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Kinetics and Safety Analysis of Peracetic Acid

Chiara Vianello[a], Ernesto Salzano[b], Giuseppe Maschio*[a]

[a]Dipartimento di Ingegnerzia Industriale, University of Padova, Via F. Marzolo 9, 35131 Padova (IT)
[b]Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater Studiorum - Università di Bologna, Via Terracini 28, 40131 Bologna (IT).
giuseppe.maschio@unipd.it

Peroxyacids are commonly used in chemical processing, synthesis and bleaching. Recently, they have been demonstrated to be very versatile for the epoxidation of unsaturated oil, aiming at the synthesis of polyepoxide (plasticizer, resins and adhesives). These processes are characterized by high yields and selectivity. However, due to their hazard and instability, the peroxy reactants are often obtained from the corresponding organic acid in situ by combination with hydrogen peroxide, in the presence of a mineral (sulphuric or phosphoric) acid as catalyst.

In this paper, the kinetic of decomposition of the peroxyacetic acid in water phase have been studied by using simple thermal screening calorimetry, with or without the catalyst.

1. Introduction

The aim of Green Chemistry is a cleaner and safer environment obtained by using materials and processes that minimize the use and generation of hazardous and noxious substances. In this light, large efforts have been devoted, in the last years, to the epoxidation of unsaturated vegetable oil, aiming at the synthesis of polyepoxide (plasticizer, resins and adhesives) by peroxyacids, which have been recently demonstrated to be very versatile for a range of chemical production. These processes are characterized by high yields and selectivity. However, due to their instability, peroxy reactants are often obtained from the corresponding organic acid in situ by combination with hydrogen peroxide, in the presence of a mineral (sulphuric or phosphoric) acid as catalyst. (Santacesaria et al., 2011; Salzano et al., 2012). Furthermore, the processes are highly exothermic (about 230 kJ/mol for each double bond) and therefore can undergo thermal runaway reaction leading to a dramatic rise in the reactor temperature and eventually to explosion (Campanella et al., 2008; Leveneur et al., 2012).

The study focuses on the kinetics of decomposition of peroxyacetic acid (PAA) generated in situ by reacting concentrated hydrogen peroxide and acetic acid (AA), either with or without sulphuric acid as catalyst and in the presence of oil phase, thus simulating the epoxidation reaction. The analysis has been performed by using a thermal screening calorimetry, which has been largely tested for similar processes.

2. Experimental equipment

Thermal screening of substances and reaction mixtures is a major constituent of chemical hazard assessment, either for the identification of process conditions under which a thermal explosion can occur, or for the definition of several safety parameters as Self Accelerating Decomposition Temperature (SADT), heat of reaction, and more in general kinetics parameters for the decomposition reaction. In this study, the experimental data have been carried out by using a Thermal Screening Unit (TSU) by HEL, a pseudo-adiabatic, Non Differential Thermal Analysis instrument, designed for the fast and efficient hazard screening of liquids, solids and heterogeneous systems.

In TSU, the sample is contained in a pressure tight metal test cell of 10 cm^3. The expansion vessel has a volume of 170 cm^3, about thirty times the volume of the cells. The TSU has been designed to work until 500 °C e 250 bar (HEL, 2008). When an exothermic or endothermic process is detected, the sample

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temperature deviates from the background-heating rate, thus identifying the detected onset temperature (T_{ONSET}).

In the experimental tests performed in this work, the thermal behavior of peroxyacetic acid generated in situ by reacting concentrated hydrogen peroxide (35 %wt of aqueous solution) with acetic acid (AA), in the presence or not of sulphuric acid as catalyst, has been detected. The concentration of the acetic acid is glacial (100 %wt) and the sulphuric acid is 98 %wt. Table 1 shows the molar fraction of mixture used in the experimental tests. The molar concentration of the peroxy-acid has been obtained by assuming the stechiometric concentration:

$$RCOOH + H_2O_2 \leftrightarrow RCOOOH + H_2O \quad (1)$$

Table 1. Molar fraction of mixture

Mixture	H_20_2	Acid	H_2O	H_2SO_4
$AA+H_2O_2$	0.195	0.122	0.683	-
$AA+H_2O_2+H_2SO_4$	0.194	0.122	0.680	0.004

The cell used to all test is made by Hastelloy C276.The tests carried out are of two types: ramped test with ramp rate of 2 °C/min and isothermal tests at different temperature, for kinetic analysis.

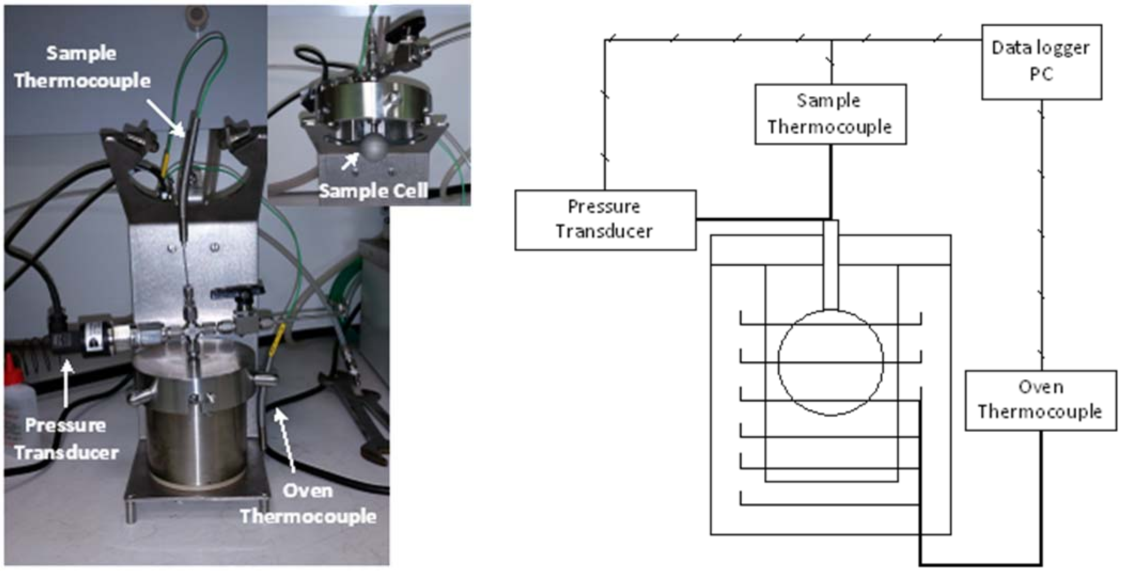

Figure 1. The Thermal Screening Unit by HEL used in this work.

3. Results: Thermochemistry

The experimental profiles for the thermal decomposition obtained in TSU by using the ramp rate of 2 °C/min for the mixture of acetic acid in hydrogen peroxide 35 %wt and the mixture of acetic acid in hydrogen peroxide 35 %wt and sulphuric acid are reported in Figure 2. For each mixtures two tests have been performed, namely Test A and Test B. The onset temperature may be observed in Figure 3, where the derivative of sample temperature is shown. The onset of decomposition temperature has been calculated by zooming the variation of the derivative near the spike, as shown in Figure 3.

Results, in terms of safety parameters, are summarized in Table 2, where the time, the temperature and the pressure corresponding to the onset and to the maximum of the spike for the divergent reaction, and the maximum value of first derivative of temperature with time, are reported.

The maximum temperature reported in Table 2 includes the heat losses because TSU performs the calorimetric analysis in a pseudo-adiabatic system. Hence, a correction factor (Φ) to account for the non-perfect adiabaticity has to be defined as:

$$\phi = 1 + \frac{w_{cell} \cdot c_{p,cell}}{w_{sample} \cdot c_{p.sample}} \quad (2)$$

where w is weight [g] of the cell or sample and the heat capacities c_p [J/g·°C] are calculated at average temperature $T^* = 0.5\cdot(T_{max}-T_{onset})$ calculated on the basis of NIST database coefficients. The heat capacity of Hastelloy C276, $c_{p,cell}$, is defined by the correlation reported by Thais & Kohn (1964):

$$c_{p,cell} = 4.185(0.1026 + 4.04 \cdot 10^5 T + 1.38 \cdot 10^{-17}\, T^5) \tag{3}$$

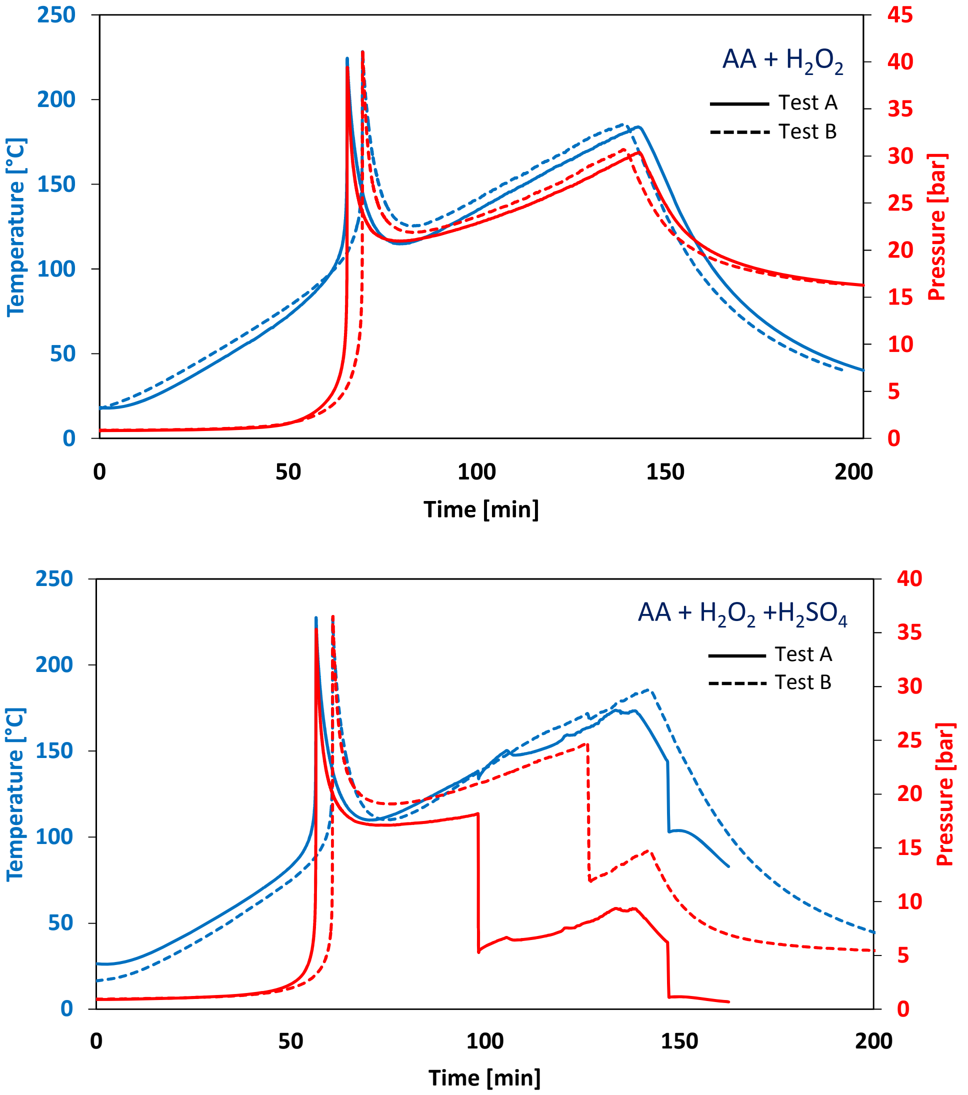

Figure 2. Thermal behaviour, in terms of sample temperature and measured pressure (dashed line, right axis), for the two mixture analysed in this work.

The heat of decomposition ΔH_d at the onset temperature has been then estimated through the correlation:

$$\Delta H_d(T_{onset}) = \phi c_{p,sample} \int_{t_{onset}}^{t_{max}} \left[\left(\frac{dT}{dt}\right) - \left(\frac{dT}{dt}\right)_{baseline}\right] dt + \Delta H_{ev} \tag{4}$$

where dT/dt is the rate of temperature rise above the onset temperature, i.e. the reference value that corresponds to zero thermal activity of the sample and ΔH_{ev} is the heat of evaporation of water (hence neglecting evaporation of other components). Eventually, the adiabatic temperature rise is simply:

$$\Delta T_{ad} = \frac{\Delta H_d}{c_{p,sample}} \tag{5}$$

Table 3 collects the obtained results for the given parameters.

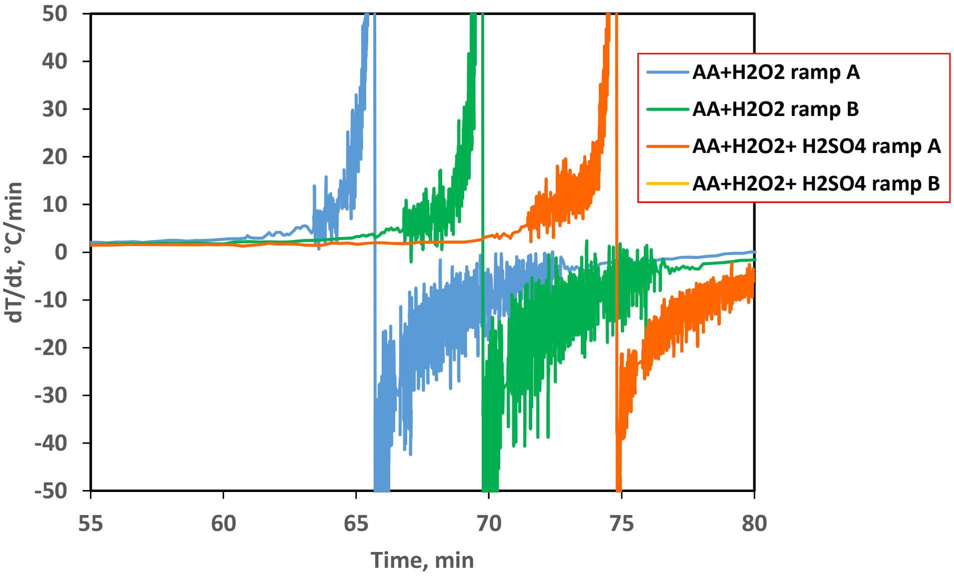

Figure 3. First derivative of sample temperature for the three mixtures analysed in this work. Right side reports the zoom of the derivative around the corresponding spikes.

Table 2. Safety parameter of mixture tested in this work

Reactants	Test	t_{onset} [min]	T_{onset} [°C]	t_{max} [min[	T_{max} [°C]	P_{onset} [bar]	P_{max} [bar]	$(dT/dt)_{max}$ [°C/min]	ΔT_{max} [°C)
$AA+H_2O_2$	A	63.61	107.94	65.71	224.41	6.51	39.42	2053.40	116.47
$AA+H_2O_2$	B	65.98	110.87	69.77	228.22	5.75	41.05	1864.40	117.35
$AA+H_2O_2+H_2SO_4$	A	56.21	117.44	56.57	227.52	8.01	35.32	2276.00	110.08
$AA+H_2O_2+H_2SO_4$	B	60.46	116.61	60.86	226.78	7.70	36.51	2246.20	110.17

Table 3. Heat of decomposition and adiabatic temperature of tests

Mixture		Weight [g]	φ	ΔH_d [J/g]	ΔT_{ad} [°C]
$AA+H_2O_2$	A	1.61	3.54	1878.66	670.68
$AA+H_2O_2$	B	1.61	3.53	1889.17	672.50
$AA+H_2O_2+H_2SO_4$	A	1.62	3.20	1698.40	608.77
$AA+H_2O_2+H_2SO_4$	B	1.64	3.19	1694.60	607.83

It is worth noting that the heat of reaction of PAA is ΔH = 2.04 kJ g^{-1} (Pasturenzi et al., 2012).

Through the processing of the experimental data of temperature and pressure, the decomposition behaviour has been evaluated in terms of gas moles n_{gas} (Yield, Y_{gas}, v/v) with respect to the oxygen moles n_{H2O2} obtained by hydrogen peroxide decomposition, by using ideal gas law and the following correlations:

$$P_{gas} = P_{exp} - P_{air} - P_{water} \cdot y_{water} \tag{6}$$

$$Y_{gas} = \frac{n_{gas}}{n_{H2O2}/2} \tag{7}$$

where P_{exp}, P_{air}, P_{water} are the measured pressure, the calculated air and the vapour pressure, respectively, y_{water} is the vapor fraction in the mixture calculated by the process simulator Aspen Plus™. Results are reported in Figure 4. The trends of oxygen yield calculated for the different mixtures are similar for the two substances.

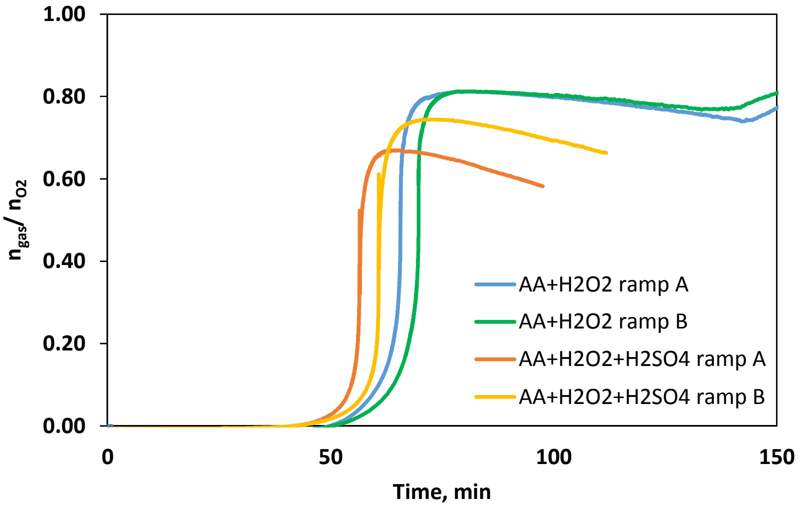

Figure 4. Yield of oxygen calculated from experimental data of pressure for the two mixtures.

4. Results: Kinetic

For an nth order reaction, Townsend and Tou (1980) showed that the pseudo rate coefficient (k) can be derived from adiabatic data. As proposed by McIntosh and Waldram (2003) an analogous evaluation can be performed by using data from a ramped screening test through the following correlation:

$$k = \frac{dT/dt}{[\Delta T_{ad}]\cdot[1-(T_{ad}/\Delta T_{ad})]^{n}} \tag{8}$$

$$\ln(k) = \ln\left(C_O^{n-1}A\right) - \frac{E}{RT} \tag{9}$$

where T_{ad} is the adiabatic temperature rise at the point where (dT/dt) is measured, C_0 is the reactant concentration at time zero and n is the order the reaction. Figure 5 shows the Arrhenius plot of *ln(k)* calculated from experimental data for the two mixtures here analyzed. Table 4 shows the kinetic parameters obtain for tests.

Table 4. Kinetic parameters as obtained by TSU methodology

Mixture		E [kJ mol^{-1}]	A [min^{-1}]	n
AA+H_2O_2	A	102.545	1.03E+12	1
AA+H_2O_2	B	104.765	7.95E+11	1
AA+H_2O_2+H_2SO_4	A	89.766	7.64E+10	1
AA+H_2O_2+H_2SO_4	B	105.488	8E+12	1

5. Conclusions

The decomposition of peroxy-acids may be the main contribution to the divergent behaviour in the case of in situ synthesis of corresponding organic acids with hydrogen peroxide. Peroxy-acetic acid is safer than formic acid in the case of absence of catalyst in terms of decomposition, even if it is considered as one of the most toxic of the peroxy-acid (Swern, 1970).

The kinetic of decomposition has been preliminary analysed from adiabatic thermal analysis in a simple instrument. Future work will be devoted to the isothermal decomposition reaction and to the analysis of the same mixtures in the presence of sulphuric and phosphoric acid as catalysts.

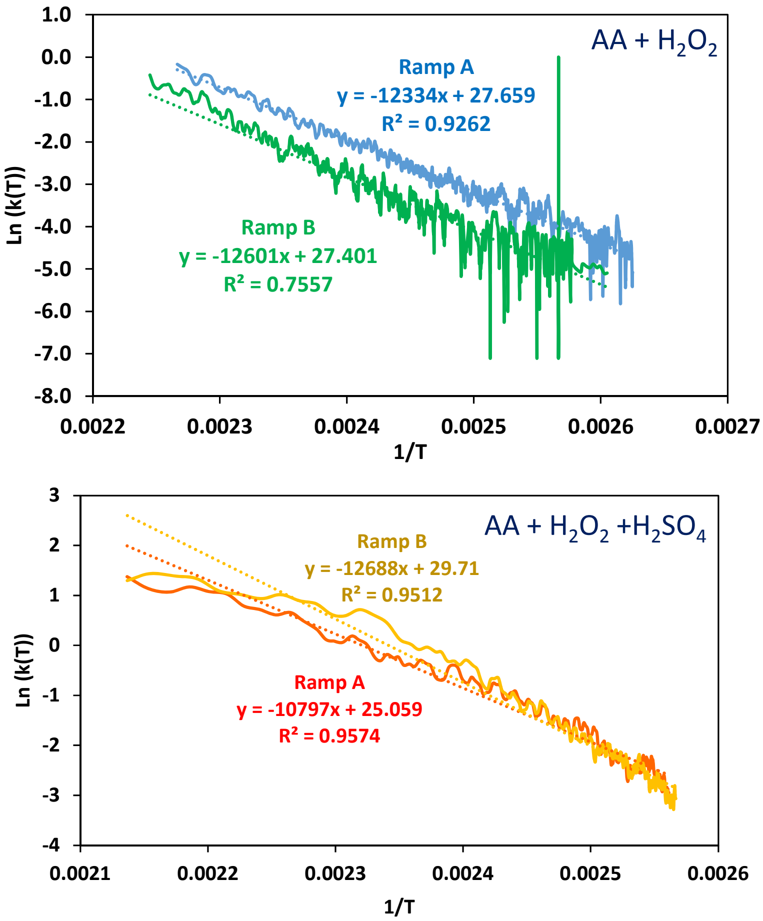

Figure 5. Arrhenius plot for AA acid with H_2O_2 and AA acid with H_2O_2 and H_2SO_4

References

Campanella A., Fontanini C., Baltanás M.A., 2008, High yield epoxidation of fatty acid methyl esters with performic acid generated in situ", Chem. Eng. J., 144, 466-475 .

HEL, 2008, TSu Operating Manual. HEL, 50 Moxon Street, Barnet, Herts, EN5 5TS, England

Leveneur S., Thones M., Hébert J-P., Taouk B., Salmi T., 2012, From Kinetic Study to Thermal Safety Assessment: Application to Peroxyformic Acid Synthesis, Industrial & Engineering Chemistry Research, 51, 13999−14007.

McIntosh R.D., Waldram S.P., 2003, Obtaining more, and better, information from simple ramped temperature screening tests. Journal of Thermal Analysis and Calorimetry, 73(1), 35–52.

Pasturenzi C., Dellavedova M., Gigante L., Lunghi A., Canavese M., Sala Cattaneo C., Copelli S., 2014. Thermochemical stability: A comparison between experimental and predicted data, Journal of Loss Prevention in the Process Industries, 28, 79-91.

Salzano E., Garcia-Agreda A., Russo V., Di Serio M., Santacesaria E, 2012, Safety criteria for the epoxydation of soybean oil in fed-batch reactor. Chemical Engineering Transactions, 26, 39–44.

Santacesaria E., Tesser R., Di Serio M., Turco R., Russo V., Verde D., 2011, A biphasic model describing soybean oil epoxidation with H_2O_2 in a fed-batch reactor. Chemical Engineering Journal, 173(1), 198–209.

Swern, D., 1970, Organic Peroxides, Editor, Wiley-Interscience, New York, USA.

Thais R.R., Kohn J.P., 1964, Heat Capacity of Hastelloy Alloy X at Temperatures between 37 °C and 1100 °C, Journal of Chemical and Engineering Data, 9, 546-547.

Townsend D.I., Tou J.C., 1980, Thermal hazard evaluation by an accelerating rate calorimeter. Thermochimica Acta, 37(1), 1–30.

Vianello C., Salzano E., Maschio G., 2015, Safety Parameters and Preliminary Decomposition Kinetic of Organo-peroxy Acids in Aqueous Phase. Chemical Engineering Transaction vol. 43, 2371-2377