Research paper

A study on the characteristics of azole-metal complexes (III)
- Thermal behaviors of 1H-1,2,4-triazole metal complexes

Wasana Kowhakul*†, Mieko Kumasaki**, Yuji Wada***,
Mitsuru Arai*, and Masamitsu Tamura****

*Environmental System course, Graduate School of Frontier Sciences, the University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-0033, JAPAN
† Corresponding address: wasana@explosion.chem.t.u-tokyo.ac.jp

**National Institute of Industrial Safety, 1-4-6 Umezono, Kiyose, Tokyo 204-0024, JAPAN

***AIST Tsukuba Central 1,Tsukuba, Ibaraki, 305-8561, JAPAN

****Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, JAPAN

Received: May 20, 2005 Accepted: April 12, 2006

Abstract

1H-1,2,4-triazole(1Htri)-metal complexes were investigated as promising gas generators for airbag inflators. The SC-DSC measurements, sensitivity tests, and deflagration tests were conducted to investigate the influences of the metals on the decomposition characteristics of the complexes. The SC-DSC measurements revealed the 1Htri-metal interaction stabilize the complexes. Regarding the sensitivity tests, 1Htri-metal complexes were categorized in the same class 7 of friction sensitivity test and class 8 of drop hammer sensitivity test. Besides, electrostatic sensitivity test, only copper and silver complexes were different from its pure azole which both complexes were categorized as class 3 according to JIS. Furthermore, the deflagration test indicated the proportion of metals in the substance had a substantial impact on burning rate, which was as verified by the relation of metal percentage and maximum pressure rate.

Keywords: 1H-1,2,4-triazole, Thermal decomposition, DSC, Complexes, Deflagration

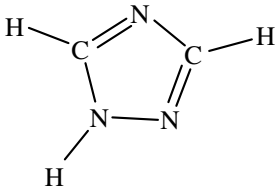
1. Introduction

Energetic materials are employed as gas generators in airbags because they easily release a large amount of decomposition gas, inflate an airbag, and protect passengers during life-threatening accidents. Many researchers have been attracted in developing new energetic materials for gas generators because of their practical use.

The important properties for gas generators are as follows[1]: (1) Generate a large amount of decomposition gas in a short period, (2) No gas toxicity, (3) Low residue after decomposition, (4) High thermal stability, (5) Low sensitivity to physical stimulation such as mechanical impact, friction and static electricity, (6) Low cost, (8) No change in properties with time. This research focused on characterization of promising gas generators in terms of thermal stability, sensitivity to friction, impact, and static electricity. Besides, the gas generating performance was examined.

For the promising gas generators, high nitrogen contents are required from the standpoint of gas toxicity. If the substances with 100% nitrogen percentage, Nitrogen-Clusters, were available, they would give clean gases when they decomposed. However, Nitrogen-Clusters only exist in theoretical calculation. Generally, the higher nitrogen percentage it has, the unstable it is; there are only a few energetic materials whose nitrogen percentage is more than 50%. Among those substances, triazole can not only give a large quantity of nitrogen gas but also have satisfactory stability[2]. Owing to high nitrogen content, they are used as gas generators.

In order to obtain better properties for gas generators, we have applied some chemical modifications to triazole; we have designed triazole-metal complexes. Transition metals are commonly used to improve reaction rates for propellant because of their catalytic characteristics[3]. As a



1H-1,2,4-triazole

Fig. 1 The structure of 1H-1,2,4-triazole (1Htri).

result, the response to stimuli becomes better.

Among myriad of triazole and transition metals, we chose 1H-1,2,4-triazole(1Htri) in this report which are the elementary structures of triazole (see Fig. 1). Copper, Cobalt, Nickel and, Silver were selected because of their catalytic characteristics[4), 5)].

2. Experiments

2.1 Samples

1Htri (98% purity), $Cu(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, and, $AgNO_3$ were purchased from Wako Chemical, Japan.

1Htri - Ag complex

5.0 mmol of 1Htri was dissolved in 15 ml of water and 2.5 mmol of $AgNO_3$ which dissolves in 15 ml of water was added and the resulting solution stirred at room temperature. The solution was filtered off. To obtain a white precipitate was dried under reduced pressure.

Anal. Calcd. for $[Ag(C_2N_3H_3)(NO_3)_2]\cdot H_2O$: C = 9.4 , H = 1.9 , N = 21.8 Found: C = 9.6 , H = 1.0 , N = 18.9

The other 1Htri-metal complexes were synthesized and analyzed according to the previous studies[5), 6)]: $[Cu(C_2N_3H_3)_2(NO_3)_2]\cdot H_2O$, $[Co_2(C_2N_3H_3)_7(NO_3)_4]\cdot 2H_2O$ and $[Ni\ (C_2N_3H_3)_6(H_2O)_6](NO_3)_6\cdot 2H_2O$ were obtained.

In order to clarify the effects of coordination, the mixtures of each metal nitrate and 1Htri were also prepared according to the metal-complex composition[7)].

2.2 SC-DSC

SC-DSC was carried out using DSC20 with the operation system STAR^e System (Mettler Toledo K.K.). In this study, stainless steel cells were selected as the high-pressure sample containers[8)]. The experiments were carried out at a heating rate of 10 K min^{-1} under a steady state flow of nitrogen (N_2). An almost constant sample mass of 1.0 mg was weighed. They were heated in the scanning mode from 30 ℃ to 500 ℃ . The temperature and heat flow calibrations were conducted by the recommended procedure using pure indium metal with a melting point of 429.6 K and heat of fusion of Δ Hf= 287.1 J g^{-1}.

The SC-DSC data on the recording chart were analyzed as follows:

(1) The line connecting the point before the exothermic reaction starts and the point after it ends was used as the baseline.

(2) The temperature at which exothermic reaction starts (T_{DSC}) is determined from the intersection of the tangential line at the inflection point and the baseline.

2.3 Sensitivity tests

2.3.1 Electrostatic sensitivity test

An electrostatic sensitivity tester measured the sensitivity to static electricity. The apparatus in this study was designed by Mizushima *et al.*[9)]. It equipped the upper and lower electrodes with fixed distance, which of electrodes connected to a set of condensers at predetermined capacitances. The sample was sandwiched between the two electrodes, and ignited by condenser discharge.

2.3.2 Friction sensitivity test

The Julius Peter friction tester (BAM) was used to determine the friction sensitivity of the metal complexes. The 1/6 explosion point was determined by rubbing the complexes on a moving plate with a fixed pin.

2.3.3 Drop hammer test

The sensitivity to mechanical impact was measured by the drop hammer test according to Japanese Industrial Standards (JIS). A drop hammer tester was made in Hosoya Firework. Co. Ltd. In the experiments, sample of approximately 0.03 gram was placed in a brass cup. The cup was placed in the device and the weight was dropped from a predetermined height. The tests were repeated following up and down method to determine 50 percent ignition energy.

2.4 Deflagration test

The 52 ml deflagration test (see Fig. 2) was carried out to evaluate combustion characters of 1Htri-metal complexes. The test apparatus is a closed vessel equipped with a pressure transducer (PE-200 kws), thermocouples, and gas outlet and safety relief valve. The combination igniter of Ti/KNO_3 powder (100 mg) as a primary ignition agent, and B/KNO_3 pellet (250 mg) as a secondary ignition agent was used to ignite the 1Htri-metal complexes. In this work, $KClO_3$ was using as an oxidizing agent.

All of samples in deflagration tests were prepared based on the stoichiometric composition and the zero of oxygen

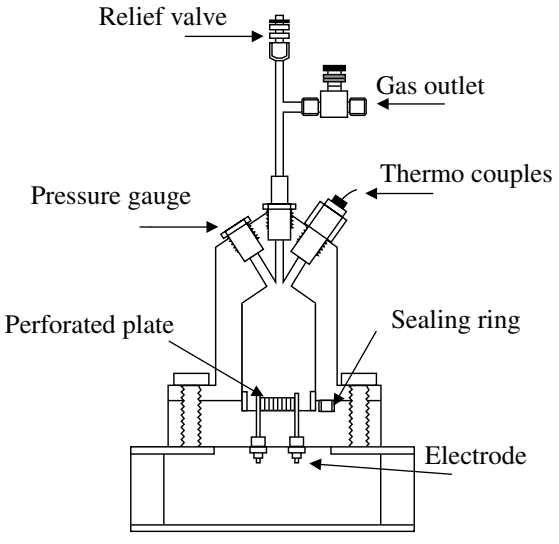


Fig. 2 The 52ml deflagration apparatus.

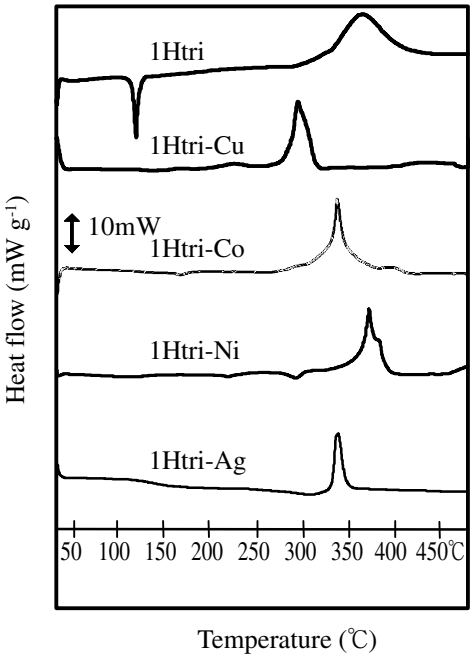


Fig. 3 SC-DSC curves for the 1Htri-metal complexes.

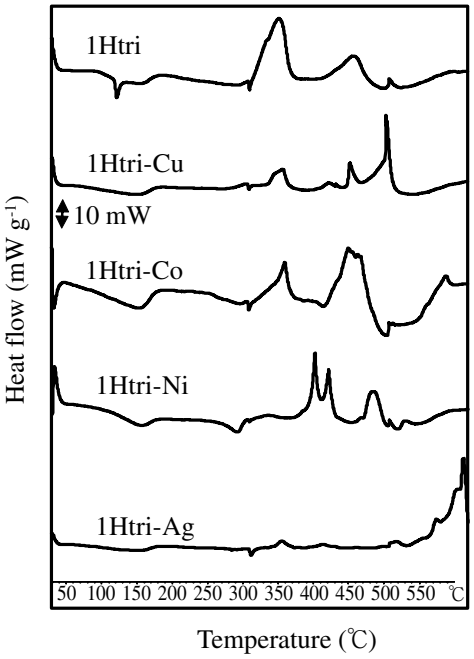


Fig. 4 SC-DSC curves for the 1Htri mixed with metal nitrates.

balance as equations (I) and (II):

$4C_2N_3H_3$ (1Htri)+$5.5KClO_4$ → $8CO_2$+ $6N_2$+$6H_2O$+5.5KCl (I)

mMetal complex [$M(C_2N_3H_3)n$]+ $nKClO_4$ →

aCO_2+ bN_2+cH_2O+dKCl+fMetal oxide (II)

3. Results and discussion

3.1 SC-DSC

Figure 3 shows SC-DSC curves of 1Htri-metal complexes. The value of T_{DSC} and Q_{DSC} are summarized in Table 1. Before decomposition temperature, 1Htri exhibited endothermic peak that corresponded to melting. In case of the complexes, the endothermic peak disappeared. The phenomena might be due to the change of their electronic state[2].

In the metal complexes, 1Htri molecules are slightly ionic positively[2] therefore, ionic 1Htri molecules and metal link in complex via coulomb force strongly while neutral molecules link together via Van der Waals force in pure azole crystal. Since the Coulomb force is stronger than the Van der Waals force, metal complexes made it difficult to melt compared to 1Htri molecular crystals.

Moreover, exothermic peak of complexes became sharp compared to the pure azoles. Figure 4 shows the exothermic behavior of 1Htri-metal nitrate mixture. The difference between two types of samples suggested that coordination, i.e. Metal-1Htri interaction also accelerated exothermic reaction.

The value of acceleration of thermal decomposition (D_{DSC}) was calculated by differentiating the curves with respect to time (Fig. 5). The figure indicated cobalt has less effect on accelerating reaction than other metals. On the other hand, copper provide good performance.

Table 1 T_{DSC} and Q_{DSC} of 1Htri-metal complexes.

Sample	T_{DSC} (℃)	Q_{DSC} (J g^{-1})	Q_{DSC} (kJ $mole^{-1}$ 1Htri)
1Htri	343	850	59
1Htri-Cu	297	1525	262
1Htri-Co	343	1496	189
1Htri-Ni	379	1418	262
1Htri-Ag	344	1103	283

3.2 Sensitivity tests

Table 2 summarized the results of the each sensitivity test. 1Htri and 1Htri-metal complexes were in the same class in its friction sensitivity and drop hammer sensitivity tests, in which every sample explode at load353N, class 7

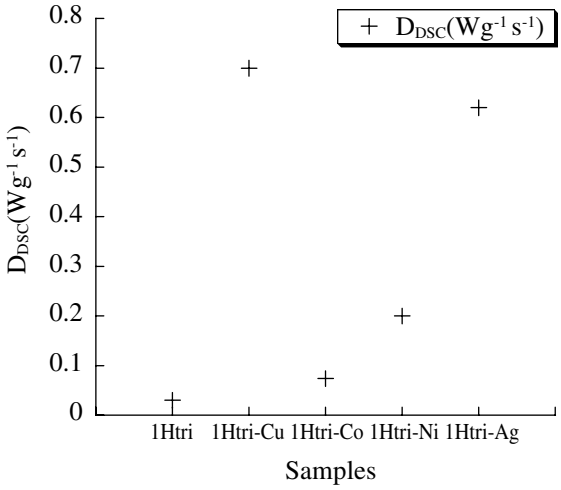


Fig. 5 D_{DSC} of 1Htri-metal complexes.

Table 2 Each sensitivity test results of 1Htri-metal complexes.

Sample	Electrostatic sensitivity (E_{50} J^{-1})	Standard deviation (σ)	Drop hammer ($H_{1/6}$ cm^{-1})	Friction sensitivity ($M_{1/6}$ N^{-1})
1Htri	1.26(class 4)	0.36	6.76 (class 2)	78～157(class 5)
1Htri-Cu	0.19(class 3)	0.69	>50 (class 8)	>353(class 7)
1Htri-Ni	0.49(class 4)	0.17	>50 (class 8)	>353(class 7)
1Htri-Co	0.69(class 4)	0.61	>50 (class 8)	>353(class 7)
1Htri-Ag	0.34(class 3)	0.18	>50 (class 8)	>353(class 7)

and class 8, repectively.

The electrostatic sensitivity was determined to be class 3 for copper and silver complexes. However, nickel and cobalt complexes, the tests were carried out in the same class 4 of its pure 1Htri, which were according to JIS.

3.3 Deflagration test

The results of the deflagration test of 1Htri-metal complexes were shown in Fig. 6 and Table 3. As silver complexes, the sample for deflagration could not be prepared because it could not form the pellet. The deflagration behaviors of 1Htri were changed by the coordination of 1Htri to metal ions. (dP/dt) max was decreased; in particular, 1Htri-Ni complex showed about twice the (dP/dt) max of 1Htri.

It could be distinguished among the burning rate and the proportion of metal in each complex. Even if the burning rate of 1Htri-metal complexes were decreased, it would decrease corresponding to the proportion between the catalysts and substances[10]. The arrangements of metal proportion in complexes were 1Htri-Co, 1Htri-Cu and 1Htri-Ni respectively and the qualities of burning rate were agreed with this arrangement.

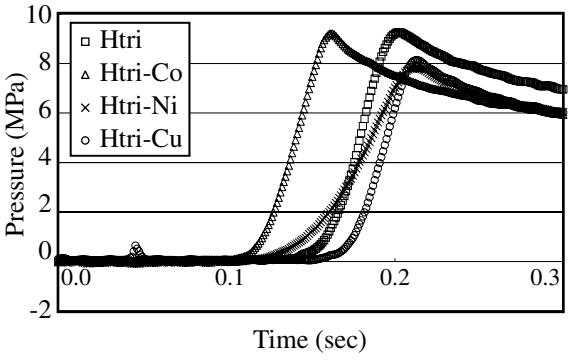


Fig. 6 The 52ml deflagration test result curves.

Table 3 The deflagration test results of 1Htri-metal complexes.

Sample	Pmax[MPa]	(dP/dt)max [MPa s^{-1}]	%Metal in complex
1Htri	9.3	287.4	
1Htri-Cu	8.1	244.2	16.3
1Htri-Co	9.2	257.7	18.5
1Htri-Ni	7.8	150.4	15.9

4. Conclusion

In this work, the experiment on SC-DSC and Deflagration test was conducted in order to investigate the influences of metal in azole complexes on decomposition characteristics. From this study, it can be concluded as following:

First, thermal stability of azole metal complexes improved because of 1Htri-metal interaction.

Second, catalytic effects on enhancing D_{DSC} were clarified. This can be observed as steep exothermic peaks in SC-DSC graphs.

Third, 1Htri-metal complexes were categorized in the same class 7 of friction sensitivity test and class 8 of drop hammer sensitivity test. Besides, electrostatic sensitivity test, only both copper and silver complexes were different from its pure azole that categorized as class 3 according to JIS.

Finally, the proportion of metal in the substance has a substantial impact on burning rate as verified by the relation of metal percentage and values of maximum pressure rate.

Acknowledgements

The authors are grateful to Hosoya Firework Co., Ltd. for their assistance at sensitivity tests.

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