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Hazard evaluation of self-decomposition materials by the combination of pressure and heat flux measurements☆

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Abstract

Thermal decomposition of unstable chemicals is always accompanied by heat release and gas generation. To ascertain such relationship, a heat flux calorimeter C80D fitted with a pressure-sensitive transducer provided simultaneous knowledge about pressure and heat flux behavior of a reactive agent. Consequently, $(\mathrm{d}P/\mathrm{d}t)_{\max}$ was a parameter to reflect the characteristics of gas production potential during decomposition with the rate of reaction, which can be determined by thermal data, and was considered as a criterion to evaluate the hazardous characteristics for unstable substance. The results were compared with those in the UN standard PVT tests and the modified closed pressure vessel test (MCPVT), which have intense outer heating. It indicates that the decomposition measured in the C80D represents the inherent factor of materials and rate of reaction is the dominant factor to contribute to the intensity of the decomposition in other PVTs.

Keywords: Pressure; Heat flux; Unstable substances; Hazardous evaluation

1. Introduction

There currently exist a number of empirical hazards screening tests having the objectives of providing a relative ranking or classification of organic peroxides and self-reactive materials, such as the United Nations standard pressure vessel tests [1] (the Koenen test, the Dutch PVT, the USA PVT) and a modified closed pressure vessel test (MCPVT) [2,3]. However, the nature characteristic of thermal decomposition of self-decomposition materials, although fundamental to evaluate the practical behavior in a certain type of pressure vessel test, is still not widely recognized because of the sensitivity of the test method and the test condition that an apparatus can perform. The use of a Setaram C80D heat flux calorimeter with a very low scanning rate provides an easy approach to identify and determine the intrinsic characteristics of an unstable substance associated with the exothermic decomposition in a closed vessel. This technique allowed for simultaneous measurement of the pressure and the heat flux behavior of a reactive agent, and provided sufficient knowledge on accurate exothermic onset temperature, rate of heat release, heat of reaction, pressure and rate of pressure increase. In addition, a glass cup was inserted into the stainless steel vessel to avoid the possible catalysis effect from the material of the container.

Fourteen organic peroxides and self-reactive materials were measured and the results were compared with the data of the Koenen test, the Dutch PVT, the USA PVT and the MCPVT. The intrinsic evaluation in C80D could help to thoroughly understand the thermal decomposition mechanism and intensity related to thermal data and gas evolution. $(\mathrm{d}P/\mathrm{d}t)_{\max}$ was reviewed as a criteria to determine the hazardous characteristics of unstable substances.

2. Experimental

2.1. C80D

Shown in Fig. 1, two vessels holding sample and reference were surrounded by a calorimetric block, which acted as a heat sink and temperature controller. The pressure-sensitive

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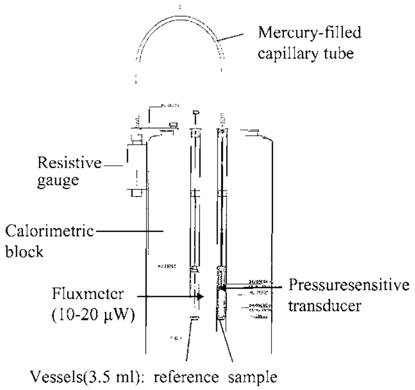

Fig. 1. C80D.

transducer was fitted on the top of the sample vessel and was connected to a pressure gauge using resistive gauge by a mercury-filled capillary tube, leaving the reference vessel to be closed with a threaded plug. The heat flow was detected by a fluxmeter with a sensitivity of 10–20 μW. The temperature range was between room temperature and 300 °C and the maximum pressure was 35 MPa. In the test, the weights of the sample and alumina as the reference were both 500 mg. The scanning rate was 0.1 K/min. The stainless steel vessel of 3.5 ml was normally used and in comparison an inner glass cup of 1 mm in thickness was inserted to investigate the interferences from metal or inert glass wall on the decomposition of the samples. The samples in the experiments were listed in Table 1.

2.2. *Modified closed pressure vessel test (MCPVT)*

In a similar type of the closed pressure vessel of 6 ml, the MCPVT was also carried out under a higher heating rate of 10 K/min and sample weight of 1 g. The details of this test were described in previous works [4,5]. The results were compared with those in the C80D and in the UN standard PVT tests [1].

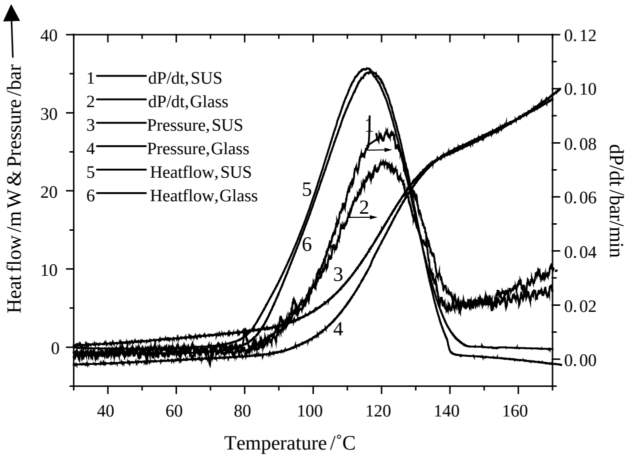

Fig. 2. Heat flow, pressure and d*P*/d*t* for materials of low decomposition rate (the case of BPB) (*TBP, DBTO, and TBHP have the similar curves; **SUS means tests conducted in stainless steel vessel and Glass means tests in glass vessel, ***the direction of the arrow is exothermic, the same as below).

3. Results and discussion

3.1. *Pressure and heat flux*

Figs. 2–9 show the curves of heat flow, pressure and pressure increase rates (d*P*/d*t*) versus temperature of the samples in both stainless steel (SUS) and glass vessel under 0.1 K/min in the C80D apparatus. Under such a slow scanning rate, the C80D could provide a very mild environmental heating condition, in which the outer intense heating rarely affected the decomposition of the sample. All heat generations were not used for self-heating, but dissipated into the large heat sink. Therefore, this was the unique advantage to evaluate the intrinsic thermal hazard conceptually.

For organic peroxides and other relevant materials as a class of similar unstable compounds, this technique indicates that the rates of heat and pressure releases always

Table 1
Samples used in the experiments

Code	Sample	Purity (wt.%)	Active oxygen (%)	State
TBPA	*t*-Butyl peroxy acetate	50.3	6.06	Liquid
CHP	Cumen hydroperoxide	83.2	8.41	Liquid
DTBP	Di-*tert* butyl peroxide (in toluene)	99.0	10.72	Liquid
BPB	*t*-Butyl peroxy benzoate	99.0	8.08	Liquid
DBTO	2,5-Dimethyl-2,5-di-(*t*-butyl peroxy) hexane-3	85.5	10.05	Liquid
MEKP	Methyl ethyl Ketone peroxide	55.5	10	Liquid
DCP	Di-cumyl peroxide	99.9	5.8	Solid
BPO	Benzyol peroxide	74.3	4.96	Solid
TCP	Bis-(4-*t*-butyl cyclohexyl) peroxy dicarbonate	97.3	3.61	Solid
LPO	Lauroyl peroxide	99.3	3.93	Solid
ADCA	Azodicarbonamide	98.0	–	Solid
AIBN	2,2′-Azobis(isobutyronitrile)	97.0	–	Solid
ABCN	1,1′-Azobis(cyclohexane-1-carbonitrile)	99.0	–	Solid
TBHP	*tert*-Butyl hydroperoxde	69	12.25	Liquid

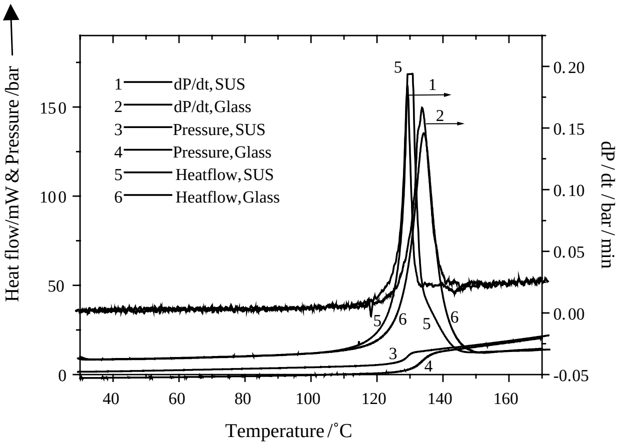

Fig. 3. Heat flow, pressure and d*P*/d*t* for materials of moderate decomposition rate (the case of CHP) (TBPA has the similar curves).

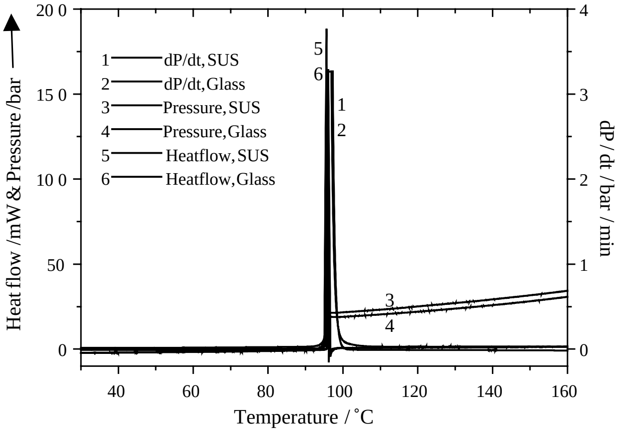

Fig. 4. Heat flow, pressure and d*P*/d*t* for materials of rapid decomposition rate (the case of BPO) (AIBN, ADCA, TCP, and ABCN have the similar curves).

simultaneously changed during the exothermic decomposition. Gas evolution rates, d*P*/d*t*, like heat evolution rates, followed the Arrhenius dependence on temperature. It suggests that the decompositions were classified by the shapes of the exothermic and pressure trace, especially by the shapes of the rate of pressure rise or rate of heat release. Figs. 2–9 distinguished all examples of rapid, moderate and low rate of reaction. Liquid decompositions, such as BPB, DTBP,

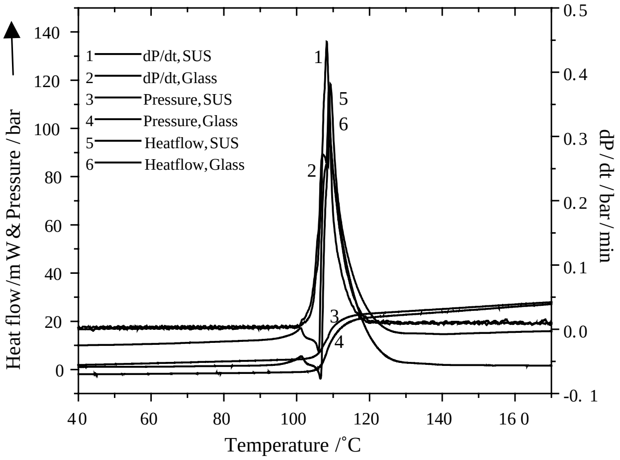

Fig. 5. Heat flow, pressure and d*P*/d*t* for ABCN (decomposition was accompanied by melting at the initial stage at below 108 °C).

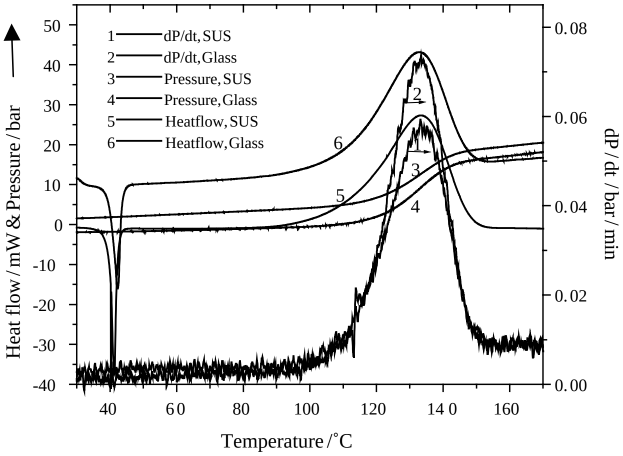

Fig. 6. Heat flow, pressure and d*P*/d*t* for DCP (decomposition took place after melting, LPO has the similar curves).

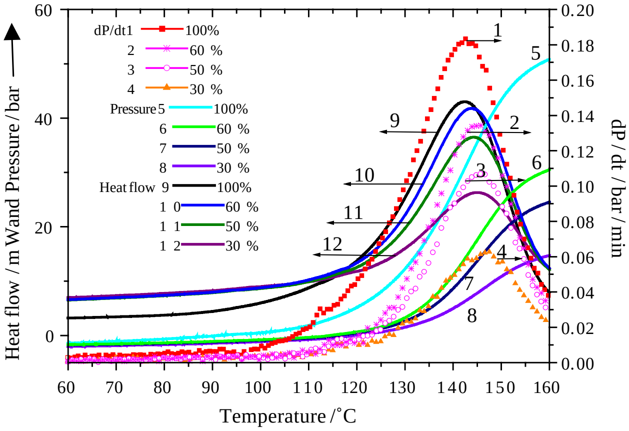

Fig. 7. Heat flow, pressure and d*P*/d*t* for DTBP in toluene.

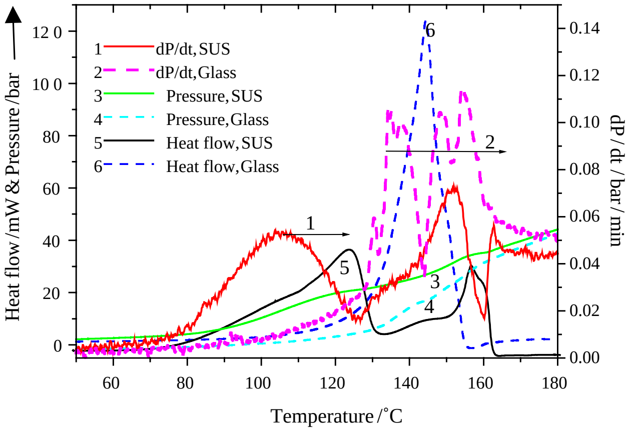

Fig. 8. Heat flow, pressure and d*P*/d*t* for TBHP in SUS and glass cells.

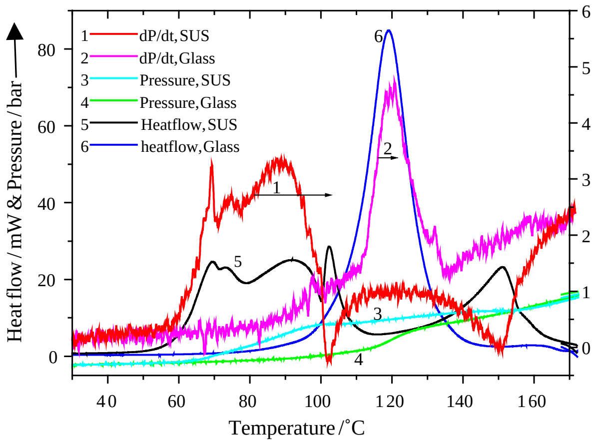

Fig. 9. Heat flow, pressure and d*P*/d*t* for MEKP in SUS and glass cells.

DBTO, and TBHP, presented the feature of low rate reactions, based on the fact that their maximum rates of pressure rise in Fig. 2, $(\mathrm{d}P/\mathrm{d}t)_{\mathrm{max}}$ values were all lower than 0.1 bar/min. TBPA and CHP in Fig. 3 had a little bit higher $(\mathrm{d}P/\mathrm{d}t)_{\mathrm{max}}$ values of 0.15 and 0.18 bar/min. The pressure of these materials behaved as ideal noncondensable gas, following the equation of $\mathrm{PV} = \mathrm{NRT}$ in all the process. At the stage of decomposition, the gas was produced stoichiometrically and pressure rose the increase of the reaction rate. At the end of decomposition, the product pressure continued to increase with the temperature linearly. The rate of pressure rise, d*P*/d*t* was a broad curve during the decomposition. It gradually increased from the onset temperature and attained the maximum when the rate of reaction reached the maximum. Rapid decompositions always occurred in solid, as BPO, AIBN, ADCA, TCP, and ABCN in Fig. 4. Their $(\mathrm{d}P/\mathrm{d}t)_{\mathrm{max}}$ values were 4.5, 4.1, 3.1, 2.5 and 0.5 bar/min, respectively. For a very rapid reaction, heat sink in the C80D was inadequate at 0.1 K/min because the transient heat generation was much larger than outer heating rating and extra heat was used to increase the reaction temperature, leading to a sharp heat flow and pressure increase peak. Detonation type of reaction was found in BPO whose both d*P*/d*t* and heat flow are very steep and significant. When lower scanning rate, as 0.01 K/min, was applied, the trace of reaction was the same as those of liquids because the heat accumulation in sample could have sufficient time to be transferred. The decomposition of some solids was more complex. Fig. 5 implied the effect of phase transformation, like melting, on the decomposition of ABCN. At the initial stage of the decomposition, it was accompanied by the melting of the sample, thus heat flows of ABCN increased a little due to the net result of the exothermal effect of reaction and endothermic effect of melting, whilst the pressure did not go up and d*P*/d*t* was negative. The vigorous decomposition occurred at about 108 °C. For LPO and DCP in Fig. 6 the decomposition took place after melting, so these two samples decomposed in liquid state, and were recognized as low decomposition.

3.2. *Effects of solvent and the vessel*

Some factors involved in the C80D measurements are discussed in this section. In Fig. 7, DTBP, besides pure one, was dissolved in toluene by 30, 50 and 60%. The heat flow and pressure reduced with the decrease of DTBO concentration. It implies that solvent could only dissipate reaction heat and hence the pressure at the expense of latent heat, but had little influence on the initial and the maximum temperatures of decomposition.

Another phenomenon was that as seen in Figs. 2–7, in most reactions, the profiles of heat flow and pressure in the stainless steel vessel and inner glass cup were exactly in the same trace. It implies that the sensitivity of the apparatus was not reduced due to a glass cell inserted and all heat flow transferred from the sample to the wall and then was captured by the thermopiles. By this means, the possible catalysis from wall could be detected. For most materials in this paper, no significant effect from vessel's materials was detected. TBHP (Fig. 8) and MEKP (Fig. 9) were the only exceptions. In stainless steel vessels, these two samples underwent several stages of reactions, corresponding to several peaks of heat flows and rates of pressure rise. While in glass cell, only one peak emerged. MEKP was classified as a rapid reaction among liquids since its $(\mathrm{d}P/\mathrm{d}t)_{\mathrm{max}}$ was up to 4.6 bar/min. It was reported that accidents caused by MEKP during last decades ranked the first order among organic peroxides, and the accidental frequency by MEKP was even twice of those caused by the second one, BPO [6]. Redox decomposition with the use of stainless steel container was suspected to be one of the main reasons of accidents. So the hazardous characteristics of MEKP by catalysis should be noticed.

3.3. *Relations of heat release and pressure in C80D*

This procedure can analytically illustrate the insights into the relations of pressure with thermal calorimetry data through simulation. Considering a decomposition starting from an initial pressure and temperature (onset condition), the pressure in a constant, unvented volume is given by [7,8]:

$$P = P_{\mathrm{onset}}\frac{T}{T_{\mathrm{onset}}} + n_{\mathrm{g}}\frac{\mathrm{RT}}{V} \tag{1}$$

where P_{onset}, T_{onset} and P, T are the initial and transient pressures and temperatures; n_{g} is the amount of the decomposition gas/mole and V is the volume of the closed vessel.

The maximum rate of pressure rise $(\mathrm{d}P/\mathrm{d}t)_{\mathrm{max}}$ in a closed volume is derived by the differential equation:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)_{\mathrm{max}} = \left[\frac{P_{\mathrm{onset}}}{T_{\mathrm{onset}}} + \frac{N_{\mathrm{gmr}}R}{V}\right]T^{*}_{\mathrm{mr}} + \frac{m_0 P_{\mathrm{s}}}{V}\mathrm{SV}_{\mathrm{g}} \tag{2}$$

where N_{gmr} is the gas decomposition parameter at the maximum reaction rate [mole noncondensable gas/mole substance], m_0 is the initial mass of sample.

Table 2
Relations of heat release and pressure in C80D

	TBPA	DTBP	BPB	DCP	BPO[a]	BPO[b]
N_{ncg}	0.97	1.43	1.01	1.02	1.09	0.87
Mw_P (g/mole)	132.3	146.2	194.2	270.3	242.2	242.2
T_{mr} (K)	393.1	413.5	389.2	406.2	372.0	358.8
x_{mr}	0.68	0.56	0.56	0.62	0.48	0.50
ln A (1 per s)	24.3	25.5	21.7	33.7	43.6	43.6
E_a (kJ/mol)	107.8	117.9	99.4	143.2	158.2	158.2
$(dP/dt)_{max}$ calculated (bar/min)	0.23	0.24	0.10	0.11	0.17	0.04
$(dP/dt)_{max}$ measured (bar/min)	0.17	0.22	0.13	0.07	4.52	0.08

[a] Tested under the heating rate of 0.1 K/min.
[b] Tested under the heating rate of 0.01 K/min.

The first term of Eq. (2) relates to a pure gas generating decomposition from the initial filled gas and hence is usually small in comparison with the second term which is contributed by the noncondensable decomposition gas, such that:

$$\left(\frac{dP}{dt}\right)_{max} = \frac{m_0 P_s}{V} SV_g \tag{3}$$

where SV_g is a classification index for a decomposition reaction without solvent boiling and represents a maximum standard gas constant volume generation rate of noncondensable gas having units [m^3/kg per s] and given by:

$$SV_g = \frac{N_{ncg}}{Mw_P} \frac{RT_{mr}}{P_s} (x_{mr} k_{mr}) \tag{4}$$

N_{ncg} is the intrinsic product decomposition parameter [mole noncondensable gas/mole substance]; Mw_P the molecular weight of the peroxide [g/mole]; R the gas constant [8.314 J/mole per K]; P_s the standard evaluation pressure, $P_s = 1201325$ Pa; T_{mr} the absolute temperature at the maximum reaction rate [K]; and x_{mr} and k_{mr} the conversion ratio and rate constant at T_{mr}.

$$x_{mr} = \frac{\int_{t_0}^{t_i} ((dH)/(dt)) \times dt}{\int_{t_0}^{t_\infty} ((dH)/(dt)) \times dt} \tag{5}$$

$$k_{mr} = A_{exp} \left(\frac{-E_a}{RT_{mr}}\right) \tag{6}$$

A and E_a are the kinetic parameters determined by the results from the C80D, respectively.

It indicates that $(dP/dt)_{max}$ is taken as overall criterion functioned by the factors associated with decomposition rate and gas evolution, such as the maximum rate of reaction under a certain volume. Table 2 lists the calculation results base on the Eqs. (4)–(6) and the actual measured ones. Here only several liquids are estimated and the results of $(dP/dt)_{max}$ calculated according to the thermal characteristics are in good agreement with the measured ones. But for BPO, the method is invalid when tested under the heating rate of 0.1 K/min. When tested under the heating rate of 0.01 K/min, the results of BPO evaluated by thermal data is consistent with the real one.

The reason is that for medium or low decomposition, gas production under a slow scanning rate follows ideal condition and the severity of the reaction is directly proportional to the gas production rate. However, for rapid or detonation types of decomposition, the case is more complicated. Propagation or detonation potential is the main added hazard, thermal data to evaluate $(dP/dt)_{max}$ is much lower than the real one for BPO. Further development of estimating $(dP/dt)_{max}$ should be considered.

Table 3
Result comparison in UN tests, MCPVT and C80D

	UN classification			MCPVT				C80D			
Sample	Koe nen	Dutch PVT	USA PVT	T_0 (°C)	T_{max} (°C)	P_{max}[a] (MPa)	$(dP/dt)_{max}$ (MPa/s)	T_0 (°C)	dH/dt (mW)	$(dP/dt)_{max}$ (bar/min)	ΔH (J/g)
TBPA			M	158	239	5.0	19.6	76	41.8	0.15	955.7
CHP	L[b]		N	219	316	4.6	81.42	90	168.2	0.18	1597.4
BPB	V	V	M	134	232	10.1	184.3	58	35.3	0.08	1464.3
DTBP	N	M	N	191	249	10.1	83.8	78	44.2	0.1	1101.6
DBTO	M		V	173	299	12.7	197.2	72	67.8	0.2	1685.8
MEKP				157	297	8.4	169.5	65	84.8	4.6	1646.2
DCP		M	L	168	278	2.2	15.0	82	24.6	0.06	832.7
BPO	V	M	V	102	193	8.1	412.7	94	460.0	4.5	1057.5
TCP				78	170	2.6	111.8	59	372.0	2.5	753.8
LPO		L	M	107	230	2.4	20.8	75	22.2	0.05	678.3
ADCA	M	L		196	294	12.4	108.9	132	296.1	3.1	1162.9
AIBN	V	M		116	241	9.5	387.5	62	392.0	4.1	1219.8
ABCN				134	266	3.2	55.6	103	108.8	0.5	749.2
TBPE	V	M		113	195	5.4	63.2	40	38.4	0.09	1165.4
TBHP			N	123	199	2.9	2.7	76	144.2	0.1	1896.5

[a] 1 MPa: 600 bar/min.
[b] “V”, “M”, “L”, and “N” stand for decompositions of “violent”, “medium”, “low” and “no”.

3.4. Comparison of classification of UN standard PVTs and MCPVT with C80D

Table 3 shows ranking results in the Koenen test, the Dutch PVT and the USA PVT, the data in the MCPVT (under 10 K/min) and in the C80D.

The ranking in the C80D based on $(\mathrm{d}P/\mathrm{d}t)_{\max}$ is MEKP, BPO, AIBN, ADCA, TCP > ABCN, DBTO, CHP > TBHP, DTBP, TBPEH, TBPA, LPO, BPB, DCP.

The ranking in the MCPVT based on $(\mathrm{d}P/\mathrm{d}t)_{\max}$ is BPO, AIBN, MEKP, DBTO > BPB, TCP, ADCA > CHP, DTBP, TBPEH, ABCN, TBPA, DCP, LPO, DTHP.

It is BPB, AIBN, BPO > DBTO, ADCA > CHP > DTBP in the Koenen PVT test; BPB, TBPEH > BPO, DCP, DTBP, AIBN, TBPEH > ADCA, LPO in the Dutch PVT; and BPO, DBTO > BPB, TBPA, LPO > TEPIC > DCP, DTBP, TBHP in the USA PVT, respectively.

The divergence between other PVTs and the C80D lies in that decomposition becomes much more intense under high external heating and it gives rise to much larger $(\mathrm{d}P/\mathrm{d}t)_{\max}$ values in other PVTs. Although there are several exceptions, one can get a general consistent classification when comparing among different methods.

It implies that the rate of decomposition plays a major role to classify the material, so those solid materials having rapid types of decomposition tested in the C80D are seen also as an intense decomposition in the MCPVT and other PVTs. While for liquids, those having the medium or low decomposition rates are ranked similar “medium” or “low” in the MCPVT and other PVTs. However, it is not always the case. For example, BPB and DBTO in the C80D are not rapid, but in the MCPVT are violent, so it seems that in these cases heat enthalpy affects the decomposition in the MCPVT. Because the heat generations of BPB and DBTO are the highest in liquids, they have a larger $(\mathrm{d}P/\mathrm{d}t)_{\max}$ due to the heat release in short time under intense outer heating and all heat contribute to rate of reaction and it is adequate to raise the reaction temperature and pressure.

4. Conclusion

Rate of pressure and rate of heat release in the C80D have the same tendency for all samples, indicating that exothermal decomposition mainly accompanied by the production of gas and there is a correlation between heat release and pressure, which was investigated in this paper. The effects of catalysis and solvent were clarified. It was also found that $(\mathrm{d}P/\mathrm{d}t)_{\max}$ is an overall parameter which encompasses intrinsic factors, such as rate of reaction, heat generation, and decomposition temperature in the C80D, and was considered as a criterion to evaluate the hazardous characteristics for unstable substances. The simulation of $(\mathrm{d}P/\mathrm{d}t)_{\max}$ values by thermal data matches those actual measured ones. Furthermore, it appears that the mechanism of decomposition of samples, which included rapid decomposition and moderate or low decomposition, had a significant influence on the intensity of the decomposition. Decomposition happening under a considerable mild surrounding condition in the C80D with the heating rate of 0.1 K/min showed an intrinsic character of unstable chemicals. In the MCPVT and some other UN PVT tests, which have an intense outer heating, the decomposition for rapid reaction is in the same order as in the C80D and the intrinsic factor, that is, rate of reaction was the dominant factor to contribute to the intensity of the decomposition. While for a moderate or low decomposition, enthalpy more likely influenced the intensity of the decomposition.

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