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## Thermal stability analysis of two imidazolium nitrate ionic liquids via STA, DSC, and ARC

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### PURPOSE OF THE ABSTRACT

In essence, ionic liquids (ILs) are salts with melting points at or below 100 °C, which are composed of organic cations and organic or inorganic anions. Owing to their distinctive properties, such as low melting point, wide liquid range, extremely low vapor pressure, sound thermal stability and wide electrochemical windows etc., ILs are used in a number of application areas. 1-Butyl-3-methylimidazolium nitrate [Bmim]NO<sub>3</sub> and 1-butyl-2,3-dimethylimidazolium nitrate [Bmmim]NO<sub>3</sub>, two typical ILs, can be used to activate copper nanoparticles for CO<sub>2</sub> separation. However, imidazole nitrate may lead to disasters or other serious hazard problems if the cooling system fails or operates at the incorrect process temperature. Therefore, it is necessary to further investigate the thermal stability of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> before used. The aim of this research was to investigate the thermal stability of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> by simultaneous thermogravimetric analyzer (STA), differential scanning calorimetry (DSC), and accelerating rate calorimeter (ARC).

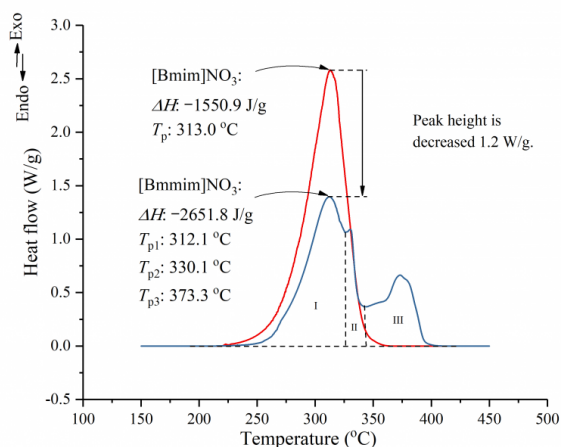
Non-isothermal decomposition of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> were carried out at five heating rates. Notably, TG and DTG curves moved toward high temperatures with increasing the heating rate from 0.5 to 8.0 K/min both of two ILs. The onset decomposition temperature (Tonset) of [Bmim]NO<sub>3</sub> was 283.4 °C under the heating rate of 4.0 K/min, which was approximately 15.0 °C lower than Tonset of [Bmmim]NO<sub>3</sub>. The TG curves of [Bmmim]NO<sub>3</sub> had three different mass loss stage, which means that [Bmmim]NO<sub>3</sub> may exist multiple decomposition reactions. Meanwhile, according to the results of DSC experiments, there were three exothermic peaks in DSC curves, as revealed in Fig. 1. The heat of reaction (?H) of [Bmmim]NO<sub>3</sub> was 2651.8 J/g, which was almost 1.7 times higher than the value of [Bmim]NO<sub>3</sub>. The results indicated that methyl substitution at the imidazolium C2 clearly increased the thermal stability. However, the increased methyl substitution of [Bmmim]NO<sub>3</sub> had a complicated decomposition reaction and released more energies.

Adiabatic experiments indicated that both [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> could cause a runaway reaction. From Fig. 2 it follows that the exothermic phenomena of [Bmim]NO<sub>3</sub> occurred at around 244.0 °C, which 10.0 °C lower than the value of [Bmmim]NO<sub>3</sub>. The exothermic process of [Bmim]NO<sub>3</sub> ended up with a final temperature of 380.7 °C and [Bmmim]NO<sub>3</sub> ended up at the same temperature. However, [Bmmim]NO<sub>3</sub> would be produced more gases, which caused the maximum pressure 11.1 bar higher than [Bmim]NO<sub>3</sub>. The thermal curves which combined DSC and ARC of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> were obtained. In accordance with DSC tests, the reaction characteristics and rudimentary thermal hazards under non-isothermal conditions were received. From the ARC tests, the correspondence of DSC results by the maximum temperature rate ((dT/dt)<sub>max</sub>) and maximum pressure rate ((dP/dt)<sub>max</sub>) under adiabatic conditions was validated. Obviously, (dT/dt)<sub>max</sub> of [Bmim]NO<sub>3</sub> was higher than [Bmmim]NO<sub>3</sub>. However, the (dP/dt)<sub>max</sub> of [Bmim]NO<sub>3</sub> was lower than [Bmmim]NO<sub>3</sub>. The

phenomena may be due to the higher carbon content of [Bmmim]NO<sub>3</sub>, which led to incomplete decomposition and produced more gases.

To sum up, although the methyl substitution at the imidazolium C2 could cause a higher thermal decomposition temperature, the potential hazard would be greater. Therefore, [Bmim]NO<sub>3</sub> is more practical than [Bmmim]NO<sub>3</sub>.

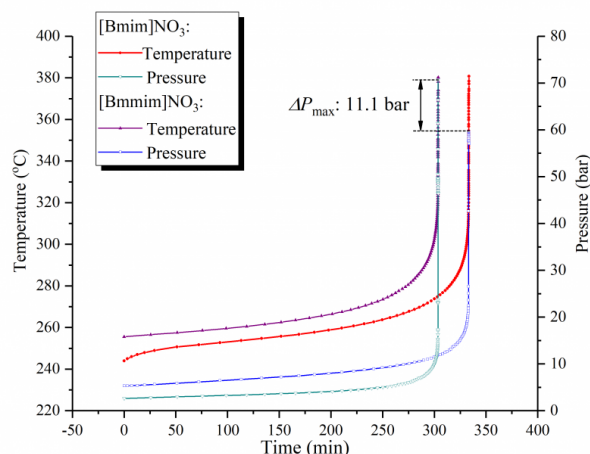
## FIGURES



**FIGURE 1**

Fig. 1. DSC curves of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> at the heating rate of 4 K/min.

DSC curves of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> at the heating rate of 4 K/min. The results indicate that [Bmmim]NO<sub>3</sub> releases more energy than B when heated.



**FIGURE 2**

Fig. 2. Pressure and temperature versus time for the thermal decomposition of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> by ARC.

This figure shows the runaway reaction of [Bmim]NO<sub>3</sub> and [Bmmim]NO<sub>3</sub> under adiabatic conditions.

## KEYWORDS

Ionic liquid | Thermal stability | Thermal decomposition | Runaway reaction

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