

ChE 411

Thermal Analysis of DMSO Decomposition under Acidic Conditions

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Introduction

Dimethyl Sulfoxide, or DMSO, has been used as an organic aprotic solvent in a variety of industrial settings. Although used due to its low toxicity relative to other solvents and high solubility, the use of DMSO presents many issues as well. DMSO undergoes a violent decomposition reaction near its boiling point of 189°C. This exothermic reaction has been known to heat up reactors beyond expected conditions and drastically increase pressure in a short time frame. The results can be catastrophic, and many incidents have occurred due to this phenomenon resulting in loss of life. ^[1]

Observations have shown that the thermal behavior of the decomposition of DMSO changes in the presence of contaminants. ^{[2][3][4]} This project analyzes the behavior of the DMSO decomposition under different amounts of acid contamination. Four acids with a wide range of pKa values are tested: Water, Methanol, Phenol, and Acetic Acid. Two equivalent ratios of DMSO to acid are tested: 9 to 1 and 5 to 1. In particular, it has been shown that a Linear Free Energy Relationship (LFER) exists between the onset temperature of the DMSO decomposition and the pKa of the acid being added to the DMSO. These experiments serve to explore this relationship and determine the effects of a higher acid concentration upon this LFER.

Methods

ARSST Usage ^[5]

The ARSST comes preloaded with multiple test modes: polynomial control, PID control, isothermal hold, multi-step heat and search, etc. The polynomial control method was utilized for these experiments. Multiple runs had issues with inability of the ARSST to heat the sample up to adequate decomposition temperatures due to incorrect equipment configuration. Therefore, most of the data was obtained using the 'create ramp polynomial and extrapolate' mode. This mode spends the first 60°C gauging the energy required to raise the sample 1°C. Using this data, a polynomial is created to reliably heat the sample at a constant temperature rise rate.

A test run is performed by loading the sample into the test cell with a stir bar, as shown in Figure (1).

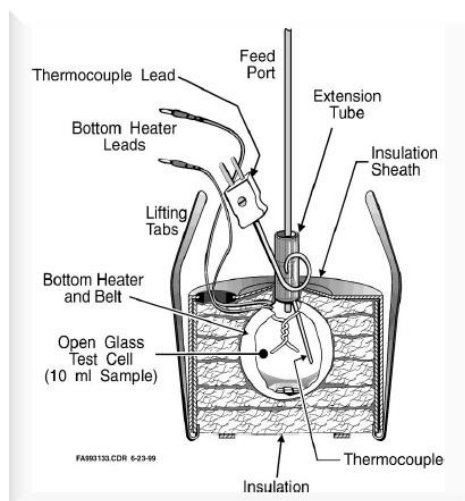


Figure (1): ARSST Test Cell Apparatus

Due to the corrosive nature of the acids being tested, the electrical components within the ARSST are coated with vacuum grease before being connected and are covered with electrical tape. Vacuum grease is also placed upon the outer rim of the lid of the ARSST to create a better seal to prevent loss of pressure over time. A high-pressure Nitrogen tank provides an inert atmosphere for the ARSST of up to 500psig. Each test is run with an initial backpressure of 300psig, preventing boiling of the solvent for a wider temperature range. The ARSST is placed upon a magnetic stir plate which stirs the stir bar within the 10 mL test cell.

Calculation of Onset Temperature [5]

The onset temperature is the temperature at which the heat generated by the contained reaction becomes detectable. In the case of the ARSST, the onset temperature is determined through extrapolation of the linear portion of the graph shown in Figure (2) down to a temperature rise rate of $0.1\text{ }^{\circ}\text{C min}^{-1}$. The graph below has a log scale for both the temperature rise rate and temperature axes.

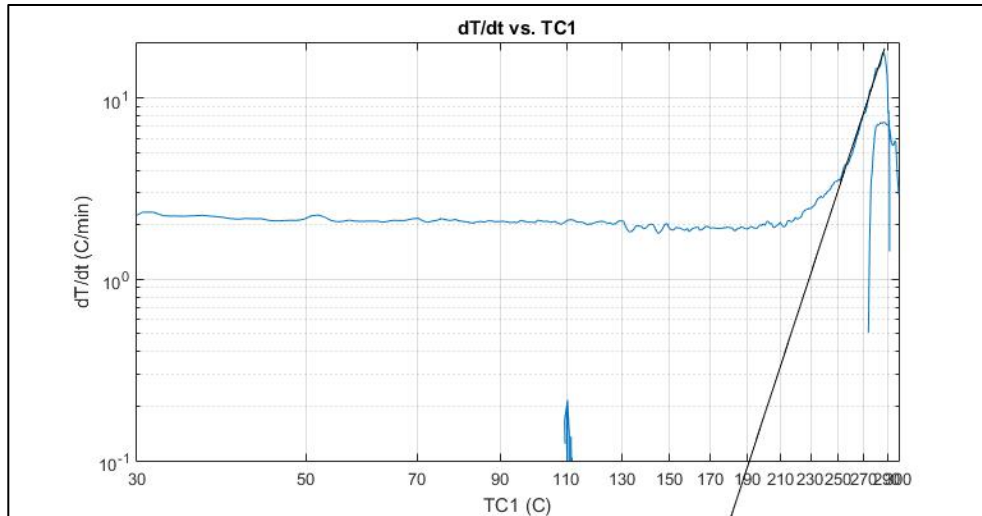


Figure (2): Onset Temperature Determination – Non-Fluctuating Data

While simple, this method of calculating the onset temperature relies on the data for the temperature rise rate being relatively smooth. In many cases, various factors, including improper thermocouple placement, slightly defective heat belts, and unexpected changes in heat capacity, can result in fluctuating temperature rise rate data, as shown below in Figure (3).

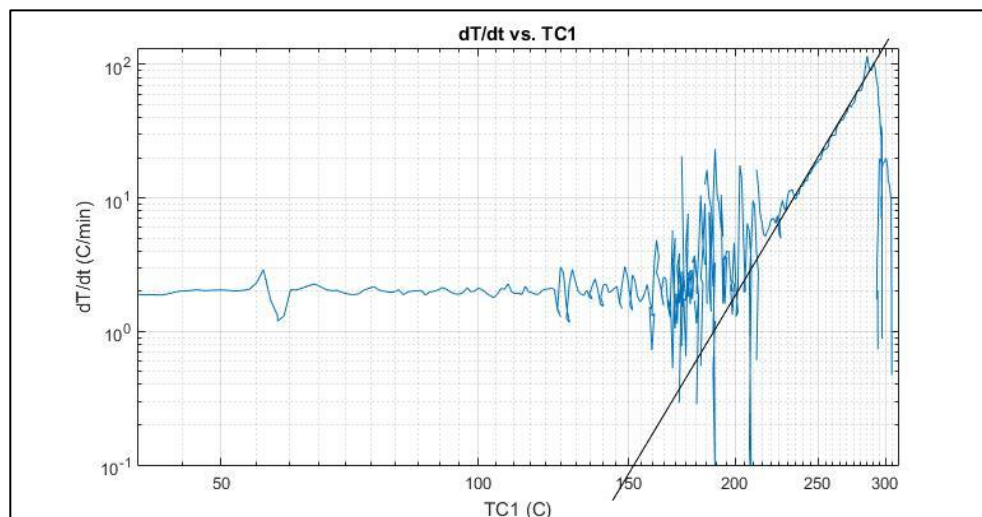


Figure (3): Onset Temperature Determination – Fluctuating Data

To combat the inherent inaccuracy of this method of onset temperature calculation, a program was created in Matlab utilizing the Method of Least Squares to more accurately calculate the onset temperature. This program finds the maximum temperature of the initial exothermic event and iterates through a range of temperature values before this maximum temperature to

determine the first data set which yields a line of best fit with an R^2 value greater than 0.98 through the temperature rise rate values. With this line, the onset temperature can be calculated without the influence of human error. Calculating the onset temperature in this manner decreases variance for similar reaction systems.

Calculation of Heat of Reaction ^[5]

The Heat of Reaction may be calculated using Equation (1) by knowing the phi factor of the system, the heat capacity of the sample, the adiabatic temperature rise, and the initial amounts of reagents placed within the test cell. In the case of the DMSO decomposition, it was assumed that the initial conversion of the reaction was 0.

$$\Delta H_R = \frac{-\phi C_s \Delta T_{AB}}{\frac{m}{m_T} (1 - X_0)} \quad (1)$$

Equation (2) describes the phi factor of the test apparatus. The phi factor of the system corresponds to the degree of adiabaticity of the test cell apparatus. The closer the phi factor is to a value of 1, the more adiabatic the system is. The ARSST utilizes a small 10 mL glass test cell within which the reagents are charged. Insulation is wrapped around the test cell to decrease the phi factor. The ARSST's strength lies in its test cell having a very small phi factor of between 1.02 and 1.10, depending upon the chemical being tested. Erroneous test results can be obtained if air is trapped within the insulation, as the phi factor of the system would be different than that calculated. The glass test cell used has a heat capacity of $0.2 \text{ cal g}^{-1} \text{ K}^{-1}$ and a mass of 1.45g. Table (1) list the heat capacities of the chemicals used.

Table (1): Heat Capacities of Selected Chemicals

| Compound | Heat Capacity ($\text{J g}^{-1} \text{ K}^{-1}$) |
|-------------|--|
| DMSO | 1.9122 |
| Water | 3.5838 |
| Methanol | 2.5281 |
| Phenol | 1.4300 |
| Acetic Acid | 2.1782 |

$$\phi = \frac{m_s C_s + m_b C_b}{m_s C_s} \quad (2)$$

With the masses added to the test cells and the heat capacities of these chemicals, the average heat capacity of the sample may be obtained with Equation (3).

$$C_s = \frac{m_{acid} C_{acid} + m_{DMSO} C_{DMSO}}{m_{acid} + m_{DMSO}} \quad (3)$$

The adiabatic temperature rise, ΔT_{AB} , describes the temperature rise detected within the system that is due to the reaction occurring rather than the external heating rate. Equation (4) can be used to calculate the adiabatic temperature rise, while Equation (5) calculates the temperature rise due to external heating.

$$\Delta T_{AB} = T_{max} - T_{onset} - \Delta T_{ext} \quad (4)$$

$$\Delta T_{ext} = \left(\frac{dT}{dt} \right)_{ext} (t_{max} - t_{onset}) \quad (5)$$

Calculation of E_a [6]

Following the methods prescribed by Townsend and Tou, the activation energy may be calculated using the pseudo rate constant in Equations (8) and (9). Kinetically, the rate constant is correlated to the temperature of the system according to Equation (6).

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

Equation (7) uses the temperature rise rate of the system as a method of calculating conversion and thus the rate of the reaction.

$$\frac{dT}{dt} = k \left(\frac{T_f - T}{\Delta T_{AB}} \right)^n \Delta T_{AB} C_0^{n-1} = k^* \left(\frac{T_f - T}{\Delta T_{AB}} \right)^n \Delta T_{AB} \quad (7)$$

$$k^* = k C_0^{n-1} = A C_0^{n-1} \exp\left(\frac{-E}{RT}\right) \quad (8)$$

Rearranging Equation (7) gives a useful way to calculate the pseudo-rate constant, given that the reaction order may be accurately obtained. Once k^* has been calculated, the activation energy can be obtained from the slope of Equation (10).

$$k^* = \frac{dT}{dt} \left(\frac{T_f - T}{\Delta T_{AB}} \right)^{-n} \Delta T_{AB}^{-1} \quad (9)$$

$$\ln(k^*) = \ln(C_0^{n-1}A) - \frac{E}{R} \left(\frac{1}{T} \right) \quad (10)$$

Results

Tests were performed using the ARSST with the specified acid and DMSO concentrations. Figure (4) and Figure (5) show the temperature and temperature rise rate data plotted against time for acids tested with a 9 to 1 molar ratio of DMSO to acid.

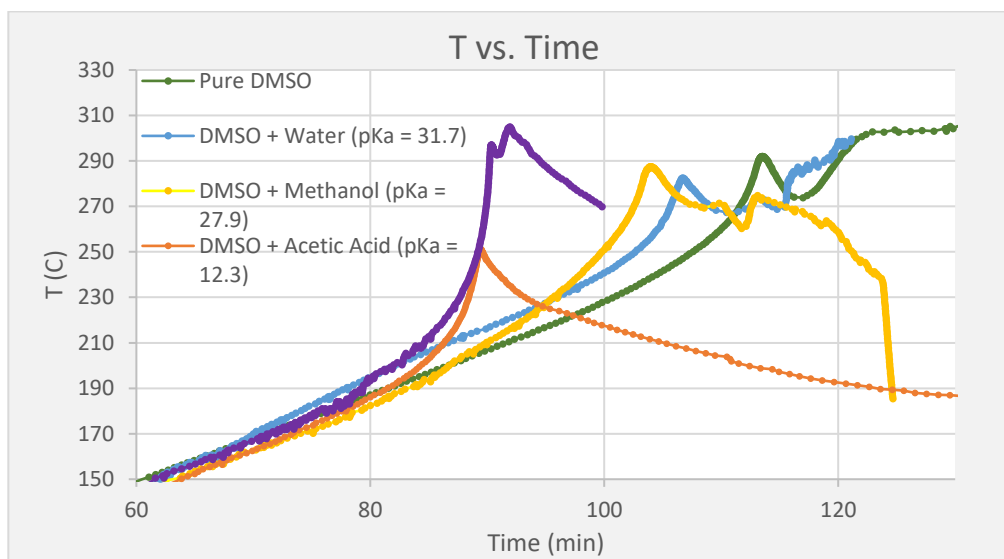


Figure (4): Temperature vs. Time Plot for 9 to 1 DMSO to Acid Molar Ratio

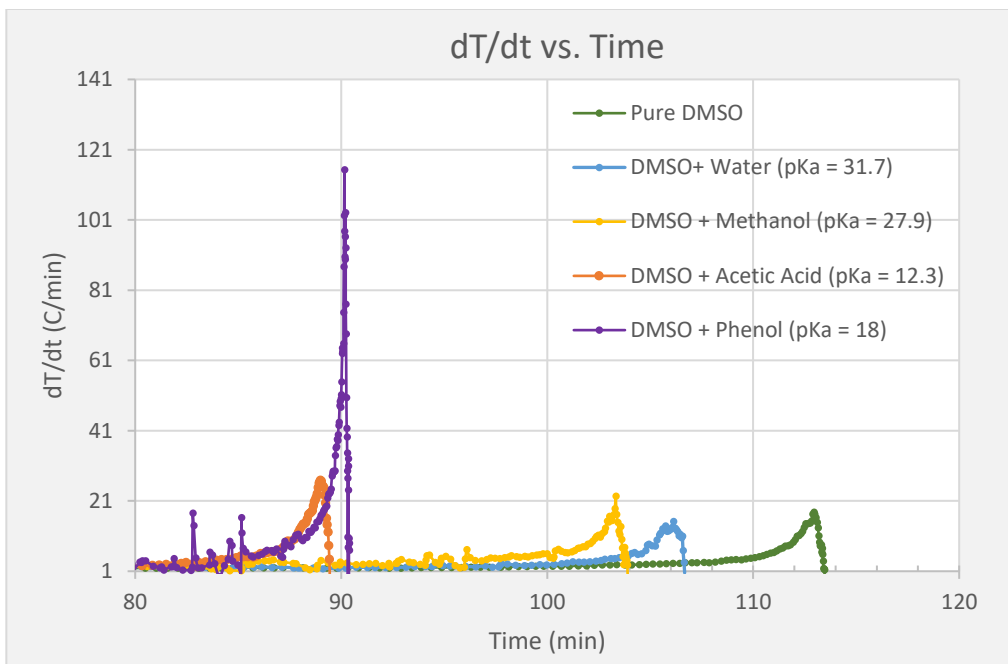


Figure (5): Temperature Rise Rate vs. Time Plot for 9 to 1 DMSO to Acid Molar Ratio

Likewise, Figure (7) Figure (6) show the same results for a 5 to 1 DMSO to acid molar ratio.

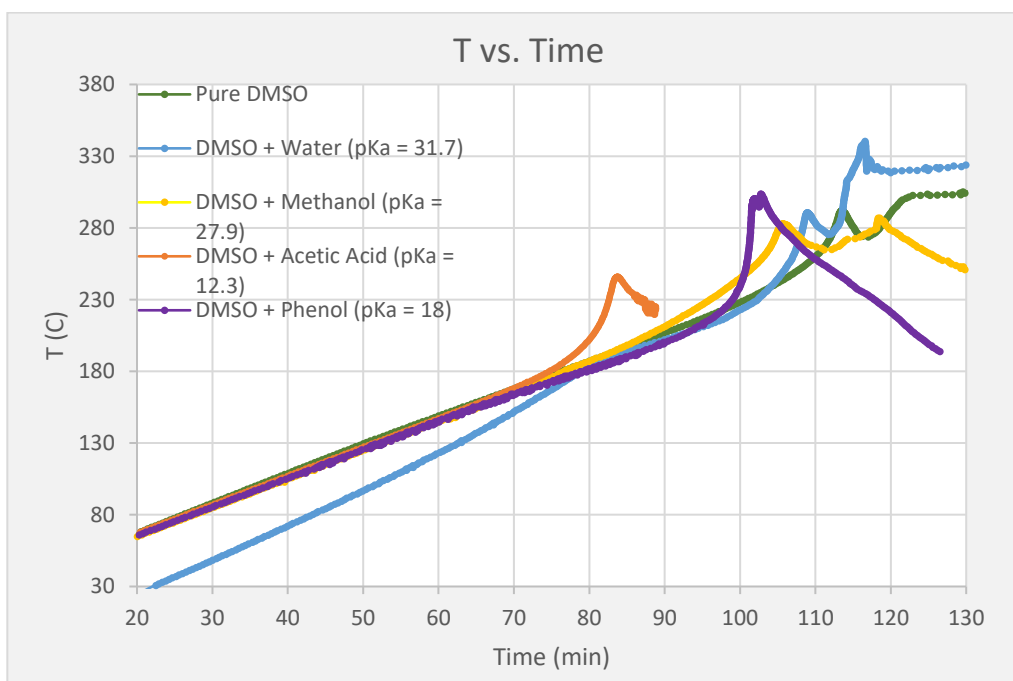


Figure (6): Temperature vs. Time Plot for 5 to 1 DMSO to Acid Molar Ratio

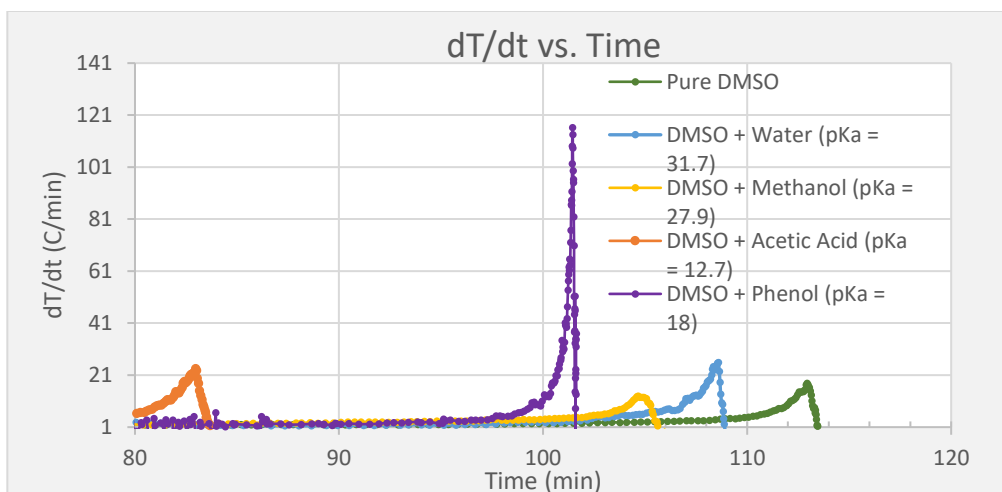


Figure (7): Temperature Rise Rate vs. Time Plot for 5 to 1 DMSO to Acid Molar Ratio

These figures illustrate the relative magnitudes of the exotherms detected upon DMSO decomposition as well as the time at which they occur relative to each other. As the pKa of the acid decreases, the time and temperature at which the exotherm occurs also decreases for both cases. The graphs of the temperature rise rate do not show a significant correlation between the pKa of the acid and the magnitude of the exotherm. However, it does appear to be true that most of the exothermic events with an acid yield higher temperature rise rates than the case with pure DMSO. In particular, the DMSO and phenol mixture shows a significant increase in the magnitude of the exothermic event. Table (2) and Table (3) summarize the results obtained by analyzing the data according to the equations given within the methods section.

Table (2): Thermal Properties of DMSO Decomposition at a 9 to 1 DMSO to Acid Ratio

| Compound | ϕ | pKa | T_{onset} (°C) | ΔT_{AB} (°C) | $\left(\frac{dT}{dt}\right)_{\text{max}}$ (°C) | E_a (kJ mole ⁻¹) 1) | $\Delta H_{\text{R}}^\circ$ (kJ mole ⁻¹) |
|-------------|--------|-------------------|----------------------------|--------------------------------|--|--------------------------------------|--|
| DMSO | 1.064 | 35 ⁽¹⁾ | 185.19 | 37.98 | 15.97 | 204.53 | -77.24 |
| Water | 1.057 | 31.7 | 189.00 | 35.34 | 13.93 | 230.39 | -74.83 |
| Methanol | 1.058 | 27.9 | 182.37 | 57.11 | 22.38 | 300.00 | -122.38 |
| Phenol | 1.060 | 18 | 154 | 37.24 | 115.36 | 173.8 | -83.02 |
| Acetic Acid | 1.057 | 12.3 | 135.36 | 50.3 | 26.88 | 161.12 | -111.47 |

⁽¹⁾: pKa value of 35 is not physically significant, but extrapolated

Table (3): Thermal Properties of DMSO Decomposition at a 5 to 1 DMSO to Acid Ratio

| Compound | ϕ | pKa | T _{onset} (°C) | ΔT_{AB} (°C) | $\left(\frac{dT}{dt}\right)_{max}$ (°C) | E _a (kJ mole ⁻¹) 1) | ΔH_{R^0} (kJ mole ⁻¹) |
|-------------|--------|-------------------|----------------------------|-------------------------|---|---|---|
| DMSO | 1.064 | 35 ⁽¹⁾ | 185.19 | 37.98 | 15.97 | 204.53 | -77.24 |
| Water | 1.061 | 31.7 | - ⁽²⁾ | - ⁽²⁾ | - ⁽²⁾ | - ⁽²⁾ | - ⁽²⁾ |
| Methanol | 1.058 | 27.9 | 181.03 | 44.35 | 13.05 | 302.88 | -99.48 |
| Phenol | 1.061 | 18 | 150 | 37.24 | 116.20 | 184.42 | -89.22 |
| Acetic Acid | 1.057 | 12.3 | 116.39 | 51.31 | 23.5 | 129.53 | -121.58 |

⁽¹⁾: pKa value of 35 is not physically significant, but extrapolated

⁽²⁾: Fluctuations in the temperature rise rate data give rise to an inaccurate onset temperature, which affects all further calculations

The low phi factor in the DMSO test case gives rise to a baseline onset temperature which is nearly the normal boiling point of DMSO, 189°C. ^{2]} As expected, the onset temperature of each reaction mixture decreases when both the pKa of the acid added decreases and when the concentration of the acid increases. Figure (8) illustrates this relationship. Some data points are emitted as erroneous temperature rise rate data gives an incorrect onset temperature.

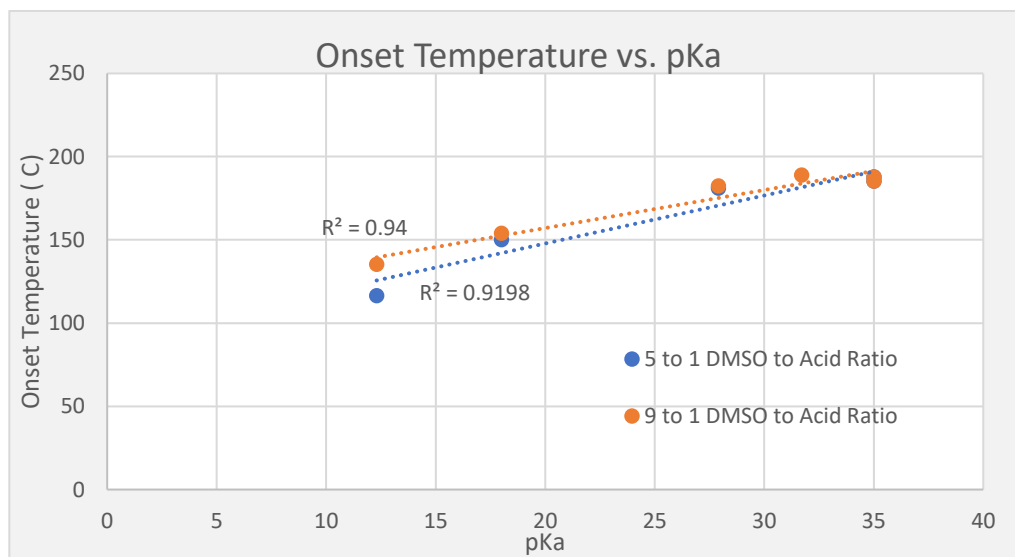


Figure (8): Onset Temperature vs. pKa Plot

In the case of the decomposition of the DMSO and water for the 5 to 1 ratio, the data was too unreliable to obtain an estimate for the onset temperature. This may be due to the escape of water from the liquid phase, despite the presence of a significant backpressure within the system. The results obtained for the water and DMSO reaction mixtures are, predictably, very similar to those of a pure DMSO system.

To obtain the activation energy, Equation (10) was plotted with the Least Squares Method, and the reaction order which yielded the best correlation was chosen. The data was plotted from the point at which the exotherm could be detected to the point at which the maximum temperature rise rate was reached. While this range of data gives a linear correlation, insufficient data is present to definitively obtain a reaction order, which significantly affects the activation order. The heat of reaction did increase in nearly every case where an acid was present. Although no perfect correlation is readily apparent, the increase in adiabatic temperature rise is likely the cause of the increased heat of reaction.

In conclusion, the presence of an acid during the decomposition of DMSO has significant effects upon the reaction kinetics. The onset temperature decreases in a linear fashion with respect to pKa, and more acidic conditions yield a lower onset temperature. The magnitude of the energy released during each exothermic event does not scale with the strength of the acid added but has a unique effect for each acid that was tested. The calculated activation energy displays a weak downward trend as acid strength increases. Similar studies have shown a strong trend between acid strength and activation energy for the DMSO decomposition. ^[7]

Future Work

To fully determine the relationship between acid strength and onset temperature of the DMSO decomposition, a wider range of acids needs to be tested. In addition, a wider range of acidic conditions, ranging from a 10:1 to a 2:1 molar ratio needs to be tested. These tests would allow determination of whether the Linear Free Energy Relationship breaks down at higher acidic concentrations. To more accurately determine the onset temperature, the multi-step heat and search mode could be used with the ARSST, gradually increasing the temperature until the reaction readily occurs. In addition, testing with a DSC could be performed to measure the

magnitude of the exothermic event detected upon DMSO decomposition under different acidic conditions.

References

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