

Thermal decomposition of acetic anhydride–nitric acid mixtures

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Abstract

The adoption of $\text{Ac}_2\text{O}/\text{HNO}_3$ mixtures for the nitration of organics or the preparation of nitric esters is not free from some risks of explosion. The behaviour of these mixtures at varying $\text{Ac}_2\text{O}/\text{HNO}_3$ molar ratios is studied by means of adiabatic and scanning calorimetry. A simplified kinetic model, based on two lumped reactions (one of which leads to the formation of tetranitromethane) is developed to simulate the thermal decomposition of the investigated system under adiabatic conditions. The use of this model allows satisfactory prediction of the temperature profiles in the reactor whereas calculated pressures are generally overestimated due to some model inadequacies to account for the absorption of gaseous decomposition products into the reacting solution. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The adoption of $\text{Ac}_2\text{O}/\text{HNO}_3$ mixtures for aromatic nitrations and the preparation of nitric esters has been reported for laboratory and industrial uses [1]. This system offers the advantage of reduced undesired secondary reactions compared to mixed acid solutions [2,3].

$\text{Ac}_2\text{O}/\text{HNO}_3$ mixtures are on the other hand characterized by a certain explosive behaviour which is generally ascribed to the formation of acetyl nitrate, a species known to undergo violent explosions on heating above 333 K [4]. Spontaneous explosions of acetyl nitrate solutions have been also reported at ambient temperature as a result of prolonged storage. More than one accident has been recorded in the past in industrial applications of this system [5].

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Literature information [6] indicates that the chemical behaviour of the system is rather complex, the intermediate acetyl nitrate being capable of decomposing with the formation of tetranitromethane and carbon dioxide.

However only scant information is available on the mechanism and kinetics of the reactions through which the thermal decomposition of $\text{Ac}_2\text{O}/\text{HNO}_3$ mixtures develops, thus preventing the reliable modeling of their behaviour at varying reaction conditions.

The present work aims, therefore, at studying the tendency of these mixtures to undergo violent thermal explosions and related kinetics. These results may allow the prediction of the effects of some process deviations during the nitration of organics or the preparation of nitric esters by means of $\text{Ac}_2\text{O}/\text{HNO}_3$ mixtures and help choose safe operating conditions. All the investigations have been carried out by means of adiabatic and scanning calorimetric techniques, coupled with chemical analysis.

2. Experimental

The experimental adiabatic runs have been carried out by means of both an Accelerating Rate Calorimeter (ARC) [7] (by Columbia Scientific Industries) and a Phi-Tec II calorimeter (by Hazard Evaluation Laboratory) [8]. For scanning experiments a PC Combilab (by Systag) equipped with a Radex oven [9] was used.

All the ARC runs were performed using stainless steel bombs with the following set parameters: wait time 600 s, heat step temperature 10 K, self-heating rate threshold value $3.3 \times 10^{-4} \text{ K s}^{-1}$. The Phi-Tec runs were performed using glass cell reactors in the standard “closed can” modality. The AcOH/HNO_3 mixtures were pre-heated to the desired temperature by adding in a second step the required amount of acetic anhydride. All Radex runs were performed using stainless steel reactors. The reaction mixtures were prepared in situ at 278 K, charged into the reactor and submitted to temperature ramp starting from ambient temperature with heating rate of $2.5 \times 10^{-2} \text{ K s}^{-1}$ up to 393 K for runs devoted to study the first exothermic event or 553 K for complete scanning.

The quantitative analyses of tetranitromethane were carried out by means of a 1090 Hewlett-Packard HPLC equipped with an S5C6 Phenomenex reverse phase column and a diode array detector. The mobile phase was $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (50:50) with a flow of $8.33 \times 10^{-6} \text{ l s}^{-1}$. The oven temperature was set at 303 K and the signal acquired at a wave length $\lambda = 220 \text{ nm}$.

The gas analyses were performed by using a Perkin-Elmer Autosystem XL equipped with a packed Carboxen 1000 column (length 5 m, internal diameter 2.1 mm) and a TCD detector. The following temperature ramp has been used: 403 K for 192 s, 0.420 K s^{-1} up to 513 K. The carrier gas was helium with a flow of $1.67 \times 10^{-4} \text{ l s}^{-1}$.

3. Results and discussion

The reactive behaviour of the system $\text{Ac}_2\text{O}/\text{HNO}_3$ has been previously investigated by carrying out adiabatic runs by means of the Phi-Tec Calorimeter on the solutions prepared as indicated in Table 1.

Table 1

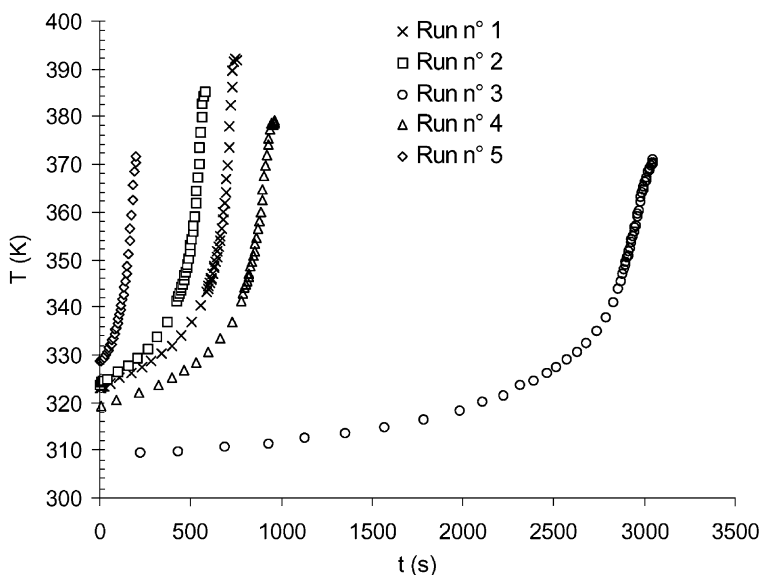
Experimental conditions adopted for adiabatic (Phi-Tec) runs carried out on $\text{Ac}_2\text{O}/\text{HNO}_3$ systems

Run number	$n_{\text{HNO}_3}^0$ (moles)	$n_{\text{Ac}_2\text{O}}^0$ (moles)	$R = n_{\text{Ac}_2\text{O}}^0/n_{\text{HNO}_3}^0$	n_{AcOH}^0 (moles)	Φ
1	0.179	0.0894	0.5	0.399	1.55
2, 3, 4	0.224	0.0894	0.4	0.399	1.51
5	0.447	0.0894	0.2	0.399	1.39

The results of these runs (Fig. 1) indicate that the investigated system undergoes exothermic decomposition with recorded adiabatic temperature rise increasing with the increase in the initial molar ratio $R = n_{\text{Ac}_2\text{O}}^0/n_{\text{HNO}_3}^0$ (see Runs 1, 2 and 5). Runs 3 and 4 were performed by using initial solutions of the same composition ($R = 0.4$) as Run 2 by starting from different temperatures. Recorded adiabatic temperature rises in the three runs were practically coincident. Similar results were recorded for final pressures (Fig. 2) although a little discrepancy was observed for the value of Run 3 compared to those for Runs 2 and 4.

For each run substantial pressure values are observed thus confirming the hazardous nature of these mixtures.

To better characterize their behaviour, at the end of the Run 3, the liquid sample was recovered and submitted to a scanning test, starting from ambient temperature, with a heating rate of $2.50 \times 10^{-2} \text{ K s}^{-1}$ up to 553 K. The results of this run showed the occurrence of a second exothermic event during which a large amount of gas is evolved. A second set of scanning experiments allowed to demonstrate that, starting from different initial R, the decomposition process is characterized by two distinct exothermic events (Fig. 3).

Fig. 1. Temperature vs. time in adiabatic runs performed on different $\text{Ac}_2\text{O}/\text{HNO}_3$ by means of Phi-Tec.

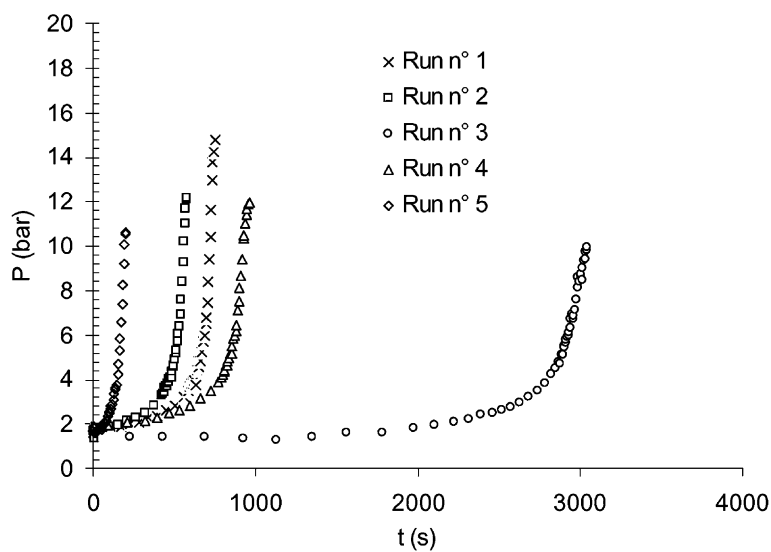


Fig. 2. Pressure vs. time in adiabatic runs performed on different $\text{Ac}_2\text{O}/\text{HNO}_3$ by means of Phi-Tec.

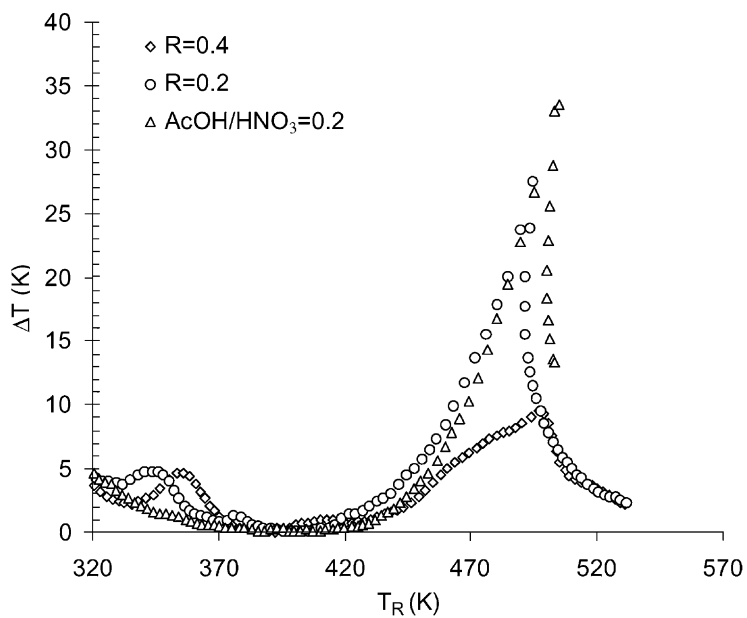


Fig. 3. Radex scanning results (reactor-oven temperature difference vs. reactor temperature) obtained for different $\text{Ac}_2\text{O}/\text{HNO}_3$ mixtures and AcOH/HNO_3 system that simulate the mixture $\text{Ac}_2\text{O}/\text{HNO}_3$ with $R = 0.2$.

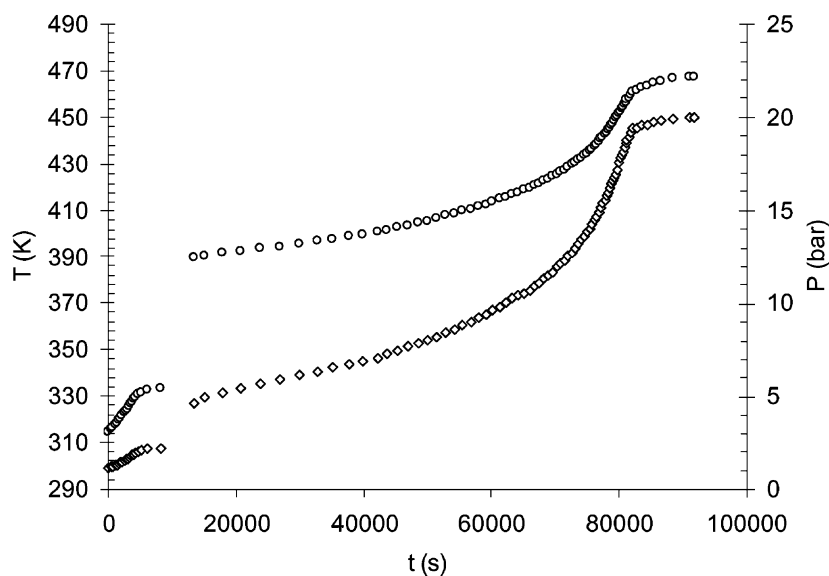


Fig. 4. Temperature (○) and pressure (◇) vs. time data obtained in an ARC adiabatic run performed on a $\text{Ac}_2\text{O}/\text{HNO}_3$ system with $R = 0.4$ (thermal inertia: $\Phi = 3.22$, sample mass: $m_s = 1.16$ g).

A similar behaviour has been observed during adiabatic ARC runs too (Fig. 4), thermal decomposition proceeding through two exothermic steps.

It is noteworthy to observe that also a mixture of acetic and nitric acid shows the occurrence of an exothermic peak during a scanning run in the temperature range 423–543 K (see Fig. 3). This result suggests that this exothermic event could be ascribed for all the investigated mixtures to the oxidation of organic compounds present in the solution by means of nitric acid.

To throw light on the reaction network through which the thermal decomposition of the $\text{Ac}_2\text{O}/\text{HNO}_3$ system develops, chemical analyses were performed on liquid and gaseous samples, at the end of the first exothermic event in experimental runs performed starting from different initial $\text{Ac}_2\text{O}/\text{HNO}_3$ molar ratios. Gaseous samples collected after cooling the reactor were composed almost exclusively of CO_2 .

The results of the analyses of liquid samples are reported in Table 2.

Table 2

System composition and tetranitromethane yield obtained at the end of the first exothermic peak during Radex scanning runs^a

R	$n_{\text{Ac}_2\text{O}}^0$ (moles)	$n_{\text{C}(\text{NO}_2)_4}$ (moles)	$n_{\text{C}(\text{NO}_2)_4}/n_{\text{Ac}_2\text{O}}^0$
0.2	2.93×10^{-3}	0	0
0.4	3.79×10^{-3}	1.37×10^{-3}	0.360
0.5	4.04×10^{-3}	2.22×10^{-3}	0.550

^a Tetranitromethane is reported as converted moles of acetic anhydride.

$$\frac{d}{dt}[\text{HNO}_3] = -k_1[\text{AcONO}_2] - 2k_2[\text{AcONO}_2][\text{HNO}_3] \quad (3)$$

along with a thermal balance equation in adiabatic conditions

$$\left(\Phi \frac{m \times c_p}{V}\right) \frac{dT}{dt} = -k_1[\text{AcONO}_2](-\Delta H_1) - k_2[\text{AcONO}_2][\text{HNO}_3](-\Delta H_2) \quad (4)$$

with m and V respectively the mass and the volume of the reacting solution, $c_p = 2.09 \text{ J mol}^{-1} \text{ K}^{-1}$ the specific heat of the sample and Φ the thermal inertia.

Moreover,

$$k_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)$$

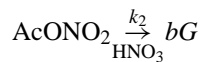
$$k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right)$$

$$[\text{AcONO}_2] = K_{\text{eq}} \frac{[\text{Ac}_2\text{O}][\text{HNO}_3]}{[\text{AcOH}]}$$

and for $t = 0$: $[\text{Ac}_2\text{O}] = [\text{Ac}_2\text{O}]_0$, $[\text{HNO}_3] = [\text{HNO}_3]_0$, $[\text{AcOH}] = [\text{AcOH}]_0$ and $T = T_0$.

The numerical integration of Eqs. (2–4) by means of a commercial software package (Matlab 5.3) [11] allowed the attainment of best estimated values for kinetic parameters A_1 , E_1 , A_2 , E_2 (Table 3), by comparing experimental and calculated results of the Runs 1–5 in a single optimization procedure (Fig. 5).

For a possible application of these results to real situations an attempt to model the reactor overpressurization has also been made. For this purpose, Reaction 2 has been lumped as



with G being a gaseous pseudo-component. Since for $R = 0.2$, at the end of the first exothermic event in the scanning runs, a residual pressure of 2.50 bar was recorded at 293 K, the coefficient “ b ” has been calculated by assuming an ideal behaviour for gaseous pseudo-component

$$b = \frac{n_G}{n_{\text{Ac}_2\text{O}}} \approx 0.1$$

where $n_{\text{Ac}_2\text{O}} = 2.92 \times 10^{-3} \text{ mol}$ are the converted moles of acetic anhydride. The model developed above was revised to account for the increase of the pressure in the reactor due to the formation of gaseous compounds. The total pressure was thus calculated by taking

Table 3

Best estimated parameter obtained by fitting all experimental adiabatic data points (Runs 1–5 in Table 1) by using the proposed mathematical model

A_1 (s^{-1})	E_1 (kJ mol^{-1})	A_2 ($\text{l mol}^{-1} \text{s}^{-1}$)	E_2 (kJ mol^{-1})
$4.37 \pm 0.833 \cdot 10^{+14}$	120 ± 0.837	$3.43 \pm 1.00 \times 10^{+15}$	127 ± 1.67

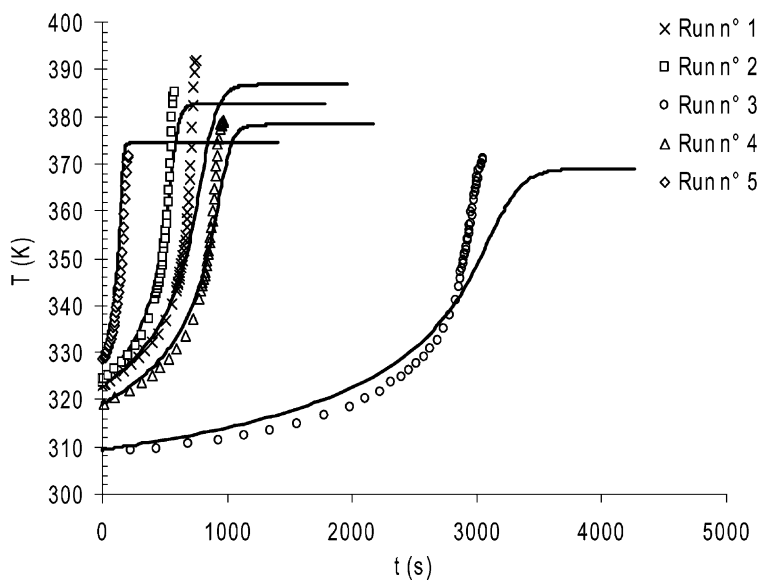


Fig. 5. Experimental adiabatic Temperatures versus time (Phi-Tec Runs 1–5) and calculated curves obtained using the proposed mathematical model with the parameters reported in Table 3.

into account the contribution of formed gases and the vapor pressure of the liquid solution present in the reactor

$$P = P^0 + RT \left(\frac{n_G + V_L [C(\text{NO}_2)_4]}{V_G} \right)$$

where: P^0 is the vapor pressure of the liquid mixture at temperature T (see Fig. 6) and V_L its volume, V_G is the volume of the gas phase and $[C(\text{NO}_2)_4]$ the molar concentration of tetranitromethane in the liquid phase. The values of V_L and V_G for considered runs are reported in Table 4.

In a first simplified approach the latter contribution is accounted for by empirical polynomial expressions previously determined on the basis of experimental results on acetic–nitric acid solutions (Fig. 6).

In Fig. 7 some examples of comparison between calculated and experimental pressure profiles are shown. These results indicate that the developed model overestimates the final pressure in the reactor.

Table 4
Volumes of liquid mixture and gas phase for the runs considered for the pressure calculation

Run number	R	V_L (l)	V_G (l)
2	0.4	40.6×10^{-3}	31.8×10^{-3}
5	0.2	49.9×10^{-3}	22.5×10^{-3}

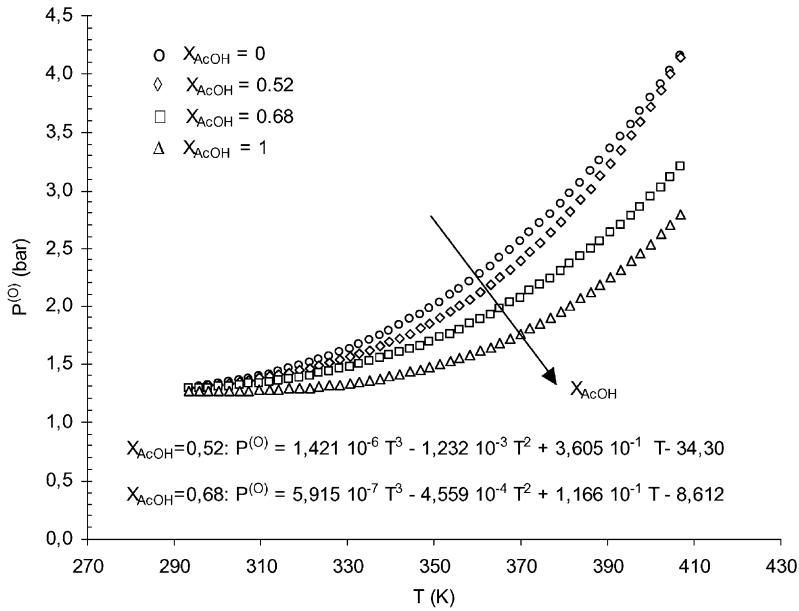


Fig. 6. Vapor pressure of different AcOH/HNO₃ systems. The curves have been parametrised with respect to the molar fraction of the acetic acid (X_{AcOH}).

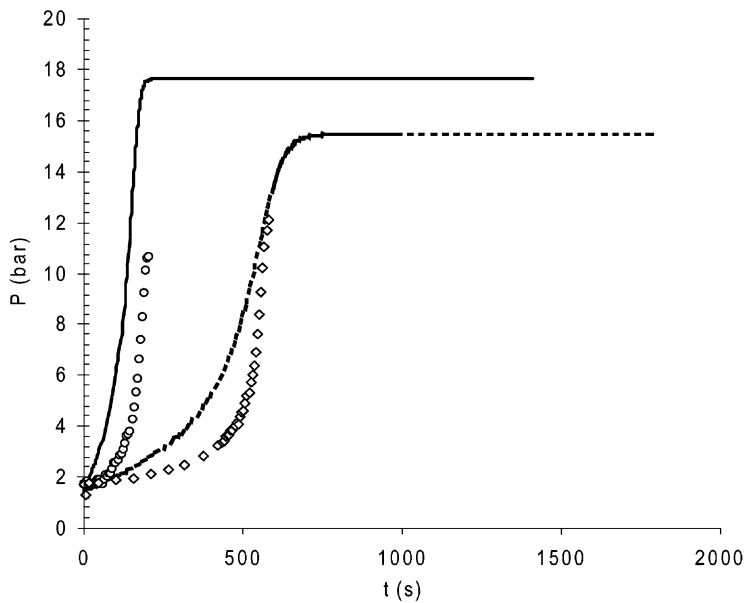


Fig. 7. Experimental pressure coming from adiabatic Phi-Tec tests ($R = 0.2$ (\circ), $R = 0.4$ (\diamond)) compared with those calculated by using the mathematical model ($R = 0.2$ (—); $R=0.4$ (---)).

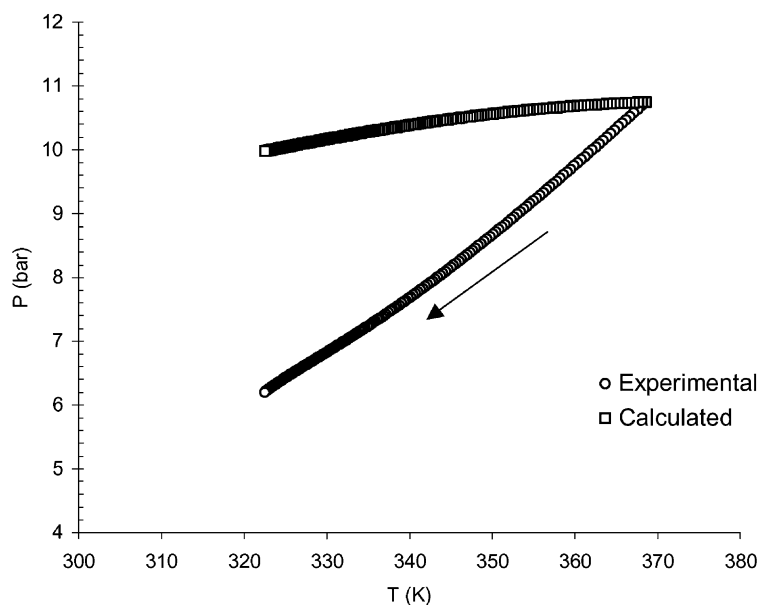


Fig. 8. Cooling curves for an adiabatic Phi-Tec run performed on a system $\text{Ac}_2\text{O}/\text{HNO}_3$ with $R = 0.2$. (○) Experimental, (□) Calculated.

The reason for this discrepancy could be ascribed to some limitations of the model itself as that of considering all reaction gaseous products to be released to the free space above the liquid. In fact some experimental evidence seems to suggest that evolved gaseous species could be partially absorbed in the liquid solution. In Fig. 8 the experimental pressure curve during the cooling of the reactor and that calculated by subtracting from the final pressure the vapour contribution and correcting for the temperature are reported. The experimental curve lies always below the calculated data points, thus indicating a tendency of the liquid absorbing some gaseous compounds.

4. Conclusions

The behaviour of $\text{Ac}_2\text{O}/\text{HNO}_3$ mixtures of different initial molar ratios has been studied by means of adiabatic and scanning calorimetry. These mixtures have been proved to undergo thermal decomposition with the development of large amounts of gases. A simplified kinetic model has been developed and used to simulate the decomposition of investigated mixtures under adiabatic conditions. The model, based on two lumped reactions, gives satisfactory results when used to predict the temperature profiles in the reactor whereas calculated pressures are overestimated due to some model inadequacies to account for the absorption of gaseous decomposition products into the reacting solution.

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