DECOMPOSITION KINETICS OF 1-BUTYL-2,3-DIMETHYLLIMIDAZOLIUM TETRAFLUOROBORATE AND THE EFFECTS OF IMPURITIES USING TGA

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ABSTRACT

Thermal gravimetric analysis (TGA) has been used to determine the kinetics of decomposition for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (DMBIBF₄) and the effects of impurities on the decomposition rates. Data was collected from both isothermal and constant heating rate TGA experiments for the decomposition of DMBIBF₄. The isothermal data was fit to a global kinetic model and the Arrhenius parameters were determined. The constant heating rate data was used to determine the activation energy using an isoconversional model. The effects of up to 10 mass-% water, NH₄BF₄, NH₄CI, and DMBICl impurities on DMBIBF₄ decomposition rates were also determined.

INTRODUCTION

Imidazolium based room temperature ionic liquids (RTILs) have received considerable attention due in part to their high thermal stability. However, recent studies have indicated that the long term thermal stability is significantly lower than the temperatures reported using TGA with a single temperature ramp rate (1,2).

We recently determined the kinetics of decomposition for DMBIPF₆ (2). However, the systematic increase in Eₐ with conversion and the small mass loss at 300°C suggests that there were some impurities in the prepared salt. This contaminant is likely due to the slow hydrolysis of PF₆⁻ that occurs when hexafluorophosphate ionic liquids contact an aqueous phase (3). To reduce the presence of contaminants in the "pure" ionic liquid, we analyzed the decomposition kinetics of DMBIBF₄, which is less prone to hydrolysis in the presence of water.
In an attempt to fully characterize the thermal stability of a "typical" imidazolium based RTIL, we have conducted both isothermal and isoconversional (constant temperature ramp program) TGA experiments in a nitrogen atmosphere on DMBIBF$_4$. Because TGA measures the rate of evaporation of degradation products and not the actual chemical reaction, information on specific chemical reactions and mechanisms cannot be determined from TGA measurements alone (2,4). Nevertheless, this data can be used to determine a global kinetic model, which is useful in predicting mass loss rates at any temperature or heating rate program and provides information on the long term storage limitations. In addition, we have investigated the effects of contaminants (up to 10 wt-%) on the decomposition rates of DMBIBF$_4$.

EXPERIMENTAL

Materials

Preparation of Salts. 1-butyl-2,3-dimethylimidazolium chloride (DMBICl) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (DMBIBF$_4$) were prepared using the procedures described previously (5). Coulometric Karl Fischer Titration (Mettler Toledo, DL39) indicated the dried salts had less than 150 ppm (0.2 mol-%) water. (Ammonium tetrafluoroborate (Aldrich, 99.99%) and ammonium chloride (Aldrich, 99.99%) were used as received.

Measurements

Thermogravimetric Analysis. A thermogravimetric analyzer (TA Instruments, Hi-Res TGA2960) was utilized to measure the decomposition temperatures of the various salts. 5.0 ± 0.2 mg samples were placed in open ceramic pans and heated at a constant scan rate (1 – 20 °C/min) while purged with 100 ml/min N$_2$. For the isothermal measurements, 5.0 ± 0.2 mg samples were heated as quickly as possible without exceeding the final temperature (200° - 400°C). For all TGA analyses, the mean of two or three replicate measurements was reported. The temperature of both the onset (5% mass fraction loss) and peak mass loss rate have uncertainties of $\sigma = \pm 3$°C.

Addition of Impurities. DMBICl and water contaminants were introduced and well mixed with DMBIBF$_4$ in a glove box prior to loading the TGA sample pan. The DMBICl/DMBIBF$_4$ mixtures formed a single phase only after heating the mixture beyond the melting point of DMBICl. The ammonium salts were insoluble and formed a 2-phase mixture in DMBIBF$_4$, thus they were added to the sample pan just prior to running the TGA.

RESULTS AND DISCUSSION

There are two common methods for determining the TGA decomposition kinetics of solids and non-volatile liquids: isothermal and isoconversional using a constant temperature ramp program. As indicated in Figure 1, the decomposition of DMBIBF$_4$ follows pseudo-zero-order kinetics over the conversion fraction range, 0 < a < 0.81.
Similar behavior has been observed for the thermal decomposition of 2-nitrobenzoic acid, calcium maleate dehydrate, and calcium fumarate trihydrate (6,7). In the case of 2-nitrobenzoic acid, this behavior was attributed to the evaporation of 2-nitrobenzoic acid prior to a gas phase decomposition mechanism. Galway and Mohamed attribute the apparent zero order decomposition kinetics of the calcium hydrates to the composite outcome of two (or more) competing decomposition mechanisms, such as a nucleation and growth process overlapping with a deceleratory reaction (7). The negligible vapor pressure of imidazolioum based RTILs, the deceleratory process observed at conversion factors above 0.81 coupled, and the observed decrease in char yield with increasing temperature ramp rates (see Figure 2) all strongly indicate the existence of competing decomposition reactions and suggests decomposition mechanisms similar to those proposed for the calcium hydrates.

![Graph: Isothermal decomposition of DMBIBF₄ in N₂.](image)

Vyazovkin and Lesnikovich have indicated that the kinetic parameters calculated from isothermal data are generally model independent, but very dependent upon the chosen kinetic model for non-isothermal data (8). Thus the preferred method for obtaining the Arrhenius parameters are from isothermal data.

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The kinetic parameters were determined from isothermal decomposition data using an Arrhenius type equation. For decomposition reactions, the reaction rate constant is replaced by the rate of the reaction $(da/dt)$ divided by the kinetic model $(f(\alpha))$, as indicated in equation 1.

$$\ln \left( \frac{da/dt}{f(\alpha)} \right) = \ln A - \frac{E_a}{RT}$$  \[1\]

The conversion fraction $(\alpha)$ at any time was calculated from the weight of the sample at that time $(wt)$, the initial weight $(w_0)$, and the final weight $(wf)$ of the sample using equation 2.

$$\alpha = \frac{w_i - w_f}{w_i - w_f}$$  \[2\]

The change in the conversion rate with time equals the mass change with time obtained directly from the TGA experiment divided by the total mass lost over the experiment. The constant mass loss rate over time indicates that the decomposition follows zero order kinetics, thus the kinetic model is simply $f(\alpha) = 1$. An Arrhenius type plot, shown in Figure 3, yields a straight line (R = 0.9946), indicating that the TGA decomposition of DMBIBF$_4$ does follow a pseudo-zero-order reaction mechanism under isothermal conditions. The parameter values were calculated to be $E_a = 21.12$ kcal/mol and $A = 2.876 \times 10^6$. 

Figure 2. Comparison of char yields under different heating rates for DMBIBF$_4$ decomposition in N$_2$. 
As indicated previously, the decomposition of DMBIBF\textsubscript{4} likely proceeds by several mechanisms. In addition, the formation of char can change the decomposition rate or lower the sample temperatures as the reaction proceeds. And, the best fit reaction model, in this case an apparent zero order reaction, reveals little, if anything, about the actual decomposition mechanism. Thus, it may be more appropriate to model the decomposition using a model free isoconversional method. We used the Ozawa-Flynn-Wall method\textsuperscript{(9,10)} using data obtained from constant heating rate decompositions, which is one of the three most commonly used isoconversional methods.

The natural logarithm of the heating rate versus the inverse of the temperature at a specific conversion rate is plotted for DMBIBF\textsubscript{4} in Figure 4. The slopes of the lines are equal to $-E_a\times b/R$, where $b$ is a constant and its value is dependent on the value of $E_a$ at the given conversion. The final value of the activation energy at each conversion rate is found iteratively using the method developed by Flynn\textsuperscript{(11)}. The pre-exponential factor, $A$, can be found from equation (3), where the temperature integral is typically evaluated using an approximation, such as the Coats-Redfern equation\textsuperscript{(12)}.

$$g(\alpha) = \frac{A}{\beta} \int\left[\frac{E_a}{RT}\right] dT$$  \hspace{1cm} [3]
The activation energy was found to be fairly constant over the conversion range $0.10 \leq \alpha \leq 0.90$ and was calculated to be $29.9 \pm 0.1$ kcal/mol. Due to some recently reported misgivings of the Coats-Redfern equation, we have not used equation 3 to determine the pre-exponential factors for the various models (13).

![Figure 4. Ozawa-Flynn-Wall isoconversional analysis of DMBIBF₄.](image)

We also investigated the effects of impurities on the decomposition temperatures of DMBIBF₄. As shown in Figure 5, the addition of up to 10% water, NH₄BF₄, DMBICl, and NH₄Cl all had a negligible effect on the decomposition temperatures of DMBIBF₄. Although the decomposition temperatures were not altered, the presence of chloride ions in the decomposition stream resulted in nucleophilic attack of some of the DMBIBF₄. DMBICl decomposes by $S_n1$ or $S_n2$ nucleophilic decomposition, yielding imidazole and alkyl halide products (14). NH₄Cl decomposition products are NH₃, HCl, and some bare H⁺ and Cl⁻ ions (15). The production of Cl⁻ leads to further decomposition of DMBIBF₄, whereas the production of alkyl chlorides does not lead to subsequent decomposition of DMBIBF₄. Evidence for this effect can be seen in the mass loss curves, as shown in Figure 6.
Figure 5. Effects of contaminants on the decomposition temperatures of DMBIBF$_4$.

Figure 6. Effects of chloride contaminants on the mass loss of DMBIBF$_4$. 

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CONCLUSIONS

A kinetic model to describe the TGA decomposition in N_2 of DMBIBF_4 has been developed from isothermal decomposition data. Zero-order behavior was observed for DMBIBF_4 when \( \alpha < 0.90 \), followed by a strongly deceleratory process for the decomposition of char formed during the early stage decomposition. From an Arrhenius type plot, the activation energy of the initial decomposition stage was determined to be 21.12 kcal/mol and the pre-exponential factor was found to be \( 2.876 \times 10^6 \). Using the isoconversional method of Ozawa-Flynn-Wall, the activation energy was determined to be \( 29.9 \pm 0.1 \) kcal/mol for the conversion factor range \( 0.10 \leq \alpha \leq 0.90 \).

The decomposition temperature was generally not affected by the presence of contaminants. The exception is when the impurity, such as NH_4Cl, produces unassociated chloride ions as a decomposition product. This results in decomposition of some DMBIBF4 at temperatures associated with DMBICl decomposition.

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