Acetic Anhydride Hydrolysis at High Acetic Anhydride to Water Ratios

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ABSTRACT: The hydrolysis of acetic anhydride in the presence of water is an exothermic reaction that produces acetic acid. Most of the research has focused on low ratios of acetic anhydride to water. The major concern in the industry is the accidental addition of a small amount of water to large quantities of acetic anhydride stored in tanks, or as handled in a manufacturing process. This paper focuses on isothermal and adiabatic experiments that were conducted to understand the effect and rate of hydrolysis at high ratios of acetic anhydride to water. The acetic acid produced in the reaction also affects the rate of reaction. Detailed calorimetric data and specific rate expressions that have been developed are presented in this paper. © 2014 Wiley Periodicals, Inc. Int J Chem Kinet 46: 151–160, 2014

INTRODUCTION

In industrial facilities handling acetic anhydride (Ac_2O), the inadvertent addition of water (H_2O) to a tank containing acetic anhydride is a significant safety risk. The reaction of acetic anhydride and water produces acetic acid (AcOH) and releases heat. Pressure generated by the vapor pressure of the hot material can lead to vessel rupture and release of the vapors that are flammable and toxic.

The reaction of acetic anhydride with water to give acetic acid has been studied by a number of authors. Because most of the work on this reaction has been done in a large excess of water, most of the authors describe the reaction rate as pseudo-first order in acetic anhydride [1–12] although a few describe it as overall second order; first order in acetic anhydride and first order in water [8,13,14]. Very few data have been reported for systems at high acetic anhydride to water ratios, but it suggests that the reaction rate in concentrated acetic anhydride is slower than in dilute systems [8].

The response in the presence of acetic acid either present in the acetic anhydride or formed by the reaction must also be considered. Different authors have reported different effects of acetic acid [5]. In some cases, acetic acid slowed the reaction, whereas in others, it increased the observed reaction rate. Golding and Dussault's [5] results showed that in dilute acetic anhydride solutions (Ac_2O–water weight ratio < 0.2), acetic acid slowed the reaction slightly. Orton and Jones [8] showed that increasing the acetic acid concentration from 50 wt% to 97 wt% results in a reduction in the reaction rate constant (Ac_2O–water weight ratio varying from 0.25 to 0.015).

Various techniques have been used to measure the rate of the acetic anhydride hydrolysis reaction. Glasser and Williams [4] used an isothermal calorimetric

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technique to determine the extent of reaction versus time. Shatynski and Hanesian [9] used adiabatic calorimetry to collect rate data on the reaction. The isothermal methods give data for only one temperature per experiment. However, they allow for the examination of any other changes with extent of the reaction such as acetic-acid formation. The adiabatic experiments give data on rate versus a number of temperatures in each experiment. However, any impact of other effects is lumped together with the impact of temperature. In this work, both isothermal experiments and adiabatic experiments were conducted.

EXPERIMENTAL

Isothermal experiments were conducted in a Mettler RC-1 Reaction Calorimeter (Mettler-Toledo AG, Schwerzenbach, Switzerland). The glass MP10 Mettler reactor with a nominal 1-L volume was used in the experiments. The RC-1 comprises a controlled jacketed reactor, an electrical immersion calibration heater, an agitator, thermocouples, and a temperature-controlled, positive displacement ISCO pump (Teledyne Isco, Lincoln, NE, USA) used for the injection of reactants. The stirrer was used and operated at 200 rpm. A temperature-controlled heat-transfer oil is circulated through the jacket of the reactor. The oil temperature is controlled to maintain the desired temperature of the sample in the reactor. The RC-1 constantly measures the difference between the reactor sample temperature, T_r, and the jacket temperature, T_j. The heat-transfer coefficient between the reactor contents and the jacket, U, is determined by calibrations using an electrical immersion heater. The heat capacity, C_p, of the reactor contents is determined from a temperature ramp. The calibrations and C_p determinations are done at the beginning and end of each experiment. The heat transfer surface, S, is determined from the reactor geometry and the liquid level in the reactor. The heat-generation rate at any time can then be calculated from

$$Q_t = \mathrm{U} \times \mathrm{S} \times (T_r - T_j) \tag{1}$$

In the tests, the acetic anhydride and acetic acid were charged to the reactor and brought to the desired temperature after the standard calibrations were done. Deionized water was placed in a temperature-controlled ISCO pump. At the start of the reaction, the total amount of water was quickly injected into the reactor by the ISCO pump. The reaction was then allowed to proceed to completion while the data were collected. After the reaction was complete, the final calibrations to determine U and the final C_p were done.

Adiabatic experiments were conducted in the Fauske Vent Sizing Package (VSP2) reactor [15] (Fauske and Associates LLC, Burr Ridge, IL, USA). The VSP2 consists of a thin-walled reaction vessel (test cell) of a nominal 0.12-L volume. The test cells used for this work were 304 SS weighing about 38 g each. The test cell is located inside a heavy-wall containment vessel. High-pressure N_2 is introduced into the containment vessel so that the pressure difference between the test cell and the containment vessel is minimized to avoid damage to the test cell from overpressurization. This prevents the thin-walled test cell from bursting if high pressure is developed during a reaction. A heater outside the lower portion of the test cell is used to raise the sample temperature during the test. A second guard heater surrounds the test cell and keeps the surroundings at the same temperature as the test cell so that adiabatic conditions are maintained during the test. A magnetic stirrer is used to provide agitation during the reaction.

In the adiabatic experiments, the acetic anhydride and acetic acid were charged to the test cell. The test cell was placed into the containment vessel and the containment vessel was sealed. The test cell was then brought to the desired starting temperature. Tubing that passed through the containment vessel wall allowed for the introduction of water to the test cell. At the start of the experiment, the water was quickly injected into the test cell and the valve in the tubing was closed. An effort was made to heat the water before injection but its temperature was lower than the test cell temperature for the higher-temperature experiments.

The acetic anhydride and glacial acetic acid used in the tests was obtained from Sigma–Aldrich (St. Louis, MO, USA). The acetic anhydride purity was stated to be 99.5%. Water used in the tests was deionized.

RESULTS AND DISCUSSION

Isothermal Experiments

The RC-1 calorimeter was used for the isothermal experiments. The RC-1 calculates the rate of heat release from the reaction from Eq. (1). The reaction rate at time t can then be calculated from

$$\mathrm{Rate}_t = Q_t/\Delta \mathrm{H}_{rxn} \tag{2}$$

The extent of the reaction at any time can be determined by comparing the heat released up to that time to the total heat release for the reaction:

$$\mathrm{X}_t = \mathrm{H}_t/\Delta \mathrm{H}_{rxn} \tag{3}$$

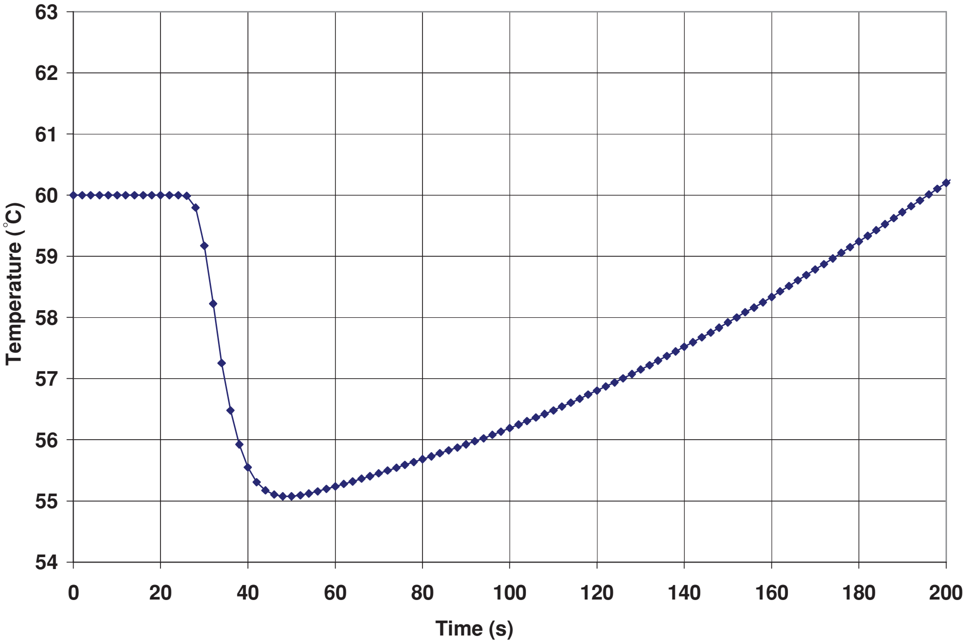

Figure 1 Change in temperature due to significant endothermic heat of mixing seen when adding 1.96 wt% water to acetic anhydride at 60 °C. Heat of hydrolysis and the calorimeter controls quickly return the temperature to 60 °C.

Upon addition of water to the acetic anhydride, a significant endothermic heat of mixing was observed. In the isothermal experiments, the water was at the same temperature as the acetic anhydride when it was introduced. Figure 1 shows the temperature of the reaction mass immediately after the addition of 1.96 wt% water to acetic anhydride with no acetic acid added. The heat of mixing was not estimated separately from the total enthalpy change for the experiments. The measured enthalpy change at 30 °C was −55.9 kJ/mol; at 60 °C, it was −55.1 kJ/mol. Zogg et al. [11] reported a total enthalpy change of −60 kJ/mol at 25 °C and −57 kJ/mol at 55 °C. Visentin et al. [10] reported a total enthalpy change of −61 kJ/mol at 25 °C and −58 kJ/mol at 55 °C.

The solubility of water in acetic anhydride has been found to be 2 wt% at 20 °C [16]. The RC-1 experiments were carried out using a water concentration just below 2 wt% so as to ensure a single liquid phase in the reaction mass.

The RC-1 temperature control via the reactor jacket and the heat generated from the reaction quickly raised the temperature back to the desired level after the injection of the water. However, the temperature upset caused by the heat of mixing and the RC-1 control system's effort to return the temperature to the set point mean that the data during the very early portion cannot be used to determine reaction kinetics.

Toward the end of the reaction, the temperature difference between the jacket and the reaction mass becomes very small as the reaction slows. At some point, the difference is too small to be accurately measured and the data are not usable. Because of these issues at the beginning and the end of each experiment, only the data from about 5% conversion to about 80% conversion were used in determining kinetics for the reaction.

The reaction was taken to be overall second order; first order in acetic anhydride and first order in water:

$$\text{Rate} = k \times [H_2O] \times [Ac_2O] \tag{4}$$

The heat generation rate, Q, was determined by the RC-1 calorimeter for each data point. Equation (2) was then used to determine the rate at each data point. The concentration of water and acetic anhydride at each point was calculated from the starting concentrations and the extent of reaction from Eq. (3) as follows:

$$[H_2O] = [H_2O]_0 \times (1 - X_t) \tag{5}$$

$$[Ac_2O] = [Ac_2O]_0 - [H_2O]_0 \times X_t \tag{6}$$

The reaction rate constant, k, could then be calculated for each data point from Eq. (4).

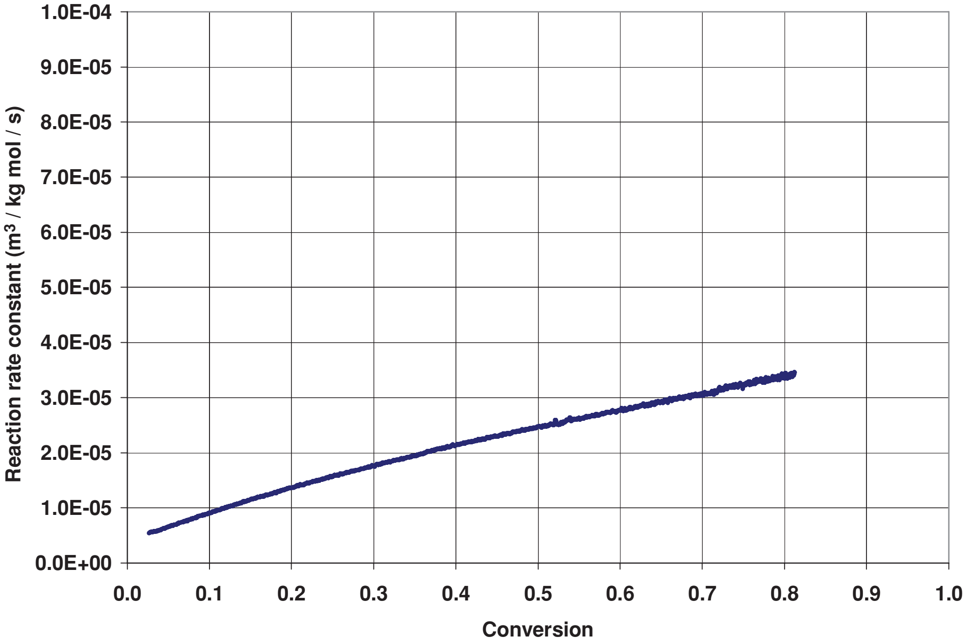

Figure 2 Change in reaction rate constant seen with increasing conversion for an Ac_2O–water ratio of 50:1 at 60 °C.

One experiment was conducted at 30 °C in an excess of water (0.1:1 Ac_2O–water weight ratio). Then three experiments at different temperatures were conducted at a 50:1 Ac_2O–water weight ratio. Figure 2 shows the reaction rate constant versus the conversion for the experiment at 60 °C and an Ac_2O–water weight ratio of 50:1.

Figure 2 shows the reaction rate constant changing as the reaction proceeds. In contrast to this result at the high Ac_2O–water ratio, Fig. 3 shows the rate constant versus conversion for the 0.1:1 Ac_2O–water experiment. While the reaction-rate constant changes with conversion at high Ac_2O–water ratio, it is constant at low Ac_2O–water ratio. The increase in the rate constant with conversion was also seen in the experiments with 50:1 Ac_2O–water at 30 °C and at 90 °C.

To determine the reaction-rate constant at the beginning of the experiment for the high Ac_2O–water cases (when acetic acid was zero), the rate constant versus the conversion curve was extrapolated back to zero conversion. The results are shown in Table I.

Figure 4 shows the results from the RC-1 experiments and compares them to some values found in the literature. The results of Asprey et al. [13] are shown as are the results of Glasser and Williams [4] and of Cleland and Wilhelm [3]. The results of Glasser and Williams [4] and of Cleland and Wilhelm [3] were published as first-order rate constants but were converted to second order by dividing by the water concentrations used in their experiments. Also shown is the result for a higher Ac_2O–water ratio experiment reported by Orton and Jones [8].

The comparison shows that the present work at low Ac_2O–water ratio agrees well with the other results at low ratios. The reaction-rate constants at high Ac_2O–water ratios are clearly smaller than those at low ratios.

Plotting ln(k) versus 1/T for the 50:1 Ac_2O–water ratios using the initial values at zero acetic acid concentration, and fitting the points by least squares gives an Arrhenius expression for the reaction rate constant:

$$k = 827.079\,\mathrm{m}^3/\mathrm{kg}-\mathrm{mol/sec} \times \exp\left(-52{,}886\,\mathrm{J/mol/R/T}\right) \qquad (7)$$

The activation energy determined from these tests, 52,886 J/mol, is larger than the values reported by Glasser and Williams [4] (45,187 J/mol), Cleland and Wilhelms [3] (44,392 J/mol), and Asprey et al. [13] (45,606 J/mol). However, Haji and Erkey [17] reported an activation energy of 53,408 J/mol, and Ramaswamy et al. [18] reported the activation energy to fall in the range of 53,100 to 54,000 J/mol. Golding and Dussault [5] suggested that the activation energy increases with increasing the acetic anhydride concentration, although no reason was given for this. The data shown in Table II seem to support their assertion.

It was proposed that the acetic acid formed in the reaction was catalyzing the reaction leading to the

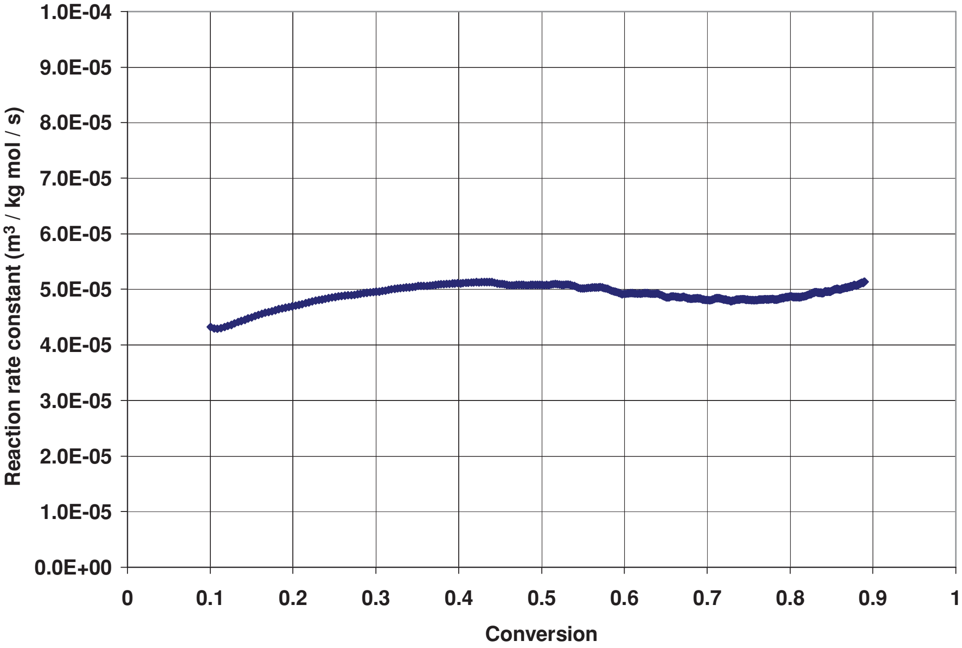

Figure 3 Change in reaction rate constant seen with increasing conversion for an Ac_2O–water weight ratio of 0.1:1 at 30 °C

Table I Initial Reaction Rate Constants for the Ac_2O + Water Reaction

Ac_2O–Water Weight Ratio	Temperature (°C)	k (m^3/kg-mol/s)
0.1:1	30	4.68E-05
50:1	30	6.50E-07
50:1	60	4.05E-06
50:1	90	2.09E-05

increase in the reaction-rate constant versus the conversion shown in Fig. 2. To test this, additional experiments were conducted in the RC-1 with acetic acid added to the acetic anhydride before the water was added. The results of these experiments extrapolated back to the initial acetic acid concentrations are shown in Table III. These results confirm that the reaction is catalyzed by acetic acid at large Ac_2O–water ratios. The work by Orton and Jones [8] and by Golding and

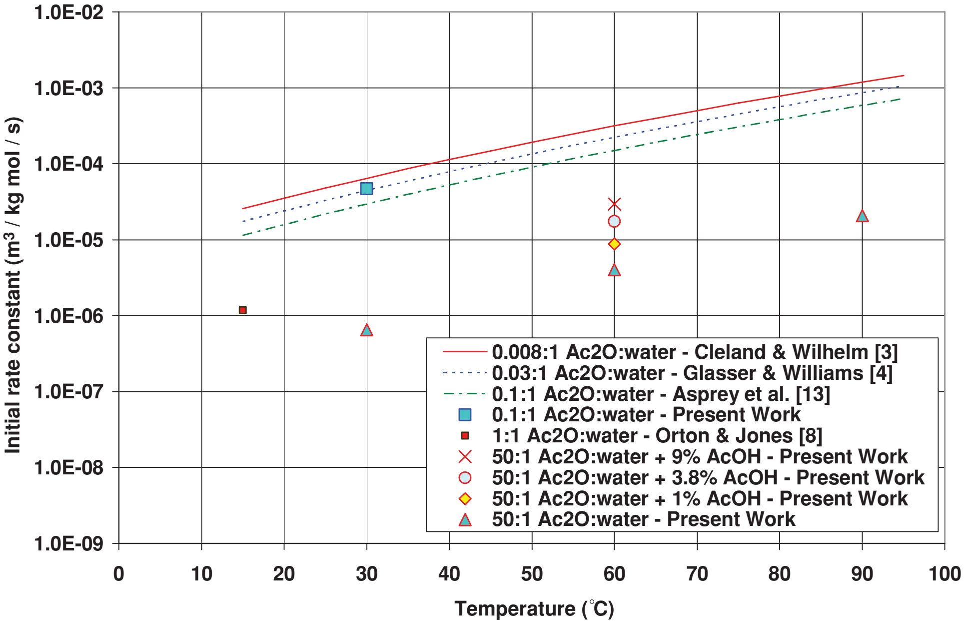

Figure 4 Comparison of literature results for initial reaction rate constants to the values determined in current work.

Table II Activation Energy and Acetic Anhydride Concentration

Ac_2O Concentration (mol/L)	Ac_2O–Water Weight Ratio	Activation Energy (kJ/mol)	Reference
0.02	0.002	42.95	8
0.075	0.008	46.09	3
0.25	0.03	49.44	4
0.66	0.07	53.408	6
1.0	0.1	45.606	13
8.3	5.1	53.6	18
10.1	50	52.886	Current Work

Table III Initial Reaction Rate Constants When Water Is Added to Ac_2O in the Presence of Acetic Acid

Ac_2O–Water Weight Ratio	Acetic Acid (wt%)	Temperature (°C)	k (m^3/kg-mol/s)
50:1	0	60	4.05E-06
50:1	1	60	8.80E-06
50:1	3.8	60	1.75E-05
50:1	9.0	60	2.95E-05

Dussault [5] show the rate slowing with acetic acid but their experiments were done in a large excess of water.

An autocatalytic reaction can be expressed as two reactions: catalyzed and not catalyzed. In the current case, these reactions can be written shown in Eqs. (8) and (9) as

$$Ac_2O + H_2O \rightarrow 2AcOH \tag{8}$$

$$Ac_2O + H_2O + AcOH \rightarrow 3AcOH \tag{9}$$

The rate expression for the reaction of Eq. (8) was shown above in Eq. (4). The rate expression for Eq. (9) is

$$\mathrm{Rate}_{\mathrm{catalyzed}} = k' \times [H_2O] \times [Ac_2O] \times [AcOH]^{\mathrm{n}} \tag{10}$$

where [AcOH] is the acetic-acid concentration at the given time (not the initial value).

The net reaction rate is then given as

$$\begin{aligned}\mathrm{Rate} = k \times [H_2O] \\ \times [Ac_2O] + k' \times [H_2O] \\ \times [Ac_2O] \times [AcOH]^n\end{aligned} \tag{11}$$

which can be rewritten as

$$\mathrm{Rate} = k'' \times [H_2O] \times [Ac_2O] \tag{12}$$

where

$$k'' = (k + k' \times [AcOH]^n) \tag{13}$$

The acetic-acid concentration can be calculated throughout the course of the reaction based on the conversion. The reaction-rate constants calculated for the data can then be plotted as a function of the acetic-acid concentration (Fig. 5). The plot shows good agreement between the various runs at 60 °C.

Data from the RC-1 experiments at 30 °C and 90 °C combined with the data from the 60 °C experiments allow for determining the value of k' and n in Eq. (11). A value of 0.85 was found to be the best average value for n and k' is given by

$$\begin{aligned}k' = 7465\,(\mathrm{m}^3/\mathrm{kg} - \mathrm{mol})^{0.85}/\mathrm{sec} \\ \times \exp(-55{,}342\,\mathrm{J/mol/R/T})\end{aligned} \tag{14}$$

where k′ has units of $(m^3/kg\text{-}mol)^{0.85}/s$. Thus, the value of k″ for a 50:1 Ac_2O–water weight ratio is

$$\begin{aligned}\mathrm{k}'' = (827.079\,\mathrm{m}^3/\mathrm{kg} - \mathrm{mol/sec} \\ \times \exp(-52{,}886\,\mathrm{J/mol/R/T}) \\ + 7465\,(\mathrm{m}^3/\mathrm{kg} - \mathrm{mol})^{0.85}/\mathrm{sec} \\ \times \exp(-55{,}342\,\mathrm{J/mol/R/T}) \\ \times [\mathrm{AcOH\ kgmol/m}^3]^{0.85})\end{aligned} \tag{15}$$

Figure 6 shows a comparison of the value of k″ calculated from the RC-1 experiments and the fit from Eq. (15).

Adiabatic Experiments

Adiabatic VSP2 experiments were conducted at 3:1 and 19:1 Ac_2O–water ratios. The adiabatic experiments were conducted at higher water ratios which would lead to two liquid phases in the reaction mass. These experiments combine the effects of changing

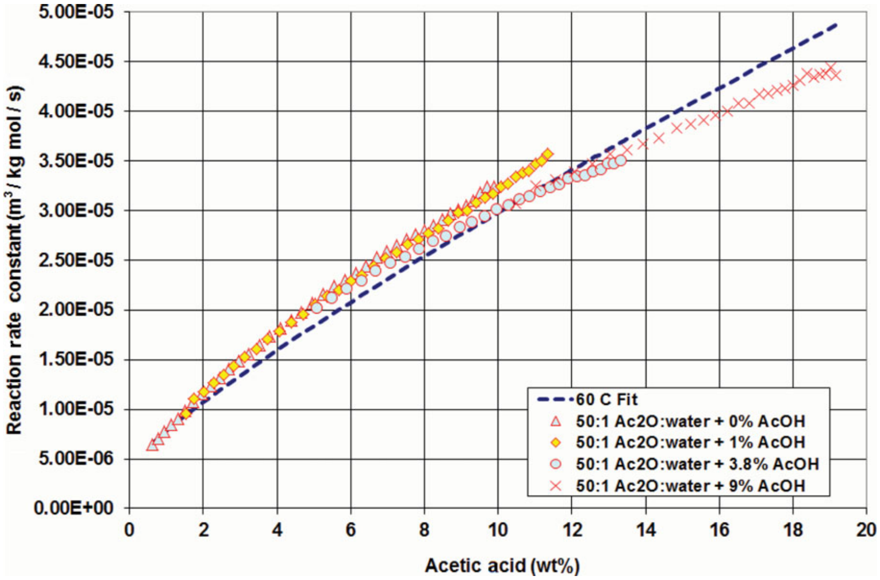

Figure 5 Reaction rate constant vs. acetic acid concentration for four experiments at 60 °C. The rate constant calculated from Eq. (15) is also shown.

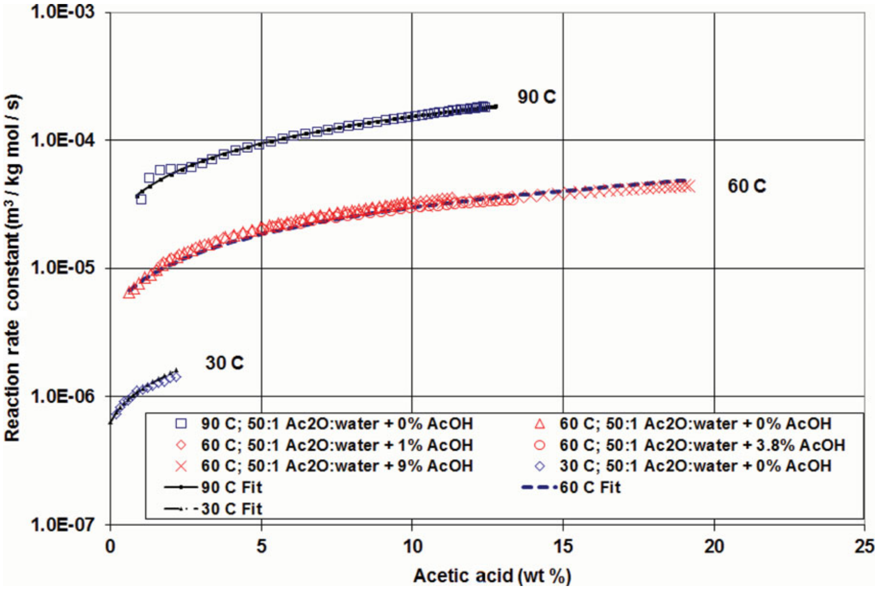

Figure 6 Predicted values of k″ using Eq. (15) vs. measured data from the RC-1 experiments.

solubilities, composition, and temperature as one might expect to see in a large-scale reaction (for example an Ac_2O storage tank accidentally charged with water). In all of the adiabatic experiments, the acetic anhydride contained 1 wt% acetic acid at the start of the experiment.

The rate of the reaction can be related to the temperature-rise rate measured by the VSP instrument:

$$\mathrm{d}X/\mathrm{d}t = \mathrm{d}T/\mathrm{d}t/\Delta T_a \tag{16}$$

The conversion at any temperature can be calculated from

$$X_T = (T - T_0)/\Delta T_a \tag{17}$$

The water and acetic anhydride concentrations can then be calculated from Eqs. (5) and (6). The reaction rate constant at each data point can then be calculated

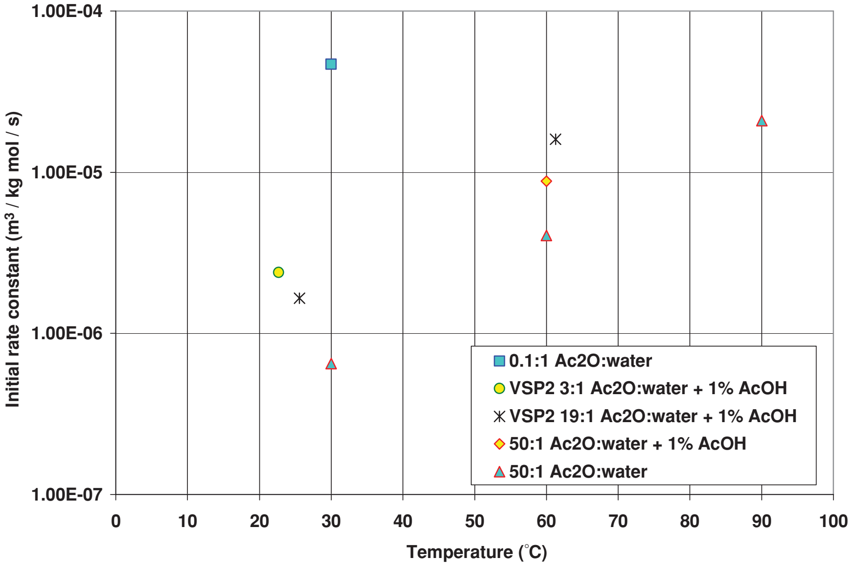

Figure 7 Initial reaction rate constants for the adiabatic experiments at a 19:1 and a 3:1 Ac_2O–water ratio and for isothermal experiments at 50:1 and 0.1:1 Ac_2O–water ratios.

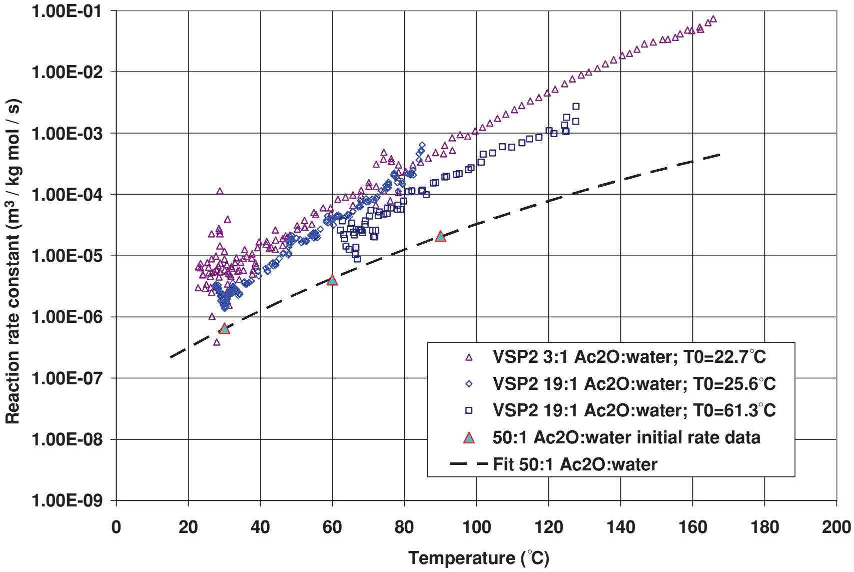

Figure 8 Reaction rate constants for the adiabatic experiments at a 19:1 and a 3:1 Ac_2O–water ratio as compared to the initial reaction rate constants (zero AcOH) for a 50:1 Ac_2O–water ratio.

from

$$dX/dt = k \times 1/[H_2O]_0 \times [H_2O] \times [Ac_2O] \tag{18}$$

Two adiabatic runs were made with an Ac_2O–water ratio of 19:1. One run started at 26 °C and the other at 61 °C. The rate constants at these initial temperatures (and, therefore, initial acetic acid concentrations) were calculated from the data and are shown in Fig. 7. An adiabatic run was also made at a 3:1 Ac_2O–water ratio. The initial reaction-rate constant for this run is also shown in Fig. 7. From these data, it is apparent that lower Ac_2O–water ratios give higher initial reaction-rate constants.

Figure 8 shows the reaction-rate constant versus the temperature from the adiabatic VSP2 runs compared

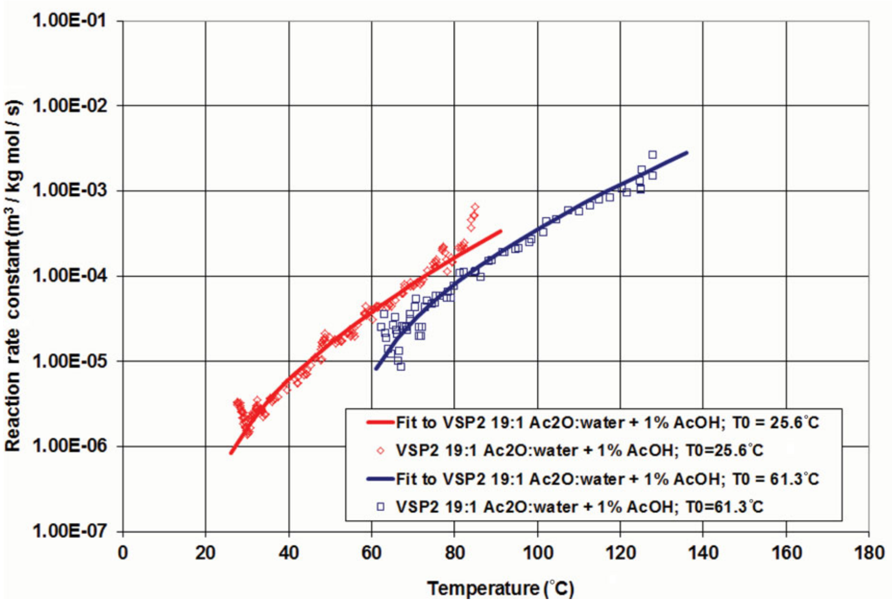

Figure 9 Reaction-rate constant calculated from Eq. (15) is compared with the values calculated for the adiabatic experiments at a 19:1 Ac_2O–water ratio with two different starting temperatures.

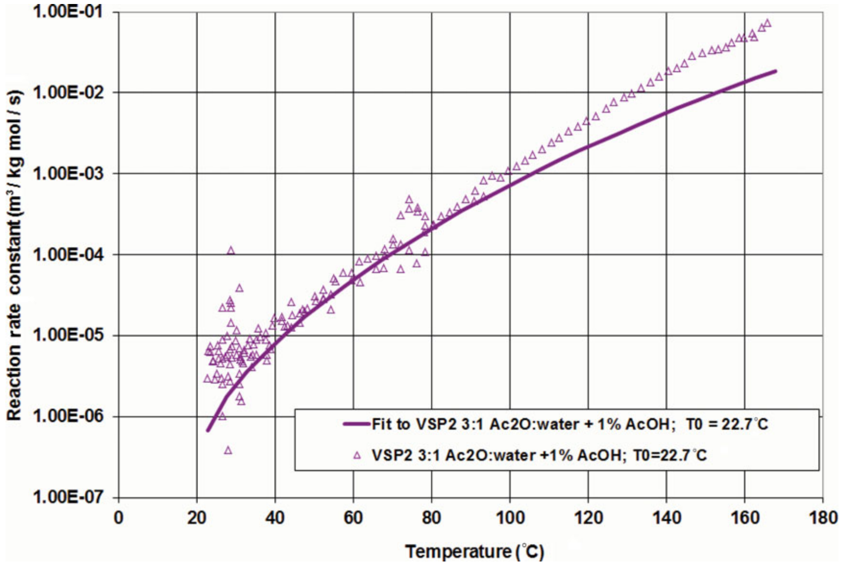

Figure 10 Reaction-rate constant calculated from Eq. (15) is compared with the values calculated for the adiabatic experiment at a 3:1 Ac_2O–water ratio.

to the data from the isothermal experiments. The increase in the rate constant with temperature seen for the adiabatic runs is higher than the change due to temperature from the isothermal runs. This may be due to the formation of acetic acid during the course of the reaction such that the acetic-acid concentration is increasing as the temperature increases. Because the reaction mass contains more water, it likely formed two phases during a portion of the experiment. It is possible that some of the increase in the apparent reaction-rate constant could also be attributed to the change in solubility of the two phases with temperature.

Reaction rate constants were calculated from Eq. (15) and are compared to the values from the VSP2 runs in Figs. 9 and 10. While Eq. (15) does not consider the lower initial Ac_2O–water ratio of the VSP2 runs or the impact of limited solubility, it gives a relatively good agreement for the VSP2 runs at a 19:1 Ac_2O–water ratio; the agreement for the 3:1 Ac_2O ratio run is not as good.

CONCLUSIONS

The rate of hydrolysis of acetic anhydride in the presence of water is strongly dependent on the ratios of acetic anhydride to water. Most of the previous research work has focused on the low acetic anhydride to water ratios. Detailed isothermal and adiabatic calorimetric experiments were conducted at high Ac_2O–water ratios and compared with results for the low Ac_2O–water ratios.

Specific rates for the reaction at 3:1, 19:1, and 50:1 ratios were determined. The effect of acetic acid on the reaction also depends on the Ac_2O–water ratio. At high ratios, acetic acid increases the reaction rate. At low ratios, it has little effect.

A rate expression describing the impact of the acetic acid on the rate constant at high Ac_2O–water ratios has been developed.

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