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Thermal degradation study of decabromodiphenyl ether. Translating thermo-analytical results into optimal chromatographic conditions

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Abstract: This study aims to investigate the thermal degradation behavior of decabrominated diphenyl ether (BDE 209), a flame retardant (FR) which accounts for more than 90% of the total polybrominated diphenyl ethers reported for indoor dust samples collected from Eastern Romania. Simultaneous TG/DTA was applied under various heating rate and atmospheres. The results of this study showed that BDE 209 undergoes thermal degradation in a single step, regardless of the heating rate or atmosphere, with an initial degradation temperature between 297 and 330 ^{0}C, depending on the heating rate, and a partial overlapping of melting and thermal degradation in the initial stages which might suggest that the common degradation noticed for the higher brominated FRs analysis might also occur during sample preparation or during injection of the extracts in the GC systems and not necessarily during column elution. The main findings of this research were aimed at designing proper GC analytical methods for the selected halogenated contaminants.

Keywords: brominated flame retardants, BDE 209, thermal degradation, TG-DTA, chromatographic analysis.

Introduction

Flame retardants (FRs) are materials that inhibit or resist the spread of

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fire that are added to polymers which are used in plastics, textiles, electronic circuitry or other materials.[1,2] The extensive use of FRs in various materials (furniture, plastics, electronics equipment, textiles, etc.) has led to the widespread and substantial contamination of the indoor environment, e.g. indoor air and dust.[3-5] Indoor environment as well as dietary intake is of special concern for the increasing human exposure to such chemicals for which various adverse health effects have been reported.[4] However, due to voluntary withdrawals, bans and widespread restrictive regulations regarding the manufacture and use of some FRs,[6-8] the need for substitutes have substantially increased.[9] Consequently, there are some reports on (already) elevated levels in indoor environments of many substitutes, such as novel brominated FRs (decabromodiphenyl ethane (DBDPE) or 1,2-bis-(2,4,6 tribromo-phenoxy) ethane) or organophosphate FRs.[5,9-12] Currently, efforts are undertaken at international level to establish the extent of migration of chemicals from products, the consequent human exposure and the effects of such exposure.[13]

Even if the properties of brominated FRs, such as polarity or vapor pressure, suggest that different procedures should be applied for their analysis from environmental samples when compared to classical persistent organic pollutants (POPs), the analytical methodology for the FRs measurement are in most of the cases based on protocols previously established for POPs. In order to achieve the sensitivity needed for the brominated FRs detection from environmental samples, the instrumental analyses of such compounds are mostly based on the use of GC-MS. While analytical methods are readily available for quantifying lower brominated diphenyl ethers (BDE) congeners found in the Penta-BDE and Octa-BDE technical mixtures, the analysis of higher brominated compounds, in particular of decabromodiphenyl ether (BDE 209), has proven to be difficult.[14]

Conventional GC techniques suitable for the determination of other halogenated contaminants are not satisfactory for the determination of polybrominated diphenyl ethers (PBDEs), especially for higher brominated congeners.[15] High temperatures are needed for the GC injection and column systems, while some higher PBDE congeners are thermally-labile compounds, particularly BDE 209, which begins to degrade at temperatures above 300 °C.[16,17] However, generally, the elution temperatures of such compounds in GC systems are very close or even higher than the degradation temperatures reported for brominated FRs.[18] As a consequence, if their degradation into GC systems is not fully considered, this generates an increased uncertainty for their quantification and therefore errors occur when estimating the human exposure to such compounds. Even if the thermal degradation of such compounds due to instrumental conditions applied for their identification and quantification is reported in scientific literature in the field,[5] there are no systematic studies by proper thermos-analytical methods to report on their behavior. Due to their degradation during sample preparation or into GC systems during their analysis, errors might be generated for assessing their levels, while such errors lead to underestimation of the human exposure to such compounds.

Therefore, throughout the present study we have investigated thermal degradation behavior of decabromodiphenyl ether (BDE 209), a FR which accounts for more than 90% of the total BDEs reported from indoor dust samples from Eastern Romania,[10] by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) under different atmospheres (nitrogen, helium and air) and with different heating rates.

Results and discussions

TG/DTG and DTA analyses were performed simultaneously and the obtained recordings for BDE 209 thermal degradation under nitrogen flow at 2, 10 and 20 (from top to down) K/min are presented in Figure 1. Atmosphere in which FRs thermal degradation occur is also important to be considered since several GC instruments setup might use either nitrogen or helium as carrier gas, while some sample preparation steps for FRs extraction from several matrices are generally performed in air. Therefore, degradation experiments were also performed under different atmospheres, namely: helium, air and nitrogen and TG/DTA recordings for BDE 209 degradation at a heating rate of 10 K/min are presented in Figure 2.

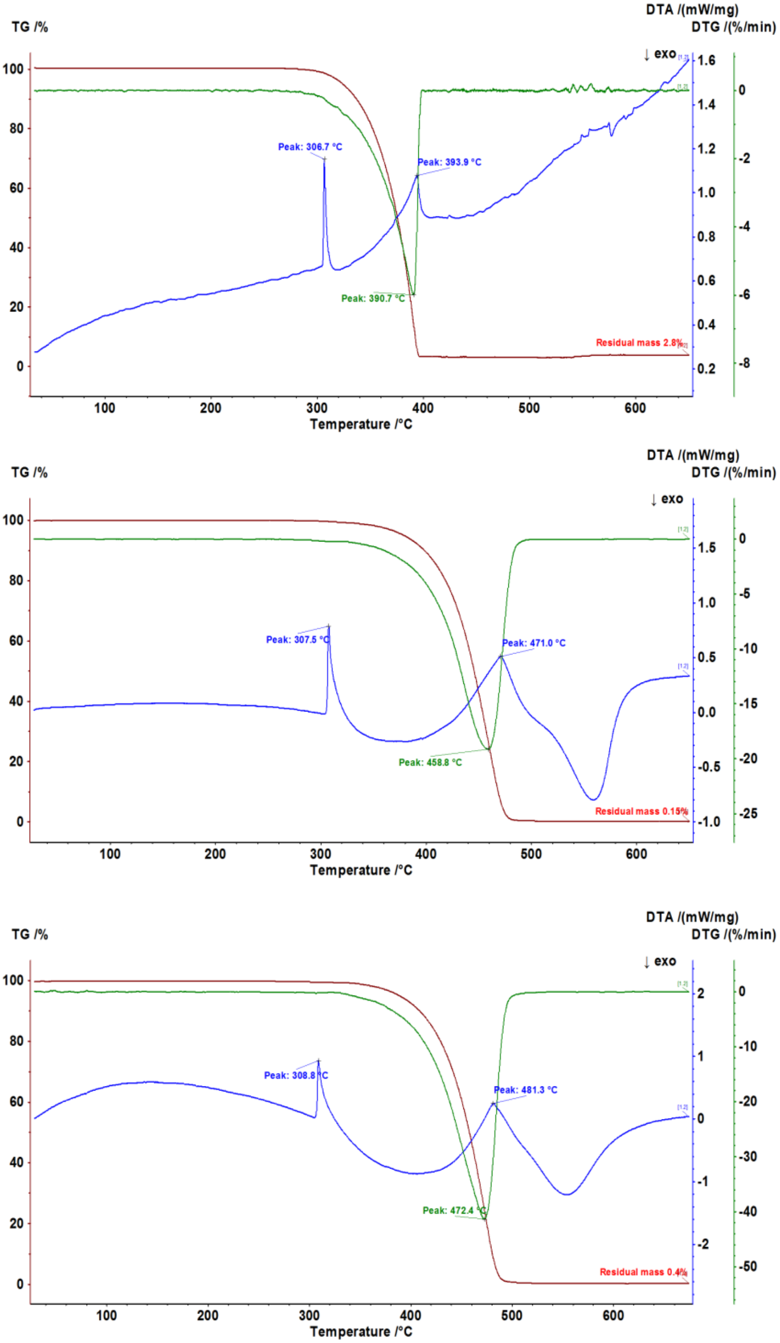

Figure 1. TG/DTG and DTA recordings for BDE 209 degradation at 2, 10 and 20 (from top to down) K/min under N_2.

By analyzing the TG/DTG curves it could be noticed that thermal degradation of BDE 209 occurs in a single step, with complete weight loss, regardless of heating rate and atmosphere, with an initial degradation temperature slightly shifted towards higher values with increasing heating rate. This is an important observation since various GC oven temperature programs might apply different heating rates depending on the analytes targeted for analysis: lower heating rates are generally used especially when targeting in a single run lower brominated FRs together with other organohalogenated contaminants such as chlorinated pesticides, while higher heating rates are employed when target analytes are highly brominated FRs, especially BDE 209.

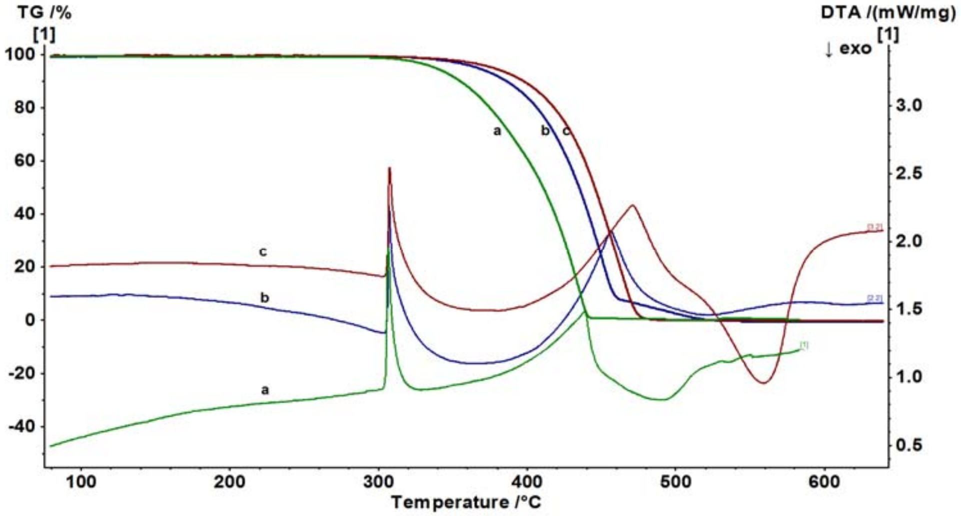

Figure 2. TG/DTA recordings for BDE 209 degradation at 10 K/min in different atmospheres: helium (a), air (b) and nitrogen (c), respectively.

DTA recordings suggest a partial overlapping of melting and thermal degradation in the initial stages, followed by a second endothermic degradation step at higher temperatures that shifts with increasing heating rate. This hypothesis is supported by the fact that the first peak is completely reversible if consecutive heating and cooling cycles are employed, as depicted in Figure 3.

Marked asymmetry and an inflexion point are noted in the DTA degradation peak, suggesting a change in the reaction mechanism after maximum degradation rate is attained, without any correspondence in the TG curves. As DTA and TG measurements are based on different fundaments, this apparent disagreement does not necessarily have a physical significance. DTA is much more sensitive than TG and the inflexion could indicate a variation in the degradation mechanism, as it is also observed in DTG.

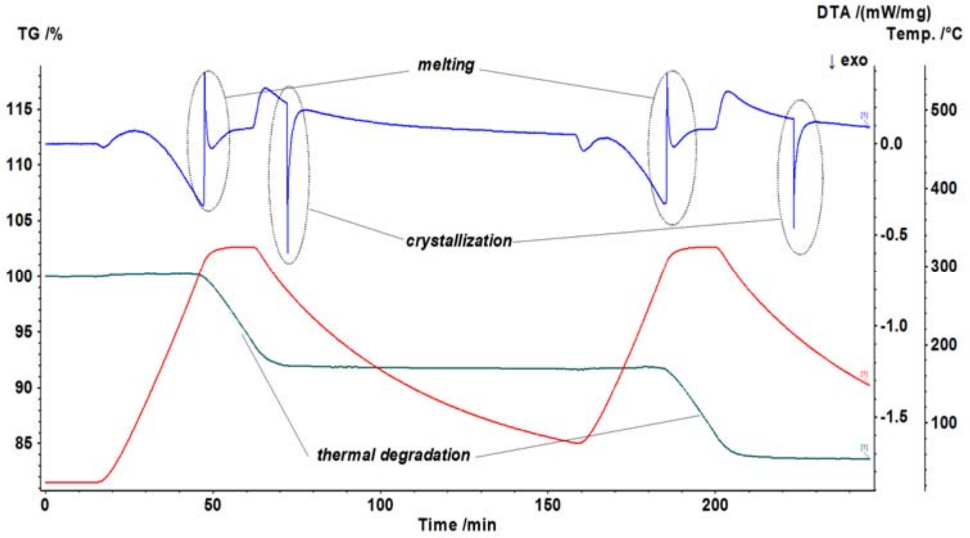

Figure 3. DTA and TG recordings for BDE 209 under nitrogen at 10 K/min, for two consecutive heating/cooling cycles from 25 to 320 ^{0}C.

The characteristic temperatures and melting enthalpy (obtained by integrating the melting peak) from DTA analysis are presented in Table 1, while Table 2 shows the characteristic temperatures and weight loss obtained from TG/DTG recordings for the BDE 209 thermal degradation.

The initial and maximum melting temperatures are largely insensitive to heating rate increasing, as expected from a first order transition, exhibiting an increase of 1.3 and 2.2 degrees, respectively. In contrast, the kinetically driven degradation is markedly shifted towards higher temperatures with increasing heating rate. As it can be seen by analyzing the initial and maximum temperatures for melting, respectively degradation, the two processes partially overlap for heating rates lower than 15 K/min and only at 20 K/min a complete separation is obtained. Since both melting and pyrolysis are endothermic processes, the greater the overlap (as for the lowest heating rates) the higher the combined thermal effect measured in DTA. Thus, we expect that the value of 21.2 J/g obtained for 20 K/min to be an accurate estimation of the melting enthalpy for BDE 209.

Table 1. Characteristic temperatures and melting enthalpy from DTA analysis in nitrogen.

Heating rate (K/min)	T_i (^{0}C)	T_m (^{0}C)	T_f (^{0}C)	ΔH_m (J/g)
2	304.0	306.7	315.2	42.1
5	304.1	304.4	314.8	37.2
10	305.1	307.5	329.1	32.4
15	305.3	306.6	330.7	26.1
20	305.3	308.8	331.8	21.2

In a similar manner, the results of thermal analysis under different atmospheres and at a constant heating rate of 10 K/min, namely the initial and maximum melting temperatures, melting enthalpies and weight loss percentages are presented in Tables 3 and 4.

Table 2. Characteristic temperatures and weight loss for BDE 209 degradation in nitrogen.

Heating rate (K/min)	T_i (^{0}C)	T_m (^{0}C)	T_f (^{0}C)	Weight loss (%)
2	297.1	390.7	399.2	97.2
5	302.2	437.1	462.3	99.9
10	303.6	458.8	498.1	99.85
15	306.7	470.8	512.5	94.46
20	330.8	472.4	531.2	99.6

Table 3. Characteristic temperatures and melting enthalpy from DTA analysis at 10 K/min under different atmospheres.

Atmosphere	T_i (^{0}C)	T_m (^{0}C)	T_f (^{0}C)	ΔH_m (J/g)
Helium	306.2	307.8	321.5	33.6
Nitrogen	305.1	307.5	329.1	32.4
Air	304.5	307.2	329.4	34.3

Table 4. Characteristic temperatures and weight loss for the degradation of BDE 209 at 10 K/min under different atmospheres.

Atmosphere	T_i (^{0}C)	T_m (^{0}C)	T_f (^{0}C)	Weight loss (%)
Helium	297.7	434.6	449.2	99.79
Nitrogen	303.6	458.8	498.1	99.85
Air	302.9	449.5	540.4	99.9

As it can be seen from Figure 2 and Table 3, BDE 209 melting is largely insensitive to the nature of the furnace atmosphere. However, the initial degradation temperature is lower under helium as compared to nitrogen and air (Table 4) and an additional degradation step is made evident by the inflexion point in TG at 394.5 ^{0}C, suggesting a lower thermal stability under helium. This is an important finding which might be further used when choosing the proper GC analysis conditions in terms of carrier gas selection. Figure 4 presents a typical mass-chromatogram when injecting a standard solution containing only BDE 209. Thermal degradation of BDE 209 generates the formation of the lower brominated congeners, in Figure 4 being presented the formation of the nona-BDEs. Therefore, TG experiments performed in the present study suggested that BDE 209 thermal stability is lower under helium atmosphere when compared to air and nitrogen.

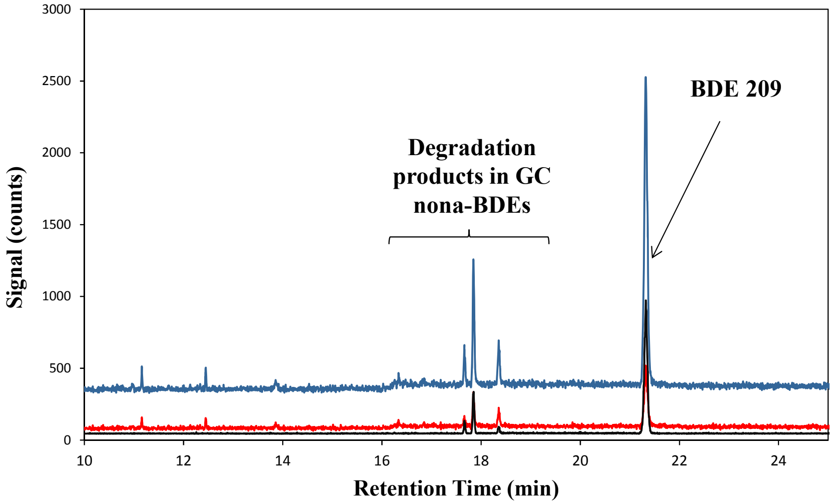

Figure 4. Typical mass-chromatogram (total ion chromatogram - blue; *m/z* = 81 - red; *m/z* = 79 - black) for the GC with MS detection for the analysis of BDE 209.

Although the use of air as GC carrier gas is not suitable mainly due to inactivation of the capillary GC columns stationary phases, helium is generally the most used carrier gas employed in GC experiments due to its properties of ensuring the maximum linear velocity for the targeted analytes. However, our results suggest that the type of carrier gas used in common GC setups might influence the analysis accuracy of highly brominated FRs in general and of BDE 209 in particular.

Experimental

Thermal degradation experiments were performed on a Netzsch STA 449 F1 Jupiter with simultaneous recording of TG and DTA, using alumina crucibles. A constant flow of 40 mL/min of gas (nitrogen, helium and air, respectively) was used. Linear heating rates of 2, 5, 10, 15 and 20 K/min were used with sample mass of about 4 mg. Temperature and sensitivity calibrations (DTA) were performed using Netzsch certified standards. DTG curves were numerically obtained as the time derivative of the thermogravimetric data using the Netzsch Proteus 6.0 software (Netzsch).

Conclusions

BDE 209 undergoes thermal degradation in a single step, regardless of the heating rate or atmosphere, with an initial degradation temperature between 297 and 330 ^{0}C, depending on the heating rate, and a partial overlapping of melting and thermal degradation in the initial stages. This might suggest that the common degradation noticed for the higher brominated FRs analysis might also occur during sample preparation or injection of the extracts into the GC systems and not necessarily during column elution since temperatures above 300 ^{0}C are not commonly applied for the GC oven temperature programs.

Acknowledgements

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References

1. World Health Organization/ International Classification for Patient Safety (WHO/ICPS). Environmental Health Criteria 162: Brominated Diphenyl Ethers. Geneva: World Health Organization; **1994**.

2. World Health Organization/ International Classification for Patient Safety (WHO/ICPS). Environmental Health Criteria 192: Flame Retardants–General introduction. Geneva: World Health Organization; **1997**.

3. Rudel, R.A.; Perovich, L.J. Endocrine disrupting chemicals in indoor and outdoor air, *Atmos. Environ.*, **2009**, *43*, pp. 170-181.

4. Harrad, S.; Abdallah, M.; de Wit, C.; Östman, C.; Bergh, C.; Covaci, A.; Darnerud, P.O.; de Boer, J.; Diamond, M.; Huber, S.; Leonards, P.; Mandalakis, M.; Ostman, C.; Haug, L.S.; Thomsen, C.; Webster, T.F. Indoor contamination with hexabromocyclododecanes, polybrominated diphenyl ethers, and perfluoroalkyl compounds: an important exposure pathway for people?, *Environ. Sci. Technol.* **2010**, *4*, 3221-3231.

5. Covaci, A.; Harrad, S.; Abdallah, M.A.E.; Ali, N.; Law, R.J.; Herzke, D.; de Wit, C.A. Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour, *Environ. Int.* **2011**, *37(2)*, 532-556.

6. EU Directive 2003/11/EC, Official Journal L 042, 15/02/**2003**.

7. EU Directive 2005/84/EC, OJ L344/40, 27/12/**2005**.

8. EC 2008, European Court of Justice ruling in joint cases C-14/06 and C-295/06, *http://curia.europa.eu*.

9. Nagorka, R.; Conrad, A.; Scheller, C.; Süßenbach, B.; Moriske, H.J. Diisononyl 1,2-cyclohexanedicarboxylic acid (DINCH) and Di(2-ethylhexyl) terephthalate (DEHT) in indoor dust samples: Concentration and analytical problems, *Int. J. Hyg. Environ. Health.* **2011**, *214(1)*, 26-35.

10. Van den Eede, N.; Dirtu, A.C.; Neels, H.; Covaci, A. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust, *Environ. Int.* **2011**, *37(2)*, 454-461.

11. Abb, M.; Heinrich, T.; Sorkau, E.; Lorenz, W. Phthalates in house dust, *Environ. Int.* 2009, *35*, 965-970.

12. Bergh, C.; Torgrip, R.; Östman, C. Simultaneous selective detection of organophosphate and phthalate esters using gas chromatography with positive ion chemical ionization tandem mass spectrometry and its application to indoor air and dust, *Rapid Commun. Mass Spectrom.* **2010**, *24(19)*, 2859-2867.

13. Calafat, A.M.; Wong, L.Y.; Silva, M.J.; Samandar, E.; Preau, J.L.; Jia, L.T.; Needham, L.L. Selecting Adequate Exposure Biomarkers of Diisononyl and Diisodecyl Phthalates: Data from the 2005–2006 National Health and Nutrition Examination Survey, *Environ. Health Perspect.*, **2011**, *119(1)*, 50–55.

14. de Boer, J.; Wells, D.E. Pitfalls in the analysis of brominated flame retardants in environmental, uman and food samples–including results of three international interlaboratory studies, *Trends Analyt. Chem.* **2006**, *25*, 364-372.

15. Björklund, J.; Tollbäck, P.; Hiärne, C.; Dyremark, E.; Östman, C. Influence of the injection technique and the column system on gas chromatographic determination of polybrominated diphenyl ethers, *J. Chromatogr. A*, **2004**, *1041*, 201-210.

16. World Health Organization/ International Classification for Patient Safety (WHO/ICPS). Environmental Health Criteria 162: Brominated Diphenyl Ethers. Geneva: World Health Organization; **1994**.

17. Dumitras, M.; Maftei, D.; Airinei, A.; Tudorachi, N.; Dirtu, A.C. NPK analysis of the thermal degradation of decabromodiphenyl ether, *Rev. Chim.* **2016**, submitted.

18. Dirtu, A.C.; Ravindra, K.; Roosens, L.; Van Grieken, R.; Neels, H.; Blust, R.; Covaci, A. Fast analysis of decabrominated diphenyl ether (BDE 209) using low-pressure gas chromatography-electron capture negative ionization-mass spectrometry, *J. Chromatogr. A*, **2008**, *1186 (1-2)*, 295-301.