

OXIDATION OF ASCORBIC ACID WITH HYDROGEN PEROXIDE: INVESTIGATION WITH A REACTION CALORIMETER

ALBERTO SCHIRALDI^{1*}, MATTEO SCAMPICCHIO², STELLA COSIO¹, Hasan S. M. KAMRUL²

¹University of Milan, Dep. Food Environmental Nutrition Sciences, Milano, Italy

²Free University of Bolzano, Piazza Università 1, 39100, Bolzano, Italy

The oxidation of ascorbic acid (AA) implies first the formation of dehydro-ascorbic acid (DHA) and, in a second step, a further oxidation that breaks the molecule in smaller mass compounds, like oxalic acid and 1,2-ethandiol-1,2-dicarboxy acid. The overall process is therefore the result of two consecutive steps.

The process was investigated in isothermal conditions with a reaction calorimeter at different concentration, pH and temperatures.

The instrument used is a chemical process analyser CPA202 developed by ChemiSense® and designed to suppress uncontrolled temperature differences between the content of the reactor and its. This means that all the heat exchanged from the reactor to the thermostat bath flows through the heat transducer, which is located between the bottom of the reactor and a Peltier element used as a heat pump. Figure 1 shows the trend of the recorded signals.

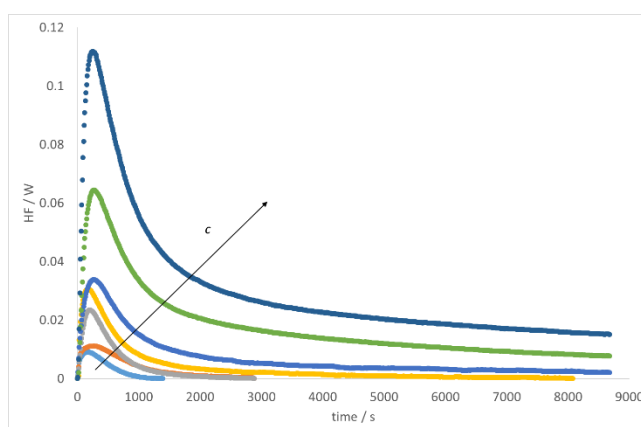
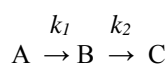


Figure 1. Isothermal calorimetric traces recorded for various concentrations of Ascorbic Acid.

A two consecutive step kinetic model allows fitting the experimental trends, provided that a damping factor, $\exp(-\tau/t)$, is introduced to account for the delay of heat transfer (about 100 s). Both steps follow a first order kinetics (although other combinations were also considered):



$$\alpha_A = \exp(-k_1 t)$$

$$\alpha_B = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

$$\alpha_C = 1 - \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] - \exp(-k_1 t)$$

$$\dot{Q}_1 = k_1 \Delta H_1 \exp(-k_1 t)$$

$$\dot{Q}_2 = \Delta H_2 \frac{k_1 k_2}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$$

$$\dot{Q} = a \exp(-k_1 t) - b \exp(-k_2 t)$$

$$P = \dot{Q} \exp\left(-\frac{\tau}{t}\right)$$

$$\lim_{t \rightarrow \infty} P = 0$$

Taking into account that the overall thermal effect is exothermic, the reaction enthalpies were assumed both negative, or one positive and the other negative. Figure 2 reports an example of best fit.

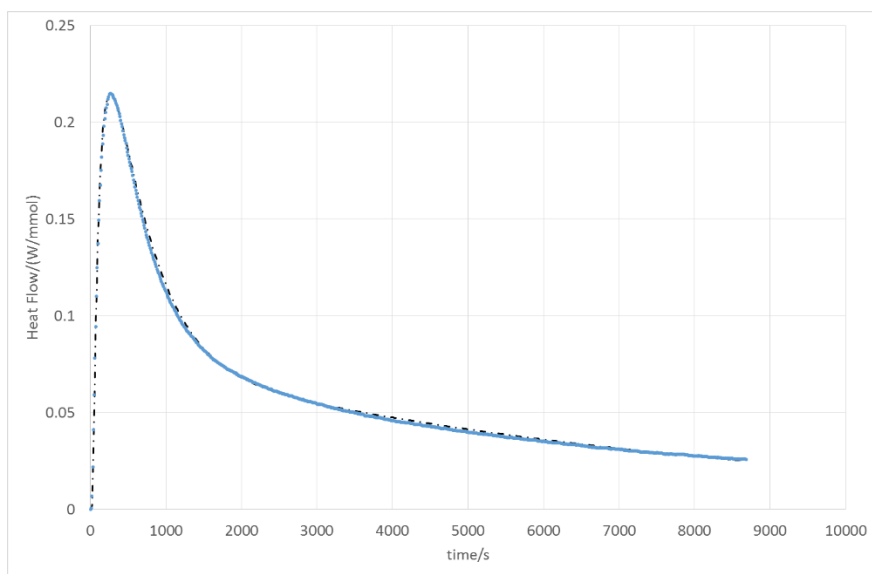


Figure 2. The best fit (dotted line) of the experimental calorimetric trace (continuous line) with a two-step consecutive process. Both steps were exothermic.

As for the pH role, it was found that at low pH the process is much faster (see Figure 3)

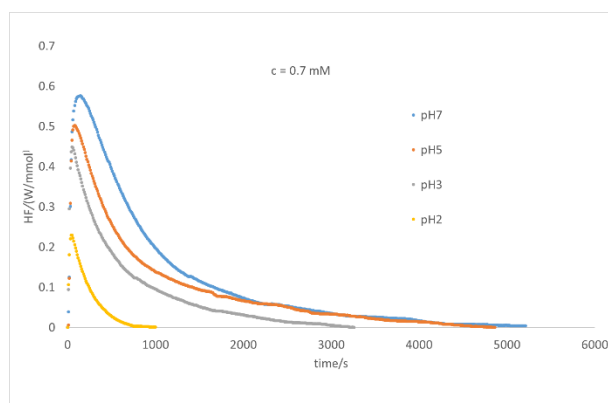


Figure 3. Effect of the pH on the oxidation rate.