Pyrolysis mechanism of urazole by evolved gas analysis

Satoru Yoshino · Atsumi Miyake

Abstract In order to obtain a better understanding of the pyrolysis mechanism of urazole, molecular orbital (MO) calculations and evolved gas analysis were carried out. The MO calculations were performed using the density functional method (B3LYP) at the 6-311++G(d,p) levels by Gaussian 03. The geometrical structure of urazole and its tautomers were examined theoretically. Identification and real-time analysis of the gases evolved from urazole were carried out with thermogravimetry-infrared spectroscopy (TG-IR) and thermogravimetry-mass spectrometry (TG-MS). The evolved gases were identified as HNCO, N_2, NH_3, CO_2, and N_2O at 400 °C, but were different at other temperatures.

Keywords Urazole · Evolved gas · Molecular orbital analysis · Real-time analysis

Introduction

Gas-generating agents have recently received considerable attention due to their possible applications in air-bag systems. These agents require specialized control in order to operate effectively. The essential features are thermal stability, release of large volumes of gas, high combustion speed, non-explosiveness, non-toxicity (both agents and generated gas), and long-term stability. Since 1,2,4-triazole-3-one (TO) has an identical framework to 5-nitro-1,2,4-triazole-3-one (NTO), which is known for its high combustion performance and thermal stability [1–4], TO is a promising next generation gas generating agent. To design a molecule with optimized combustion performance and thermal stability, it is necessary to clarify the effects of substituents on the thermal properties of TO derivatives. Some thermal behavior of triazole derivatives and thoes complex have been reported [5, 6]. Urazole (Fig. 1) is one such TO derivative, and has two carbonyl groups at positions 3 and 5 of the triazole ring. Several studies have been carried out on the gas generating properties of urazole and the effects of oxidizer composition, including small scale deflagration tests [7, 8], but the pyrolysis mechanism of urazole is not yet fully understood. For this reason, in this investigation, evolved gas analysis and molecular orbital (MO) calculations were carried out.

Experimental

In this study, urazole (Kanto Chemical Co., Inc.) with a reagent-grade purity (97%) was used without further purification.

Thermal behavior was analyzed by Thermogravimetry/differential thermal analysis (TG/DTA; Shimadzu Co. Ltd., DTG-50) under an argon gas flow rate of 20 mL min^{-1}. Samples (about 2 mg) were measured in an aluminum pan at a heating rate of 10 K min^{-1} from room temperature (R.T.; 25–30 °C) to 400 °C.

Thermogravimetry-infrared spectroscopy (TG-IR) was used to identify the gases evolved during pyrolysis of urazole. The apparatus consisted of a TG system (Shimadzu Co. Ltd., DTG-50) and an IR spectrometer (Shimadzu Co. Ltd., IRPrestige-21). The gases evolved after pyrolysis of the samples during the TG measurements were fed to a gas cell for IR analysis through a stainless steel transfer line.

S. Yoshino (✉) · A. Miyake
Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan
e-mail: d07tf010@ynu.ac.jp

Fig. 1 Numbering schemes and molecular structures of the urazole
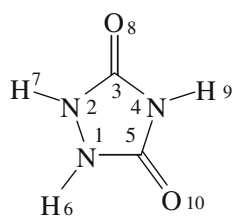
TG-IR analysis was carried out using an aluminum pan under an argon gas flow of 20 mL min^{-1}, a heating rate of 10 K min^{-1}, a measurement range of R.T. to 400 °C, and with a scanning resolution of 8 cm^{-1}. All spectra were integrated 15 times.

In addition, thermogravimetry-mass spectrometry (TG-MS) was used for real-time analysis of the gases evolved during the pyrolysis of urazole. This apparatus consisted of a TG system (Rigaku Co., TG8120) and a mass spectrometer (Shimadzu Co. Ltd., GCMS-QP2010). Measurements were carried out using an aluminum pan under a helium gas flow of 200 mL min^{-1}, with a heating rate of 10 K min^{-1}, a measurement range of R.T.−400 °C, and an oven temperature of 200 °C. The evolved gas components were identified on the basis of IR and MS reference spectra, available in the spectral libraries of the National Institute of Standards and Technology (NIST) and from a previous study [9].

Molecular orbital calculations were performed using the Gaussian 03 program [10]. Geometry optimizations of the structures and vibration analysis were archived within the framework of density functional theory (DFT) using the B3LYP method at the level of 6-311++G(d,p) (restricted closed-shell).

Results and discussion

Molecular orbital calculations

1,2,4-Triazole satisfying Huckel's rule are known to exhibit aromaticity. Urazole, on the other hand, is considered to be less stable than 1,2,4-triazole, since it does not satisfy Huckel's rule and has two carbonyl groups at position C3 and C5. Geometry optimizations were first performed on the structures of urazole tautomers (Fig. 2), calculated at the B3LYP/6-311++G(d,p) level, to determine the most stable compound. The total energies of the urazole tautomers are summarized in Table 1. The lowest value is found for structure **1**, which is considered to be the most stable isomer. The optimized bond lengths and angles for structure **1** are summarized in Table 2. Urazole was found not to have a planner structure. These results agree with the previous calculations of Jensen [11]. To
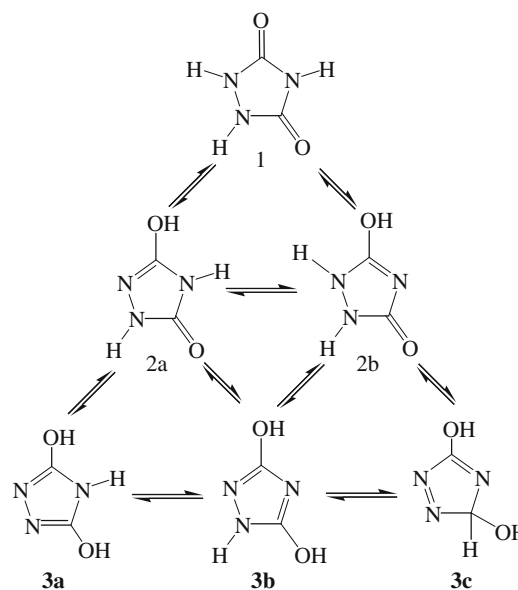
Fig. 2 Molecular structures of the urazole (**1**) and its tautomers

Table 1 The total energies (hartree) of the urazole (1) and its tautomers at B3LYP/6-311++G(d,p) levels

Compound	Total energy/hartree
1	−392.854
2a	−392.840
2b	−392.826
3a	−392.814
3b	−392.816
3c	−392.771

Table 2 Geometry optimized structures of urazole (**1**) at B3LYP/6-311++G(d,p) levels

Bond	Length/Å	Bond	Angle/°
N1N2	1.426	N1N2C3	107.86
N2C3	1.404	N2C3N4	104.75
C3N4	1.390	C3N4C5	112.69
N4C5	1.390	N4C5N1	104.75
N1H6	1.014	N1N2H7	113.39
N2H7	1.014	N2C3O8	113.39
C3O8	1.204	C3N4H9	126.84
N4H9	1.008	N4C5O10	123.66
C5O10	1.204	C5N1H6	128.41

investigate the properties of the urazole structure when the bond length in the triazole ring is extended, a relaxed scan was carried out using structure **1** as the initial structure.
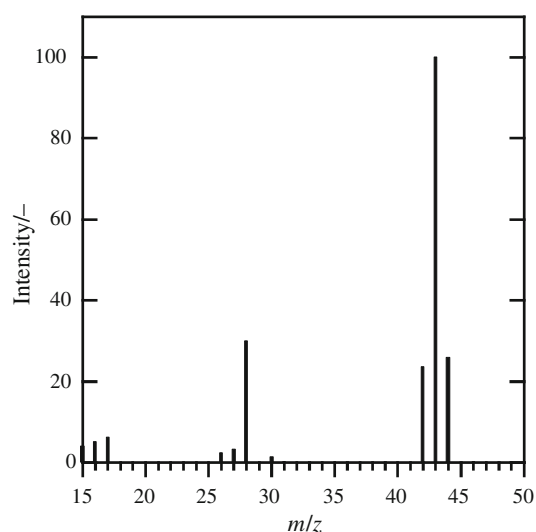
The length of the N1–N2 bond was found to increase with that of C3–N4 bond. The length of the C3–N4 bond was also found to increase with that of N1–N2 bond.

Identification of evolved gases

Analysis of the gases evolved from urazole was carried out using TG-IR and TG-MS. An IR spectrum and an averaged MS spectrum of gasses evolved in the range of 210–360 °C is shown in Figs. 3 and 4, respectively. The peaks in the IR spectrum can be assigned to νCO_2: 2,300–2,400 cm^{-1}, $\nu HNCO$: 2,250–2,275 cm^{-1}, νN_2O: 2,225 cm^{-1}, $\nu C=O$:
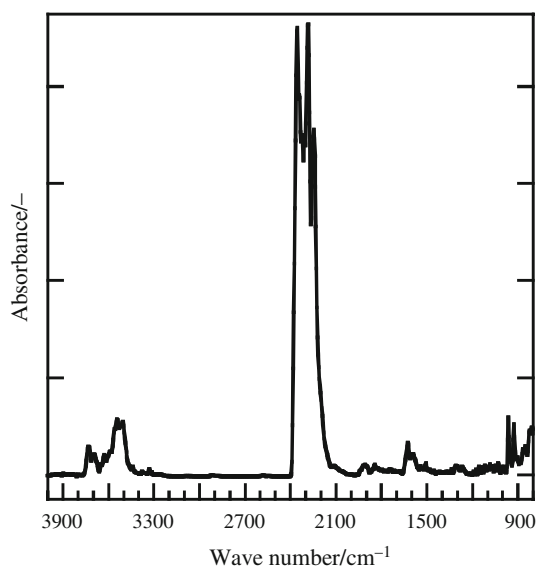
Fig. 3 IR spectrum of gases evolved from urazole using TG-IR, a heating rate of 10 K min^{-1}

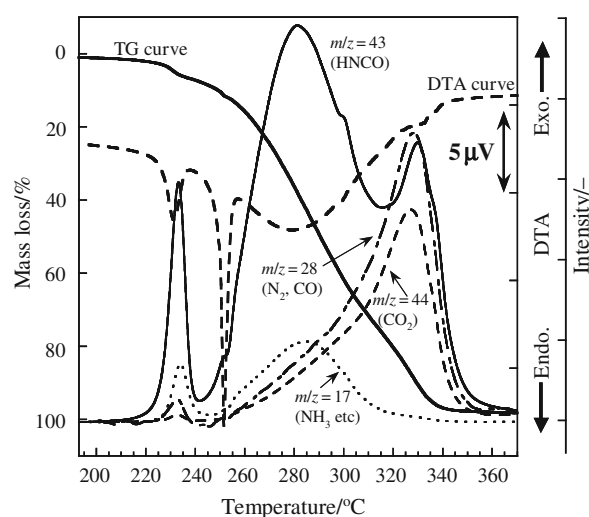1,500–1,600 cm^{-1}, and δNH_3: 950 cm^{-1}. The peaks in the mass spectrum correspond to mass-to-charge (m/z) ratios of 44, 43, 42, 28, and 17. The $m/z = 42$ peak can be assigned to ionized HNCO ($m/z = 43$). From the above results, it was determined that the gases which evolved from urazole at 400 °C were HNCO, N_2, CO_2, NH_3, and N_2O. Additionally, the $m/z = 43$ peak due to HNCO exhibited the highest intensity.
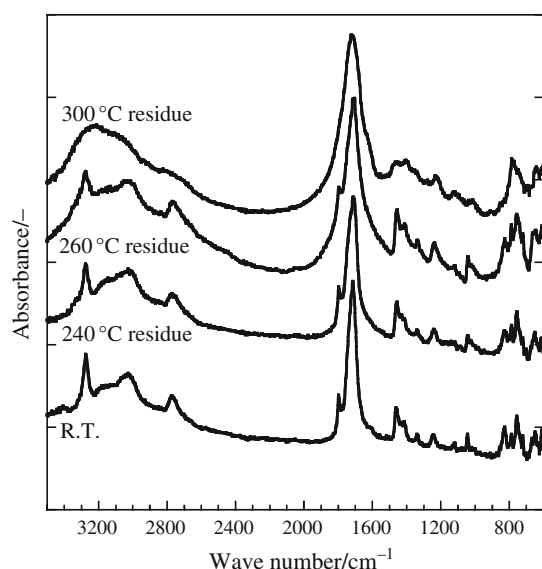
Real-time analysis of evolved gases

Real-time analysis of the evolved gases was carried out using TG-MS. Figure 5 shows TG/DTA curves for urazole in addition to intensity curves for the various MS peaks. At 220 °C, the TG curve indicated that mass loss had occurred. The DTA curve exhibited two endothermic peaks at 231 and 252 °C, and it has been reported that the melting point of urazole is 249 °C [12].

The intensity curve for $m/z = 43$ exhibited three peaks in the range 220–360 °C. The first peak at 220–240 °C is considered to be due to a phase change or an alteration in the chemical structure of urazole, since the evolved gases were observed with an endothermic peak. To further investigate this, urazole residues were analyzed at R.T., 240, 260, and 300 °C using IR measurements. Figure 6 shows the IR spectra of each residue. Since slight differences can be observed between the spectra at R.T., 240 and 260 °C, the endothermic peaks in the DTA curves at 231 and 252 °C are thought to correspond to a phase change of urazole. Since the melting point of urazole is 249 °C, the endothermic peak at 231 °C may be due to a structural phase transformation. These results suggest that urazole

Fig. 4 MS spectrum (70 eV) of gases evolved from the urazole using TG-MS, a heating rate of 10 K min^{-1}

Fig. 5 TG/DTA curve and intensity curves for the MS peaks ($m/z = 44, 43, 28, 17$)

Fig. 6 IR spectra of the urazole residues at the various temperatures (R.T.: 240, 260, 300 °C)

undergoes a phase change upon decomposition at 231 °C, and melts at 252 °C.

The second peak in the MS component curve for $m/z = 43$ in the range 240–310 °C is due to endothermic thermal decomposition of urazole. In the temperature range 310–360 °C, it is considered that the products of urazole become decomposed, since an inflection point was observed at around 310 °C in the TG curve, and the intensity of the $m/z = 17$ peak was smaller, and that of the $m/z = 28$ and 44 peaks was larger than at 240–310 °C. From these results, it was found that the gases which evolved from urazole at low temperatures (220–310 °C) were HNCO, NH$_3$, N$_2$, CO$_2$, and N$_2$O, and at high temperatures (310–360 °C) were HNCO, N$_2$, CO$_2$, and N$_2$O.

Discussion of initial decomposition mechanism

The initial decomposition mechanism in urazole at temperatures of 220–310 °C was considered based on the results of the analysis of evolved gasses and MO calculations. Since the HNCO intensity is highest at 220–310 °C, there are two possible mechanisms for HNCO production from urazole. The first is the dissociation of the N1–N2 and C3–N4 bonds of the urazole structure, and the second is the dissociation of N2–C3 and N4–C5 bonds. Since, according to the MO calculations, the length of N1–N2 bond increases with that of the C3–N4 bond, the former mechanism seems more likely. Initial decomposition occurs by a ring-opening reaction (N1–N2 and C3–N4 bonds) of the triazole ring.

Conclusions

Based on investigation of the pyrolysis mechanism in urazole, the following conclusions can be drawn.

(1) Urazole underwent a phase change upon decomposition at 231 °C, and melted at 252 °C.
(2) The gases evolved from urazole at 400 °C were HNCO, N$_2$, NH$_3$, CO$_2$, and N$_2$O.
(3) HNCO was the major evolved component during the thermal decomposition of urazole.
(4) At low temperatures (220–310 °C), the evolved gases were HNCO, NH$_3$, N$_2$, CO$_2$, and N$_2$O.
(5) At high temperatures (310–360 °C), the evolved gases were HNCO, N$_2$, CO$_2$, and N$_2$O.
(6) The initial decomposition mechanism of urazole is suggested to be a ring-opening reaction of the triazole ring.

References

1. Sinditskii VP, Smirnov SP, Egorshev VY. Thermal decomposition of NTO: an explanation of the high activation energy. Propell Explos Pyrotech. 2007;32:277–87.
2. Thangadurai S, Karatha KPS, Sharma DR, Shukla SK. Review of some newly synthesized high energetic materials. Sci Tech Energ Mater. 2004;65:215–26.
3. Hara Y, Taniguchi H, Ikeda Y, Takayama S, Nakamura H. The thermal decomposition and hazards evaluation for 3-nitro-1, 2, 4-triazol-5-one. Sci Tech Energ Mater. 1994;55:183–7.
4. Rothgery EF, Audette DE, Wedlich RC, Csejka DA. Preparation, crystal structure, thermal decomposition mechanism, and thermodynamical properties of H[Pr(NTO)$_4$(H$_2$O)$_4$]·$_2$H$_2$O. Thermochim Acta. 1991;185:19–25.
5. Badea M, Olar R, Marinescu D, Basile G. Thermal behavior of some new triazole derivative complexes. J Therm Anal Calorim. 2008;92:209–14.
6. Li N, Chen SP, Gao SL. Crystal structure and thermal analysis of diaquadi (1, 2, 4-triazol-5-one)zinc(II) ion nitrate. J Therm Anal Calorim. 2007;89:583–8.
7. Arai M, Tsukahara T, Ueda Y, Ichikawa K, Tamura M. Proceedings of 23th international pyrotechnics seminar, Tsukuba, September 30–October 4, 1997, p. 53–63.
8. Arai M, Tsukahara T, Tamura M. Proceedings of 26th international pyrotechnics seminar, Nanjing, October 1–4, 1999, p. 7–14.
9. Fischer G, Geith J, Klapotke TM, Krumm B. Synthesis, properties and dimerization study of isocyanic acid. Z Naturforschung. 2002;57b:19–24.
10. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR et al. Gaussian 03 revision E 01. Wallingford CT: Gaussian Inc.; 2004.
11. Jensen JO. Vibrational frequencies and structural determinations of urazole. Spectrochim Acta A. 2003;59:637–50.
12. Gordon PG, Audrieth LF. Hydrazine derivatives of the carbonic and thiocarbonic acids. VI. A new synthesis of urazole. J Org Chem. 1955;20:603–5.