

Study on the thermal stability of 2-hexyne, 1-pentyne, ethyl isocyanide, and *n*-butyl isocyanide as sulfur-free gas odorants

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Abstract In Japan, *tert*-butyl mercaptan (TBM) is mainly employed as an odorant of LPG. However, the sulfur component in TBM gives the adverse effect for environment and human body and/or has a negative impact on reforming catalyst of fuel cell and other types of cogeneration systems. In this way, the development of sulfur-free odorant is expected. This study focuses on the thermal stability and combustibility of 2-hexyne, 1-pentyne, *n*-butyl isocyanide (BIC), and ethyl isocyanide (EIC) that is expected as the candidate odorants. As the result of DSC measurement, the comparison of T_{DSC} indicated that 2-hexyne and 1-pentyne are more thermally stable than BIC and EIC. However, in 2-hexyne and 1-pentyne, the slight exothermic peaks were observed at lower temperature region before those main

exothermic peaks. In 2-hexyne, copper or aluminum increased the heat amount of that slight exothermic peak observed before main peak. In 1-pentyne with zinc, T_{DSC} was approximately decreased to 279 °C from 337 °C of 1-pentyne alone. As the results of ARC measurement, in the presence of oxygen, the exothermic heat of 2-hexyne and 1-pentyne was observed at approximately 50–100 °C. This heat release may be corresponding to the slight heat release observed by DSC, and it thought to be results from the reaction with atmospheric oxygen. In this way, for the practical application of 2-hexyne and 1-pentyne as odorants, it is important to suppress the invasion of oxygen in the cylinder to low as much as possible in respect of the storage of the candidate odorant. As a result of thermal equilibrium calculation, even if either candidate odorant is added at about 100 ppm, there is little influence on propane combustibility from the adiabatic flame temperature, species of combustion gas and their yields.

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Introduction

At present, the odorants have been added into supply fuel such as liquefied petroleum gas (LPG) that is mainly consumed as a fuel for domestic use. The odorants can indicate the leakage to the occupants to take an action for escape. As the component of the odorant, the organic sulfur compound such as *tert*-butyl mercaptan (TBM) is used in Japan.

From the viewpoint of the effective utilization of energy and the deletion of greenhouse effect gas such as carbon dioxide, the residential fuel cell utilizing LPG and other

types of cogeneration systems come to the front. However, the sulfur component has a negative impact on reforming catalyst of fuel cell. Thus, it is necessary to remove the sulfur component that is included in LPG.

The sulfur component contained in LPG is derived from two ways. One is the residue in production process. The other is the odorant itself. The hazardous component such as sulfur dioxide is exhausted when the organic sulfur compound burns. Furthermore, it is undesirable on the environmental protection and human body. Moreover, in the situation that the high desulfurization of gasoline and diesel oil which become the competition fuel for LPG is powerfully advanced, the development of sulfur-free odorant is expected with respect to not only improving the usage of LPG more friendly to the environment but also maintaining the competitive edge on a global level as well as LPG being no longer a fuel used merely in gas burners. Nowadays, sulfur content in gasoline and diesel oil sold at gas stations have been reduced to below 10 ppm.

In such situation, the investigation on the sulfur-free odorant for LPG was initiated by The High Pressure Gas Safety Institute of Japan and has started since the 2005 fiscal year. Some of the authors searched for an extensive compound, and the candidate substances were selected. These candidate substances were evaluated from various viewpoints such as the odor intensity, the quality of odor, the boiling point, the chemical stability, the vapor–liquid equilibrium in propane, and concentration performance. From the results of this research, 54 kinds of compounds that consist of 17 kinds of unsaturated hydrocarbons such as alkynes and olefines, 19 kinds of organic compounds containing oxygen such as aldehydes and ketones, and 18 kinds of organic containing nitrogen such as amine and isocyanides were selected. Moreover, with researching its quality again, four candidate substances, 2-hexyne, 1-pentyne, ethyl isocyanide (EIC), and *n*-butyl isocyanide (BIC) as summarized in Table 1 were narrowed down.

In order to utilize these substances as gas odorant, the detailed investigation on thermal stability and combustibility of the candidate substances is required. From this, we evaluated the thermal stability and fundamental combustibility of 2-hexyne, 1-pentyne, EIC, and BIC by comparison with the conventional odorant, TBM.

Table 1 List of the candidate substances employed in this study

Substance name	Chemical formula
2-Hexyne	$\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CCH}_3$
1-Pentyne	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
<i>n</i> -Butyl isocyanide (BIC)	$\text{CH}_3(\text{CH}_2)_3\text{N}\equiv\text{C}$
Ethyl isocyanide (EIC)	$\text{CH}_3\text{CH}_2\text{N}\equiv\text{C}$
<i>tert</i> -Butyl Mercaptan (TBM)	$(\text{CH}_3)_3\text{CSH}$

Experimental

Materials

As the experimental sample, 2-hexyne (Wako Pure Chemical Industries, Ltd., 98%), 1-pentyne (Wako Pure Chemical Industries, Ltd., 97%), EIC (custom-made, 95%), BIC (Aldrich, 97%), and TBM (Tokyo Chemical Industry Corp., Ltd., 98%) were used without further purification. In order to investigate the reactivity with LPG and the metallic constituent, LPG produced by Takachiho Chemical Industrial Co, Ltd and four kinds of metals, iron (Wako Pure Chemical Industries, Ltd., 99.9%, <45 μm), copper (Wako Pure Chemical Industries, Ltd., 99.9%, <75 μm), aluminum (Kojundo Chemical Laboratory Co, Ltd., 99.99%, <45 μm), and zinc (Wako Pure Chemical Industries, Ltd., 99.9%, 75–90 μm and Wako Pure Chemical Industries, Ltd., 99.9%, 125–150 μm), were used.

DSC

A DSC produced by TA Instruments (Q200) was used in the present experiment. The sample was heated from room temperature to 500 $^\circ\text{C}$ at the rate of 10 K min^{-1} to measure the onset temperature, T_{DSC} and the heat of reaction, Q_{DSC} . Using sealed cells made of SUS-303 stainless steel as sample container, the thermal behavior of approximately 2–3 mg of the sample was observed in an air atmosphere. Besides, in order to examine the reactivity with the metals which are possible to contact with the candidate substances in distribution and/or consumption stages, the thermal behavior of 2–3 mg of the sample with 1.5 mg of the metal were observed.

ARC

An adiabatic calorimeter (Arthur D. Little, accelerating rate calorimeter: ARC2000) was used in the present experiment. For ARC measurement, a sample bomb made of hastelloy C was used. The sample mass was approximately 1.0 g. Four kinds of nitrogen, air, oxygen, and propane were employed as atmosphere gases in the sample bomb. In the experiments in nitrogen, air, and oxygen, each candidate substance was first loaded in the sample bomb under atmospheric air and this sample bomb was set to the ARC. And then, it was pressurized to 1 MPa with each gas. On the other hand, in the experiment in propane, liquefied propane of approximately 1 g was initially loaded in the sample bomb. Each candidate substances were secondary put in this sample bomb and it was set to the ARC. It is noticed that a small amount of air was contained in the experiments under nitrogen, oxygen, and propane atmosphere because the atmosphere gas was charged under

atmospheric air. The temperature change of the sample was measured by the heating–waiting–searching mode of the ARC. In this measurement, the heat temperature step is 5 °C, slope sensitivity is 0.02 °C min⁻¹, and wait time is 20 min.

Combustibility of the candidate substances

In order to evaluate the combustibility of the elemental candidate substance and the effect of it on the combustibility of liquefied petroleum gas, thermal equilibrium calculation code [1] which was developed by NASA Lewis Research Center was employed. Mixture fraction between propane and candidate odorant was varied in seven stages as 1, 0.5, 0.1, 0.01, 0.001, 0.001, and 0 at mole ratio. In order to estimate burning behavior in both oxygen rich and poor conditions, equivalent ratio is also varied in five stages as 0.8, 0.9, 1.0, 1.1, and 1.2.

Results and discussions

Thermal behavior of each candidate substance

Figure 1 shows the DSC curves of the candidate substances and TBM under the conditions of SUS-303 sealed cell and an air atmosphere. The exothermic peaks were shown in the candidate substances, while only the endothermic peak was obtained in TBM.

In 2-hexyne, T_{DSC} and Q_{DSC} of the exothermic peak were 404 °C and 1,413 Jg⁻¹. In 1-pentyne, T_{DSC} and Q_{DSC} of exothermic peak were 337 °C and 2,242 Jg⁻¹. Other than those main exothermic peaks, in 2-hexyne and 1-pentyne, the slight exothermic peaks were observed at

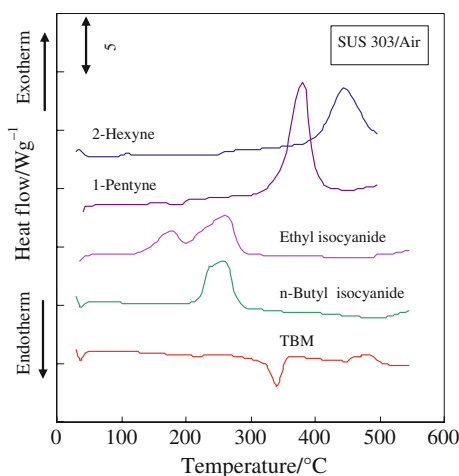


Fig. 1 DSC curves for four the candidate substances, 2-hexyne, 1-pentyne, ethyl isocyanide, *n*-butyl isocyanide, and TBM under the condition of SUS sealed cell and an air atmosphere

lower temperature. Its T_{DSC} and Q_{DSC} of that peak of 2-hexyne were 98 °C and 40 Jg⁻¹. In 1-pentyne, its T_{DSC} and Q_{DSC} were 128 °C and 23 Jg⁻¹. In addition, the base line of thermal curves of 2-hexyne and 1-pentyne was changed at 200–260 °C. This temperature point shifted to higher temperature region with the increase of sample mass. From these results, it is suggested that the change of the baseline corresponds to vaporization of the samples.

In BIC and EIC, two exothermic peaks overlapped were obtained. T_{DSC} and Q_{DSC} of BIC were 220 °C and 1,050 Jg⁻¹ and those of EIC were 135 °C and 1,610 Jg⁻¹. These values of Q_{DSC} indicate the summarized value of these two peaks.

The thermal behavior of TBM was different from those of the candidate substances, and an endothermic peak was obtained. Furthermore, the values of T_{DSC} and Q_{DSC} were 322 °C and 380 Jg⁻¹, respectively. The exothermic peak was also obtained and T_{DSC} and Q_{DSC} were 450 °C and 150 Jg⁻¹, respectively.

From these results, 2-hexyne and 1-pentyne showed the lower onset temperature among the candidate substances. It is, however, considered that the thermal hazard is very small because Q_{DSC} is lower at about 40 Jg⁻¹. Provided these peaks are vanishingly small, we consider that 2-hexyne and 1-pentyne were more thermally stable than BIC and EIC which released the heat from lower temperature, while they were less stable than TBM.

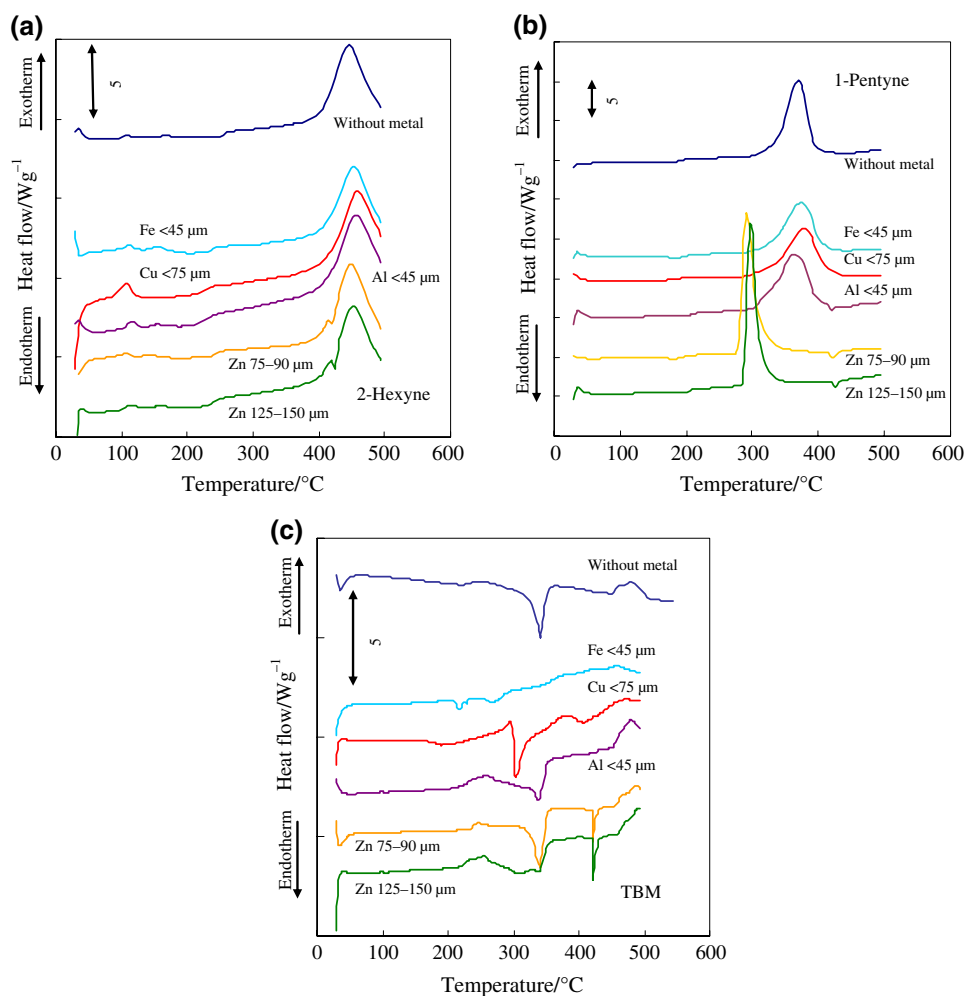
Reactivity with metal

When the thermal behavior of 2-hexyne and 1-pentyne with iron, copper, aluminum, and two types of zinc with different particle diameter was observed, the thermal curves as shown in Fig. 2 were obtained.

In 2-hexyne, the each metal hardly changed the main exothermic peak observed at approximately 400 °C from the viewpoint of T_{DSC} , Q_{DSC} , and the thermal curve shape. However, in the case of 2-hexyne with copper or aluminum, Q_{DSC} of the peak observed at the temperature of around 100 °C showed about 70 Jg⁻¹. This value is larger than that of 1-hexyne alone. Q_{DSC} of the slight peak of 2-hexyne with other metals showed 23–42 Jg⁻¹. These values were similar or less value in comparison with 2-hexyne alone.

In the measurement of 1-pentyne, the iron, copper, and aluminum hardly changed the exothermic peak observed at approximately 400 °C from the viewpoint of T_{DSC} , Q_{DSC} , and the thermal curve shape. On the other hand, zinc decreased the value of T_{DSC} to approximately 280 °C from 340 °C of 1-hexyne alone. Furthermore, it changed the shape of the thermal curve. From this result, Zn comparatively influenced the thermal stability of 1-pentyne. The exothermic peak near 130 °C that appeared in 1-pentyne

Fig. 2 DSC curves in the coexistence with various metals. **a** 2-hexyne, **b** 1-pentyne, **c** TBM



alone was hardly observed in the case of 1-pentyne with each metal.

In the case of TBM, the metals changed the thermal curve, and the obvious exothermic, however, was not observed in lower temperature than 400 °C.

ARC measurements

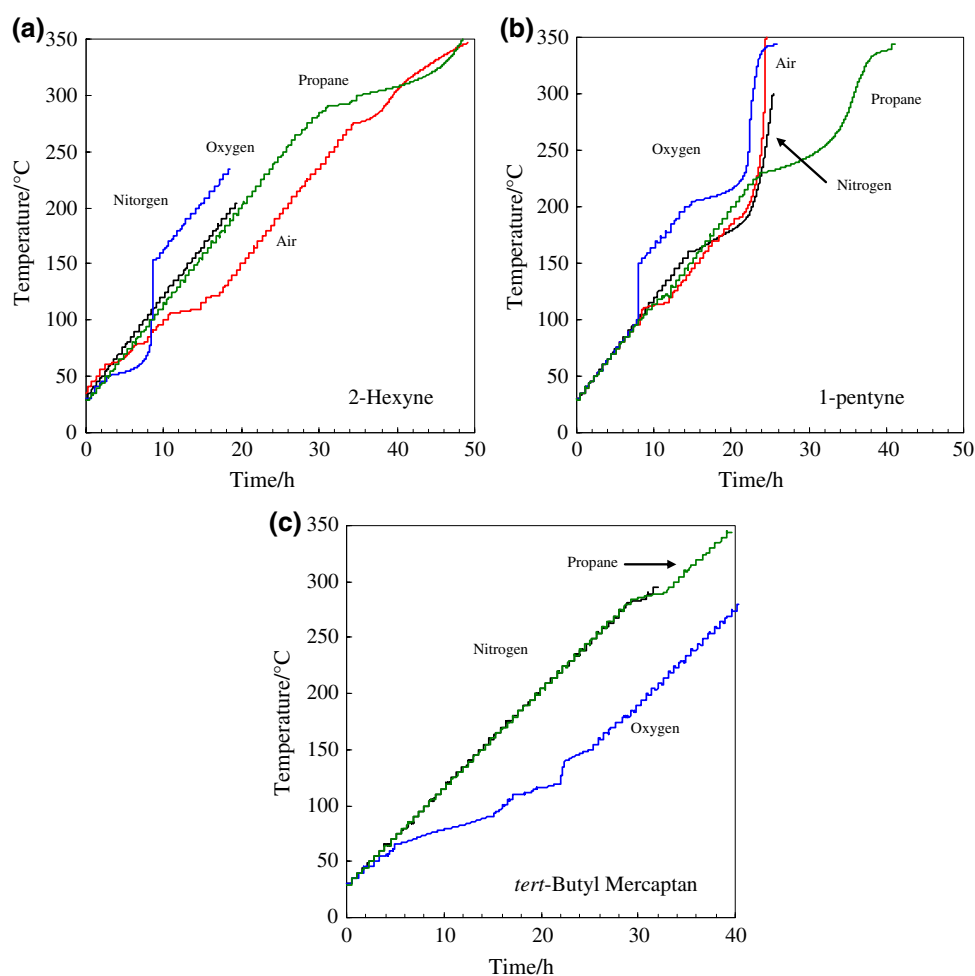
From the results of the Sect. “**Thermal behavior of each candidate substance**”, T_{DSC} of the main exothermic peak observed in 2-hexyne and 1-pentyne was comparatively high. However, these substances had the slight exothermic peak at low temperature region. In this section, the heat release behavior at low temperature was investigated with ARC.

Figure 3a shows the temperature change of 2-hexyne in an oxygen, air, nitrogen, and propane atmosphere. In a nitrogen or propane atmosphere, no temperature change induced by the exothermic reaction was detected in this temperature range up to 200 °C. However, the exothermic heat was observed under the both air and oxygen

atmosphere at 56 and 45 °C, respectively. Furthermore, its heat amount in an oxygen atmosphere was larger than that of air, which indicates that the heat release depended on the amount of atmospheric oxygen. Moreover, in the heat release in an oxygen atmosphere, a pressure reduction in the sample bomb was detected during the heat release of 2-hexyne. From these results, it is considered that 2-hexyne reacted with atmospheric oxygen. As mentioned above, in DSC measurement, 2-hexyne had the slight exothermic peak at low temperature region. This heat release may be corresponding to the heat release at approximately 50 °C observed by ARC, and it thought to be results from the reaction between 2-hexyne and atmospheric oxygen.

Figure 3b shows the temperature change of 1-pentyne. 1-pentyne released the heat in an oxygen atmosphere at 97 °C with a pressure reduction in the sample bomb. Furthermore, in an air atmosphere, slight heat release was observed at approximately 100 °C. On the other hand, in a nitrogen atmosphere, no heat release was observed in this temperature region. From these results, similar to 2-hexyne, the slight exothermic peak observed in DSC

Fig. 3 Variation of temperature under several atmosphere in the sample bomb with time under the adiabatic condition



measurement at low temperature region may be originated from the reaction between 1-pentyne and atmospheric oxygen. The heat release at more than 160 °C observed by ARC measurement is thought to be corresponding to the main heat release observed in DSC measurements.

Figure 3c shows the temperature change of TBM. Any exothermic heat does not observed up to temperature range of 300 °C under the nitrogen atmosphere. The exothermic heat was observed at 282 °C under the propane atmosphere. In an oxygen atmosphere, some heat releases were observed and first exothermic step was at 65 °C. Exothermic behavior of TBM under the oxygen atmosphere is milder than those of the other candidate substances under the same condition.

In comparison between the candidate substances and TBM in the presence of oxygen, it is considered that the thermal hazard of candidate substances was high. In addition, especially on 2-hexyne and 1-pentyne, comparatively large heat release was observed. In this way, for the practical application of 2-hexyne and 1-pentyne as odorants, the consideration of not only the decomposition of the substance itself but also the reaction with oxygen will be

required. Furthermore, it is important to suppress the invasion of the oxygen in the cylinder to low as much as possible in respect of the storage of the candidate odorant.

Effect for combustibility

Figure 4 shows the variation of adiabatic flame temperature against mixture fraction of candidate odorant in the fuel under the condition of stoichiometric ratio value being unity. As each symbol clearly overlapped, even if the amount of addition of either candidate odorant is less than 0.01 mole ratio, there is little influence on the adiabatic flame temperature.

Figure 5 shows the typical result of combustion products for stoichiometric ratio being unity. The plot of the left end of Fig. 5 is calculated result in the case of the propane without odorant as a fuel and the right end is that of 2-hexyne only. It is seldom effective on the species of combustion product and their yield. Similar tendency was observed even if the equivalent ratio was changed from 0.8 to 1.2 for four kinds of the candidate odorant taken up in this study.

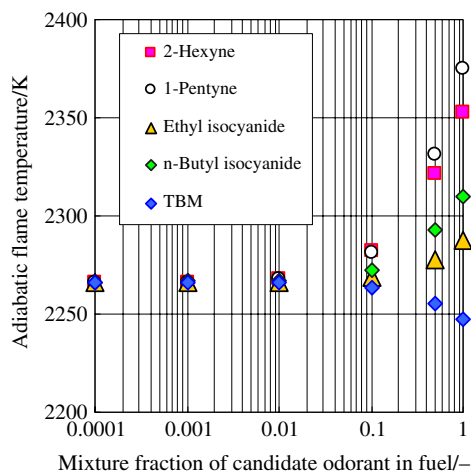


Fig. 4 Variation adiabatic flame temperature against the mixture fraction of candidate odorant in fuel

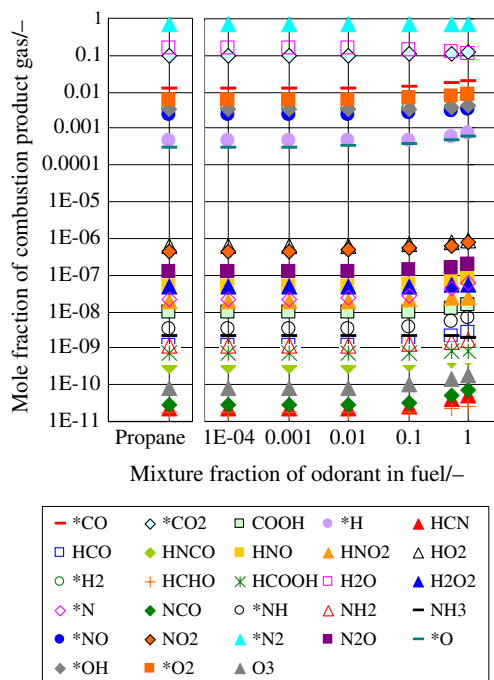


Fig. 5 Variation mole fraction of combustion product against the mixture fraction of 2-hexyne in fuel

Even if either candidate odorant is added at about 100 ppm, there is little influence on propane combustibility from the adiabatic flame temperature, species of combustion gas, and their yields.

Conclusions

1. 2-hexyne and 1-pentyne are more thermally stable than EIC and BIC in four kinds of the candidate substances taken up in this research. However, in 2-hexyne and 1-pentyne, the slight exothermic peaks were observed at lower temperature region before those main exothermic peaks.
2. In 2-hexyne, iron, copper, aluminum, and zinc hardly changed the main exothermic peak from the viewpoint of T_{DSC} , Q_{DSC} , and the thermal curve shape. On the other hand, copper or aluminum increased the heat amount of the slight exothermic peak observed before main peak.
3. In 1-pentyne with zinc, the reduction in T_{DSC} of approximately 60 K was observed. Iron, copper, and aluminum hardly changed the main exothermic peak from the viewpoint of T_{DSC} , Q_{DSC} , and the thermal curve shape.
4. In the case of 2-hexyne and 1-pentyne in the absence of oxygen, no temperature change induced by the exothermic reaction was detected in this temperature range up to 150 °C. On the other hand, in the presence of oxygen, the exothermic heat was observed at approximately 50–100 °C. This heat release may be corresponding to the slight heat release observed by DSC, and it thought to be results from the reaction with atmospheric oxygen. In this way, for the practical application of 2-hexyne and 1-pentyne as odorants, it is important to suppress the invasion of oxygen in the cylinder to low as much as possible in respect of the storage of the candidate odorant.
5. Even if either candidate odorant is added at about 100 ppm, there is little influence on propane combustibility from the adiabatic flame temperature, species of combustion gas, and their yields.

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