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FT-IR analysis of flame resistant chemical mixture

Younsu Kim[1,†], Jihyung Seo[1,†], Yoong Kee Choe[2], Youngku Sohn[1,3], and Jeongkwon Kim[1,3,★]
[1]*CNU Chemistry Core Facility, Chungnam National University, Daejeon, Korea*
[2]*Research Center for Computational Design of Advanced Functional Materials, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba 305-8568, Japan*
[3]*Department of Chemistry, Chungnam National University, Daejeon, Korea*

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Abstract: In this study, flame retardant mixtures of decabromodiphenylethane (DBDPE) and Sb_2O_3 were analyzed using Fourier transform infrared (FT-IR) spectroscopy. The experimentally obtained wavenumbers of DBDPE and Sb_2O_3 were 1321 and 949 cm^{-1}, respectively, whereas those obtained by theoretical calculation were 1370 and 818 cm^{-1}, respectively. Strong correlation was observed between the mixing molar ratios and observed peak area ratios, suggesting that FT-IR analysis can be used to obtain relative amounts of the individual components of flame retardant mixture.

Key words: Flame retardants, FT-IR, decabromodiphenylethane, Sb_2O_3, antimony trioxide

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1. Introduction

Plastics, synthetic fibers, and resins made from petroleum are among the most commonly used materials in daily life. Since these materials are composed of carbon, hydrogen, and oxygen, they are highly flammable.[1] Therefore, flame retardants are essential substances that are included as petrochemical additives.[2] Flame retardants are classified into organic and inorganic types according to their composition; organic flame retardants are more commonly used than inorganic types. Among organic types, bromine-containing flame retardants such as polybrominated diphenyl ethers, hexabromocyclododecane, tetrabromobisphenol-A, and decabromodiphenylethane (DBDPE) are the most abundant due to their excellent heat resistance and high cost-effectiveness.[3] However, regulations limiting the use of bromine-containing flame retardants continue to expand because they generate carcinogens and environmentally hazardous by-products.[4,5] Therefore, bromine-containing flame retardants are often mixed with an inorganic additive such as antimony trioxide (Sb_2O_3) to enhance flame retardancy and reduce the content of carcinogens in the combustion products.[6,7] To determine the properties of mixed flame retardants, it is important to analyze each component accurately since physicochemical characteristics can differ significantly according to composition.[8,9] Fourier Transform Infrared (FT-IR) spectroscopy has been used for the qualitative analysis

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[†] These authors contributed equally to this work.

★ Corresponding author
Phone : +82-(0)42-821-5477 Fax : +82-(0)42-821-8896
E-mail : jkkim48105@cnu.ac.kr

of flame retardants[10,11] since it provides simple and reproducible results. In this study, flame retardant mixtures of DBDPE and Sb_2O_3 were analyzed using FT-IR spectroscopy to investigate whether this method can provide sufficiently accurate quantitative information on the components of flame retardant mixtures.

2. Experimental

2.1. FT-IR experiments

DBDPE and Sb_2O_3 were obtained from CHEMLINK (Seoul, Korea). FT-IR spectra were obtained using an FT-IR spectrometer (Nicolet iS10, Thermo Scientific, CNU Chemistry Core Facility) using a scan number of 128, a resolution of 8, a wavenumber range of 400-4000 cm^{-1}, and Smart iTR Diamond ATR mode. FT-IR data acquisition was performed using the OMNIC9 software package. Mixtures of DBDPE and Sb_2O_3 were prepared by changing the mixing mass ratios of the individual components from 0 % to 100 % in increments of 10 %. Prior to FT-IR analysis, we prepared and thoroughly mixed a 1-g sample of each mixture using a vortex mixer. The areas of the FT-IR peaks were obtained using ImageJ 1.53a software (National Institutes of Health, USA).

2.2. Computational details

Geometry optimization followed by analytical vibrational frequency calculations to simulate the vibrational spectra of DBDPE and Sb_2O_3 were conducted using density functional theory (DFT) employing the ωB97XD functional.[12] We used the def2-TZVP sets as basis sets.[13] Sb atomic core electrons were represented by effective core potential (ECP). All basis sets and ECP data were obtained from the Basis Set Exchange (BSE).[14] The initial molecular structure of DBDPE was obtained using the molecular drawing function implemented in the Avogadro program.[15] At temperatures below 570 °C, the solid phase of Sb_2O_3 is senarmonite, which is a cubic molecular crystal[16] consisting of Sb_4O_6. Therefore, we removed a Sb_4O_6 structure from this crystal structure to perform geometry optimization and frequency calculations. All computations were performed using the Gaussian 16 program suite.[17]

3. Results and Discussion

3.1. FT-IR spectra of individual retardants

To determine whether FT-IR data for flame retardant mixtures of DBDPE and Sb_2O_3 could be used to provide quantitative information on each compound, we first analyzed the individual compounds of DBDPE and Sb_2O_3. The FT-IR spectra of DBDPE and Sb_2O_3 are shown in *Fig.* 1. Unique absorption peaks were observed for each compound, at 1321 and 949 cm^{-1} for DBDPE and Sb_2O_3, respectively. Sb_2O_3 showed an additional broad peak around 700 cm^{-1} due to Sb–O–Sb vibration;[18] however, this peak was not

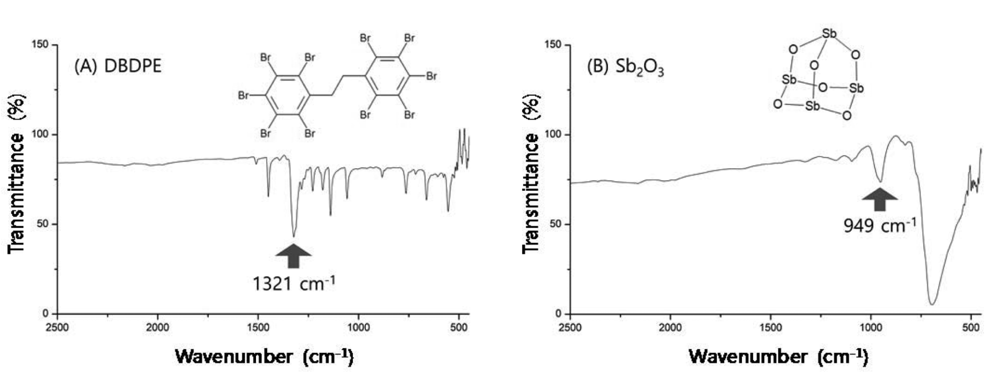

Fig. 1. Fourier transfer infrared (FT-IR) spectra of (A) decabromodiphenylethane (DBDPE) and (B) Sb_2O_3. Unique absorbance peaks were observed at 1321 and 949 cm^{-1} for DBDPE and Sb_2O_3, respectively. The spectra are displayed from 400 to 2500 cm^{-1} because no peaks were observed at wave numbers > 2500 cm^{-1}.

used for subsequent quantitative analysis because its absorption had already saturated the FT-IR spectrum. To our knowledge, no previous study has reported the FT-IR spectrum of DBDPE, although FT-IR spectra have been reported for decabromodiphenylether, with a distinct peak around 1350 cm^{-1}.[19] Decabromodiphenylether was introduced on the market earlier than DBDPE.[20] The structural similarity between decabromodiphenylether and DBDPE has contributed to the closeness of the absorption peaks of decabromodiphenylether (1350 cm^{-1}) and DBDPE (1321 cm^{-1}). For Sb_2O_3, there was a report showing the absorption peak at 949 cm^{-1}.[21]

To calculate the theoretical absorption wavenumbers for DBDPE and Sb_2O_3, we performed computational analysis using the Gaussian 16 program suite. Theoretically generated FT-IR spectra and their corresponding vibration modes for the absorption of DBDPE and Sb_2O_3 are shown in *Fig.* 2. The theoretically calculated wavenumber of the DBDPE peak (1370 cm^{-1}) was close to that obtained experimentally (1321 cm^{-1}). However, the theoretical

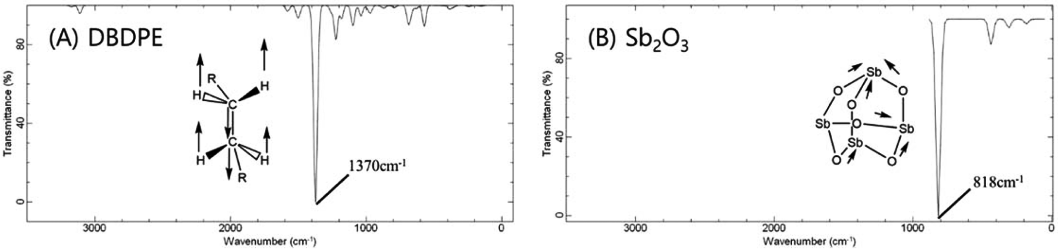

Fig. 2. Theoretical FT-IR spectra and vibration modes for (A) DBDPE and (B) Sb_2O_3. The calculated absorption peaks were 1370 and 818 cm^{-1} for DBDPE and Sb_2O_3, respectively.

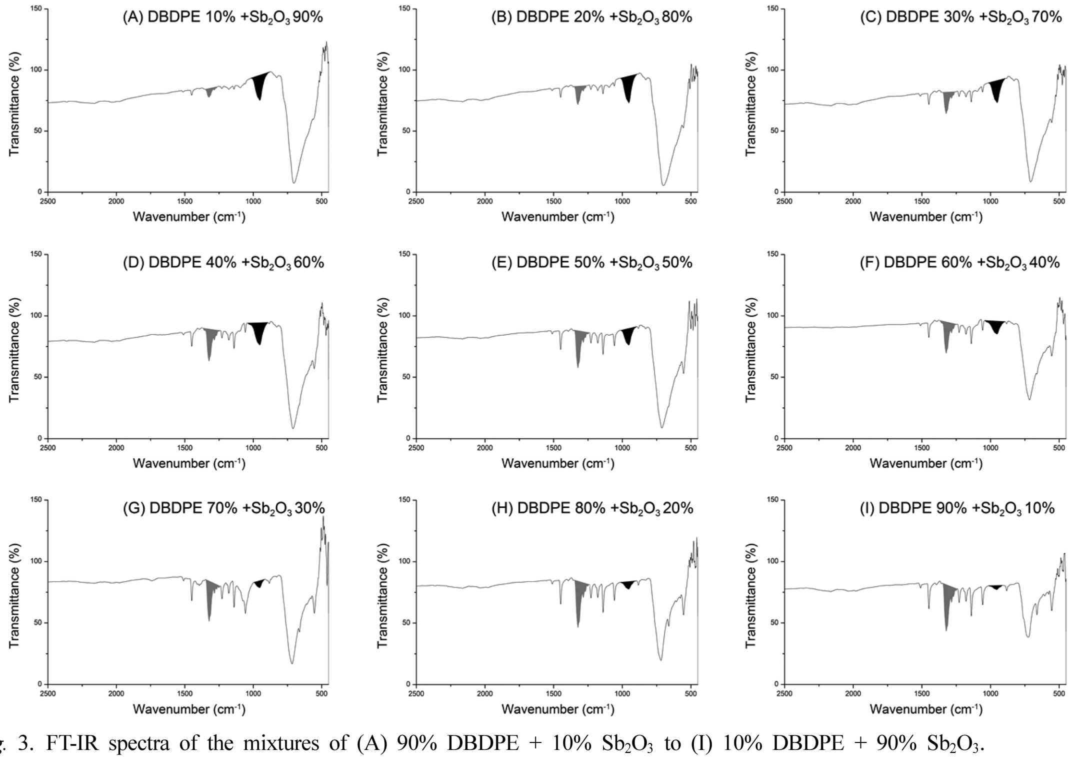

Fig. 3. FT-IR spectra of the mixtures of (A) 90% DBDPE + 10% Sb_2O_3 to (I) 10% DBDPE + 90% Sb_2O_3.

Table 1. Peak area ratios and mixing molar ratios of decabromodiphenylethane (DBDPE) and Sb_2O_3

Mixing mass ratio	Peak area for the peak at		Ratio of DBDPE/(DBDPE+Sb_2O_3)	
	1321 cm^{-1} for DBDPE	949 cm^{-1} for Sb_2O_3	Peak area ratio	Mixing molar ratio
0	0	17495	0	0
0.1	4418	17853	0.20	0.15
0.2	8800	19257	0.31	0.29
0.3	10841	16808	0.39	0.41
0.4	15062	18907	0.44	0.52
0.5	18601	12071	0.61	0.62
0.6	22962	10500	0.69	0.71
0.7	19562	3640	0.84	0.79
0.8	24722	5256	0.82	0.86
0.9	26596	2803	0.90	0.94
1	27992	0	1	1

wavenumber of the Sb_2O_3 peak (818 cm^{-1}) was significantly different from that obtained experimentally (949 cm^{-1}), likely because Sb_2O_3 is present as a cubic molecular crystal with a unit cell of Sb_4O_6,[16] whereas our calculations were performed using a single Sb_4O_6 molecule.

3.2. Comparison between mixing molar ratio and peak area ratio of flame retardant mixtures

To explore the relationship between the mixing molar ratio and peak area ratio of the flame retardant mixtures prepared using different mixing ratios of DBDPE and Sb_2O_3, the FT-IR spectra of the mixtures were obtained as shown in *Fig.* 3. The peak areas of DBDPE at 1321 cm^{-1} and Sb_2O_3 at 949 cm^{-1} are listed in *Table* 1. The mixing mass ratios were converted into mixing molar ratios by considering the molar mass of each compound (*Table* 1).

The relationship between the peak area ratio and the mixing molar ratio is shown in *Fig.* 4. We observed strong linearity ($R^2 = 0.9865$), which demonstrates that the experimentally obtained peak area ratios of DBDPE and Sb_2O_3 were well represented in the FT-IR analysis, and that this method can be used to obtain the mixing molar ratios of DBDPE and Sb_2O_3.

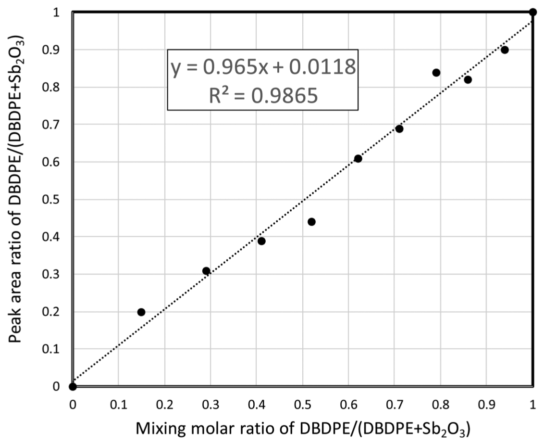

Fig. 4. Relationship between peak area ratios and mixing molar ratios of DBDPE and Sb_2O_3.

4. Conclusions

Individual FT-IR spectra of DBDPE and Sb_2O_3 were experimentally obtained and compared with theoretically generated spectra. FT-IR analysis of flame retardant mixtures composed of DBDPE and Sb_2O_3 showed high linearity between the mixing molar ratio and peak area ratio of DBDPE and Sb_2O_3, demonstrating that the FT-IR data of the flame retardant mixture can be used to provide quantitative information on its components. The current result will be beneficial to those who would like to quantitatively analyze the flame retardant mixture in a simple and reproducible way using a FT-IR spectrometer.

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Authors' Positions

Younsu Kim	: Researcher	Youngku Sohn	: Professor
Jihyung Seo	: Researcher	Jeongkwon Kim	: Professor
Yoong Kee Choe	: Senior Researcher		