Safety Parameters and Preliminary Decomposition Kinetic of Organo-Peroxy Acids in Aqueous Phase

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

[a]Dipartimento di Ingegnerzia Industriale, University of Padova, Via F. Marzolo 9, 35131 Padova, Italy
[b]Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche,Via Diocleziano 328, 80124 Napoli, Italy
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 peroxy-formic and acetic acid in water phase have been studied by using simple thermal screening calorimetry, however in the absence of the catalyst. This work is preliminary and will be extended to the actual process condition.

1. Introductions

In the last years, the limited reserves of fossil fuel and environmental issues have increased the interest towards the use of renewable raw materials for the production of polymers, as an alternative to petroleum derivatives. Among others, several industrial and scientific investigators have focused their activity on the development of polymeric materials from vegetable oils, and more in particular towards polyepoxide, which are largely used as plasticizers and stabilizers for polyvinyl chloride (PVC) resins, adhesive, structural materials and other uses. That is typically obtained through the epoxidation of unsaturated bonds of oil by peroxy-acids ($R\text{-}CO_3H$). In these cases, due to their hazard and instability, the peroxy-acid is generally generated in situ by reacting concentrated hydrogen peroxide with acetic or formic acid in the presence of a mineral acid (sulphuric or phosphoric) as a catalyst, in water phase (Santacesaria et al., 2011; Salzano et al., 2012).

Due the clear importance of these processes, several works have been devoted to the synthesis and to the decomposition of those instable organo-peroxy substances (Campanella et al., 2008; Leveneur et al., 2012) This study is focused on the experimental definition of thermal behavior and decomposition kinetic of peroxy-acetic (PAA) or peroxy-formic (PFA) acid by using a simple apparatus, the Thermal Screening Unit (TSU) and to the definition of safety parameters for the aims of process development. The peroxy acids are obtained by using H_2O_2 35 %wt and mixing the reactants together at ambient temperature. A test for the pure hydrogen peroxide has been also performed for the sake of comparison.

2. Experimental equipment

Thermal screening tests of components and reaction mixtures are often the major constituent of the chemical hazard assessment. They are useful for the identification of process conditions under which a thermal explosion can occur, and for the definition of several safety parameters as the 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 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 peroxyformic acid and peroxyacetic acid generated in situ by reacting concentrated hydrogen peroxide (35 %wt of aqueous solution) with formic acid (FA) and acetic acid (AA) has been detected. We assume the self-catalysed reaction for the two organic acids to form the corresponding peroxy substances. The concentration of formic acid is equal to 98 %wt and the acetic acid is glacial (100 %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:

$$RCOOH + H_2O_2 \leftrightarrow RCOOOH + H_2O \tag{1}$$

Table 1. Molar fraction of mixture

Mixture	H_2O_2	Acid	H_2O
PA+H_2O_2	0.188	0.154	0.658
FA+H_2O_2	0.211	0.049	0.740

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.
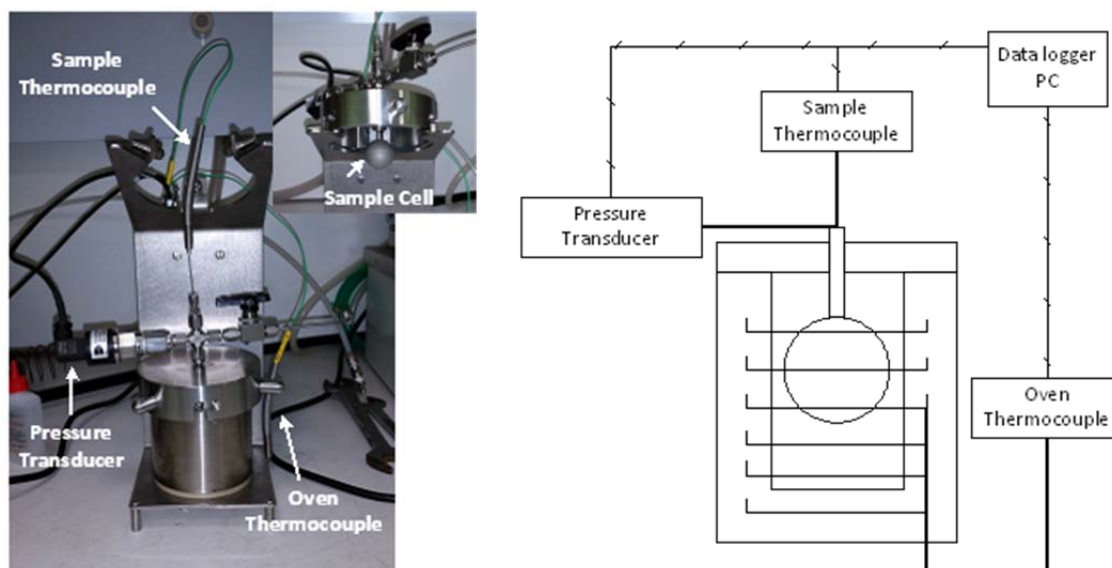

Figure 1. The Thermal Screening Unit by HEL used in this work.

3. Results: Thermochemistry

The experimental profiles for the thermal decomposition obtained in TSU by using the ramp rate of 2 °C/min for pure hydrogen peroxide and for the mixture of pure formic acid and acetic acid in hydrogen peroxide 35 %wt are reported in Figure 2. 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. Quite clearly, the onset temperature, the maximum temperature and the temperature rate of rise (i.e. the reactivity) of FA+H_2O_2 is much lower than pure PA + H_2O_2, which show a divergent decomposition behavior starting from about 70 °C.
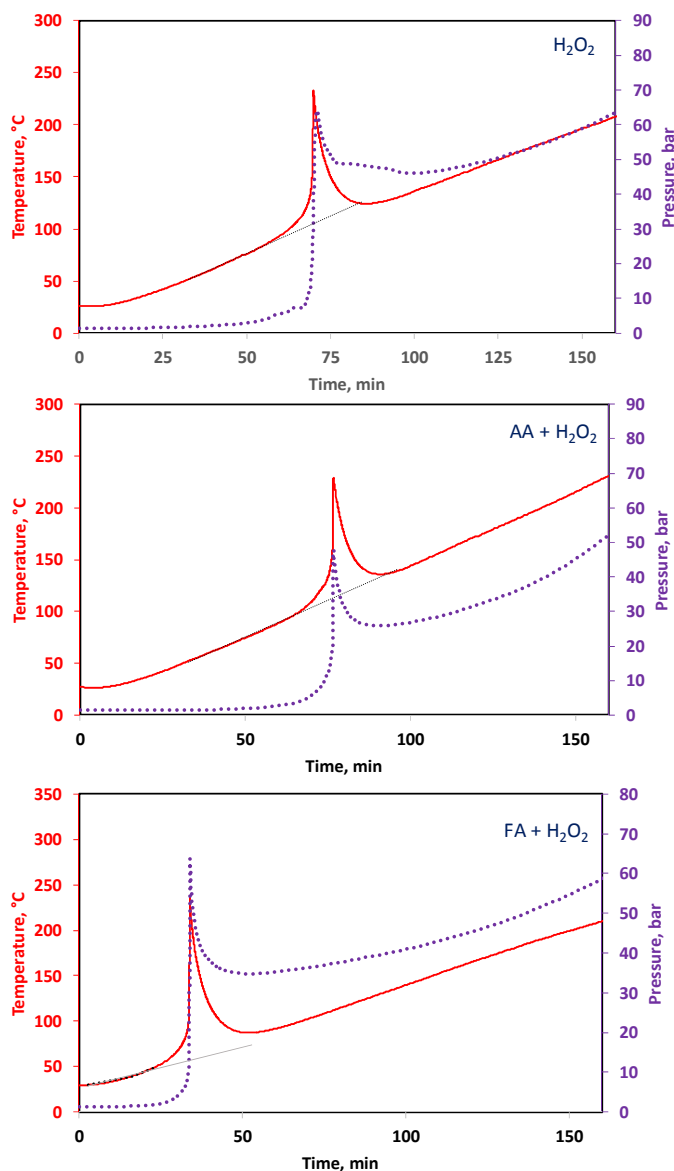
Figure 2. Thermal behavior, in terms of sample temperature and measured pressure (dashed line, right axis), for the three reactants analyzed in this work.

The maximum temperature reported in Table 1 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:

$$\phi = 1 + \frac{w_{cell} \cdot c_{p,cell}}{w_{sample} \cdot c_{p.sample}}$$ (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 $T^* = 0.5(T_{max} - T_{onset})$ 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):

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

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:

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

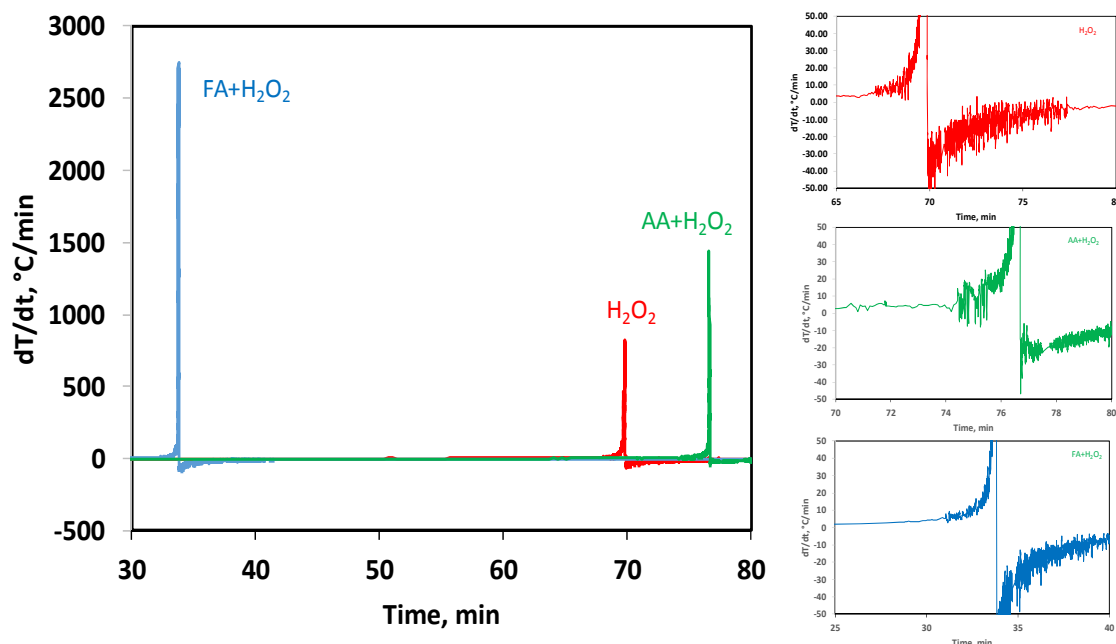Table 3 collects the obtained results for the given parameters.

Figure 3. First derivative of sample temperature for the three mixtures analyzed 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	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]
H_2O_2	66.2	69.8	69.87	232.9	7.4	31.9	819.4	122.7
AA+ H_2O_2	74.4	76.7	76.69	228.6	13.1	47.4	1,444.0	116.9
FA + H_2O_2	31.0	33.8	31.12	237.3	4.9	63.7	2,741.6	72.7

Table 3. Heat of decomposition and adiabatic temperature of tests

Mixture	Weight [g]	φ	ΔH_d [J/g]	ΔT_{ad} [°C]
H_2O_2 35%w/w	2.25	2.68	2098.48	623.38
AA + H_2O_2	1.63	3.65	1938.29	654.07
FA + H_2O_2	2.03	2.77	2809.76	655.84

It is worth noting that the heat of reaction of hydrogen peroxide (in gas phase) is ΔH= 1724 kJ g^{-1}, whereas for PAA, ΔH = 2.04 kJ g^{-1} (Pasturenzi et al., 2012).

Through the processing of the experimental data of temperature and pressure, the decomposition behavior 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:

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

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

where P_{exp}, P_{air}, P_{water} are the measured pressure, the calculated air and the vapour pressure, respectively (Table 1). Results are reported in Figure 4. The trends of oxygen yield calculated for the different mixtures are similar for the three substances: the amount of oxygen is actually corresponding to hydrogen peroxide in the case of FA, whereas AA shows higher stability to heating.
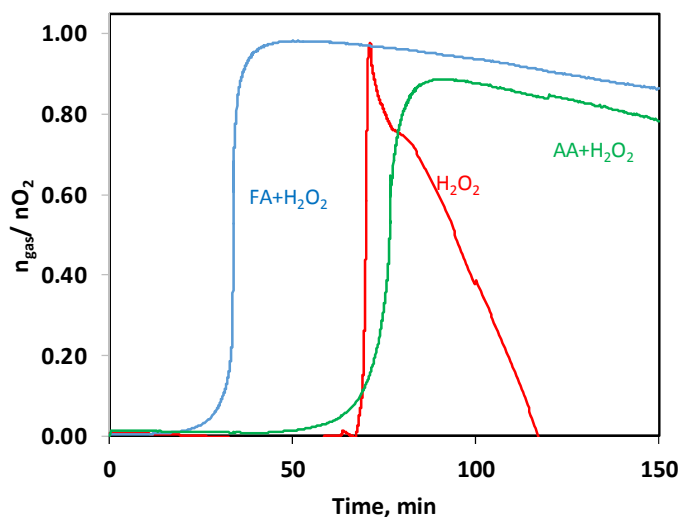

Figure 4. Yield of oxygen calculated from experimental data of pressure for the two peroxy-acid analyzed in this work and comparison with hydrogen peroxide.

4. Results: Kinetic

For an nth order reaction, Townsend and Tou (1980) show 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 pure hydrogen peroxide decomposition and for the two mixtures here analyzed.

5. Conclusions

The decomposition of peroxy-acids may be the main contribution to the divergent behavior 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 analyzed 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.
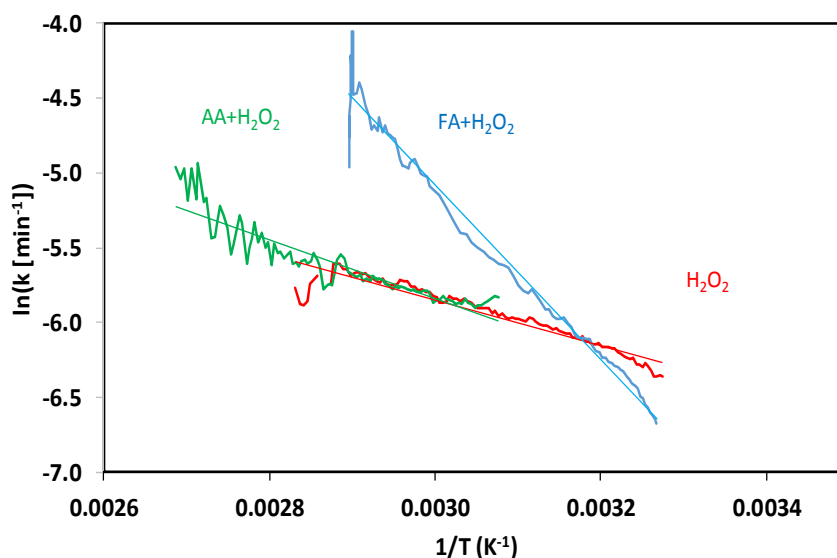
Figure 5. Arrhenius plot for hydrogen peroxide, FA and AA acid with H_2O_2.

Table 4. Kinetic parameters as obtained by TSU methodology

Mixture	E [kJ mol^{-1}]	A [min^{-1}]	n
H_2O_2	-0.011	0.149	1
AA + H_2O_2	-18.985	1.703	1
FA + H_2O_2	-44.503	96954.780	1

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.