

Thermal behavior of various metal complex nitrates (III)

— Cu complex of aminoguanidine —

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As a new gas generant, the Cu complex nitrates of aminoguanidine ($\text{Cu}(\text{NHCNNH}_2)_2(\text{NO}_3)_2$; here after, CuAG) was synthesized, and the thermal behavior was investigated.

During the isothermal decomposition reaction at 101 to 125 °C, the CuAG complex formed a stable intermediate. An autocatalysis equation can describe the reaction up to the formation of the intermediate, and the aminoguanidine of the ligand seemed to gradually decompose while maintaining the complex nitrate form. The activation energy of the reaction was 51 kJ/mol. Above 125 °C, the CuAG decomposes so rapidly that ignition occurs.

The burning rate and burning temperature at the stoichiometric composition with $\text{Sr}(\text{NO}_3)_2$ was 6.48 mm/s and 1343 °C, respectively. Concerning the gas evolution during the combustion, the N_2 and CO_2 gases account for 98.8 % of all the evolved gases, while the evolution of HCN gas was only 6.67×10^{-4} mol/mol. The evolution of CO gas was very low even during the ignition of the complex in spite of the negative oxygen balance (-0.237 g/g).

1. Introduction

Recently, automobiles sold in Japan are equipped with an airbag system for safer driving. A non-azide gas generant as a substitute for sodium azide has been studied, and tetrazole derivatives¹⁾, urazole²⁾ and azodicarboamide³⁾ were the subjects of this study.

The authors evaluated the metal complexes of organic compounds, which are composed of many nitrogen atoms, as the new gas generant. In previous reports^{4)~11)}, the thermal decomposition behavior of the metal complex of carbonylhydrazide was investigated.

In this report, the Cu complex nitrate of aminoguanidine ($\text{Cu}(\text{NHCNNH}_2)_2(\text{NO}_3)_2$; hereafter, CuAG) was synthesized, and the thermal

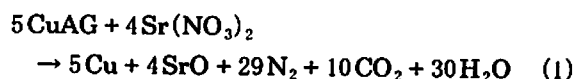
behavior was investigated.

2. Experiment

2.1 Reagents

CuAG was synthesized using a previously reported method¹²⁾. The Cu complex nitrate of the ammine was slowly added to the AG nitrate in water in a 1 to 2 molar ratio at 50 °C in a water bath. The obtained complexes were identified by elemental analysis and polarized light zeman atomic absorption spectrometry due to their insolubility in water.

The Sr nitrate oxidizing agent was Wako pure chemical reagent grade. Reagents screened to under 63 μm were mixed for sixty minutes using splittable chopsticks on parchment paper. Five kinds of samples were prepared by mixing, i.e., a stoichiometric composition and two compositions each with positive and negative oxygen balances based on eq.1. Table 1 shows these compositions.



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Table 1 Compositions of mixtures (CuAG/Sr(NO₃)₂)

Molar ratio	CuAG/Sr(NO ₃) ₂		Oxygen balance (g/100g)
	(wt./wt.)		
5 / 2	0.80/0.20		-9.14
5 / 3	0.73/0.27		-4.15
5 / 4	0.66/0.34		0.
5 / 5	0.61/0.39		+3.51
5 / 7	0.47/0.53		+13.40

2. 2 Apparatus and method

2. 2. 1 Thermal analysis

The differential thermal analysis and the gravimetric analysis were carried out using a Rigaku TAS-200 Thermal Analyzer. The sample container was an alumina cell and the sample amount was 3 mg. The sample was heated to 800 °C at a heating rate of 20 °C/min under Ar.

2. 2. 2 Isothermal decomposition

50 mg of CuAG was weighed into a glass tube sealed at one end (6 mm inside diameter and 60 mm length) and placed in an iron block having an 8 mm diameter and a 50 mm length hole. This block was inserted into an electric furnace kept at various temperatures. After being heated for a specified time, the weight of the sample was measured. The decomposition residue was analyzed by X-ray diffraction using a Rigaku rotaflex RU-200, by elemental analysis using a Yanagimoto CHN corder MT-3 type and by infrared spectroscopy using a Shimadzu FTIR-8100A.

2. 2. 3 Combustion reactivity

The heat of the reaction was measured using a Shimadzu CA-4 Type Automatic Bomb calorimeter in argon. The results of the investigation at ambient pressure showed a variation in the measurement

values of 3 % to 4 % over the pressure range of 1. 1 MPa to 3. 1 MPa. Also, there was no combustion at 0. 1 MPa, therefore, the measurement was carried out at 1. 1 MPa.

The measurement of the burning rate was carried out under the following conditions. A preliminary investigation showed that the linear burning rate in the theoretical density range of 0. 65 to 0. 70 became small as the theoretical density became large, while the weight burning rate was independent of it. Also, when the diameter of the burning tube was 6 mm, the burning rate had a maximum value. Consequently, the sample was loaded at 0. 6 of the theoretical density in a 6 mm i.d. aluminum tube. The pressure dependence was measured over the pressure range of 0. 1 to 4. 1 MPa and the influence of the composition on the burning rate was investigated at 1. 1 MPa. The burning rate was determined by the time that was needed for the combustion wave to proceed 10 mm.

The burning temperature was also measured using the same theoretical density and tube diameter used for the measurement of the burning rate. A 0. 25 mm diameter W/Re thermocouple was vertically inserted into the burning tube against the combustion direction and was connected to a Yokogawahokusinn Analyzing Recorder.

The combustion residue was analyzed by X-ray diffraction using a Rigaku rotaflex RU-200.

2. 2. 4 The evolved gas

The evolved gases in which the heat of reaction was measured were collected in a collection bag (Tedlar bag, 350 ml capacity). The amounts of the N₂, CO, CO₂ and N₂O gases evolved were quantified using a Shimadzu GC-4C Gas Chromatograph (hereafter, GC). Table 2 shows the measurement conditions for the GC. The NO and NO₂ gases were

Table 2 Gas chromatograph conditions

Gases	N ₂ , CO	N ₂ O, CO ₂
Column	Molecular sieves 5A	Activated charcoal
Particle size	60 ~ 80 mesh	60 ~ 80 mesh
Length	2m	1m
Temp.	40 °C	40 °C
Carrier gas	He, 20 ml/min.	He, 60 ml/min.

quantitatively analyzed using a Gastec gas detector tube. The NH_3 and N_2H_4 gases were quantified by the indophenol method¹³⁾ ($\lambda = 630 \text{ nm}$) and the P-aminobenzaldehyde method¹⁴⁾ ($\lambda = 458 \text{ nm}$), respectively.

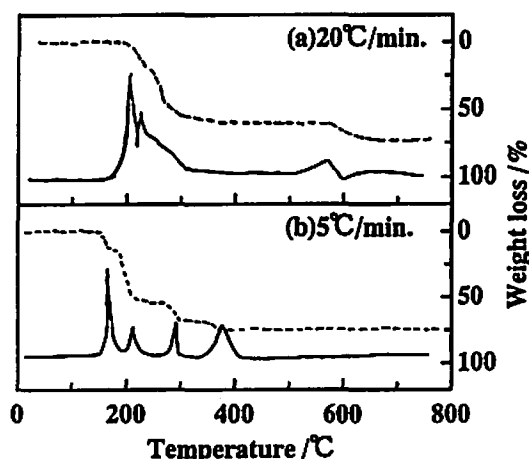


Fig. 1 DTA-TG curves of CuAG

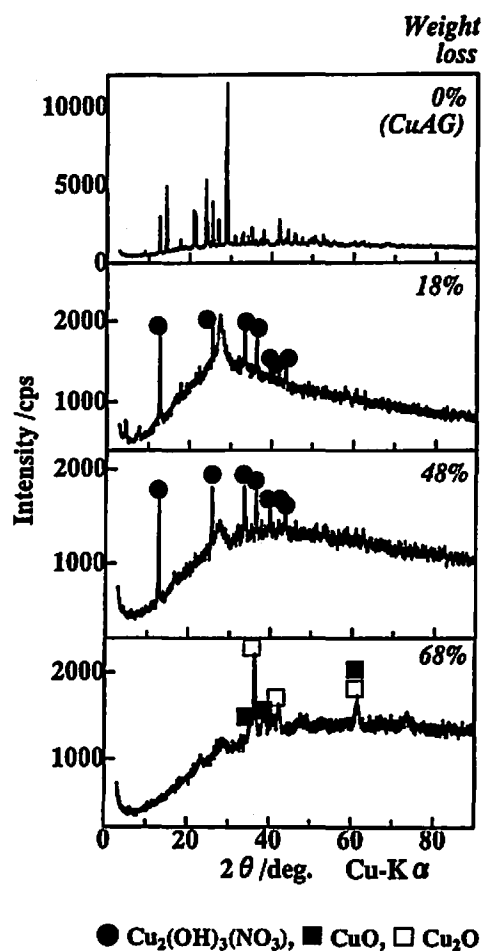


Fig. 2 XRD patterns of the residue for CuAG during the decomposition at heating rate of 5°C/min.

3. Results and discussion

3. 1 Thermal analysis

Fig.1 show the results of the thermal analysis for CuAG at various heating rates. CuAG started to exothermally decompose at 170 °C, and the decomposition reaction was complicated over a wide temperature range, as previously reported¹²⁾. At a heating rate of 5 °C/min, the weight loss converged to 18, 48, 68 % at 180, 210, 290 °C, respectively. Fig.2 shows the results of the powder x-ray diffraction for the products collected for each weight loss in Fig.1 (b), and Fig.3 shows the results of their IR spectra. The pattern of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ was confirmed up to 48 % of the weight loss, though it is difficult to consider because of a bad crystal. $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ might be formed due to H_2O being generated by the decomposition of aminoguanidine of the ligand. The formation mechanism of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ was not clear. On the other hand, in the IR spectra, the absorption attributable to the functional group of $[\text{NO}_3^-]$ was observed at 1390 cm^{-1} up to 48 % of the weight loss, and several absorption peaks attributable to the aminoguanidine,

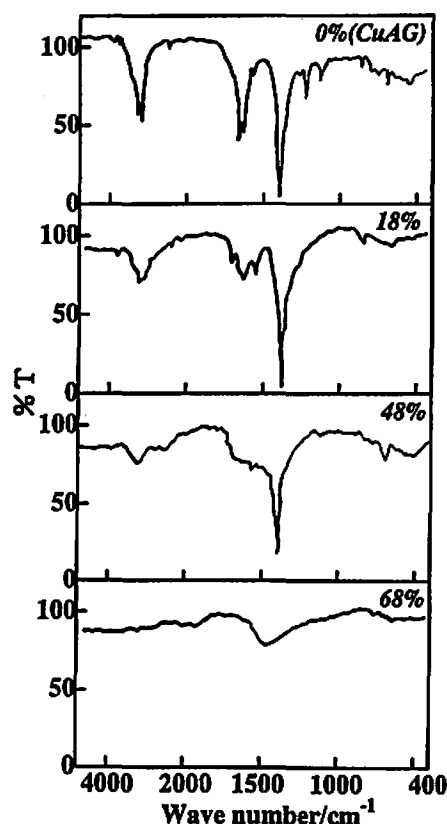


Fig. 3 IR spectra of the residue for CuAG during the decomposition at the heating rate of 5°C/min.

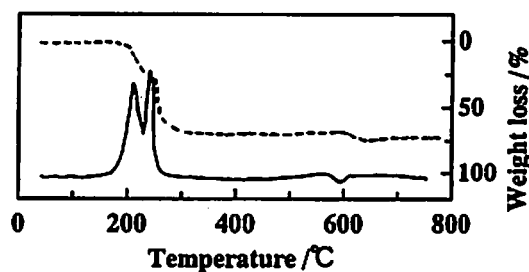


Fig. 4 DTA-TG curves for CuAG mixture

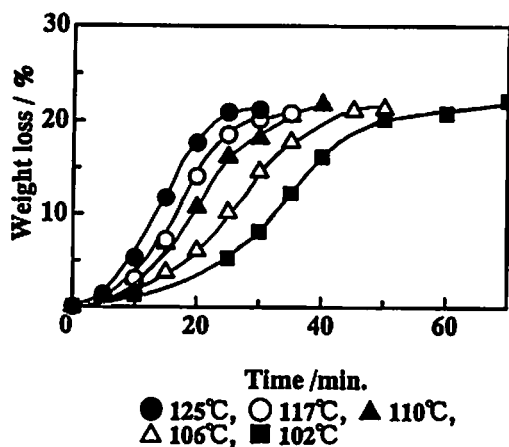


Fig. 5 The isothermal decomposition of CuAG at various temperatures

such as the NH stretching vibration at 3300 cm^{-1} and the $\text{-C}=\text{N}$ stretching vibration at 1700 cm^{-1} , became small as the decomposition reaction progressed. Aminoguanidine of the ligand might gradually decompose while maintaining the complex nitrate form under mild heating conditions.

Fig.4 shows the results of the thermal analysis for the CuAG complex mixture with $\text{Sr}(\text{NO}_3)_2$. The unreactive $\text{Sr}(\text{NO}_3)_2$ oxidizing agent was found to decompose at $560\text{ }^\circ\text{C}$. The unreacted $\text{Sr}(\text{NO}_3)_2$ was a small amount compared to the carbohydrazide complex nitrates previously reported^{7),8)}. The reactivity with $\text{Sr}(\text{NO}_3)_2$ was expected to be comparatively high.

3. 2 Isothermal decomposition

Fig.5 shows the weight loss versus time curves for only the CuAG complex during the isothermal decomposition at various temperatures from $101\text{ }^\circ\text{C}$ to $125\text{ }^\circ\text{C}$. The CuAG decomposes so rapidly that ignition occurs above $125\text{ }^\circ\text{C}$.

The weight loss converged to 21 % in the experimental temperature range, indicating the formation

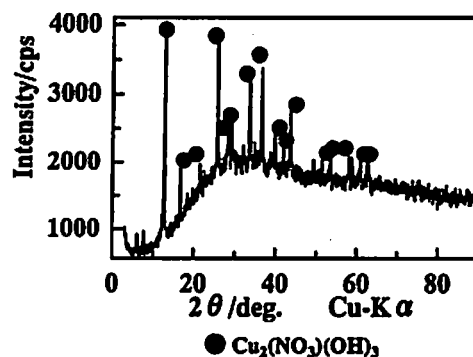


Fig. 6 XRD pattern of the residue during the isothermal decomposition at $110\text{ }^\circ\text{C}$

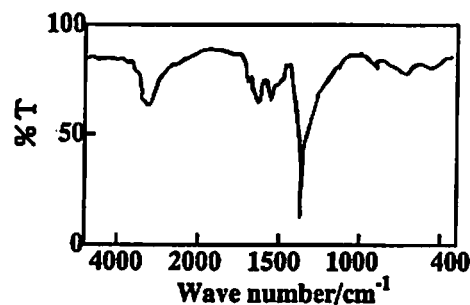


Fig. 7 IR spectra of the residue for CuAG during the isothermal decomposition at $110\text{ }^\circ\text{C}/\text{min}$.

of a stable intermediate during the course of the reaction. The decomposition did not progress even after holding at the experimental temperature for several hours. Fig.6 shows the results of the XRD for the intermediate during the isothermal decomposition at $110\text{ }^\circ\text{C}$ and Fig.7 shows the result of the IR spectrum for one experiment. The pattern of $\text{Cu}_2(\text{OH})_3(\text{NO}_3)$ was confirmed, as observed during the decomposition at the heating rate of $20\text{ }^\circ\text{C}/\text{min}$. Furthermore, the absorption attributable to the nitrate ion was also observed at 1390 cm^{-1} in the IR spectrum. The reaction mechanism seems to be same in both decomposition conditions considering from the residue in the course of reaction. The intermediate was clearly a mixture.

For the first stage of the reaction (up to 22 % of the weight loss), an applicable rate equation was investigated by the derived fractional decomposition. As shown in Fig.8, an autocatalysis equation can describe the reaction. In the case of the decomposition of CuAG, the products act as the catalysis. Arrhenius plots of the rate constants at each temperature gives the activation energy of the reaction of 51 kJ/mol (frequency factor: 7.8×10^5).

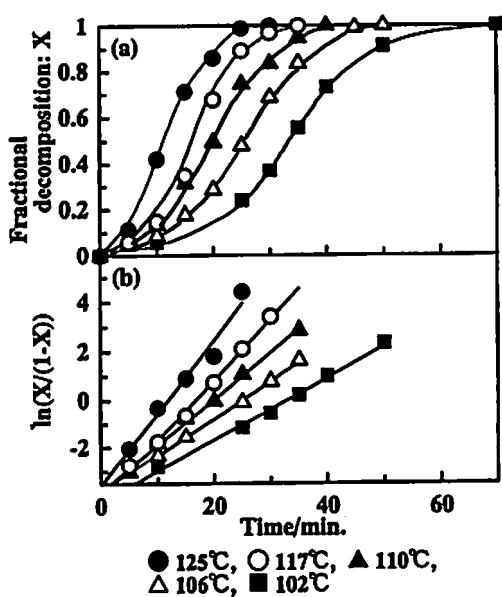


Fig. 8 Isothermal decomposition ratio (X) curves and plots of $\ln(1-X)$ against times for CuAG

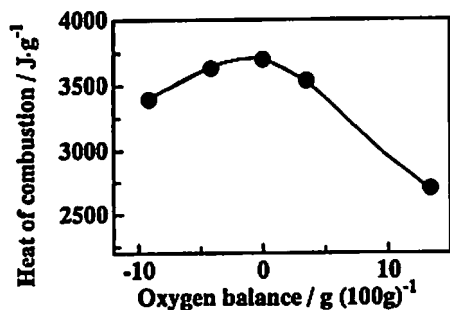


Fig. 9 Heat of combustion for CuAG/Sr(NO₃)₂

3. 3 Combustion reactivity

Fig.9 shows the composition dependence of the heat of reaction. The heat of reaction had a maximum value at the stoichiometric composition. Fig.10 shows the results of the powder X-ray diffraction for the residue of each composition. Cu and SrCO₃ were confirmed at the negative oxygen balance and stoichiometric composition. The CuAG decomposed to CuO during the decomposition under mild heating conditions, such as the thermal analysis, while it decomposed to Cu under vigorous conditions, such as the combustion. On the other hand, not Cu but CuO were confirmed at the positive oxygen balance, and unreactive Sr(NO₃)₂ was also observed in addition to CuO and SrCO₃. CuO was thought to be formed by the reaction of Cu and unreactive Sr(NO₃)₂. SrCO₃ was formed by the reaction of the reaction products SrO and CO₂.

Fig.11 shows the results of the composition

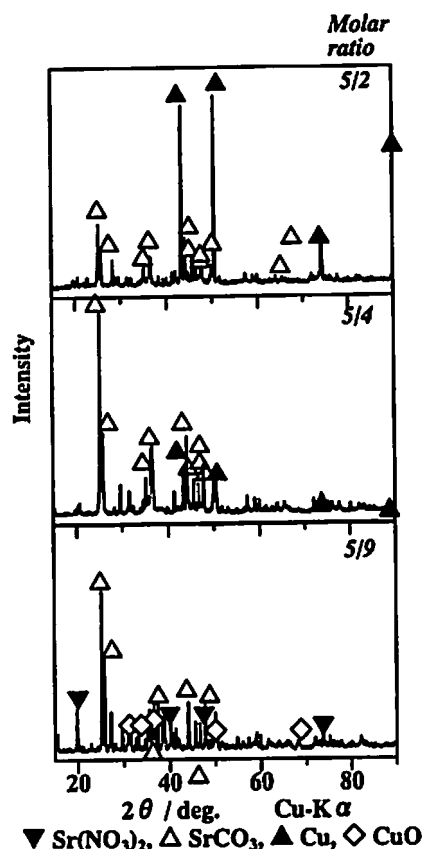


Fig. 10 XRD patterns of the combustion residue

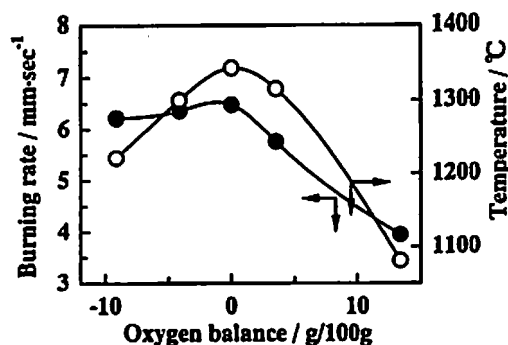


Fig. 11 Burning rate and burning temperature for CuAG/Sr(NO₃)₂

dependence of the burning rate and burning temperature. These also had a maximum value at a stoichiometric composition; the burning rate and burning temperature at the stoichiometric composition was 6.48 mm/s and 1343 °C, respectively.

Fig.12 shows the pressure dependence of the burning rate at a stoichiometric composition. The pressure exponent was estimated based on Vieille's equation ($V = aP^n$). The pressure exponent was comparatively high at 0.722, and the reaction in the gas phase was thought to be the rate-determining

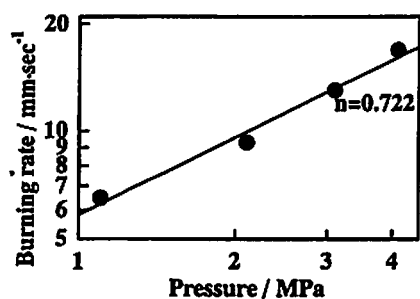


Fig. 12 Burning rate characteristics of the stoichiometric mixture

Table 3 The amount of evolved gases (unit: mol/mol)

Gases	CuAG	CuAG/Sr(NO ₃) ₂ Mixtures
	ignition	Combustion
N ₂	3.25	5.55
NH ₃	1.07	0.002435
HCN	1.41	0.0
N ₂ O	0.44	0.0
NO	0.025	0.015
NO ₂	0.0	0.0
CO	0.14	0.13
CO ₂	0.57	1.41
N number	9.89	11.11
%	98.9	95.8
C number	2.12	1.54
%	106.0	77.0

step of the combustion¹⁶⁾. The nitrate of the oxidizing agent might generate highly reactive NO_x gases. As previously reported^{7),8)}, the pressure exponent shows a tendency to be high in the case of using the nitrate as the oxidizing agent.

3. 4 The evolved gases during the combustion

Table 3 lists the analysis results of the evolved gases during the ignition for the complex only and during the combustion for the mixture. In the case of the ignition for the complex only, HCN gas attributable to the C = N bond in the structure and NH₃ gases generated more than 1 mol per 1 mol of CuAG due to the negative oxygen balance of the CuAG (-0.237 g/g). However, the evolution of CO gas was very low even during the ignition of the complex in spite of the negative oxygen balance. This phenom-

enon was a peculiarity of the CuAG complex. No carbonyl bond in the structure was given as one of the reasons. An investigation was needed to determine the relation of the complex structure and the gas evolution behavior.

On the other hand, in the mixture system with Sr(NO₃)₂, the N₂ and CO₂ gases account for 98.8% of all evolved gases, while the evolution of HCN gas was very low; 6.67×10^{-4} mol/mol. For the CO gas, there was no difference in the amount of the evolved gas compared with the one during the ignition of only the complex.

4. Conclusion

As new gas generant, the Cu complex nitrates of aminoguanidine (hereafter, CuAG) were synthesized, and the thermal behavior was investigated.

From the isothermal decomposition at 101 to 125 °C, CuAG complex formed a stable intermediate during the course of the reaction. The weight loss converged to 22%, and an autocatalysis equation can describe the reaction up to 22% of the weight loss. For this reaction, the aminoguanidine of the ligand was postulated to gradually decompose while maintaining the form of the complex. Arrhenius plots of the rate constants at each temperature provided the activation energy of the reaction, 51 kJ/mol (frequency factor; 7.8×10^5). Above 125 °C, the CuAG decomposed so rapidly that ignition occurred, and the final residue was CuO.

The burning rate and burning temperature at the stoichiometric composition with Sr(NO₃)₂ was 6.48 mm/s and 1343 °C, respectively. The final residue was not CuO but Cu. For the evolution gas during the combustion, N₂ and CO₂ gases account for 98.8% of all the evolved gases, while the evolution of HCN gas was low, 6.67×10^{-4} mol/mol. The evolution of CO gas was very little even during the ignition of the complex only in spite of the negative oxygen balance (-0.237 g/g). Having no carbonyl bonds in the structure was given as one of the reasons.

Reference

- 1) Jian Zhou WU, H. Yuzawa, T. Matsuzawa, M. Arai and M. Tamura, J. Japan Explosives Soc., 55, 66 (1994)

- 2) K. Ichikawa, M. Arai, M. Tamura and K. Waki, An academic meeting of Japan Explosives Soc., 1997 (autumn), p87
- 3) T. Kazumi, Y. Suzuki, T. Okada, T. Hasegawa and T. Yoshida, J. Japan Explosives Soc., 56, 248 (1995)
- 4) M. Akiyoshi, N. Hirata, H. Nakamura and Y. Hara, J. Japan Explosives Soc., 57, 238 (1996)
- 5) M. Akiyoshi, N. Hirata, H. Nakamura, and Y. Hara, *ibid.*, 57, 244 (1996)
- 6) M. Akiyoshi, Y. Imanishi, N. Hirata, H. Nakamura and Y. Hara, *ibid.*, 58, 68 (1997)
- 7) M. Akiyoshi, G. Kinoshita, N. Hirata, H. Nakamura and Y. Hara, *ibid.*, 58, 258 (1997)
- 8) M. Akiyoshi, G. Kinoshita, N. Hirata, H. Nakamura and Y. Hara, *ibid.*, 59, 192 (1998)
- 9) M. Akiyoshi, Y. Imanishi, N. Hirata, H. Nakamura and Y. Hara, *ibid.*, 59, 320 (1998)
- 10) M. Akiyoshi, Y. Imanishi, N. Hirata, H. Nakamura and Y. Hara, *ibid.*, 59, 328 (1998)
- 11) M. Akiyoshi, Y. Imanishi, N. Hirata, H. Nakamura and Y. Hara, *ibid.*, 59, 328 (1998)
- 12) M. Akiyoshi, Y. Imanishi, N. Hirata, H. Nakamura and Y. Hara, *ibid.*, 60, 274 (1999)
- 13) JIS K0099-1983, "Analysis method of ammonia in exhaust gases"
- 14) Analytical Chemical Handbook", Maruzen, 650 (1981)
- 15) A. P. Glazkova, Explosivestoffe, Nr. 4, 137 (1973)

種々の金属錯体硝酸塩の熱的挙動(第3報)

—アミノグアニジン銅錯体—

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新規のガス発生剤として、アミノグアニジンの銅錯体硝酸塩(以後、CuAGと略)を合成し、その熱的挙動を検討した。

101~125℃での等温分解では、CuAGは反応の途中で安定な中間体を生成する。中間体生成までの反応は、自触媒の式に最もよく適合し、この時、錯体硝酸塩の形態を維持しながら、配位子であるアミノグアニジンが徐々に分解する。分解反応の活性化エネルギーは51kJ/molであった。尚、125℃以上では、反応が急激に進行して、発火にいたる。

硝酸ストロンチウムとの量論組成での燃焼速度及び燃焼温度は、各々6.48mm/sec, 1343℃となった。燃焼時の発生ガスは、その98%が窒素及び二酸化炭素で、わずか 6.67×10^{-4} mol/molのシアン化水素ガスが検出された。また、一酸化炭素ガスは、CuAGの酸素バランスが負(-0.237g/g)であるにもかかわらず、錯体単体発火時でさえ、その発生量は少なかった。

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