature could cause prominent runaway excursions, and HCl, HNO₃, and H₂SO₄ could be classified as incompatible substance because TMCH mixed with those inorganic acids may result in the diminished TMR_{iso} .

Table 5. Scanning data of the thermal runaway decomposition at 90.0 °C by TAM III.

Samples	Mass/mg	TMR_{iso}/h	Highest heat flow/W g ⁻¹
88.0 mass% TMCH	100.0	0.58584	0.02551
88.0 mass% TMCH+ HCl (6.0 N, 10.1 mg)	99.0	0.46303	0.09479
88.0 mass% TMCH+HNO ₃ (6.0 N, 11.7 mg)	99.6	0.46303	0.14684
88.0 mass% TMCH+H ₂ SO ₄ (6.0 N, 11.5 mg)	99.4	1.23899	0.25069
88.0 mass% TMCH+H ₃ PO ₄ (6.0 N, 11.6 mg)	99.3	1.32272	0.02104

Table 6 lists the estimated results of apparent activation energy of TMCH mixed with H₃PO₄ by using Arrhenius equation, as shown in Eq. (1):

$$k_i(T) = Aexp\left(-\frac{E_a}{RT}\right)$$

(1)

where A , E_a , and R represent the frequency factor, the apparent activation energy of the stage, and the gas constant, individually. The E_a of pure TMCH and TMCH mixed with H₃PO₄ was 147.37 and 133.34 kJ mol⁻¹, respectively. When TMCH was mixed H₃PO₄, its E_a is lower than pure TMCH, indicating that the reaction could occur easily.

Table 6. Comparison of TMCH and TMCH+6.0 N H₃PO₄ of apparent activation energy analysis graph for Arrhenius plot with different isothermal temperatures at 60.0, 70.0, 80.0, and 90.0 °C.

Samples	$E_a/kJ\ mol^{-1}$	A/s^{-1}	R^2
88 mass% TMCH	147.37	3.99436E+19	0.99569
88 mass% TMCH+ H ₃ PO ₄	133.34	3.26106E+17	0.99855

Figure 7. TMCH of activation energy analysis graph for Arrhenius plot with different isothermal temperatures at 60.0, 70.0, 80.0, and 90.0 °C.

Figure 8. TMCH mixing with 6.0 N H₃PO₄ of apparent activation energy analysis graph for Arrhenius plot with different isothermal temperatures at 60.0, 70.0, 80.0, and 90.0 °C.

4 Conclusion

In view of environment protection, the calorimetric technique is very important in chemical industry for assessing the thermal hazard influence during the whole gamut of the manufacturing process. The inherent thermal hazard characteristics of TMCH and TMCH mixed with HCl, HNO₃, H₂SO₄ or H₃PO₄, were completely described in the results and discussion which depicted the thermal stability parameters of TMCH and TMCH with inorganic acids. It significantly changed not only the original reaction but also the TMR_{iso} of TMCH while TMCH was mixed with HCl, HNO₃, H₂SO₄, or H₃PO₄. When TMCH mixed with HCl, it may generate high heat flow and has second potential hazard

because it formed two prominent peaks during decomposition reaction. Therefore, those related process safety parameters were assessed by DSC and TAM III that could apply in the prevention of runaway reaction of TMCH. The incompatible behavior of the TMCH incompatible hazards should be considered carefully in industrial processes and the environment. Therefore, thermal decomposition analysis plays a vital role in environmental engineering. Furthermore, we can employ chromatography instruments, such as gas chromatography/mass spectrometer (GC/MS), thermogravimetry/GC–mass spectrometer (TG/GC/MS) coupled with Fourier transform infrared (FT/IR) spectrometer to determine the decomposition pathway of TMCH as well as mixing with incompatibles, here HCl, HNO₃, H₂SO₄, or H₃PO₄.

References

1. Y.L. Chen, Y.P. Chou, H.Y. Hou and C.M. Shu, J. Therm. Anal. Calorim., **95**, 535-539 (2009)
2. S.H. Wu, Y.W. Wang, T.C. Wu, W.N. Hu and C.M. Shu, J. Therm. Anal. Calorim., **93**, 189-194 (2008)
3. K.Y. Chen, S.H. Wu, Y.W. Wang and C.M. Shu, J. Loss Prev. Process Ind., **21**, 101-109 (2008)
4. S.H. Liu, C.P. Lin and C.M. Shu, J. Therm. Anal. Calorim., **106**, 165-172 (2011)
5. J.R. Chen, S.H. Wu, S.Y. Lin, H.Y. Hou and C.M. Shu, J. Therm. Anal. Calorim., **93**, 127-133 (2008)
6. L.K. Wu, K.Y. Chen, S.Y. Cheng, B.S. Lee and C.M. Shu, J. Therm. Anal. Calorim., **93**, 115-120 (2008)
7. H.Y. Hou, Y.S. Duh, W.H. Lin and C.M. Shu, J. Therm. Anal. Calorim., **85**, 145-150 (2006)
8. Y.S. Duh, X.H. Wu and C.S. Kao, Process Saf. Prog., **27**, 89-99 (2008)
9. A.C. Li, Y.T. Tsai, S.H. Wu, C.W. Chiu, S.J. Shen, R.H. Chang and C.M. Shu, J. Therm. Anal. Calorim., **113**, 1611-1618 (2013)
10. Y.W. Wang, C.M. Shu, Y.S. Duh and C.S. Kao, Ind. Eng. Chem. Res., **40**, 1125-1132 (2001)
11. S.H. Liu, H.Y. Hou and C.M. Shu, Thermochemica Acta, **556**, 226-232 (2013)
12. Y.T. Tsai, M.L. You, X.M. Qian and C.M. Shu, Industrial & Engineering Chemistry Research, **52**, 8206-8215 (2013)
13. C.Y. Jhu, Y.W. Wang, C.Y. Wen and C.M. Shu, Applied Energy, **100**, 127-131 (2012)
14. M. Toledo, Stare Software with Solaris Operating System, Operating Instructions, Switzerland (2004)
15. S.Y. Lin, J.M. Tseng, Y.F. Lin, W.T. Huang and C.M. Shu, Journal of Thermal Analysis Calorimetry, **93**, 257-267 (2008)
16. W.T. Chen, C.C. Ma, M.H. Lee, Y.C. Chu, L.C. Tsai and C.M. Shu, Appl. Energy, **100**, 187-192 (2012)
17. H.X. Chen and N.A. Liu, J. Therm. Anal. Calorim., **90**, 449-452 (2007)
18. J.M. Tseng, M.Y. Liu, S.L. Chen, W.T. Hwang, J.P. Gupta and C.M. Shu, J. Therm. Anal. Calorim., **96**, 789-793 (2009)
19. Y.C. Chu, F.C. Tsai, F.R. Lin, T.C. Chiang and C.M. Shu, Energy Education Science and Technology Part A, **30**, 977-982 (2013)