

Synthesis and thermal analysis of alkali metal compounds of 1,2,4-triazole-3-one

Mikito Nakano^{*}, Satoru Yoshino^{*}, Mieko Kumasaki^{*†}, and Atsumi Miyake^{*}

^{*}Graduate School of Environment and Information Sciences, Yokohama National University,
79-7 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, JAPAN

Phone: +81-45-339-3994

[†]Corresponding address: kumasaki@ynu.ac.jp

Received: January 30, 2012 Accepted: March 31, 2013

Abstract

Alkali metals were reacted with 1,2,4-triazole-3-one (TO) in order to investigate the effect of different metals on the thermal properties of ionized TO rings. Three TO alkali metal compounds, namely, TOLi, TONa, and TOK, were synthesized, and their thermal properties and structures were compared with those of TO. The structures of the TO alkali metal compounds were investigated using Fourier transform infrared spectrometry (FT-IR), nuclear magnetic resonance spectrometry (¹H-NMR), ultra violet spectroscopy (UV), elemental analysis (EA), and molecular orbital (MO) calculations. FT-IR and UV spectra showed that all TO alkali metal compounds retained the carbonyl group and five membered ring of TO. ¹H NMR results indicated that the TO alkali metal compounds retained two of the hydrogen atoms in the original TO ring structure, and EA results was consistent with the structure. MO calculations showed that the bond length of N1-N2, C5-N1, and C5-H9 increased when the valence decreased. The thermal behavior of the TO alkali metal compounds was investigated by sealed cell differential scanning calorimetry (SC-DSC). From the results of SC-DSC, an endothermic peak and an exothermic peak in TO thermal behavior were observed at different temperatures, and TO alkali metal compounds showed an endothermic peak just before exothermic peak. These major exothermic peak and endothermic peak of TO alkali metal compounds decreased in temperature on increasing the atomic number of the alkali metal.

Keywords : 1,2,4-triazol-3-one, metal compound, thermal decomposition

1. Introduction

Azole compounds have attracted considerable attention. In the past, Miyata *et al.* and Iwakuma *et al.* carried out experiments on tetrazole compounds with the purpose of finding new gas generating agents for inflators¹⁻³. Kowhakul *et al.* applied chemical modifications, *i.e.*, synthesized triazole-metal complexes, to improve the reaction rates⁴. In many studies, azole compounds based on a 1,2,4-triazole-3-one (TO) (Figure 1) framework have been investigated as next-generation energetic materials,^{5, 6}. The framework of such compounds consists of a carbonyl group attached to a five-membered ring containing three nitrogen atoms. One such compound is 3-nitro-1,2,4-triazole-5-one (NTO), a nitrate derivative. During decomposition, NTO exhibits a high burning rate

and releases a large amount of gas. NTO also exhibits a low sensitivity to heat.⁷⁻⁹. A previous study reported that the amount of energy released by NTO is almost equivalent to the energy released by 1,3,5-trinitroperhydro-1,3,5-triazine or 1,3,5,7-tetra-nitroperhydro-1,3,5,7-tetrazocine; however, NTO has greater thermal stability¹⁰. This property enables NTO to be used as a propellant powder for military explosives¹¹. Many studies have also investigated the thermal properties, thermal decomposition mechanism, density, and crystal structure of NTO metal salts^{9, 12-15}.

Another example of TO derivatives is 1,2,4-triazolidine-3,5-dione, which also exhibits a high burning rate and releases a large amount of gas. The azole compound is a potential gas generating agent. The thermal

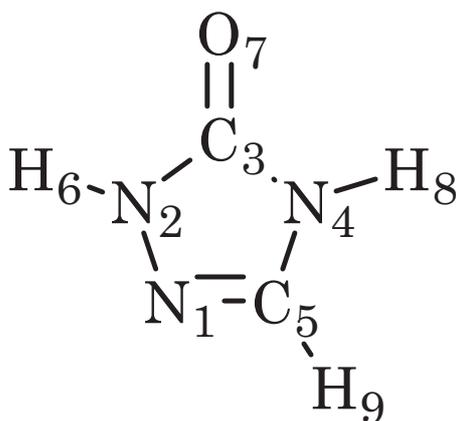


Figure 1 Molecular structure of TO.

decomposition mechanism of 1,2,4-triazolidine-3,5-dione have been hypothesized on the basis of results from molecular orbital calculations and thermal analysis^{16,17}.

NTO and 1,2,4-triazolidine-3,5-dione have several properties in common, including the high thermal stability of the high-nitrogen-content chemicals. The thermal stability and high burning rate of these compounds are attributed to the common framework they share. On analyzing the effect of substituents TO on thermal stability, it was found that the substituent of TO does in fact affect the thermal property. However, studies focusing on the effect of TO ring ionization on thermal behavior are necessary to further clarify the thermal properties of TO.

Ionic interaction caused by a positively charged metal is considered as one of the chief methods to ionize TO. However, to investigate the influence of ionization caused by a combination of various metals on the thermal properties of TO, a detailed thermal analysis must be carried out.

In the present study, TO and TO alkali metal compounds were synthesized to study the effect of metal addition on the thermal behavior resulting from metal-TO interaction. To express the relationship in terms of atomic number, three alkali metals, Li, Na, and K, having valence as same as that of hydrogen, were chosen. The thermal behaviors and molecular structures of TO and the three TO alkali metal compounds were investigated and compared to determine the effects of the metal added on the thermal behavior. Understanding these effects helps us to predict the thermal properties of triazole-metal compounds from their chemical compositions, and paves way for the development of new energetic materials and gas generating agents.

2. Experiments

2.1 Reagents

For the synthesis of TO, triethyl orthoformate (Kanto Chemical Co., Inc.) and semicarbazide hydrochloride (Kanto Chemical Co., Inc.) were used as the starting materials. $0.1 \text{ mol}\cdot\text{L}^{-1}$ potassium hydroxide solution (Wako Pure Chemical, Ltd.), $0.1 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide solution (Wako Pure Chemical, Ltd.), and $4.0 \text{ mol}\cdot\text{L}^{-1}$ lithium hydroxide solution (Wako Pure Chemical, Ltd.)

were used to synthesize TOK, TONa, and TOLi compounds, respectively.

2.2 Synthesis

The detailed procedure for preparation of TO is provided in an earlier report¹⁸. Triethyl orthoformate was added to semicarbazide hydrochloride and stirred for 3h at 60°C . The obtained TO was then filtered and recrystallized from ethanol. Individual TO alkali metal compound was synthesized using the obtained TO (50 mg) and the corresponding alkali metal hydroxide solution (50 mL of $0.1 \text{ mol}\cdot\text{L}^{-1}$). The solution was heated to 60°C and stirred for 2h. The TOLi solution was colorless, while the TONa and TOK solutions were yellow. After stirring, the solvent was evaporated at 50°C to obtain a colorless solid. To remove the remaining unreacted TO, the residue was stirred in 250 mL of acetone and filtered twice. The thus-obtained TO alkali metal compounds were colorless and deliquescent solid.

2.3 Instruments

The TO alkali metal compounds were characterized by elemental analysis (EA, Elementar: vario EL CHNOS Elemental Analyzer), Fourier transform infrared spectrometry (FT-IR, JASCO : FT/IR-420) using the KBr method, ultraviolet spectroscopy (UV, Shimadzu: UV-1800), and nuclear magnetic resonance spectrometry (^1H -NMR, Bruker : DRX500) using DMSO as the solvent. The thermal properties of the TO alkali metal compounds were investigated by stainless steel sealed cell differential scanning calorimetry (SC-DSC, Mettler Toledo : HP DSC 827e) at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ over a measurement range $30\text{-}500^\circ\text{C}$.

3. Results and discussion

3.1 Structure determination of the TO alkali metal compounds

During the synthesis, side reactions such as fragmentation or opening of the TO framework is common because of the basicity and high temperature of the reaction conditions. In order to confirm the synthesis of the TO alkali metal compounds, the presence of the TO framework in the final product was investigated. UV spectra provide information on conjugated and π -electron systems such as five-membered rings and carbonyl groups in TO, while, IR spectra provide information on the vibrational modes specific to a substituent group. The interaction motif caused by an alkali metal can be determined by identifying the number of hydrogen atoms in each compound via NMR.

Figure 2 shows the UV spectra of TO and the TO alkali metal compounds. In the UV spectrum of TO, the signal observed in the 190-210 nm region results from the five-membered ring and carbonyl group¹⁹; the TO alkali metal compounds also exhibited similar absorption spectra. We therefore conclude that the five-membered ring of the TO framework is conserved even after the treatment in basic aqueous solution and the reaction with alkali metals.

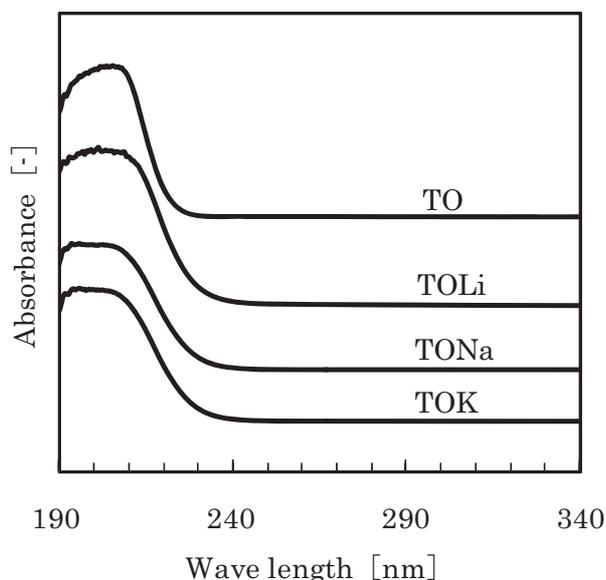


Figure 2 UV spectra of TO and the TO alkali metal compounds.

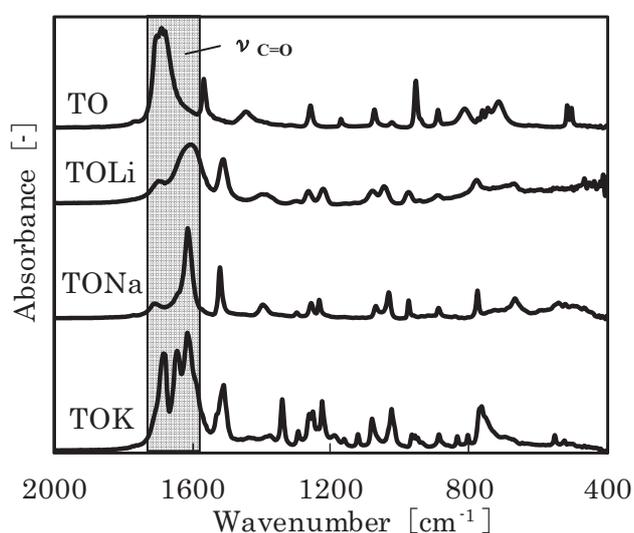


Figure 3 IR spectra of TO and the TO alkali metal compounds.

Figure 3 shows the IR spectra of TO and the TO alkali metal compounds. The IR spectrum of TO exhibits a carbonyl peak (C=O) at 1700 cm^{-1} , while the IR spectra of the TO alkali metal compounds exhibit carbonyl peaks at 1600 cm^{-1} , providing further confirmation that the TO structure did not decompose during the synthesis.

Table 1 shows the yields and elemental analysis of TO and the TO alkali metal compounds, where the values shown in parentheses are the calculated values. The experimental results for the TO alkali metal compounds exhibited larger values for hydrogen and smaller values for carbon and nitrogen, compared to the values determined by calculations. This was attributed to the deliquescence of the TO alkali metal compounds.

Figure 4 shows the $^1\text{H-NMR}$ spectra of TO and the TO alkali metal compounds. In the spectrum of TO, peaks corresponding to N-H (11.31 ppm and 11.43 ppm) and C-H (7.71 ppm) were observed¹⁹. The integrated intensity of

Table 1 EA results of TO and the TO alkali metal compounds.

Sample	Composition	Yield[%]	Result of elemental analysis		
			C	H	N
TO	$\text{C}_2\text{H}_3\text{N}_3\text{O}$	89	28.54 (28.40)	3.56 (3.55)	49.65 (48.40)
TOLi	$\text{C}_2\text{H}_2\text{N}_3\text{OLi}$	90	25.29 (26.40)	2.794 (2.22)	43.41 (46.17)
TONa	$\text{C}_2\text{H}_2\text{N}_3\text{ONa}$	72	20.40 (22.44)	2.841 (1.88)	32.23 (39.24)
TOK	$\text{C}_2\text{H}_2\text{N}_3\text{OK}$	66	19.50 (19.51)	1.637 (1.637)	33.59 (34.10)

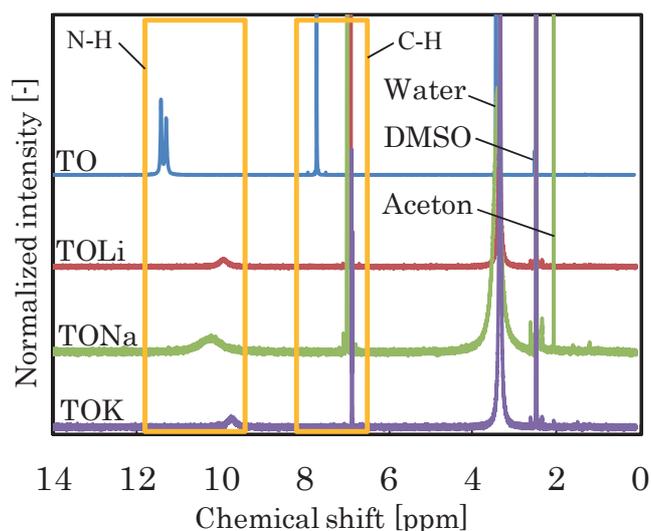


Figure 4 $^1\text{H-NMR}$ spectra of TO and the TO alkali metal compounds in the range of 0.00 to 14.00 ppm.

the N-H and C-H signals gave a ratio for the number of hydrogen atoms as 2.09 : 1.00.

All the TO alkali metal compounds exhibited broad peaks around 10.00 ppm and sharp peaks around 7.00 ppm. On the basis of the results in the previous study¹⁹, the broad signals are derived from hydrogen atoms in the N-H bonds, and the sharp signals are derived from hydrogen atoms in the C-H bonds. In the spectrum of TOLi, peaks corresponding to C-H and N-H were observed at 6.91 ppm and 9.95 ppm, respectively. The integrated intensities of the N-H and C-H peaks gave a ratio for the number of hydrogen atoms as 0.89 : 1.00. In the spectrum of TONa, peaks corresponding to C-H and N-H were observed around 7.00 ppm and 10.25 ppm, respectively. The integrated intensities of the N-H and C-H peaks gave a ratio for the number of hydrogen atoms as 0.81 : 1.00. For TOK, peaks corresponding to C-H and N-H were observed around 7.00 ppm and 9.89 ppm, respectively. The integrated intensity of signal of the N-H and C-H peaks gave a ratio for the number of hydrogen atoms as 0.95 : 1.00. The disappearance of one N-H peak, the downfield displacement of another signal observed at 10.00 ppm, and the reduction in the relative ratio of the C-H and N-H signals are attributed to the elimination of a hydrogen during the synthesis. Therefore, the TO alkali metal compounds contain only two hydrogen atoms attached to

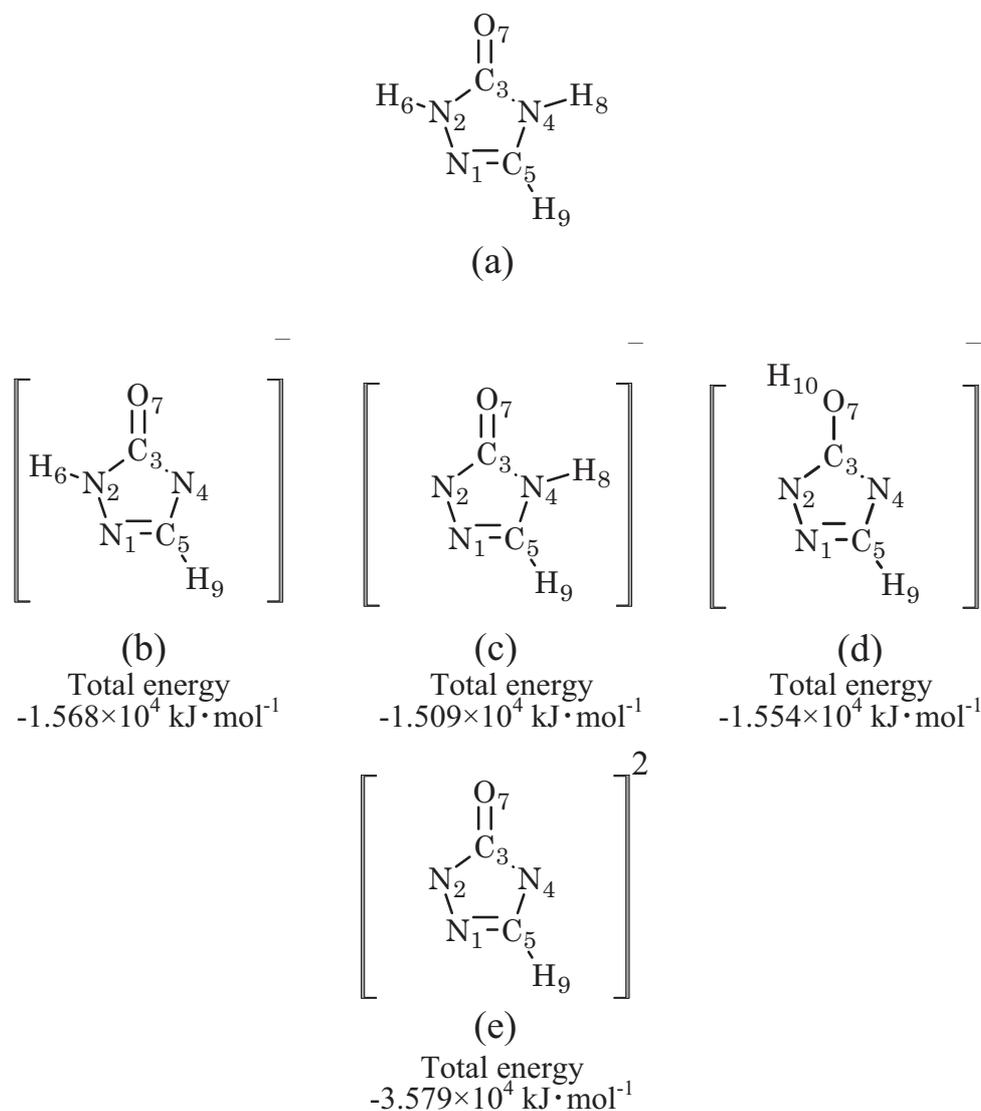


Figure 5 Structures of TO and ionized TO.

the five-membered ring. The downfield shift of the C-H peak from 7.71 ppm to 7.00 ppm is due to the change in the electronic density of the five membered ring caused by the elimination of hydrogen.

3.2 Structural change caused by ionization

To study the structural change caused by ionization, ab initio MO calculations were carried out using Gaussian 03 W²⁰. Geometry optimization was performed on the structures of TO and ionized TO (Figure 5), calculated at the MP2/6-311+G(d,p) level. Table 2 summarizes the optimized bond length and angle. The optimized structure of (b) and (d) showed more distortion than do the structure of (c). The bond length of N1-N2, C5-N1, and C5-H9 increased with decreasing ionic valence.

To determine the most stable structure of negatively charged TO, the total energies of (b), (c), and (d) were compared with that of (a). Since the energy of (c) is lower than that of (b) and (d), the most stable structure of the monoanionic form of TO is considered to be (c). The most stable structures of the TO alkali metal compounds are presumed to be as shown in Figure 6.

3.3 Thermal behavior of TO and the TO alkali metal compounds

Figure 7 shows the SC-DSC curves of TO and the TO alkali metal compounds. TOLi showed an exothermic peak at 155°C and an endothermic peak just before an exothermic peak at 330°C. TONa showed endothermic peaks at 117°C and 160°C and an endothermic peak just before an exothermic peak at 325°C. TOK showed an endothermic peak just before an exothermic peak at 285°C.

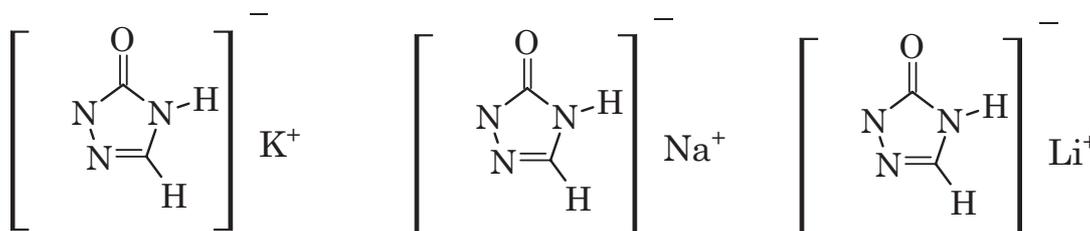
In an earlier study on TO¹⁸, an endothermic peak was observed and attributed to melting at 230°C and an exothermic peak was observed and attributed to decomposition at 332°C in the gas phase. In contrast, the TO alkali metal compounds showed an endothermic peak just before an exothermic peak at around 300°C. Furthermore, in the alkali metal compounds, the onset temperature of the endothermic peak just before the exothermic peak decreased with the increasing atomic number of the alkali metal.

4. Conclusions

The following conclusions can be drawn from our

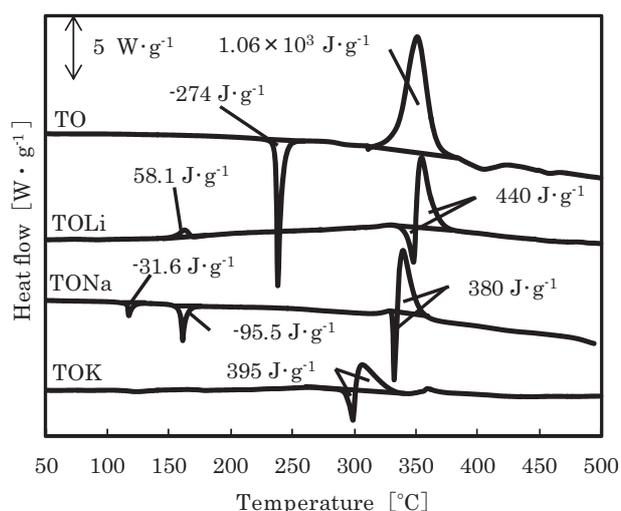
Table 2 Geometry optimized structures of TO and ionized TO at MP2/6-311+G (d,p) level

Bond	(a)	(b)	Length[Å]		
			(c)	(d)	(e)
N1-N2	1.36890	1.37078	1.38485	1.38184	1.38849
N2-C3	1.38210	1.39819	1.36308	1.33813	1.38517
C3-N4	1.39984	1.37389	1.41892	1.33972	1.39865
N4-C5	1.37179	1.35594	1.36719	1.36526	1.35663
C5-N1	1.30983	1.33767	1.32406	1.34602	1.35663
N2-H6	1.00780	1.00696	-	-	-
C3-O7	1.21873	1.25240	1.25450	1.38063	1.29411
N4-H8	1.00830	-	1.00706	-	-
C5-H9	1.07936	1.08551	1.08279	1.08553	1.09439
C7-H10	-	-	-	0.96389	-
			Angle [°]		
N1-N2-C3	114.941	113.236	109.193	104.469	107.524
N2-C3-N4	100.583	105.232	105.719	116.696	110.423
C3-N4-C5	109.150	104.215	107.172	98.964	102.12
N4-C5-N1	111.779	117.343	109.914	115.231	115.482
C5-N1-N2	103.546	99.973	108.002	104.640	104.451
N1-N2-H6	120.017	120.832	-	-	-
N2-C3-O7	130.210	123.791	131.397	121.028	124.914
C3-N4-H8	122.998	-	123.826	-	-
N4-C5-H9	124.355	122.729	124.699	122.811	123.29
C3-O7-H10	-	-	-	102.641	-

**Figure 6** Structures of the TO alkali metal compounds.

study :

- (1) Three TO alkali metal compounds (TOLi, TONa, and TOK) were successfully synthesized. All three compounds were white deliquescent solids. TOLi was colorless while TONa and TOK were yellow in aqueous solution.
- (2) UV and FT-IR analysis confirmed that the TO framework maintained its five-membered ring and carbonyl group even after reaction with the alkali metals. NMR spectra indicate that a hydrogen on the five-membered ring was replaced with the alkali metal ion during the reaction, which was supported by EA results.
- (3) Geometry optimization indicated that the bond length of N1-N2, C5-N1, and C5-H9 increased with increasing ionic valence. The most stable structures of the TO alkali metal compounds were considered to be those shown in Figure 6.
- (4) DSC indicates that the TO alkali metal compounds showed an endothermic peak just before an exothermic peak at $\sim 300^\circ\text{C}$, and the onset temperature of the

**Figure 7** DSC curves of TO and the TO alkali metal compounds.

endothermic peak decreased with increasing atomic number of the alkali metal.

Acknowledgements

The authors are grateful to Mr. Ishihara at the Instrumental Analysis Center of Yokohama National University. This study was supported by the 39th Foundation for the Promotion of the Industrial Explosives Technology (2011).

References

- 1) K. Iwakuma, Y. Miyata, S. Date, M. Kohga, and K. Hasue, *Sci. Tech. Energetic Materials*, 68, 95–101 (2007).
- 2) Y. Miyata, S. Date, and K. Hasue, *Sci. Tech. Energetic Materials*, 68, 131–135 (2007).
- 3) Y. Miyata, K. Morita, K. Iwakuma, M. Abe, S. Date, and K. Hause, *Sci. Tech. Energetic Materials*, 68, 153–159 (2007).
- 4) W. Kowhakul, M. Kumasaki, Y. Wada, M. Arai, and M. Tamura, *Sci. Tech. Energetic Materials*, 67, 87–90 (2006).
- 5) S. Yoshino, and A. Miyake, *J. Therm. Anal. Calorim.*, 102, 513–516 (2010).
- 6) K. Y. Lee, and M. D. Coburn, U. S. Patent, 4,733, 610, (1988).
- 7) S. Ye, K. Tonokura, M. Koshi, *Combust. Flame*, 132, 240–246 (2003).
- 8) G. Singh, and S. P. Felix, *J. Hazard. Mater.*, A90, 1–17 (2002).
- 9) H. H. Licht, *Propellants, Explos., Pyrotech.*, 25, 126–132, (2000).
- 10) M. W. Smith, M. D. Matthew, and D. Cliff, DSTO-TR-0796, (1999).
- 11) P. B. Kulkarni, T. S. Reddy, J. K. Nair, A. N. Nazare, M. B. Talawar, T. Mukundan, and S. N. Asthana, *J. Hazard. Mater.*, A123, 54–60 (2005).
- 12) S. S. Yun, J. K. Kim, and C. H. Kim, *J. Alloys Compd.*, 408, 945–951 (2006).
- 13) S. Jirong, H. Rongzu, K. Bing, and L. Fuping, *Thermochim. Acta*, 331, 49–60 (1999).
- 14) S. Jirong, H. Rongzu, K. Bing, and L. Fuping, *Thermochim. Acta*, 335, 19–25 (1999).
- 15) T. Yoshida, Y. Shimizu, K. Hara, S. Chijiwa, and J. Onishi, U. S. Patent, 5, 827, 996, (1998).
- 16) S. Yoshino, and A. Miyake, *J. Therm. Anal. Calorim.*, 99, 145–148 (2010).
- 17) S. Yoshino, S. Ihara, M. Tajima, K. Matsunaga, and A. Miyake, *Sci. Tech. Energetic Materials*, 70, 16–22 (2009).
- 18) D. R. Haines, N.J. Leonard, and D. F. Wiemer, *J. Org. Chem.*, 47, 474–482, (1982).
- 19) Alan R. Katritzky, Christopher A. Ramsden, Eric F.V. Scriven, and Richard J.K. Taylor, *Comprehensive Heterocyclic Chemistry*, Pergamon Press, 5, 739 (1984)
- 20) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, (2004).

1,2,4-triazole-3-oneアルカリ金属化合物の合成と熱挙動に関する研究

中野未樹人*, 吉野悟*, 熊崎美枝子*†, 三宅淳巳*

TOのイオン化合物の熱挙動について検討するため、TOのリチウム化合物、ナトリウム化合物、カリウム化合物を合成した。そして、金属の添加がおよぼす影響について検討するため、それぞれの熱挙動および構造をTOと比較した。TOアルカリ金属化合物の構造は、赤外分光分析 (FT-IR)、核磁気共鳴分光分析 (¹H-NMR)、紫外分光分析 (UV)、元素分析 (EA) と量子化学計算の結果 (MO) より検討した。FT-IRおよびUVの結果よりカルボニル基と五員環構造が確認された。また、NMRおよびEAの結果から五員環には二つの水素原子が結合していると考えられた。量子化学計算の結果からはTOは価数が減少すると、五員環の1位と2位の結合、5位と1位の結合および5位と水素の結合が伸びることが明らかとなった。熱挙動の検討には密閉セルを用いた示差走査熱量測定を用いた。SC-DSCの結果より、TOは吸熱挙動と発熱挙動が離れて観察されるのに対し、TOアルカリ金属化合物は吸熱挙動の直後から発熱挙動が観察された。また、TOアルカリ金属化合物の主要な吸熱ピークおよび発熱ピークは金属の原子番号が大きくなるに従って低下した。

*横浜国立大学大学院環境情報学府 〒240-8501 神奈川県横浜市保土ヶ谷区常盤台79番7号
Phone: 045-339-3994

†Corresponding address: kumasaki@ynu.ac.jp