Kinetics and Safety Analysis of Peracetic Acid

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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 peroxycetic 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 peroxycetic 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\textsuperscript{3}. The expansion vessel has a volume of 170 cm\textsuperscript{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 (TONSET).

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 steechiometric concentration:

$$RCOOH + H_2O_2 \rightarrow RCOOH + H_2O$$  \(1\)

### Table 1. Molar fraction of mixture

<table>
<thead>
<tr>
<th>Mixture</th>
<th>H$_2$O</th>
<th>Acid</th>
<th>H$_2$O</th>
<th>H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA+H$_2$O$_2$</td>
<td>0.195</td>
<td>0.122</td>
<td>0.683</td>
<td>-</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$+H$_2$SO$_4$</td>
<td>0.194</td>
<td>0.122</td>
<td>0.680</td>
<td>0.004</td>
</tr>
</tbody>
</table>

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.](image)

### 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 (\(\Phi\)) to account for the non-perfect adiabaticity has to be defined as:

$$\phi = 1 + \frac{W_{cell}/C_p,cell}{W_{sample}/C_p, sample}$$  \(2\)
where \( w \) is weight [g] of the cell or sample and the heat capacities \( c_p \) [J/g °C] are calculated at average temperature \( T^* = 0.5 \cdot (T_{\text{max}}-T_{\text{onset}}) \) calculated on the basis of NIST database coefficients. The heat capacity of Hastelloy C276, \( c_{p,\text{cell}} \), is defined by the correlation reported by Thais & Kohn (1964):

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

(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 \( \Delta H_d \) at the onset temperature has been then estimated through the correlation:

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

(4)

where \( \frac{dT}{dt} \) 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 \( \Delta H_{\text{ev}} \) is the heat of evaporation of water (hence neglecting evaporation of other components). Eventually, the adiabatic temperature rise is simply:

\[
\Delta T_{\text{ad}} = \frac{\Delta H_d}{c_{p,\text{sample}}}
\]  

(5)
Table 3 collects the obtained results for the given parameters.

![Graph showing first derivative of sample temperature for three mixtures analyzed in this work.]

**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

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Test</th>
<th>$t_{onset}$ [min]</th>
<th>$T_{onset}$ [°C]</th>
<th>$t_{max}$ [min]</th>
<th>$T_{max}$ [°C]</th>
<th>$P_{onset}$ [bar]</th>
<th>$P_{max}$ [bar]</th>
<th>$(dT/dt)_{max}$ [°C/min]</th>
<th>$\Delta T_{max}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA+H$_2$O$_2$ A</td>
<td>A</td>
<td>63.61</td>
<td>107.94</td>
<td>65.71</td>
<td>224.41</td>
<td>6.51</td>
<td>39.42</td>
<td>2053.40</td>
<td>116.47</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$ B</td>
<td>B</td>
<td>65.98</td>
<td>110.87</td>
<td>69.77</td>
<td>228.22</td>
<td>5.75</td>
<td>41.05</td>
<td>1864.40</td>
<td>117.35</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$+H$_2$SO$_4$ A</td>
<td>A</td>
<td>56.21</td>
<td>117.44</td>
<td>56.57</td>
<td>227.52</td>
<td>8.01</td>
<td>35.32</td>
<td>2276.00</td>
<td>110.08</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$+H$_2$SO$_4$ B</td>
<td>B</td>
<td>60.46</td>
<td>116.61</td>
<td>60.86</td>
<td>226.78</td>
<td>7.70</td>
<td>36.51</td>
<td>2246.20</td>
<td>110.17</td>
</tr>
</tbody>
</table>

Table 3. Heat of decomposition and adiabatic temperature of tests

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Weight [g]</th>
<th>$\varphi$</th>
<th>$\Delta H_d$ [J/g]</th>
<th>$\Delta T_{ad}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA+H$_2$O$_2$ A</td>
<td>1.61</td>
<td>3.54</td>
<td>1878.66</td>
<td>670.68</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$ B</td>
<td>1.61</td>
<td>3.53</td>
<td>1889.17</td>
<td>672.50</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$+H$_2$SO$_4$ A</td>
<td>1.62</td>
<td>3.20</td>
<td>1698.40</td>
<td>608.77</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$+H$_2$SO$_4$ B</td>
<td>1.64</td>
<td>3.19</td>
<td>1694.60</td>
<td>607.83</td>
</tr>
</tbody>
</table>

It is worth noting that the heat of reaction of PAA is $\Delta H = 2.04$ 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 $n_{H_2O_2}$ obtained by hydrogen peroxide decomposition, by using ideal gas law and the following correlations:

\[
\begin{align*}
\Delta H_d &= P_{gas} 
\Delta T_{ad} = \frac{P_{exp} - P_{air} - P_{water} \cdot y_{water}}{\frac{n_{gas}}{n_{mol}}} \cdot y_{water}
\end{align*}
\]

\[
\begin{align*}
Y_{gas} &= \frac{n_{gas}}{n_{mol_2}}
\end{align*}
\]

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.
4. Results: Kinetic

For an $n^{th}$ 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:

$$k = \frac{dT}{dt} \left[\frac{1}{\Delta T_{ad}}\left[1 - \left(\frac{T_{ad}}{\Delta T_{ad}}\right)\right]\right]^n$$

$$\ln(k) = \ln(C_0^{-1}A) - \frac{E}{RT}$$

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>
<thead>
<tr>
<th>Mixture</th>
<th>$E$ [kJ mol$^{-1}$]</th>
<th>$A$ [min$^{-1}$]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA+H$_2$O$_2$ A</td>
<td>102.545</td>
<td>1.03E+12</td>
<td>1</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$ B</td>
<td>104.765</td>
<td>7.95E+11</td>
<td>1</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$+H$_2$SO$_4$ A</td>
<td>89.766</td>
<td>7.64E+10</td>
<td>1</td>
</tr>
<tr>
<td>AA+H$_2$O$_2$+H$_2$SO$_4$ B</td>
<td>105.488</td>
<td>8E+12</td>
<td>1</td>
</tr>
</tbody>
</table>

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$_2$O$_2$ and AA acid with H$_2$O$_2$ and H$_2$SO$_4$

References

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