

The thermal behavior of various metal complex nitrates (II)

The Fe and Cr complex nitrates of urea

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The metal complex nitrates are expected to be new gas generants for automobile air bags. In this report, the thermal behavior of the Fe and Cr complex nitrates of urea was investigated using only the complex and in the mixed system with KBrO_3 .

The coordination of urea to a metal increased its thermal stability and the thermal reactivity. The thermal stability of CrUR was greater than that of FeUR.

FeUR decomposed not to Fe_2O_3 but to $\text{Fe}(\text{NO}_3)_2$, while CrUR decomposed to Cr_2O_3 during the isothermal decomposition over the temperature range of 160 to 220°C. A first-order equation can best describe the decomposition reaction for both complexes. The obtained activation energies were 160.4 kJ/mol for FeUR and 174.0 kJ/mol for CrUR. The thermal reactivity of CrUR was lower than that of FeUR. This was postulated to be caused by the fact that Cr^{3+} has three electrons in the d-orbital and these electrons increased the crystal field stabilization energy.

It was clear that the combustion reactivity of CrUR was greater than that of FeUR based on the combustion residue and the evolved gas. For FeUR, part of the nitrate ion in the molecule participated only slightly in the reaction. It was generally suggested that a part of the nitrate ion in the complex participated only slightly in the reaction in the case of the Fe complex nitrate.

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 necessary properties of the gas generant is high thermal stability, the evolution of a large volume of harmless gas during the combustion reactions, high combustion stability, etc.

The authors evaluated the metal complexes of organic compounds (carbohydrazide, semicarbazide, aminoguanidine, etc.), which are composed of many nitrogen atoms, as a new gas generant. Various

metal complex nitrates were synthesized and the gas evolution behavior was qualitatively investigated^{4)~10)}.

In this report, for the metal complex nitrates of urea ($\text{M}(\text{Urea})_6(\text{NO}_3)_3$, M=Metal; Fe, Cr, hereafter MUR), the thermal behavior was investigated for the complex only and for the mixed system with the oxidizing agent.

2. Experiment

2. 1 Reagents

The Fe complex nitrate of urea was synthesized based on the synthesis method¹¹⁾ of the Cr complex nitrate of urea. Cr nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) or Fe nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and urea were mixed in the molecular ratio of 1 to 6 in warm water. The crystal precipitated by concentration due to evaporation in a water bath at 50°C. The obtained products were analyzed by an emission spectroscopic analysis of the metal and elemental analysis.

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Table 1 Compositions of mixtures

	Molecular ratio mol/mol	Weight ratio wt./wt.
FeUR/ Sr(NO ₃) ₂	32.3/67.7	57.5/42.5
FeUR/ KClO ₄	27.6/72.4	62.3/37.7
FeUR/ KBrO ₃	22.2/77.8	50.7/49.3

Table 2 Compositions of FeUR / KBrO₃ mixtures

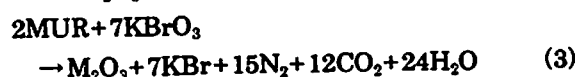
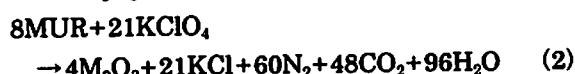
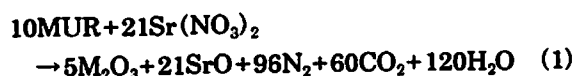
Molecular ratio mol/mol	Weight ratio wt./wt.	Oxygen balance g/100g
28.6/71.4	59.0/41.0	-4.71
25.0/75.0	54.6/45.4	-2.18
22.2/77.8	50.7/49.3	0
20.0/80.0	47.4/52.6	+1.89
16.7/83.3	41.9/58.1	+5.01

Table 3 Composition of CrUR / KBrO₃ mixtures

Molecular ratio mol/mol	Weight ratio wt./wt.	Oxygen balance g/100g
25.0/75.0	54.4/41.0	-2.18
22.2/77.8	50.6/49.4	0
20.0/80.0	47.2/52.8	+1.89

The metal complexes and the oxidizing agents screened to under 63 μm were mixed for ninety minutes using splittable chopsticks on parchment paper. All used reagents were Wako Pure Chemical reagent grade.

The thermal behavior and the ignitability were investigated in FeUR mixtures with the oxidizing agents (Table 1). In the mixture system with KBrO₃, the combustion reactivity was investigated using compositions of negative and positive oxygen balance in addition to a stoichiometric one. The compositions of the mixtures are shown in Tables 2 and 3. The mixtures were prepared based on eqs. 1~3 showing the chemical stoichiometric equation.



M: Fe, Cr

Table 4 Conditions for gas chromatography

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

2. 2 Differential thermal analysis apparatus and method

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

2. 3 Isothermal decomposition

Thirty mg of the sample was weighted into a glass tube sealed at one end (6 mm in inside diameter and 60 mm in length). This glass tube was then placed in an oil bath 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 Nippon Detam JDX-3500K and infrared absorption spectrometry using a Shimadzu FTIR-8100A.

2. 4 Combustion reactivity

The heat of combustion (reaction) was measured using a Shimadzu CA-4 Type Automatic Bomb Calorimeter at 1.1 MPa under argon. The sample was 0.5 g. The sample was ignited by switching on the electric current using the nichrome wire.

2. 5 Gas evolution behavior

The gases evolved during the measurements of the heat of combustion were collected into a collection bag (Tedlar bag, 350ml capacity). The amounts of the N₂, CO, CO₂ and N₂O gases evolved were quantified using a Shimadzu GC-4C Gas Chromatograph (hereafter, GC). Table 4 shows the measurement conditions for the GC. The NO and NO₂ gases were quantitatively analyzed using a Gastec gas detector tube. The NH₃ and N₂H₄ gases were quantified by the indophenol method¹²⁾ (λ = 630 nm) and the

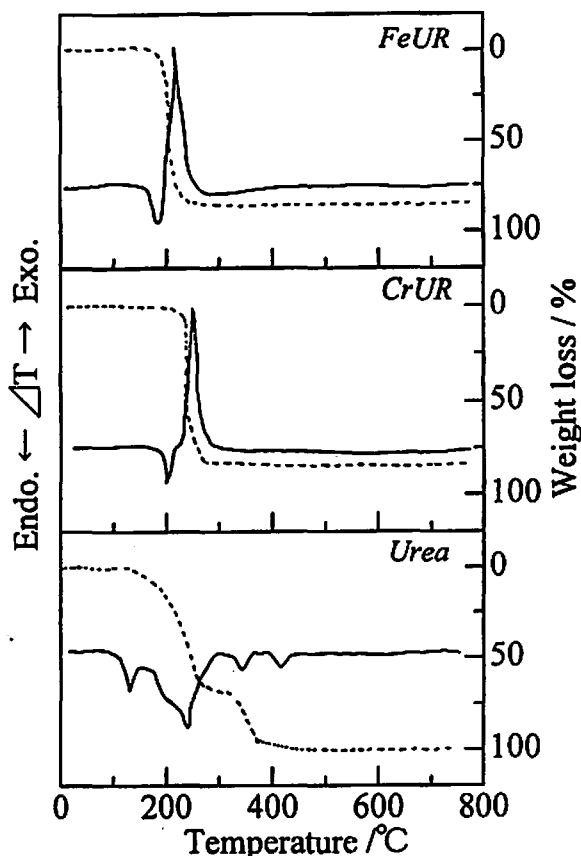


Fig. 1 DTA-TG curves for MUR (M: Fe, Cr) and urea

P-aminobenzaldehyde method¹³⁾ ($\lambda = 458$ nm), respectively.

The decomposition and combustion residues were analyzed by X-ray diffraction using a Nippon Detam JDX-3500.

3. Results and discussion

3. 1 Differential thermal analysis

Fig.1 shows the results of the differential thermal analysis for FeUR and CrUR, in which the results for the urea of the ligand are shown for reference.

FeUR started to melt at about 175°C, and then exothermally decomposed. The final weight loss was 89%, which was consistent with the theoretical one for the formation of Fe_2O_3 (86.7%).

For CrUR, the thermal behavior was apparently similar to that of FeUR, though the initial temperature of melting was 20°C higher than that of FeUR. The final weight loss was 85%, which was consistent with the theoretical value for the formation of Cr_2O_3 (87.2%). The formation of a metallic oxide was confirmed by X-ray diffraction of both complexes.

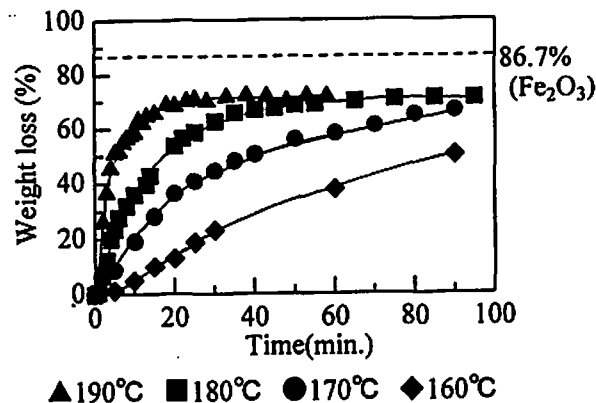


Fig. 2 The decomposition of FeUR at various temperatures

The initial temperature of the exothermic peak for FeUR was 195°C and that for CrUR was 15°C higher than that of FeUR. As previously reported about the thermal behavior of various metal complexes of carbohydrazide, the higher the initial temperature of the exothermic peak in DTA curve, the greater the thermal stability of the complex. This tendency was consistent with the order of the Irving Williams system; the stability of the complex is greater in the upper right side of the periodic table. However, the initial temperature of the exothermic peak for the UR complex of Fe, which is on the right side in comparison with Cr in the periodic table, was higher unlike the above-mentioned tendency.

On the other hand, the urea in the ligand started to melt at about 135°C, and then endothermally decomposed over wide temperature range. Coordinating the urea to a metal increased the thermal stability and the thermal reactivity.

3. 2 Thermal behavior during isothermal decomposition

3. 2. 1 Change in the weight loss

Fig.2 shows the weight loss curve versus time during the isothermal decomposition in the temperature range of 160°C to 190°C for FeUR as a representative example. In the experimental temperature range, the final weight loss converged to 71%, which was less than the theoretical value for the formation of Fe_2O_3 (86.7%). This value was consistent with the theoretical value of the formation of ferrous nitrate ($\text{Fe}(\text{NO}_3)_2$, 71.1%). Fig.3 shows IR spectrum of the products. The existence of nitrate

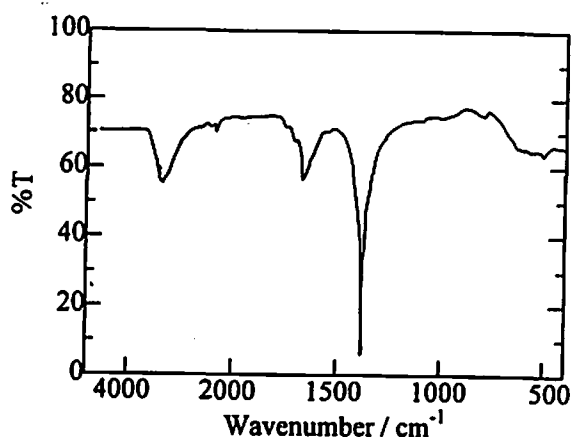


Fig 3 IR spectrum of the residue during isothermal decomposition for FeUR

ion in the residue was confirmed by the large peak at 1390cm^{-1} . Based on the weight loss and IR spectrum, not Fe_2O_3 but $\text{Fe}(\text{NO}_3)_2$ was thought to be formed by the decomposition of FeUR. Due to a bad crystal, it was not possible to do a powder X-ray diffraction. However, it is unclear whether the anhydrous salt of $\text{Fe}(\text{NO}_3)_2$ is stable or not, while hexahydrate and enneahydrate of $\text{Fe}(\text{NO}_3)_2$ were generally very familiar¹⁴⁾.

On the other hand, CrUR also had the same weight loss curve as that of FeUR, and the weight loss converged to 81%, which agreed with the theoretical value for the formation of Cr_2O_3 . CrUR decomposed to a metallic oxide in the experimental temperature unlike FeUR. The formation of Cr_2O_3 was confirmed by the powder X-ray diffraction pattern.

3. 2. 2 Activation energy of the reaction

For both urea complexes, the fractional decomposition was derived from the weight loss finally obtained, and an applicable rate equation was investigated; the result was that a first-order equation can best describe the reaction. Plots for the FeUR, as a representative example, are shown in Fig.4, in which good linearity was seen over the range of the fractional decomposition from 10 to 85 %. Fig.5 shows the arrhenius plots for both complexes. The activation energies were calculated by the rate constants at various temperatures: FeUR, 160.4kJ/mol, CrUR, 174.0kJ/mol. The thermal reactivity of CrUR was lower than that of FeUR, which was consistent with the tendency of the initial temperature of the



Fig 4 Isothermal decomposition ratio (X) curves and linear plots for a first-order reaction for FeUR

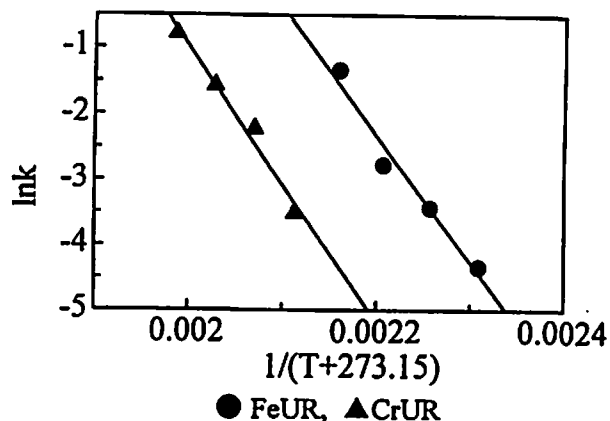


Fig 5 Arrhenius plots of the decomposition for MUR (M: Fe, Cr)

exothermic peak in the DTA curve.

Six-coordinated octahedron complexes have 5 outer d-orbitals¹⁶⁾ – 2 orbitals of high energy level opposite to the ligand and 3 orbitals of low energy level not opposite to the ligand. Three electrons of the d-orbital for CrUR occupy 3 orbitals of low energy according to Hund' law. Namely, these three electrons provide equal strain to the ligand, and the crystal field is very stable. A low thermal reactivity for CrUR was thought to be caused by the large crystal field stabilization energy.

Furthermore, the thermal reactivity for the metal complexes of urea was low compared with the re-

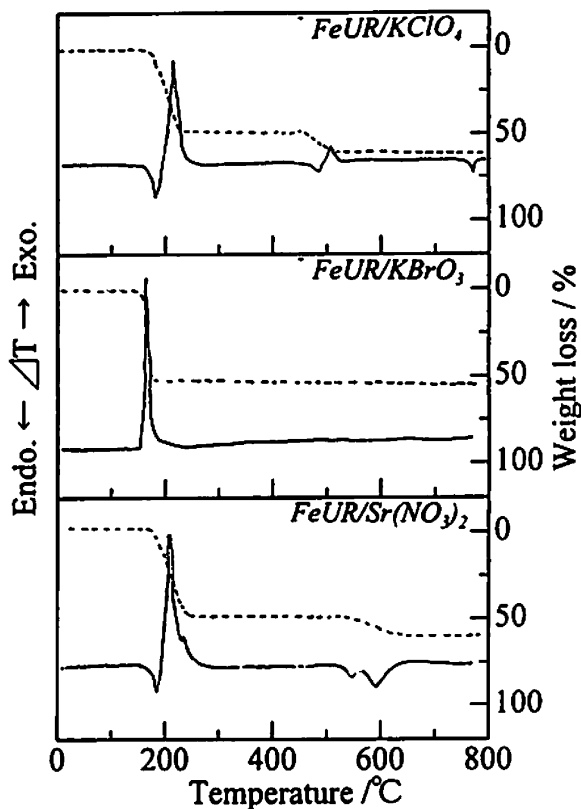


Fig. 6 DTA-TG curves of mixtures

sults obtained for the various metal complexes of carbonylhydrazide⁴¹; the activation energy obtained for the metal complexes of carbonylhydrazide was 50.2~186.9kJ/mol. The thermal reactivity of the ligand might influence that of the metal complex.

3. 3 Combustion reactivity

3. 3. 1 Differential thermal analysis of mixture system with various oxidizing agents

Fig.6 shows the results of the differential thermal analysis for FeUR mixtures with various oxidizing agents as representative examples.

For the KBrO_3 system, there was a difference in the thermal behavior between the mixtures and the complex. A vigorous exothermic reaction started about 175°C in this system unlike the complex only. The final weight loss was 64%, which was greater than the theoretical value (58.4%). The sample was thought to scatter due to the vigorous reaction.

For mixture systems with the other oxidizing agents except for KBrO_3 , there was little difference in the thermal behavior between the mixtures and the complex only. In the $\text{Sr}(\text{NO}_3)_2$ system, the endothermic reaction of the unreactive oxidizing agent

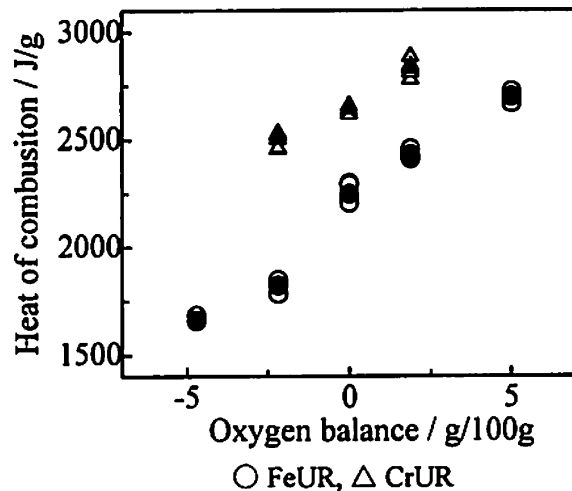


Fig. 7 Heat of combustion for MUR mixtures (M=Fr, Cr)

was confirmed about 560°C, and the weight loss at that time was 20%, which was less than mix ratio of $\text{Sr}(\text{NO}_3)_2$ in the mixture (42.5%). In the KClO_4 system, the weight loss (20%) during the decomposition of the unreactive KClO_4 above 500°C was less than the mix ratio of KClO_4 to mixture (37.6%). Consequently, the Fe complex nitrate of urea seen to moderately react with the oxidizing agents except for KBrO_3 . For CrUR, the thermal reactivity with various oxidizing agents was the same tendency as that for FeUR.

Incidentally, the combustion reactivity mentioned below was investigated in the mixture system only with KBrO_3 , because it was possible to ignite in KBrO_3 system.

3. 3. 2 Heat of combustion

Fig.7 shows the composition dependence of the heat of combustion for both complexes. They had no maximum value at the stoichiometric composition, and increased as the mix ratio of KBrO_3 increased. This was thought to be caused by the exothermic decomposition of the unreactive KBrO_3 .

Furthermore, Fig.8 shows the results of the powder X-ray diffraction of the combustion residue at the stoichiometric composition for both complexes. For the FeUR system, the diffraction pattern of KNO_3 was confirmed in addition to that of KBr and Fe_2O_3 . KNO_3 might be formed during cooling of the sample, because KNO_3 decomposes to KNO_2 above the melting point (330°C). $\text{Fe}(\text{NO}_3)_2$ was formed by

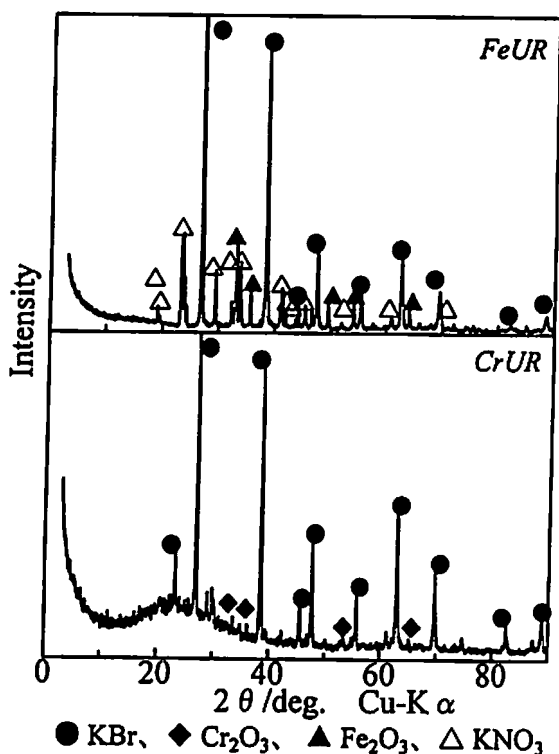


Fig. 8 XRD pattern of the combustion residue

the decomposition of FeUR as seen in the isothermal decomposition, and $\text{Fe}(\text{NO}_3)_2$ was postulated to metathetical react with KBr. In any case, part of the nitrate ion in the molecule only slightly participated in the reaction. On the other hand, for CrUR, the diffraction pattern of KBr and Cr_2O_3 was confirmed in the combustion residue. In addition, the combustion residue in this system was scattered by the vigorous reaction. There was great difference in the combustion reactivity between FeUR and CrUR.

3. 4 Evolved gases during the combustion

Table 5 shows the results of the quantitative analysis of the evolved gas using the stoichiometric compositions for both complexes during the combustion.

For CrUR, mainly N_2 and CO_2 were evolved, and these gases accounted for 99 per cent of all evolved gases. CO and NH_3 gases slightly evolved. In addition, the mass balance of nitrogen and carbon atoms were very good before and after the reaction. On the contrary, for FeUR, the evolution of N_2 gases decreased, while CO and NH_3 gases considerably generated. FeUR insufficiently reacted with KBrO_3 based on the low recovery ratio of nitrogen atom and

Table 5 The evolved gas behavior during the combustion for FeUR and CrUR (unit: mol/mol)

	FeUR	CrUR
N_2	3.09	7.54
NH_3	1.07	8.95×10^{-2}
NO	3.45×10^{-2}	1.54×10^{-2}
NO_2	1.48×10^{-3}	0
N_2O	0	0
CO	0.64	0.30
CO_2	3.59	4.61
N	7.25	15.16
%	48.3	101.1
C	4.34	4.91
%	72.3	81.8

the combustion residue mentioned above.

The combustion reactivity of FeUR with KBrO_3 was low, because part of the nitrate ion in the molecule only slightly participated in the reaction.

4. Conclusion

For two kinds of metal complex nitrates of urea (metal: Fe, Cr), the thermal behavior was investigated for only the complex and in mixed systems with an oxidizing agent.

Coordinating the urea to the metal increased the thermal stability and the thermal reactivity. The thermal stability of CrUR was greater than that of FeUR.

FeUR decomposed not to Fe_2O_3 but to $\text{Fe}(\text{NO}_3)_2$ and CrUR decomposed to Cr_2O_3 during the isothermal decomposition over the temperature range of 160 to 220°C. A first-order equation can best describe the decomposition reaction for both complexes. The obtained activation energies were 160.4 kJ/mol for FeUR and 174.0 kJ/mol for CrUR. The thermal reactivity of CrUR was lower than that of FeUR. Cr^{3+} has three d-orbital electrons and these electrons increased the crystal field stabilization energy. The low thermal reactivity for CrUR was thought to be due to the large crystal field stabilization energy.

CrUR vigorously reacted with KBrO_3 , so that the sample scattered. N_2 and CO_2 gases account for 99

percent of all the evolved gases. On the other hand, for FeUR, a part of the nitrate ion in the molecule only slightly participated in the reaction. Not only N_2 and CO_2 gases but also NH_3 and CO gases were significantly generated during the combustion. The combustion reactivity of CrUR was greater than that of FeUR.

It was generally suggested that a part of the nitrate ion in the complex only slightly participated in the reaction for the case of Fe complex nitrate.

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種々の金属錯体硝酸塩の熱的挙動(第2報) —鉄及びクロムの尿素錯体硝酸塩—

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エアバッグ用新規ガス発生剤として、有機金属錯体硝酸塩の実用可能性を検討している。その研究の一環として、Fe及びCrの尿素錯体硝酸塩について錯体単体及び酸化剤混合系での熱的挙動を比較検討した。

尿素を金属に配位させることで、その熱安定性、熱反応性は向上する。また、両錯体を比較すると、Cr錯体硝酸塩の熱安定性が高い。

160~220°Cの温度範囲で等温分解を行った結果、Fe錯体硝酸塩は酸化鉄ではなく硝酸鉄を、Cr錯体硝酸塩は酸化クロムを生成した。両錯体の分解反応は1次式によく適合し、活性化エネルギーは各々160.4kJ/mol, 174.0kJ/molとCr錯体の熱反応性は低い値を示した。これは、 Cr^{3+} の外殻d軌道電子数が3つで、結晶場安定化エネルギーが大きくなるためと推測される。

一方、臭素酸カリウムとの混合系での燃焼反応性は、反応残渣と、この時の発生ガス挙動からCr錯体の方が高いことが明らかとなった。即ち、Fe錯体では、分子内の硝酸根が反応に関与しないため、反応性が低い。一般的に、金属錯体硝酸塩において、中心金属を鉄にすると、硝酸根が反応に寄与しなくなる可能性が示唆された。

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