Evaluation of self-heating models for peracetic acid using calorimetry

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ABSTRACT

Thermal analysis of peracetic acid (PAA) with respect to the explosive properties was performed using calorimetry. The exothermic characteristics and thermal runaway profiles of PAA solutions were acquired through differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). The results revealed significant enthalpy changes and gas eruption for PAA solutions that were subjected to free-radical induced and autocatalytic reactions. The reaction kinetics and order of various PAA solutions were elucidated using calorimetry.

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1. Introduction

Organic peroxy acids are typical reagents used in oxidizing reactions in industrial applications; they are commonly known as the crosslinking agents to produce epoxides from alkenes and esters from ketones. Organic peroxides have been used extensively as promoters and catalysts because of their exceptional reactivity and oxidative capacity. Because of their chemical reactivity, organic peroxides can cause fire or explosion incidents, including heat accumulation during the catalytic reaction or storage, failure of temperature control, inadequate vent relief devices, and contamination, which might initiate autocatalytic reactions and thermal runaway (Prana et al., 2014). The safety concerns for the handling and chemical processing of organic peroxides include heat dissipation for liquid and vapor phases at elevated temperatures, impurity incompatibilities, viscosity of the reaction medium, pressure relief, and shielding from heat sources. Organic peroxy acids contain the peroxycarboxyl bond (—O=C—O—O—), which is an energetically functional group that provides free radicals to execute polymerizations and includes an easily broken weak oxygen–oxygen bond that releases heat at ambient temperature. Heat sources and contaminants (like acids or metallic ions) may induce the explosive decomposition of organic peroxides (Tobias, 1991). With improper temperature control and inadequate pressure reliefs during peroxy acid processing, a thermal runaway excursion might be followed by accidental fires or explosions (Wang et al., 2015).

Peracetic acid (PAA), which is a type of peroxy acid, is used not only as a catalyst but also as a strong oxidant in bleaching, disinfection, and epoxidation. PAA is widely used as an epoxidation agent in industrial olefin production. The reaction is performed using PAA with strong acids or combining transition metal catalysts to enhance the rapid conversion. A lower concentration of PAA is applied in the sanitation, pulp, and paper industries worldwide because it does not contain chlorine but it provides effective bleaching (Appels et al., 2011; Wood et al., 2013). It is also commonly used in the disinfection processes of wastewater treatment because of its excellent virucidal, sporicidal, and fungicidal properties (Formisano et al., 2016; Kitis, 2004). In addition, PAA reagents are used as a disinfectant in pharmaceutical, food processing, and the beverage industries. PAA can be produced using two methods: either by mixing acetic acid (AA) or acetic anhydride (AAh) and hydrogen peroxide (HP), with sulphuric acid (H_2SO_4) as a catalyst (Zhao et al., 2007) or by oxidising acetaldehyde (John and Weymouth, 1962). The first method was the

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Nomenclature

C	Concentration (mol L^{-1})
C_0	Initial concentration (mol L^{-1})
c_{pb}	Specific heat of the stainless-steel test bomb $(0.45\,\text{J g}^{-1}\,\text{K}^{-1})$
c_p	Specific heat of the PAA $(2.61\,\text{J g}^{-1}\,\text{K}^{-1})$
dC/dt	Concentration variation $(\text{mol L}^{-1}\,\text{min}^{-1})$
dP/dt	Pressure elevation rate measured by VSP2 (psi min^{-1})
$(dP/dt)_{max}$	Maximum pressure elevation rate (psi min^{-1})
dT/dt	Self-heating rate (K min^{-1})
$(dT/dt)_{ad}$	Adiabatic self-heating rate (K min^{-1})
$(dT/dt)_{vsp2}$	Self-heating rate measured by VSP2 (K min^{-1})
dx/dt	Variation of degree of conversion
E_a	Activation energy (kJ mol^{-1})
ΔH	Heat (J kg^{-1})
ΔH_d	Heat of decomposition (J kg^{-1})
ΔH_r	Heat of reaction (J kg^{-1})
k_0	Rate constant (min^{-1})
M_a	Mass of the sample (g)
M_b	Mass of the test bomb (g)
M_f	Mass of sample after a VSP2 test (g)
P_{max}	Maximum temperature measured by VSP2 (psig)
R	Ideal gas constant $(8.314\,\text{J mol}^{-1}\,\text{K}^{-1})$
T	Temperature (°C or K)
T_i	Apparent onset temperature measured by DSC ($i = 1, 2, 3\ldots$; °C or K)
T'	Temperature using ϕ correction (°C or K)
T_0	Initial self-heating temperature measured by VSP2 (°C or K)
$T_0{'}$	Initial self-heating temperature using ϕ correction (°C or K)
T_f	Final temperature after reaction (°C or K)
T_{max}	Maximum temperature measured by VSP2 (°C or K)
$T_{max}{'}$	Maximum temperature temperature using ϕ correction (°C or K)
x	Degree of conversion $(0 < x < 1)$
$\triangle T$	Temperature rise (°C or K)
$\triangle T_{ad}$	Adiabatic temperature rise (°C or K)
ϕ	Thermal inertia $\left(\frac{M_a C_p + M_b C_{pb}}{M_a C_p}\right)$

the distillation column combined with a preferred temperature range of 40–60 °C are used to prevent the formation of a potentially hazardous vapor phase (Pohjanvesi et al., 2002, 2004; Vineyard et al., 2006). A micro-structured reactor system was proposed to produce PAA, which improves the heat transfer, aiming at safe and continuous production in order to avoid unpredictable exothermic reactions which may lead to a runaway or an explosion using conventional reaction systems (Ebrahimi et al., 2011; Ebrahimi et al., 2012; Jolhe et al., 2015). However, producing $10\,\text{kg h}^{-1}$ PAA using a continuous flow micro-structured reactor, which has a volume of less than $10\,\text{dm}^3$, only can cover a small fraction of the market demand in comparison with a batch process with the capacity of $170\,\text{kg h}^{-1}$ based on a $5\,\text{m}^3$ stirred tank rector (Klaas et al., 2002; Ebrahimi et al., 2009).

The major products of the thermal decomposition of PAA are CO_2 and AA; O_2 is consumed by the reaction with methyl radicals to yield formaldehyde (H_2CO) (Schmidt and Sehon, 1963; Swern, 1971; Zhao et al., 2008). Heating of PAA starts with homolytic cleavage of the O—O bond to yield radicals (Sawaki, 1992). PAA is rapidly hydrolysed to AA and HP; after thermal decomposition of PAA at 130–150 °C, it was reported to produce CH_4, C_2H_6, C_2H_4, CH_3OH, CO_2, O_2, $HCOOH$ and $HOCH_2COOH$ (Evans and Seho, 1963; Swern, 1971; Yuan and Van Heiningen, 1997). Heating of PAA in the vapor phase from 127–360 °C starts with the peroxy bond homolysis to yield radicals. The decomposition of PAA solutions may proceed via two pathways, see Eqs. (1) and (2).

$$CH_3COOOH \xrightarrow{\triangle} CH_3COO^\bullet + {}^\bullet OH \rightarrow CH_3{}^\bullet$$
$$+CO_2 + {}^\bullet OH \xrightarrow{O_2} 2H_2CO + CO_2 \tag{1}$$

$$CH_3COOOH \xrightarrow{H_2O\,/\,\text{at }30-65\,°C} CH_3COOH + H_2O_2 \tag{2}$$
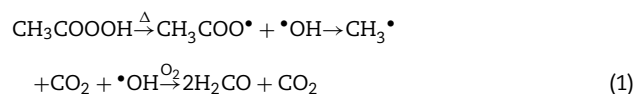
The synthesis, hydrolysis and oxidizing applications of PAA in industry is important, and some studies have evaluated the safety of PAA separate from their common applications related to commercial production. Related studies using calorimetric testing revealed that PAA solutions are more energetic and potentially more dangerous than other types of organic peroxides (Duh and Kao, 2008; Graham et al., 2011; Shen et al., 2010). Ni et al. (2016a, 2016b) have proposed a theoretical framework for the thermal runaway and risk assessment. This was achieved by combining the mathematical models and temperature thresholds for the synthesis of PAA with HP and AA in case of a cooling failure in a batch reactor. The performed probabilistic approaches are appropriate for accident risk evaluation in PAA chemical plants. According to the United Nations (UN) Recommendations on the Transport of Dangerous Goods (UN TDGs, 2000), it can be classified as an organic peroxide type D. In general, for such an energetic chemical the self-accelerating decomposition temperature (SADT) needs to be measured when the heat of decomposition is greater than $300\,\text{J g}^{-1}$; the National Fire Protection Association (NFPA) code 432 for the storage of organic peroxide formulations also recommends classifying 43 mass% PAA as a class II formulation because the decomposition is not as rapid, violent, or complete as that produced by class I formulations, which present the most severe fire hazards (NFPA, 2002). For example, a 43 mass% aqueous PAA solution, which detonates partially, does not deflagrate rapidly, and shows no violent effect when

prevailing approach for many years. However, the AAh–HP reaction is difficult to master because of the possible formation of diacetyl peroxide, which has explosive properties (Zhang et al., 2007). Therefore, the AA–HP reaction was preferably chosen for PAA synthesis. The production process of PAA, which can decompose due to heat, impurities, friction, and impact even in a chemical process, from concentrated HP is potentially explosive. In the production process of a stable aqueous PAA solution, a base is added to the reaction medium (AA, HP and an acid catalyst) that neutralizes unreacted acids. PAA in aqueous solution is produced in a continuous tubular reactor equipped with a distillation column. The potentially hazardous vapor rises through the distillation column where it is rectified to give the desired PAA concentration with minimal levels of residual HP and AA in the reactor. Using a pressure in the range of 3–27 kPa in the reactor, and 7–13 kPa in