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Benzotriazole is thermally more stable than 1,2,3-triazole

Alan R. Katritzky,[a,*] Zuoquan Wang,[a] Maia Tsikolia,[a] C. Dennis Hall[a] and Michelle Carman[b]

[a]*Center for Heterocyclic Compounds, University of Florida, Department of Chemistry, Gainesville, FL 32611-7200, USA*
[b]*University of Florida, Department of Biomedical Engineering, Gainesville, FL 32611-6131, USA*

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Abstract—TGA, DTA and DSC analyses indicate that benzotriazole is significantly more stable thermally than 1,2,3-triazole.

Recently, Prashad and co-workers[1] claimed 1,2,3-triazole 'as a safe and practical substitute for cyanide' and described benzotriazole as 'an explosive reagent' on the basis of one report.[2] Intuitively, 1,2,3-triazole would seem to be less stable than benzotriazole and evidence to support this conclusion has now been obtained.

Benzotriazole itself is an inexpensive, odorless and stable compound. Benzotriazolyl groups have been used extensively as synthetic auxiliaries for the last two decades.[3] They activate molecules towards numerous transformations and are both easily introduced and removed at the end of a reaction sequence.

Thermogravimetric analysis (TGA) of benzotriazole and 1,2,3-triazole was conducted on a Seiko TG/DTA 300. Measurements were taken from 50 to 240 °C at 1 °C/min in nitrogen using open platinum pans. As seen in Figure 1A benzotriazole evaporated between 127 and 194 °C with a peak rate at 166 °C while 1,2,3-triazole evaporated between 60 and 114 °C with a peak at 90 °C (Fig. 1B). Decomposition was not observed as open pans were used for the experiments.

Differential thermal analysis (DTA) for these two compounds was also carried out at the same time as TGA under the same conditions. The melting point for benzotriazole was ~95 °C, and evaporation of benzotriazole was complete at 193 °C (Fig. 2A). In contrast, evaporation of 1,2,3-triazole was complete at 113 °C (Fig. 2B).

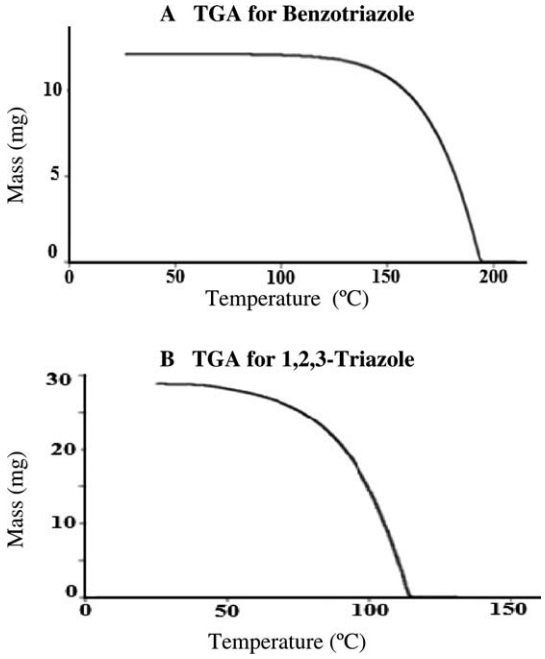

Figure 1. TGA curves for (A) benzotriazole and (B) 1,2,3-triazole.

Decomposition temperatures and thermal stabilities of these two compounds were measured by Differential scanning calorimetry (DSC) using a Seiko Instruments DSC 220C (Fig. 3). A positive deflection in the DSC corresponds to an exothermic process and a negative deflection corresponds to an endothermic one. Measurements for DSC were taken from 25 to 450 °C at a rate of

* Corresponding author. Tel.: +1 352 392 0554; fax: +1 352 392 9199; e-mail: katritzky@chem.ufl.edu

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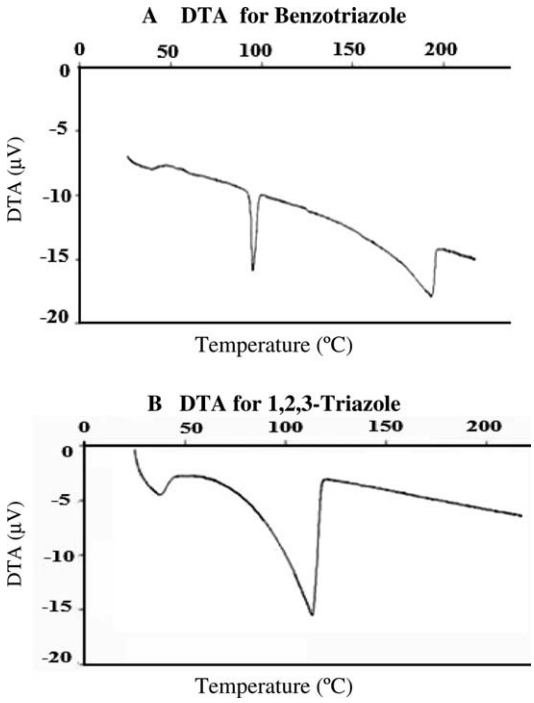

Figure 2. DTA curves for (A) benzotriazole and (B) 1,2,3-triazole.

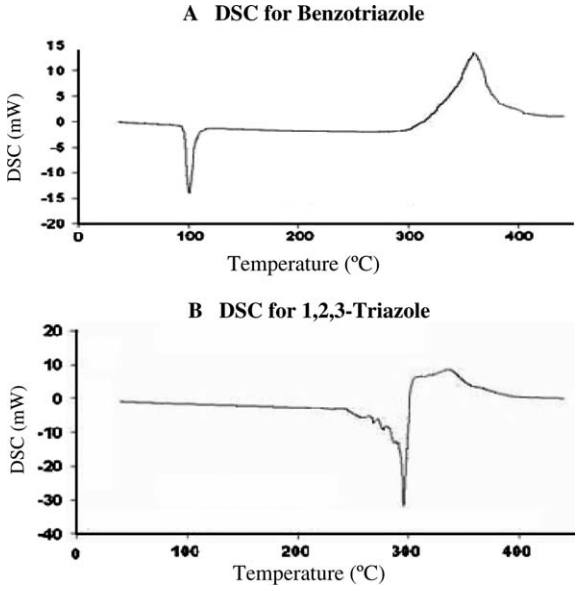

Figure 3. DSC curves for (A) benzotriazole and (B) 1,2,3-triazole.

10 °C/min under nitrogen using sealed aluminum pans and the hold time at maximum temperature was 1 min.

Benzotriazole (Fig. 3A) is shown to melt at 100 °C with a ΔH_m 98 mJ/mg and then to decompose exothermically ($\Delta H_d \sim -547$ mJ/mg) between 306 and 410 °C with its peak rate at 359 °C. By comparison, degradation of 1,2,3-triazole (Fig. 3B) occurred between 218 and 338 °C with multistep endothermic processes followed by exothermic ones (overall $\Delta H_d \sim -126$ mJ/mg).

The thermal stability experiments described herein clearly demonstrate the superior thermal stability of benzotriazole compared to 1,2,3-triazole.

To describe benzotriazole as 'an explosive reagent' (cf Ref. 1) is clearly misleading. During more than 20 years of intense research into the chemistry of benzotriazole derivatives, documented in several hundred publications, we have never observed a violent decomposition of benzotriazole. Maumee chemical company had an explosion in 1956 when attempting to distil ca. 1000 kg of the crude compound at 220 °C, but 'extensive laboratory runs, even under extreme conditions', gave no indication of any hazard.[2]

Stability decreases however, when an electronegative atom is attached to benzotriazole nitrogen. Thus the widely used 1-hydroxybenzotriazole is reported[4] to be unstable and we observed 1-chlorobenzotriazole to decompose violently at ca. 130 °C.

References and notes

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