The addition of an ammonium salt of a carboxylic acid to the oxirane ring of an epoxide such as glycidyl methacrylate is accompanied by many side reactions with water, hydroxide ions, and ammonia. The goal of this work was to determine the relative reaction rates of each of the possible reactions in order to put the esterification reaction in perspective with the side reactions. In performing this work, three experimental techniques were utilized, nuclear magnetic resonance, infrared, and calorimetry. The hydrolysis of GMA by water and ammonium hydroxide were first evaluated using the GEMINI 300 NMR of Varian, Inc. The reaction of isobutyric acid and its ammonium salt was followed by infrared using Applied Systems’ ReactIR infrared probe in conventional lab glassware. The reaction of isobutyric acid with GMA was finally studied using the METTLER TOLEDO Reactor Calorimeter RC1. Each tool showed its strengths and weaknesses. The NMR is excellent for determining the rates of reactions from the time development of the peak integrals, but is very time consuming. The infrared was excellent for determining the rates of reactions and also overcame the cumbersome-ness of the NMR in taking the data from peak measurements to reaction rates. The RC1 is excellent for determining the reaction rates, but gives no clue as to the identities of the reactants and products involved in the reaction. The ultimate tool for determining the reaction kinetics and product identification is the combination of the RC1 calorimeter with the ReactIR infrared probe. This combination allows redundant following of the rates of reactions, and gives the spectroscopic visualization of the molecular changes occurring during the reaction.

Keywords: Kinetics, hydrolysis, RC1, NMR, ReactIR, condensation, heat flow, Arrhenius plot.

Introduction

SC Johnson polymer manufactures acrylic latexes for use world-wide in the graphic arts, coatings, and adhesives businesses. In order to compete in the fast paced, highly competitive specialty markets, it is also a company interested in the preparation of specialty polymer products with a minimum expenditure in research effort with the maximum return of results from the research. To achieve the results necessary, the scientists and engineers need the right tools to do the right jobs. This requires having the best tools to describe the products and processes for optimization of the return on the research investment dollars.

The training in characterization of reactions and the reaction intermediates and products that is taught in academia does not focus on speed and accuracy, just accuracy. Therefore, using several different tools such as nuclear magnetic resonance, NMR, and infrared, IR, by tediously taking samples and acquiring tremendous amounts of data, most of which is superfluous, is of no concern when the answer to the problem is not needed for a few years. This training is the most important part of the academic experience, not necessarily the answer. In transition to the industrial environment, the speed and accuracy are both key to achieving the optimum product within the window of opportunity, so important in product launches and profitability for the corporation.

This paper is a story about this transition for SCJ Polymer in the investigation of addition of an acid functional compound to an epoxy functional moiety to test the speed and accuracy of the ability to fathom this reaction. This is not a new reaction by any means. It has been described in the literature long ago.
**Experimental**

**NMR Experimental Details**

*Water Hydrolysis*
A 0.2 g sample of GMA was weighed into 10.0 g of deuterated water. The sample was degassed and placed into the probe of the Varian Gemini 300 NMR spectrometer. The probe was heated to 80°C and the spectra were acquired.

*Ammonia Hydrolysis*
A 0.2 g sample of GMA was weighed into 10.0 g of deuterated water. One equivalent of ammonium deuteroxide, ND4OD, approximately 0.2 g, was added to the GMA solution. This sample was placed into the probe of the Varian Gemini 300 NMR spectrometer. The probe was heated to 80°C and the spectra were acquired.

**Infrared Experimental Details**

*Isobutyric Acid Reaction*
A 10.0 g sample of GMA was weighed into a four neck round bottom flask equipped with a stirrer, thermocouple, condensor, and infrared probe. The reactor contained 300.0 g of high purity water, Milli-Q water. One equivalent of isobutyric acid, IBA, approximately 10.0 g, was added to the GMA solution. The reactor and its contents were heated to 80°C and the infrared spectra were acquired automatically, every 2 minutes for a period of one hour.

*Ammonium Isobutyrate Reaction*
A 10.0 g sample of GMA was weighed into a four neck round bottom flask equipped with a stirrer, thermocouple, condensor, and infrared probe. The reactor contained 300.0 g of high purity water, Milli-Q water. One equivalent of isobutyric acid, IBA, approximately 10.0 g, and one equivalent of an aqueous ammonia solution were added to the GMA solution. The reactor and its contents were heated to 80°C and the infrared spectra were acquired automatically, every 2 minutes for a period of one hour.

**RC1 Experimental Details**

*Aqueous Hydrolysis*
The reaction of glycidyl methacrylate with water can undergo two reactions, hydrolysis of the ester and hydrolysis of the epoxy group. With the NMR, one can focus on the reaction of the oxirane by following the signals which are related to the epoxy function and its alcohol product. The NMR spectrum of the oxirane and alcohol are shown in figures 2 and 3, respectively. There are three peaks due to the epoxy group protons. Two from the methylene carbon occur at 2.88 and 3.02 δ, and the methyne hydrogen atom at 3.45 δ. The methylene atoms on the carbon between the ester oxygen and the epoxy ring have resonances at 4.1 and 4.6δ; These GMA peaks are unique and isolated well enough that following the integration with time provides a

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**Figure 1:** The major reactants and products in the reaction of GMA with iso-butyric acid in the presence of ammonium hydroxide.
reasonable way to monitor the kinetics. In strong contrast to GMA, the glyceryl methacrylate has the methylene hydrogen atoms shifted to $3.7\delta$, and they are in the form of a multiplet. These unique resonances allow the development of peak integration and the subsequent analysis of the kinetics.

This aspect is shown again in figure 4. This graph shows that there are unique atoms that can be readily isolated and evaluated to provide meaningful data for kinetic evaluation of the opening of the oxirane ring. The three peaks that change with time represent the decrease in the oxirane concentration with the concomitant increase in the alcohol concentration. No manner of reckoning with the ester hydrolysis has been attempted in this evaluation. This is due to the fact that in the D2O environment, the acid and alcohol protons readily exchange with the solvent giving rise to a sharp peak around 5 ppm.

The integration of the peaks with respect to time result in the alpha methyl protons, the vinyl protons and the water protons remaining constant throughout the experiment. The peaks associated with the epoxy group decreased with time and the peak associated with the glyceryl methacrylate increased with time. This is shown in figure 7.

For the Hydrolysis of GMA at 80°C in D2O, we can readily follow the loss of the epoxy proton resonances. By plotting the reaction time as a function of the data, one can graphically obtain the reciprocal of the rate constant from the slope of the resulting graph.
line. In this case, the data plotted as the function of ln(C_0/Concentration) yields a straight line with the slope equal to 1/k, the inverse of the rate coefficient. This is shown for peaks 6 and 8 in figures 5 and 6, respectively. The agreement of the rate coefficient by using each curve is quite reasonable.

There is yet another method to determine the rate coefficients. This technique involves using the general integrated form of the rate equation and solving for the unknown, which in this case is the rate coefficient. The results from this technique agree quite well with the graphical determination by using the following equation with the concentration of peak 6 as the example. The results are shown graphically in figures 7 and 8, respectively representing peaks 6 and 8.

Results from the fit of the equation are: k= 0.0122 for peak 6. The same treatment for the other peak, designated as peak 8 are shown below.

Results from the fit of the equation are: k= 0.0154 for peak 8. The three peaks, thus tested, provided reasonable information regarding the rate of hydrolysis of the epoxy group at 80°C. The results of the rate coefficients are contained in table 1. The two techniques of treating the data are quite consistent, and the different curves provide fairly consistent data. The same reaction at room temperature has been found\textsuperscript{1} to have a rate coefficient of 8.5·10\textsuperscript{-6} mol/minute.

Table 2 contains the results from Bronsted’s study\textsuperscript{1} of rates of reaction of other ions at 25°C in various ionic strength solutions. This table gives us a platform for comparison of further results.

The rate of reaction with ammonium deuteroxide at room temperature yields a value of 2.5·10\textsuperscript{-4}, which is in the ballpark for the other anions mentioned above.

The NMR evaluation of the reaction of ammonium deuteroxide at 80°C results in a rate coefficient of 1.84·10\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Glycid</th>
<th>Epichlorohydrin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodide</td>
<td>1.62·10\textsuperscript{-2}</td>
<td>6.0·10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>0.79·10\textsuperscript{-2}</td>
<td>3.8·10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Bromide</td>
<td>1.03·10\textsuperscript{-3}</td>
<td>3.7·10\textsuperscript{-2}</td>
</tr>
<tr>
<td>Chloride</td>
<td>1.50·10\textsuperscript{-4}</td>
<td>6.9·10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Formate</td>
<td></td>
<td>2.8·10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Benzoate</td>
<td></td>
<td>3.1·10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Acetate</td>
<td></td>
<td>3.7·10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Trimethyl Acetate</td>
<td></td>
<td>5.0·10\textsuperscript{-4}</td>
</tr>
</tbody>
</table>

Table 2. The ranking of other anions is as follows (T\textsuperscript{-} = Thiocyanate).

<table>
<thead>
<tr>
<th>Peak Evaluated</th>
<th>k- Graphical</th>
<th>k-Curve Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.01255</td>
<td>0.01263</td>
</tr>
<tr>
<td>6</td>
<td>0.0124</td>
<td>0.0122</td>
</tr>
<tr>
<td>8</td>
<td>0.0162</td>
<td>0.0154</td>
</tr>
<tr>
<td>Average</td>
<td>0.0137</td>
<td>0.0134</td>
</tr>
</tbody>
</table>

Table 1: Rate coefficients for the hydrolysis of the epoxy group at 80°C, from NMR data and applying two fitting techniques.
Infrared

The first experiment describes the reaction of GMA with isobutyric acid in water at 80°C. The spectral results are shown in figure 9. The appearance of an increase in the ester absorption frequency at approximately 1740 cm⁻¹, is the foremost indication of the formation of the ester bond during the reaction. The epoxy group absorption frequencies around 1300 cm⁻¹, are more difficult to isolate due to the low extinction coefficient. However, it is possible to see the trends in the data. When removing the first two data points, due to peak change as a function of either dilution or equilibration, the data looks reasonably good. The data is fit by a first and a second order equation. The R2 for the second order equation is much better.

The rate coefficient for the addition of isobutyric acid to GMA from this peak has a value of 0.650 for the reaction of equimolar reactants at 80°C. The scatter is fairly great at longer times due to the fact that the concentrations are determined by a ratio and a difference of small numbers. This tends to amplify the error while estimating the molar concentrations. This is not a problem in the analysis of the data using the ester peak. The peak intensities, initial and final are significantly different to preclude this multiplication of the error as seen in the epoxy band analysis. This is illustrated in figure 12. This produces a reaction rate coefficient of 6.276·10⁻² for the reaction using the ester band as the analyze peak.

The second set of data describes the reaction of butyric acid, Ammonia, and GMA. The results of this experiment are not so simple. It appears, in peak 1, that there are two reaction rates, one very slow, followed by a very fast reaction, and both are first order.
Peak 2 has some shape, but is not able to be evaluated in any simple manner.

The first part of the curve, from time = zero to 20 minutes, there appears to be a reaction that follows a different reaction order or rate than the remaining reaction. The rate coefficient for this portion of the curve follows first order kinetics and has a coefficient of $1.08 \times 10^{-2}$. The fit of this portion of the curve generates a rate coefficient of $1.07 \times 10^{-2}$, and a kinetic order of 0.38. This is indicative of a catalytic effect of the ammonium salt on the rate of reaction. The reaction order and the rate differ drastically from the expected values.

**RC1**

**Run #1:** charge the reactor with 7.08 g of a 28% aqueous ammonia solution, 10.26 g of isobutyric acid, and 718.1 g of high purity water. Raise the temperature of the reactor to 80°C. Manually add 14.59 g of GMA into the reactor over 2 minutes. Ramp the stirrer from 300 to 850 rpm over 20 minutes. Hold the reactor at 80°C until the temperature difference between the reactor and the jacket returns to a constant value. Cool the reactor and collect the contents.

**Run #2:** charge the reactor with 7.08 g of a 28% aqueous ammonia solution, 10.26 g of isobutyric acid, and 718.1 g of high purity water. Raise the temperature of the reactor to 80°C. Meter 14.59 g of GMA into the reactor over 2 minutes. Maintain the stirrer at 400 rpm throughout the reaction. Hold the reactor at 80°C until the temperature difference between the reactor and the jacket returns to a constant value. Cool the reactor and collect the contents.

**Run #3:** charge the reactor with 10.26 g of iso-butyric acid, and 709.0 g of high purity water. Raise the temperature of the reactor to 80°C. Meter 14.59 g of GMA into the reactor over 2 minutes. Maintain the stirrer at 400 rpm throughout the reaction. Hold the reactor at 80°C until the temperature difference between the reactor and the jacket returns to a constant value. Cool the reactor and collect the contents.

The addition of 14.59 g of GMA, 0.1026 mol or 1.95%, to 14.59 g of isobutyric acid, 0.1163 mol or 1.37%, should produce 0.0137 mol or 1.208 g of isobutyric acid remaining in the reactor, 750 g of matter, or 0.16 weight percent of unreacted acid. There was no detectable unreacted GMA in the product.

**Table 3: Heat of reaction data.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>kJ</th>
<th>kJ/g (GMA)</th>
<th>kJ/mol (GMA)</th>
<th>% Free Acid</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.783</td>
<td>122.21</td>
<td>17.37</td>
<td>1.057</td>
<td>ramp</td>
</tr>
<tr>
<td>2</td>
<td>2.910</td>
<td>199.45</td>
<td>28.35</td>
<td>1.012</td>
<td>no ramp</td>
</tr>
<tr>
<td>3</td>
<td>4.509</td>
<td>309.05</td>
<td>43.93</td>
<td>1.261</td>
<td>no ammonia</td>
</tr>
</tbody>
</table>

**Figure 13: Molar conc. of the ester product from GMA iso-butyric acid, and ammonium hydroxide.**

**Figure 14: The nonlinear fit of the data for the second curve.**
The reaction involves the transformation of some mass in one form to another form, and measuring the amount of heat involved in that transformation. This is shown in figure 15 for the three reactions. The form that is more interpretable to a chemist is to translate this information into the form of the conversion, or extent of the reaction, as a function of time. This transformation is shown in figure 16. The transformation function is:

\[ X = \frac{\int_{0}^{t} Q_r \, dt}{\int_{0}^{t} Q_r \, dt} \]

This describes the extent of the reaction in terms of the overall rate process, and does not isolate an individual event as contributing to the kinetic description.

The new look is then to examine the data in terms of the heat flow, or the rate of reaction as a function of conversion (figure 17).

This allows us to interpret kinetic data in a novel manner. The RC1 provides us the ability to evaluate the kinetics as a function of temperature in a manner that is much simpler than previously available. Based on the work of Ralph Landau\(^2\), we are able to examine the effect of temperature on the rates of reactions in a single experiment. The usual method of determining the activation energy, \( E_a \), is to perform kinetic experiments with at least three different runs at differing temperatures. This requires running a separate experiment and removing samples at various intervals with each run and evaluating the conversion with time. From these separate runs, one can determine the rate constant for the reaction at each temperature and subsequently plot the logarithm of the rate constants as a function of the inverse of the temperature yielding the activation energy from the slope of this line. The RC1 is a tool that can determine the activation energy with a single run.

The kinetic equations are:

\[ \frac{dC}{dt} = -k \cdot t \quad (1) \]

where \( C \) is the concentration of the analyze, \( k \) is the reaction rate coefficient, and \( t \) is the time of the reaction. The rate of the reaction as a function of temperature has been well documented and represented by the Arrhenius equation:

\[ k = A_0 e^{-E_a/RT} \]

For a first order reaction equation 1 becomes:

\[ \ln(C/C_0) = -kt \quad (2) \]

For the thermal analysis, the heat of reaction is:

\[ Q_r = (dC/dt)(\Delta H_{\text{rxn}} \cdot V) \quad (3) \]

---

*Figure 15: Heat flow as a function of time.*

*Figure 16: Conversion as a function of time.*

*Figure 17: Heat and conversion data.*
Where \( C \) is the concentration, \( \Delta H_{rxn} \) is the heat of reaction and \( V \) is the volume. At some instant in time,

\[
Q_t = -k \cdot C \cdot \Delta H_{rxn} \cdot V \quad (4)
\]

Substitution of \( Q_r \) and \( Q_{r0} \) for the heat at time = \( t \) and time = \( 0 \), respectively, the first-order equation becomes:

\[
\ln\left(\frac{Q_r}{Q_{r0}}\right) = -kt \quad (5)
\]

Using equation 5, one can utilize the heat flow from the reactor calorimeter to determine the rate coefficient for a reaction at that particular reaction temperature. By ramping the calorimeter from one temperature to another, and waiting sufficient time between the ramps to follow the heat flow for the reaction, one should be able to generate the desired Arrhenius equation data.

### The Experiment

The condensation of Glycidyl Methacrylate, GMA, with Ammonium Isobutyrate, AB, was selected for this experiment. The reagents, ammonium hydroxide, GMA, AB, and water, were all added to the reactor at room temperature. The heat flow characteristics of the reactor were measured and the reactor was ramped to 65°C, 75°C, and 85°C over a 15 minute ramp time with a twenty minute interval between the end of one ramp and the beginning of the next. The reagents were allowed to react to completion at 85°C before the reactor was returned to room temperature. The heat flow characteristics were again measured when the contents of the reactor reached thermal equilibrium at room temperature. The results of the fit to the heat flow data for the 85°C reaction are in figure 18.

### Results and Discussion

The reaction profile is shown in figure 18. The one curve represents the reactor temperature profile and the other curve depicts the heat flow. The intervals are indicated for each kinetic rate coefficient time interval for each temperature as well. The results of the data treatment are shown in figure 19. In this graph, the ratio of the heat flow at the time \( t \) divided by the heat flow at time zero which corresponds to the vertical lines in figure 18 on the ordinate and the time difference between the time of \( Q(t) - t = 0 \) is shown.

The lines in figure 19 represent the fit lines of a pseudo-first-order kinetic equation. In order to generate the Arrhenius Plot, the rate coefficients are derived from the fit functions illustrated in figure 18. These values are then altered to the natural logarithm and then plotted against the inverse of the temperature, in degrees Kelvin. Taking the logarithm of each side of the Arrhenius equation yields a linear function in which the pre-exponential \( A_0 \) now becomes the intercept and the activation energy, \( E_a \), is extracted from the slope. The answer from this work is:

\[
E_a = 7.7 \text{ kcal/(K\cdot mol)} \text{ or 32.2 kJ/(K\cdot mol)}
\]

Work was done earlier to determine the reaction rate of GMA with SCX 693^3. The results from running three separate runs at 65°C, 75°C, and 85°C,

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>0.01216</td>
</tr>
<tr>
<td>75</td>
<td>0.04815</td>
</tr>
<tr>
<td>85</td>
<td>0.09457</td>
</tr>
</tbody>
</table>

Figure 18: Reactor temperature and heat flow as a function of the reaction time.

Figure 19: Ratio of the heat flows vs. the time of the reaction.
respectively gave comparable results. The rate coefficient for each temperature is contained in table 4.

The activation energy derived from these results is 6.1 kcal or 25.4 W per mol·K. Since the reaction of a carboxylic acid group on the resin with the GMA epoxy group is the same mechanism as the reaction of the ammonium isobutyrate, the rate coefficients and the activation energy seem reasonable by comparison.

**The Conclusions**

From a single run, we are able to determine:
- the heat of reaction from integration of the heat flow over the entire reaction time,
- the maximum rate of reaction based on the heat flow curve,
- the rate coefficients for the reaction at at least three different temperatures,
- the activation energy, and thus,
- an estimate of the rate as a function of temperature.

This is a very expeditious use of the RC1 reactor calorimeter. From one run, in one day, we can now determine what would usually take several weeks and a minimum of three runs. Another case of getting more with less.

The continual monitoring of the heat of reaction provides a more extensive way of following the reaction kinetics than taking samples and performing off-line analyses. The best system is that of coupling the RC1 with on-line chemical monitoring, such as pH or the infrared spectroscopy unit available from Applied Systems, Inc.

The reproducibility of the reactor allows for more reliable data than the manually run laboratories.