

Evaluation of gas generating ability of some tetrazoles and copper (II) oxide mixtures through closed vessel test and theoretical calculation

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Received: April 22, 2008 Accepted: September 29, 2008

Abstract

The heats of formation and densities for thirteen tetrazoles were measured, and using these values, evolved gas volume, adiabatic flame temperature and product gas concentration for the mixtures with copper (II) oxide were calculated through chemical equilibrium calculation. Four-liter closed vessel test was conducted for each mixture to acquire the pressure-time history and the temperature-time history. There was a good correlation between the theoretical amounts of generated gases and the maximum pressure but there was low correlation between the theoretical amounts of generated gases and the rate of gas release. It is found that the rate of gas release of six tetrazoles are better than that of presently used tetrazole. In some tetrazoles, HCN, NO₂, and NH₃ were found even though they were not formed theoretically. It is recommended that the result of the chemical equilibrium calculation should be used on selecting the candidates for closed vessel tests.

Keywords: Tetrazole, Heat of formation, Closed vessel test.

1. Introduction

In the past, mixtures of sodium azide and oxidizers have been the dominant gas generating agents for automobile airbag system. Sodium azide has disadvantage such as producing dangerous explosives by reacting with heavy metals. Many researches on the development of substitute gas generating agents have been carried out.

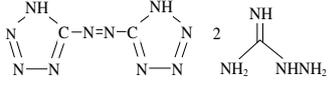
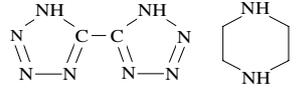
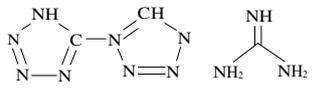
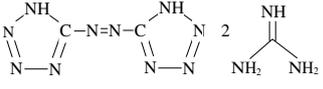
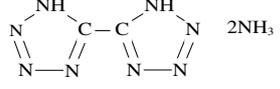
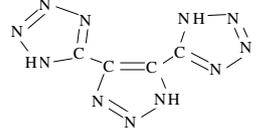
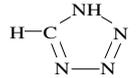
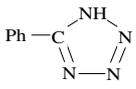
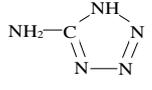
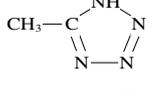
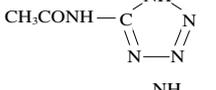
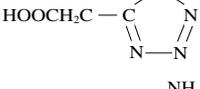
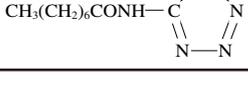
Authors have been researching on new tetrazoles¹⁾⁻¹⁰⁾ as alternative nitrogen producing agents. For evaluating the performances of airbag gas generating agents for new compounds, it has been common to conduct sixty-liter tank test, and as another screening test, small-scale closed vessel test has been suggested^{9), 10)}. These methods take times and labor to measure the performance of agents. It is assumed that chemical equilibrium calculation softwares, e.g., ICT-Thermodynamic Code¹¹⁾ are effective for estimating the necessary abilities such as the adiabatic flame temperature T_f , combustion products at T_f and 298 K, the amount of generated gases at 298 K. However, it is impossible to conduct theoretical calculations for many recently-synthesized tetrazoles if the heats

of formation are not included in the database. In this study, chemical equilibrium calculations were conducted after determining the heats of formation for those tetrazoles that have not been measured. This was followed by conducting chemical equilibrium calculations to calculate the amount of generated gases for various stoichiometric ratio tetrazole / metal oxide mixtures and compare these with the results of four-liter closed vessel tests to examine whether it is possible to estimate the ability of the mixtures to generate gases.

Copper (II) oxide CuO was selected as an oxidizer in this study because, despite its relatively low gas-generating ability, there is an advantage in that not having restriction in the production of the mixtures because tetrazole / CuO mixture is not legally classified as a low explosive such as percholates and nitrates mixtures¹³⁾.

In addition, comparison was also made between the calculated results and the observed results of the concentrations of generated gases, because it is required that the gases emitted by the airbag are harmless to the human body.

Table 1 Tetrazoles used in this experiment.

Tetrazoles	Abbreviation	Structure	Molecular weight
Aminoguanidium 5'5'-azobis-1H-tetrazolate	AGAT		314.28
Piperazium 5'5'-bi-tetrazolate	PIPE BHT		224.23
Guanidium 1,5-bistetrazolate	G15B		197.16
Guanidium 5'5'-azobis-1H-tetrazolate	GAT		284.25
Diammonia 5,5'-bi-tetrazolate	BHT 2NH ₃		172.15
4,5-di(1H-tetrazol-5-yl)[1,2,3]triazole	DTZT		205.14
1H-tetrazole	1HT		70.05
5-phenyl-1H-tetrazole	P5T		146.15
5-amino-1H-tetrazole	5-ATZ		85.07
5-methyl-1H-tetrazole	M5T		84.08
5-methyl-amide-1H-tetrazole	AD1		127.11
(1H-tetrazole 5-yl)-acetic acid	TAA		128.09
5-heptyl-amide-1H-tetrazole	AD7		211.27

2. Experimental

2.1 Samples

CuO (Kanto Chemical, Co. Inc., Kanto extra pure grade reagent) was used as an oxidizer. All tetrazole samples except for 5-ATZ and TAA (purchased from Fujimoto Chemicals Co., Ltd.) tested in this study were purchased from or kindly donated by Toyo Chemicals Co., Ltd. The names and structures of tetrazoles which were examined in this study are given in Table 1.

2.2 Measurement of heat of formation, density, melting point, and impact sensitivity

The heats of formation for tetrazole compounds were measured by using automatic bomb-type calorimeter (Shimadzu Corp., CA-4PJ). Approximately 1.0 gram

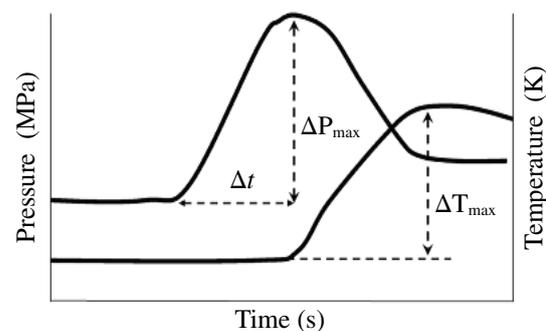


Fig. 1 Schematic diagram of the changes in pressure and temperature inside the closed vessel.

Table 2 Heat of combustion, heat of formation, density, and melting point of tetrazoles.

Tetrazoles	Heat of combustion at constant volume (kJ · mol ⁻¹)	Heat of combustion at constant pressure (kJ · mol ⁻¹)	Heat of formation (kJ · mol ⁻¹)	Heat of formation (kJ · g ⁻¹)	Density (g · cm ⁻³)	Melting point (K)
AGAT	-13,940	-4,367.4	782.06	2.49	1.59	488–490
PIPE BHT	-20,742	-4,646.0	542.62	2.42	2.17	605–611
G15B	-13,731	-2,697.9	504.01	2.56	1.61	460–466
GAT	-13,206	-3,741.3	452.22	1.59	1.69	536–540
BHT 2NH ₃	-13,708	-2,352.3	422.04	2.45	1.55	507–510
DTZT	-11,387	-2,335.9	305.68	1.49	1.75	563–573
1HT	-14,145	-987.16	301.62	4.31	1.59	423–430
P5T	-26,567	-3,881.6	269.59	1.85	1.96	487–492
5-ATZ	-12,521	-1,060.8	238.52	2.80	1.60	480–482
M5T	-19,219	-1,613.4	235.75	2.80	1.92	416–420
AD1	-15,727	-1,994.7	87.61	0.69	2.13	561–563
TAA	-13,044	-1,665.9	-86.28	-0.67	1.43	395–400
AD7	-26,996	-5,703.7	-264.78	-1.25	1.49	527–529

powder sample was weighed correctly and pressed into a cylindrical pellet embedded with nickel / chrome wire for ignition. After the sample was tightly enclosed inside the bomb, 2.5-3.0 MPa oxygen gas was introduced inside the bomb and it was ignited to achieve complete combustion. The heat of combustion of the sample was calculated through the measured temperature rise inside the water tank. The measurement was conducted at least twice, and if the difference between the maximum and the minimum exceeded 209 J · g⁻¹, the measurement was conducted again until the difference falls within 209 J · g⁻¹, and then the average of two closest data was deduced¹³⁾.

Density of each tetrazole, which is necessary for calculating the amount of generated gases per mass, was measured with picnometric method using the specific gravity bottle¹⁴⁾.

Melting point of each sample was measured by means of a melting point apparatus (Yazawa Kagaku, Co. Ltd, BY-2). In order to investigate the impact sensitivity of tetrazoles, the drop hammer test was conducted according to JIS K 4810¹⁵⁾.

2.3 Measurement of pressure rise and temperature rise in the closed vessel and quantitative analysis of combustion products

The orifice of the chimney-type strand burner was closed to act as a four-liter closed vessel, and the pressure-time change was measured at an initial pressure of 2 MPa helium gas and at an initial temperature of 298 K. The 4 gram pellets of 14 mm in diameter and 9mm in length were prepared. The side of pellet was coated with epoxy resin (Semedine Co., Ltd., 1500). The B / KNO₃ igniter (Nippon Koki Co., Ltd.) was placed on the top of the pellet and it was ignited with a heated nickel/chrome wire (diameter 0.6 mm). Pressure was measured through a strain-gauge pressure transducer (Kyowa Electronic Instruments Co., Ltd., PG-100KU) and after amplification through a signal conditioner (Kyowa Electronic Instruments Co., Ltd., CDV-230C), the output was recorded on a digital data recorder (Keyence Corp., GR-3000). The gas tem-

perature in the vessel was obtained with K-type thermocouple (diameter 1 mm). The output of the thermocouple was recorded on a digital data recorder (Keyence Corp., GR-3000). Figure 1 shows schematic diagram of the time profiles of pressure and temperature inside the closed vessel, together with the net maximum pressure increase ΔP_{\max} and the net temperature increase ΔT_{\max} , and Δt is the time difference between the start of ignition and the time when pressure increase reaches its maximum value.

Gaseous products of four-liter closed vessel test were analyzed by FT-IR gas analyzer (Temet Co., Ltd., DX-4000). Helium gas was used as the carrier gas, and CO₂, CO, NO₂, NO, NH₃, and HCN were analyzed. H₂O evolved in the combustion gas was assumed to be in a liquid state.

3. Results and discussion

3.1 Density, melting point, heat of combustion, and heat of formation

The names of the compounds, abbreviated names, chemical formula and molecular weights are given in Table 1.

Table 2 shows the heat of combustion at constant volume ΔU , the heat of combustion at constant pressure ΔH , and the heat of formation H_f and density and melting point for each tetrazole compound, which is listed in the order of H_f . The relation between ΔU and ΔH is given by the following equation:

$$\Delta H = \Delta U + \Delta \nu RT$$

where $\Delta \nu$ is the difference in the number of moles of gas products before and after reaction and R is a gas constant.

Table 2 also shows H_f of compounds tested. It is found that H_f of AD1, TAA, and AD7 are smaller than that of glycidyl azide polymer (GAP), a typical high energetic binder, at 0.96 kJ · g⁻¹¹⁶⁾. H_f (kJ · g⁻¹) of other compounds except 1HT fall in the range between 1.49-2.80 kJ · g⁻¹, close to that of 3, 3 bis-(azido methyl oxetane) (BAMO) which is 2.46 kJ · g⁻¹¹⁷⁾. 1HT has the highest H_f at 4.31 kJ · g⁻¹ which is close to that of cubane which is 5.47 kJ · g⁻¹¹⁷⁾. It indicates that tetrazoles tend to have high energy

Table 3 Theoretical amounts of generated gases.

Mixtures	Composition (mass%)	Theoretical maximum density ($\text{g} \cdot \text{cm}^{-3}$)	Theoretical amount of generated gases ($\text{mol} \cdot \text{cm}^{-3}$)	Theoretical amount of generated gases ($\times 10^{-2} \text{ mol} \cdot \text{g}^{-1}$)
DTZT / CuO	21.35 / 78.65	4.11	4.07	0.989
1HT / CuO	22.70 / 77.3	3.82	3.71	0.972
5-ATZ / CuO	23.41 / 76.59	3.76	3.62	0.963
G15B / CuO	21.59 / 78.41	3.92	3.72	0.948
BHT · 2NH ₃ / CuO	21.29 / 78.71	3.87	3.35	0.866
AGAT / CuO	20.83 / 79.17	3.95	3.41	0.863
GAT / CuO	20.34 / 79.66	4.11	3.53	0.859
TAA / CuO	21.16 / 78.84	3.71	3.07	0.826
AD1 / CuO	17.56 / 82.44	4.77	3.63	0.760
M5T / CuO	14.98 / 85.02	4.78	3.41	0.713
PIPE BHT / CuO	13.54 / 86.46	5.11	3.40	0.664
P5T / CuO	9.75 / 90.25	5.30	3.18	0.600
AD7 / CuO	9.43 / 90.57	4.93	2.53	0.513

Table 4 Adiabatic flame temperature and calculated heat of explosion of mixtures.

Mixtures	Adiabatic flame temperature (K)	Calculated heat of explosion ($\text{kJ} \cdot \text{g}^{-1}$)
1HT / CuO	2,253	1.65
5-ATZ / CuO	1,893	1.40
BHT · 2NH ₃ / CuO	1,774	1.35
AGAT / CuO	1,764	1.32
G15B / CuO	1,725	1.24
TAA / CuO	1,683	1.19
M5T / CuO	1,653	1.16
AD1 / CuO	1,585	1.11
PIPE BHT / CuO	1,547	1.08
GAT / CuO	1,515	1.01
DTZT / CuO	1,388	0.86
P5T / CuO	1,358	0.81
AD7 / CuO	1,306	0.76

density and azobis-tetrazoles such as AGAT and GAT and bis-tetrazoles such as BHT · 2NH₃ and PIPE BHT show higher H_f than other tetrazoles. According to Conkling¹⁷⁾, in case of organic compounds, a low melting point enhances ignitability and reactivity; too low a melting point can cause production and storage problems, so 373K might be a good minimum value. All compounds tested in this experiment meet this criterion. However, it was found that melting points of TAA, M5T, 1HT, and G15B were lower than that of 5-ATZ which has been used as a fuel for gas generating agents.

3.2 Impact sensitivity

All compounds did not ignite even at a drop height of 50 cm (highest point of 1 / 6 ignition point). According to the Regulations of the Japan Explosives Society¹⁸⁾, it was found that all compounds were classified as class 8 and they can be treated as insensitive organic compounds.

Table 5 ΔP_{\max} , Δt , and $\Delta P_{\max} \cdot \Delta t^{-1}$ of mixtures.

Mixtures	ΔP_{\max} (MPa)	Δt (s)	$\Delta P_{\max} \cdot \Delta t^{-1}$ (MPa · s ⁻¹)
DTZT / CuO	0.336	0.54	0.62
BHT · 2NH ₃ / CuO	0.320	0.72	0.44
AGAT / CuO	0.265	0.60	0.44
AD1 / CuO	0.236	1.08	0.22
1HT / CuO	0.286	0.96	0.30
GAT / CuO	0.260	1.08	0.24
5-ATZ / CuO	0.216	1.26	0.17
TAA / CuO	0.236	1.62	0.15
M5T / CuO	0.148	1.38	0.11
PIPE BHT / CuO	0.099	2.60	0.04
P5T / CuO	0.120	3.50	0.03
AD7 / CuO	0.080	8.90	0.01

3.3 Amount of generated gases

Table 3 gives the calculated values of the gas compositions and the amount of generated gases at 298 K for stoichiometric ratio tetrazole / CuO mixture according to chemical equilibrium calculation. Here, H₂O is treated as a liquid, therefore it is not included in the amount of generated gases. With regard to the calculation of the density of mixtures, the data of Table 3 were used for tetrazole compounds and with regard to the density of CuO, the value $6.315 \text{ g} \cdot \text{cm}^{-3}$ ¹⁹⁾ was used.

It was found that stoichiometric ratio DTZT / CuO mixture demonstrated maximum values for both the amount of generated gases per unit mass and the amount of generated gases per unit volume.

3.4 Adiabatic flame temperature and heat of explosion

T_f and heat of explosion for each tetrazole / CuO mixture that were derived from the chemical equilibrium calculation are shown in Table 4. 1 HT / CuO mixture shows the highest values. It is found that DTZT / CuO mixture which has the highest theoretical amount of generated gases has

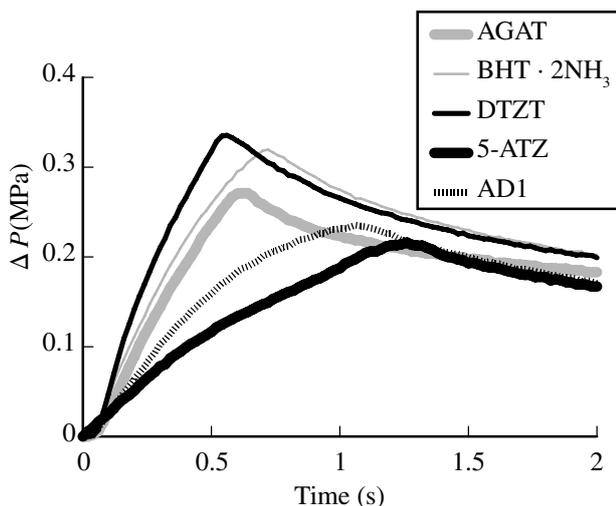


Fig.2 (a) Pressure-time history of tetrazoles / CuO mixtures from closed vessel test (higher than 5-ATZ).

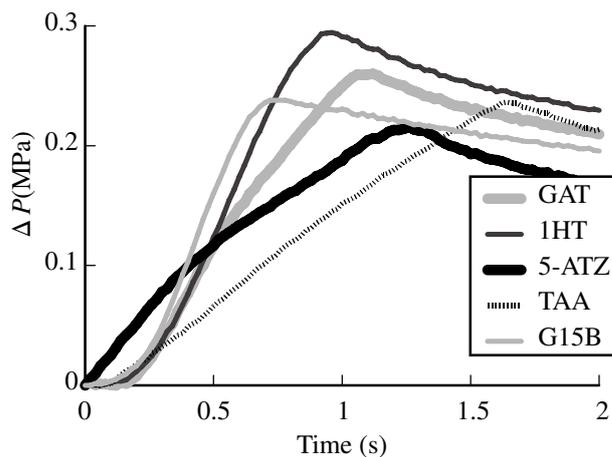


Fig.2 (b) Pressure-time history of tetrazoles / CuO mixtures from closed vessel test (intersecting with curve of 5-ATZ).

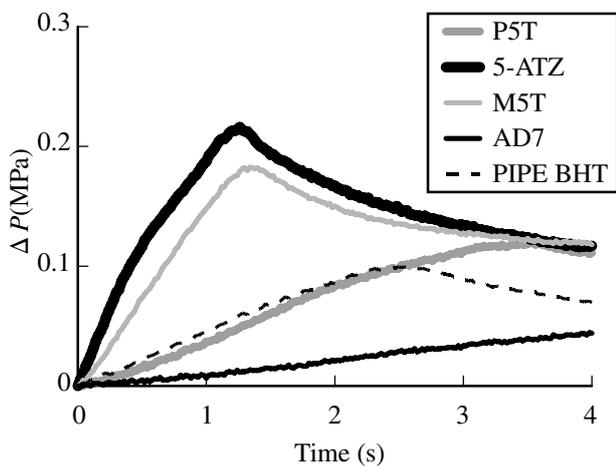


Fig.2 (c) Pressure-time history of tetrazoles / CuO mixtures from closed vessel test (lower than 5-ATZ).

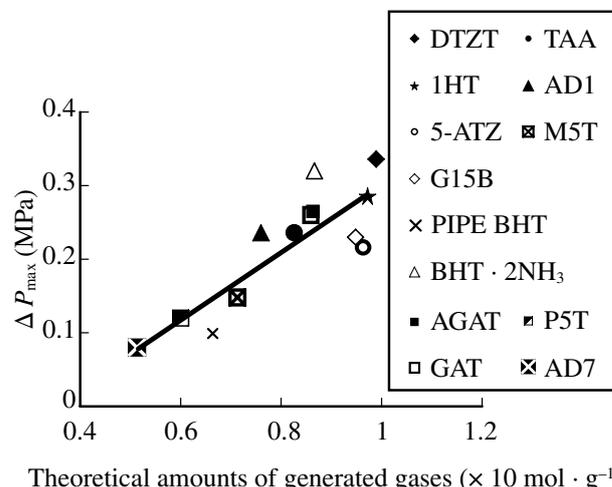


Fig.3 Relationship between ΔP_{max} and theoretical amount of generated gases.

low T_f and the heat of explosion due to its low H_f .

3.5 Four-liter closed vessel test

Figure 2 shows the pressure-time history of tetrazoles / CuO mixtures. The pressure-time curve of 5-ATZ / CuO mixture was compared with that of other mixtures. The pressure-time curve could be divided into three patterns: (a) the pressure-time curve that is higher than that of 5ATZ / CuO; (b) the pressure-time curve that intersects with that of 5-ATZ / CuO, and (c) the pressure-time curve that is lower than that of 5-ATZ / CuO.

ΔP_{max} , Δt , and $\Delta P_{max} \cdot \Delta t^{-1}$ that were obtained from Fig.2(a), (b), and (c) are shown in Table 5.

The mixture whose pressure-time curve is higher than that of 5-ATZ / CuO mixture has a shorter Δt which means a higher burning rate.

The mixtures whose pressure-time curve intersected with that of 5-ATZ / CuO mixture are less ignitable than 5-ATZ

/ CuO mixture and have shorter Δt . They require longer induction time than 5-ATZ / CuO mixture but they have higher burning rate and the amount of generated gases of these mixtures exceeded that of 5-ATZ / CuO mixture.

The mixture whose pressure-time curve is lower than that of 5-ATZ / CuO mixture has a lower burning rate.

Figure 3 shows the relationship between ΔP_{max} and the theoretical amounts of generated gases. The square of the coefficient factor was 0.862, so it was found that there exists a proportional relationship between ΔP_{max} and the theoretical amounts of generated gases. It can be concluded that the compound whose mixture shows a large theoretical amount of generated gases can give a high ΔP_{max} and it can be a good fuel candidate. As mentioned later, the net temperature rise of most mixtures were low, and the effect of temperature on the expansion of gas was small and the mixture that produces a large theoretical amount of generated gases tends to show a large ΔP_{max} .

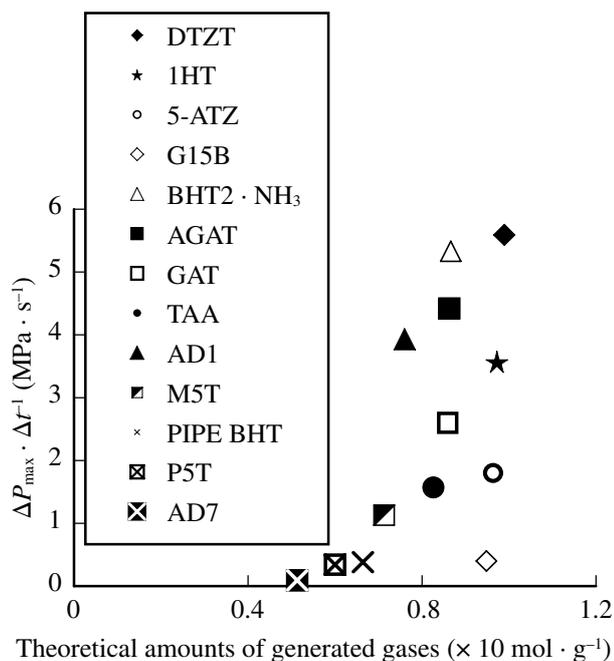


Fig. 4 Relationship between $\Delta P_{\max} \cdot \Delta t^{-1}$ and theoretical amount of generated gases.

Mixtures containing DTZT, BHT · 2NH₃, or 1HT that displayed temperature rise of several degrees gave a larger ΔP_{\max} , which indicates that temperature rise may affect their ΔP_{\max} .

Figure 4 shows the relationship between $\Delta P_{\max} \cdot \Delta t^{-1}$ and the theoretical amount of generated gases. The performance of gas generating agent was evaluated according to the value of $\Delta P_{\max} \cdot \Delta t^{-1}$ in four-liter closed vessel test⁴⁾. The values of $\Delta P_{\max} \cdot \Delta t^{-1}$ followed the order of:

DTZT > BHT · 2NH₃ > AGAT > AD1 > 1HT > GAT >
5-ATZ > TAA > M5T > PIPE BHT > G15B > P5T > AD7.

DTZT showed maximum values for both $\Delta P_{\max} \cdot \Delta t^{-1}$ and the theoretical amount of generated gases. Correlation between $\Delta P_{\max} \cdot \Delta t^{-1}$ and the theoretical amount of generated gases was not good. In order to select a candidate of gas generating agents, it may be desirable to conduct the theoretical calculation first, find a candidate that shows a large theoretical amount of generated gases and then conduct four-liter closed vessel test.

Figure 5 shows the temperature-time history of tetrazoles / CuO. No significant temperature increase were found for most mixtures.

The ranges of temperature increase for the mixtures not listed in Fig. 5 were within 1 K.

3.7 Theoretical amounts of main generated gases

Table 6 shows the theoretical amounts of main combustion gases (N₂ and CO₂) for the mixtures at 298 K. Mixtures containing 5-ATZ, 1HT, or BHT · 2NH₃ showed large amounts of generated N₂ gas per unit mass while mixtures containing 5-ATZ, 1HT, or DTZT showed large amounts of generated N₂ gas per mole.

Mixtures containing TAA, AD1, PIPE BHT, P5T, or AD7 were estimated to generate more CO₂ than N₂, and therefore it is suggested that they are not suited for N₂

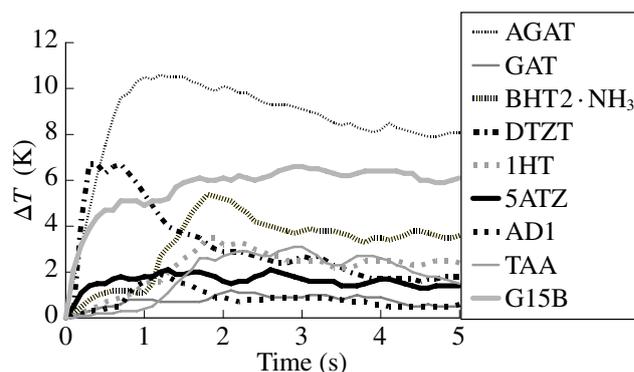


Fig. 5 Temperature-time histories of tetrazoles / CuO mixtures from closed vessel test.

source. DTZT / CuO showed large amounts of gases and its performance is better than other mixtures

3.8 Quantitative analysis of generated harmful gases

Table 7 shows measured concentrations of generated harmful gases such as HCN, NO₂, CO, and NH₃ of mixtures. Mixtures containing AGAT, PIPE BHT, GAT, DTZT, or 1HT did not produce CO gas even though the chemical equilibrium calculation suggested their production. On the contrary, HCN was not formed theoretically, which agreed with the measured results for the mixtures containing AGAT, PIPE BHT, BHT · 2NH₃, DTZT, 5-ATZ, or AD1. Theoretically, NH₃ should not be generated but all mixtures tested produced the gas. As for NO₂, all mixture should not produce the gas theoretically but only the mixtures containing AGAT, PIPE BHT, DTZT, or 1HT did not produce the gas. It was found that the mixtures containing AGAT, PIPE BHT, or DTZT produced NH₃ gas but did not produce other harmful gases.

In some tetrazoles, HCN, NO₂, and NH₃ are found even though they are not formed theoretically. They can be formed by incomplete burning because the actual burning temperature is lower than the theoretical one.

4. Conclusions

Obtaining the heat of formation of tetrazoles enables the calculation of the theoretical amount of generated gases, and the adiabatic flame temperature. In this study, tetrazoles / CuO mixtures were studied and the correlation between the theoretical amount of generated gases and the net pressure rise inside the closed vessel was also found. It is found that the order of rate of gas release is DTZT > BHT · 2NH₃ > AGAT > AD1 > 1HT > GAT > 5-ATZ > TAA > M5T > PIPE BHT > G15B > P5T > AD7.

However, there was low correlation between the theoretical amounts of generated gases and rate of gas release.

It is recommended that the result of the chemical equilibrium calculation should be used on selecting the candidates for closed vessel tests.

In some tetrazoles, HCN, NO₂, and NH₃ are found even though they are not formed theoretically.

Table 6 Main combustion gases of mixtures at 298K.

Mixtures	Theoretical amounts of generated gases ($\times 10^{-2} \text{mol} \cdot \text{g}^{-1}$)	N ₂ (mol)	N ₂ (mol%)	CO ₂ (mol)	CO ₂ (mol%)
DTZT / CuO	0.989	5.72	26.8	4.16	19.5
1HT / CuO	0.972	6.48	28.6	3.24	14.3
5-ATZ / CuO	0.963	6.88	29.4	2.75	11.8
G15B / CuO	0.948	6.02	16.9	2.92	12.7
BHT · 2NH ₃ / CuO	0.866	6.18	26.3	2.47	10.5
AGAT / CuO	0.863	5.97	25.7	2.65	11.4
GAT / CuO	0.859	5.72	25.0	2.86	12.5
TAA / CuO	0.826	3.30	15.4	4.95	20.4
AD1 / CuO	0.760	3.45	16.1	4.14	19.4
M5T / CuO	0.713	3.56	16.7	3.56	16.7
PIPE BHT / CuO	0.664	3.02	14.3	3.62	17.1
P5T / CuO	0.600	1.33	6.90	4.67	24.1
AD7 / CuO	0.513	1.11	5.50	4.02	19.8

Table 7 Harmful gases of mixtures at 298K.

Mixtures	CO (ppm) calc.	CO (ppm) found	HCN (ppm) calc.	HCN (ppm) found	NH ₃ (ppm) calc.	NH ₃ (ppm) found	NO ₂ (ppm) calc.	NO ₂ (ppm) found
AGAT / CuO	60	0	0	0	0	90	0	0
PIPE BHT / CuO	80	0	0	0	0	79	0	0
GAT / CuO	100	0	0	9.4	0	105	0	2.8
BHT · 2NH ₃ / CuO	50	100	0	0	0	141	0	0.6
DTZT / CuO	50	0	0	0	0	74	0	0
1HT / CuO	110	0	0	110	0	70	0	0
P5T / CuO	60	100	0	6.4	0	22.4	0	2.1
5-ATZ / CuO	90	100	0	0	0	144	0	3.3
M5T / CuO	80	200	0	7.5	0	61	0	0.7
AD1 / CuO	90	200	0	0	0	37.4	0	3.0
TAA / CuO	110	300	0	28.4	0	57	0	2.1
AD7 / CuO	30	100	0	0.96	0	5	0	2.8
G15B / CuO	200	160	0	2.5	0	124.0	0	2.6

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密閉容器試験と化学平衡計算によるテトラゾール系化合物と酸化銅(II)混合物のガス発生能力の評価

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テトラゾール系化合物13種類の生成熱, 密度を測定し, 得られた数値を用いて酸化銅(II)との化学量論混合物のガス発生量, 断熱火炎温度, 発生ガス濃度を化学平衡計算により求めた。各組成について4 l密閉容器試験を行い, 最大発生圧力とガス温度を求めた。ガス発生量と最大発生圧力には相関性が見られたが, ガス発生速度との相関性は良くなかった。化学平衡計算結果は密閉容器試験を行う候補者の選択に用いるのが良いであろう。6種類のテトラゾールのガス発生速度は現在使用されているテトラゾールよりも大きいことがわかった。燃焼温度が低いために, 化学平衡計算では見られない有害ガスHCN, NO₂, NH₃が実際の燃焼では観察された。

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