TGA Decomposition Kinetics of 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate and the Thermal Effects of Contaminants

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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 ($DMBIBF_4$) and the effects of impurities on the decomposition rates. 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.[1,2] 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. Data was collected from both isothermal and constant heating rate TGA experiments for the decomposition of $DMBIBF_4$. The effects of up to 10 mass-% water, NH_4BF_4, NH_4Cl, and DMBICl impurities on $DMBIBF_4$ decomposition rates were also determined.

EXPERIMENTAL

The imidazolium based room-temperature ionic liquids (RTILs) were prepared as described previously.[3] The thermal stabilities were measured using a TA Instruments, Hi-Res TGA2960 Thermogravimetric Analyzer. For the isothermal TGA study, 5.0 ± 0.1 mg samples of $DMBIBF_4$ were heated as quickly as possible without exceeding the final temperature. For the isoconversional TGA study, 5.0 ± 0.1 mg samples of $DMBIBF_4$ were heated at multiple scan rates between 0.5ºC/min and 4ºC/min. For all TGA analyses, the mean of three replicate measurements was typically reported. The temperature of both the onset (5% mass fraction loss) and peak mass loss rate have an uncertainty of □ = ± 2ºC. The mass loss rate has a relative uncertainty of □/ $\bar{x}$ = ± 10%.

RESULTS AND DISCUSSION

Although RTILs exhibit high short term thermal stability, they begin to decompose at much lower temperatures when heated for long periods of time. (cf Figure 1) The decomposition of $DMBIBF_4$ was found to follow the Avrami-Erofeev model and the corresponding Arrhenius parameters were calculated. The determined model was then used to predict the mass loss of $DMBIBF_4$ at a different scan rate (constant heating rate experiment) and at a different temperature (isothermal experiment). The presence of impurities was found to have limited effect on the $DMBIBF_4$ decomposition. The presence of Cl^- did result in an equimolar mass loss of $DMBI^+$ (presumably via nucleophilic attack), but did not appear to have a catalytic effect on the remaining $DMBIBF_4$. (cf Figure 2) The results were similar to those previously obtained in our lab for $DMBIPF_6$.

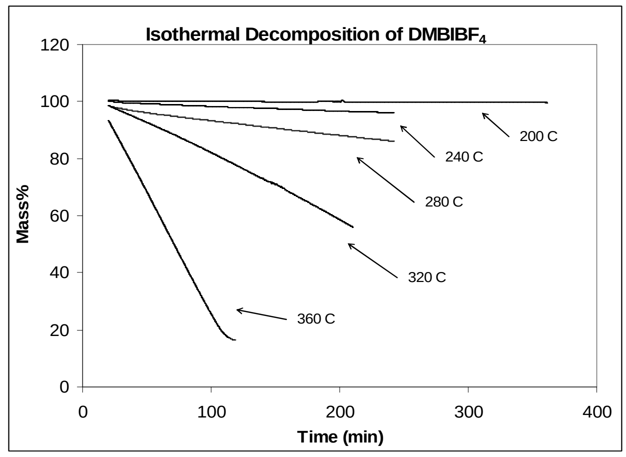

Fig 1. Isothermal decomposition of $DMBIBF_4$ in N_2.

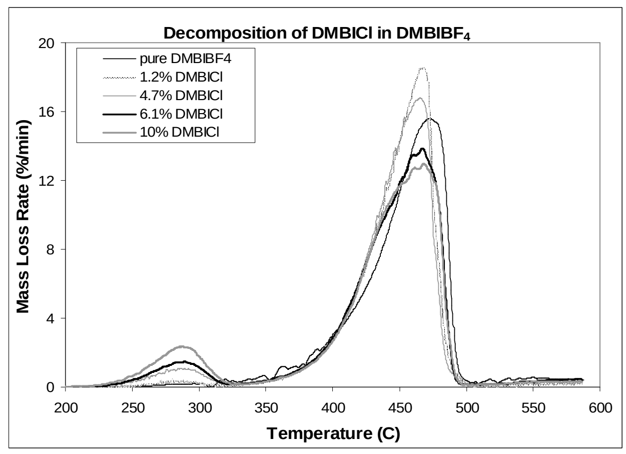

Fig 2. Effect of DMBICl contaminants on the Mass Loss Rate of $DMBIBF_4$ in N_2 at 10°C/min.

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