MEASURING THE RATES OF SOLID STATE REACTIONS BETWEEN ALCl₃ AND C₅H₆NCI USING DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Differential Scanning Calorimetry was used to measure the rates and heats of the solid state reactions between aluminum chloride and pyridinium chloride. It was found that the three reactions studied followed the same rate law derived from a two dimensional diffusion mechanism. The integrated form of this rate law is (1-\(\zeta\))ln(1-\(\zeta\)) + \(\zeta\) = kt where \(\zeta\) is the degree of transformation, k is the specific rate constant and t is the time. The rate constant for the neutralization reaction was measured at several temperatures and from these data the energy of activation was calculated. From the measured rate law, inferences about the reaction mechanism and energy transfer were made.

INTRODUCTION

Despite the fact that almost all materials of interest are solids and there is a pressing need to understand homogeneous solid state reactions, relatively little is known about the kinetics and mechanisms of solid state reactions because it is difficult to design experiments that will generate useful information. For this reason we have begun a series of experiments using differential scanning calorimetry (DSC) to measure the rates of solid state reactions (1). The reason we are using DSC is that for any exothermic reaction, heat begins to evolve at the beginning of the reaction and stops when the system equilibrates, so that the rate of the reaction is proportional to the rate at which heat is evolved. If the heat is generated quickly enough for the reaction to be followed by DSC, useful information about the kinetics of solid state reactions might be obtained.

We have selected the series of reactions between AlCl₃ and chloride salts such as NaCl (2), pyridinium chloride (3), methylethylimidazolium chloride (4), or n-butylypyridinium chloride (5) to explore the feasibility of using DSC to study solid state kinetics. These reactions are highly exothermic, very rapid for solid state reactions, have interesting Lewis acid-base chemistry and generally form products that have lower melting points than either of the reactants. They are also of particular interest to the molten salt community because, in the liquid state, the chloroaluminates formed are useful as solvents for interesting reactions and unusual species and as electrolytes in energy generating devices. The reactions whose kinetics we report on here are between pyridinium chloride, C₅H₆NCI, and AlCl₃ and are shown below.
Each product is a congruently melting compound. The melting point of C₅H₆NaAlCl₄ is approximately 120 °C, the melting point of C₅H₆NaAl₂Cl₇ is approximately 24 °C and the melting point of (C₅H₆)₂ClAlCl₄ is approximately 91 °C.

THEORETICAL BACKGROUND

A differential scanning calorimeter can be used to measure both isothermal and dynamic (temperature changing) processes and in the present study, an isothermal mode was used. This means changes as a function of time, keeping temperature constant, were recorded. Since a differential scanning calorimeter is designed, in effect, to maintain a zero temperature differential between a standard and a test sample, any heat evolved during the reaction (the test sample) will be supplied by the instrument to the reference sample and is therefore the quantity measured. If we define a quantity $\zeta$ as the degree of transformation, $\zeta = 0$ at the beginning of the reaction when the heat begins to evolve and $\zeta = 1$ when the system equilibrates and heat stops being evolved. Therefore, the rate of the reaction is $d\zeta/dt$.

For the solid state reaction,

$$A = C + \Delta H$$  [4]

$A$ is the solid at the start of the reaction, $C$ is the material after the reaction has equilibrated, and $\Delta H$ is the heat evolved during the reaction. In general,
\[ \zeta = \Delta H_{\text{partial}} / \Delta H_{\text{reaction}}. \] 

That is, the entire area under the experimental Q vs. time curve gives \( \Delta H \) for the reaction and an area corresponding to a particular time less than \( t_{\text{reaction}} \), \( (\Delta Q/\Delta t) \times \Delta t \), gives \( \Delta H_{\text{partial}} \) for that elapsed time. Dividing \( \Delta H_{\text{partial}} \) by \( \Delta H_{\text{reaction}} \) yields the value of \( \zeta \) corresponding to that rate. The process is repeated for several times at each of several temperatures. In order to ensure that the reaction has not proceeded to any significant extent before data is collected, the reactants and pans are cooled to as low a temperature as is practical prior to being loaded into the calorimeter. This concept is illustrated in Fig. 1 (7) which shows a three dimensional plot of \( \zeta \) against time and temperature, \( T \), for a generalized solid state reaction. It is apparent from the diagram that as \( T \) approaches 260 °C, \( \zeta \) approaches zero.

For first, second, or third order reactions, the temperature dependence of the reaction rate is given by the familiar Arrhenius equation so that the rate law for the reaction becomes

\[ \frac{d\zeta}{dt} = k(1-\zeta)^n = A_0[\exp - E_a/RT](1 - \zeta)^n \] 

In linear form, this equation becomes

\[ \ln(\frac{d\zeta}{dt}) = \ln A_0 - E_a/RT + n\ln(1-\zeta). \]

\( A_0, E_a, n \) and \( k \) are obtained from experimental values of \( d\zeta/dt, 1/T, \) and \( (1-\zeta) \). However, most solid state reactions do not follow a simple ordered rate law and for these reactions, the rate law is derived for various possible model reaction mechanisms. The experimental \( \zeta \) vs \( t \) curves are then compared with the model \( \zeta \) vs \( t \) curves and the best fit selected to obtain the overall reaction rate law. From the rate law, inferences about the reaction mechanism can be made. Unfortunately, differences in the \( \zeta \) vs. \( t \) curves corresponding to different mechanisms are often quite small so that very precise measurements are needed.

**EXPERIMENTAL DETAILS**

The experiments were performed on a Perkin-Elmer DSC-4 with a thermal analysis data station (TADS). Data were collected in the isothermal mode using a special isothermal program. Because the reactions between \( C_5H_6\text{NCl} \) and \( \text{AlCl}_3 \) were fairly rapid at elevated temperatures, both reactants were cooled on dry ice in a nitrogen filled glove box (moisture content less than 10 ppm), to ensure that the reaction did not proceed to any great extent prior to being placed in the calorimeter. The desired mole fractions of the reactants were prepared by weighing stoichiometric quantities of each compound that had been ground and sieved through a 40 Mesh screen, directly into a large stainless steel pan (0.7 cm diameter) inside the glove box and then sealing the pan. This conceptually simple procedure proved to be quite difficult in practice and took quite a bit of preparation time. The temperature of the sealed pans was further reduced before removing them from the glove.
box. The best mixing procedure seemed to be simply holding the sealed pan with a
tweezers and gently shaking it for a few seconds.
The cold pans were then placed in the calorimeter and brought to a high enough temperature
for the reaction to occur fairly rapidly.

\[ \Delta H_{\text{partial}} \] and \[ \Delta H_{\text{reaction}} \] were calculated by first enlarging the measured
thermogram, transferring it to heavy cardboard, cutting out the area under the curve with a
sharp scissors and weighing it on an analytical balance. A square with known dimensions
of the same cardboard was used to calibrate the area. The precision of this technique was
better than 1%.

The melting and freezing points of the products were obtained by switching to the
normal dynamic mode of the instrument. This was done to further ensure that a true
product was actually produced. Sublimation, decomposition, and vaporization all produce
endothermic thermograms similar to melting so that obtaining an exotherm is fairly good
evidence that a reaction has occurred. Since all reactants and products are very
hygroscopic, all transfer reactions were done in the controlled atmosphere glove box.

RESULTS AND DISCUSSION

Fig. 2 shows a typical thermogram obtained from our calorimeter for Eq[3] at
50 °C. The dashed line represents the baseline extrapolation procedure. Since we are
operating the instrument in the isothermal mode, the abscissa represents time and not
temperature. A temperature range of 10 °C is actually a time of one minute so the time for
this reaction is slightly longer than two minutes. All thermograms had the same general
shape as Fig. 2. Fig. 3, 4, and 5. show typical isothermal \( \zeta \) vs t plots for Eq.[1], Eq.[2],
and Eq.[3] respectively. Table I lists the average \( \Delta H_{\text{reaction}} \) and temperature range for
the reactions studied. Although there is considerable error in each of the \( \Delta H \) measurements
shown in Table I, the general trends are all in the expected direction and the data are self
consistent. For example, it must be the case that the enthalpy of reaction for Eq.[2] is
considerably larger than the enthalpy of reaction for Eq.[1] because an AlCl₃ molecule is
being added to pyridinium tetrachloroaluminate. The difference between the heats of
reaction for Eq.[1] and Eq.[2] should equal \( \Delta H_{\text{rxn}} \) for the reaction:

\[
\begin{align*}
\text{AlCl}_4^- + \text{AlCl}_3 & \rightarrow \text{Al}_2\text{Cl}_7^- \\
\end{align*}
\]

Although the measurement for this reaction proved extremely difficult, our preliminary data
indicate that, within experimental error, \( \Delta H[8] = \Delta H[2] - \Delta H[1] \).

The \( \zeta \) vs. t curves indicate that Eq. [1-3] all follow a rate law derived from a two
dimensional diffusion mechanism (8):

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\[ \frac{d\zeta}{dt} = k[-\ln(1-\zeta)]^{-1} \]  

where \( k \) is the specific rate constant. The integrated form of this rate law is:

\[ f(\zeta) = (1-\zeta)\ln(1-\zeta) + \zeta = kt \]

so that if the rate law is correct for a particular reaction, a plot of \( f(\zeta) \) vs. \( t \) would give a straight line with slope \( k \). Fig. 6 shows a plot of \( f(\zeta) \) vs. \( t \) for Eq.[1] at each of three temperatures and all three are linear, the 50 °C plot having a correlation coefficient of 0.999. Special care was taken in each of these reactions to fill the pan with exactly (to three significant figures) \( 1 \times 10^{-4} \) moles of each reactant. Fig. 7 shows an Arrhenius plot for Eq.[1] using the results of these experiments plus two additional experiments. The data or fairly linear yielding an \( E_a \) of 16 kJ/mol. The theoretical interpretation of an Arrhenius plot for inherently heterogeneous solid state reactions is open to question, but the relative linearity of the graph and the value of \( E_a \) is useful for purposes of comparison and to verify internal consistency of the data. Fig. 8 and Fig. 9 are the \( f(\zeta) \) vs. \( t \) plots for Eq.[2] and Eq.[3] respectively and again, each of these graphs is quite linear indicating a two dimensional diffusion mechanism.

The salient features of all of these reactions is their extreme rapidity and the fact that, within experimental error, they all follow the same rate law indicating a similar mechanism. The heterogeneous reactions probably proceeds evenly over two contiguous crystal surfaces. On a microscopic level, for the neutralization reaction, this can be pictured as the \( Cl^- \) ions from the surface of a crystal of \( C_5H_5NCI \) hopping to the surface of an \( AlCl_3 \) crystal followed by the formation of pyridinium tetrachloroaluminate nuclei which then grow. Details of now these nuclei grow are unclear (9) as are the details of energy transfer. The heat generated by one group of molecules reacting with another generates the activation energy for a subsequent reaction producing a kind of energy wave moving through the crystal. It is also probable that enough heat is generated in this process to cause eutectic mixtures to melt locally forming a molten salt and thus significantly increasing the reaction rate. Freezing eventually occurs and the system appears to always be in the solid state. It is also possible that these reactions are vapor driven. That is, there is a high enough vapor pressure of each reactant in the sealed pan so that a gas phase reaction occurs. The reaction product is well below its melting point and eventually precipitates causing either a eutectic to form locally or, allowing more unreacted material to vaporize and drive the reaction.

**SUMMARY**

Differential Scanning Calorimetry has been shown to be a useful technique for measuring the rates of exothermic solid state reactions. The extent of reaction, \( \zeta \), is obtained from the thermogram and is then fitted to known rate laws derived for different possible solid state reaction mechanisms. From these rate laws inferences as to the microscopic details of the solid state reaction may be drawn.
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TABLE I

Average Heats of Reaction and Temperature Range for the Solid State Reactions between AlCl₃ and C₅H₆NCl

| Reaction                  | ΔHₘₐᵥ(kJ/mol) | Temperature Range (°C) |
|---------------------------|--------------|------------------------|
| C₅H₆NCl + AlCl₃          | - 53 +/- 6   | 50 - 100               |
| 2C₅H₆NCl + AlCl₃         | - 76 +/- 1   | 50                     |
| C₅H₆NCl + 2AlCl₃         | - 120 +/- 14 | 22 - 33                |
| C₅H₆NaAlCl₄ + AlCl₃      | - 63         | 25                     |

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A series of isothermal $\zeta$ vs. time curves at different temperatures.

FIG. 3 Isothermal $\zeta$ vs. time for Eq. [1].
FIG. 4
Isothermal $\zeta$ vs. time for Eq. [2].

FIG. 5
Isothermal $\zeta$ vs. time for Eq. [3].

FIG. 6 $f(\zeta)$ vs. time for Eq. [1] at each of three temperatures.
FIG. 7 Arrhenius plot for Eq. [1].

FIG. 8 $f(\zeta)$ vs. time for Eq. [2].

FIG. 9 $f(\zeta)$ vs. time for Eq. [3].