

Examination of Structural Differences between Isomers of Common Brominated Flame Retardants using Iodo-Adducts in LCMS

Nicole Riddell^a, Alan McAlees^a, Robert McCrindle^b, and Brock Chittim^a

Introduction

Brominated Flame Retardants often exist as a multitude of structural isomers in the environment. Since isomers can have varying levels of toxicity and bioaccumulation, it is important to not only confirm the identity of these contaminants, but also to identify which structural isomers are dominant in environmental samples. Scientists most often rely on purified reference standards to accomplish this, but when these standards are not readily available, they are required to utilize costly and time consuming methods such as x-ray crystallography and/or NMR analyses. Unfortunately, these procedures are not always practical when analyzing a complex mixture of compounds.

Utilizing the properties of halogen bonding and LCMS analysis may provide an avenue for the determination of structural configurations of isomers in select cases. Halogen bonding involves the interaction of a molecule bearing a halogen atom functioning as an electron-acceptor site (halogen bond donor) and a lone-pair possessing atom working as an electron-donor site (halogen bond acceptor)^{1,2}. It is known that iodide ions can behave as bidentate halogen bonding acceptors, but it appears that the intramolecular aspects of this type of interaction have not been exploited for structural determinations.

The objective of this work was to develop a simple LCMS technique that is based on the principle of iodide adduct formation in the mass spectrometer source to provide researchers with an alternative avenue for the identification of some brominated isomers.

Experimental

All experiments were conducted using a Micromass Quattro *micro* API mass spectrometer (MS) under negative electrospray ionization (see Table 1 for source conditions). Standard solutions (see Table 2) were prepared by diluting 100 μ l of a 50 μ g/mL stock solution to 5 μ g/mL with isopropanol (800 μ l) and a 1.66 mM aqueous potassium iodide solution (KI; 100 μ l). The standard solutions were then infused directly into the MS at a rate of 10 μ l/min.

Table 1: Source Parameters

Capillary Voltage (kV)	3.0
Cone Voltage (V)	12
Source temperature (°C)	100
Desolvation Temperature (°C)	300
Desolvation Gas Flow (L/hr)	200

Table 2: Compounds investigated

α -/ β -TBECH	α -HBCD
γ -/ δ -TBECH	γ -HBCD
BDE-66	α -TBCO
BDE-17	β -TBCO
BDE-155	HCDBCO

Results and Discussion

Promoting the formation of iodo-adducts in the MS source by simultaneously introducing a solution of potassium iodide (KI) has allowed the observation of a [M+I]⁻ cluster for γ - and δ -TBECH, which otherwise do not produce a molecular ion cluster by ESI, APCI, or APPI (see Figure 1). It is interesting to note that α - and β -TBECH do not form the [M+I]⁻ adduct. This can be explained by examining the structural configuration of the isomers. Gamma- and delta-TBECH have bromine atoms in adjacent equatorial positions on the cycloaliphatic ring system. Distortion of the ring system provides one of these bromine atoms with the correct configuration to form an intramolecular bridging iodo-adduct with a bromine atom on the side chain (see Figure 1). In contrast, the bromine atoms of alpha- and beta-TBECH are in axial positions anti to one another, which prohibits the formation of the iodo-adduct.

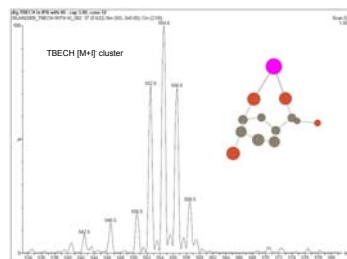


Figure 1: A mass spectrum showing the iodo-adduct cluster for a γ -/ δ -TBECH mix.

Results and Discussion continued...

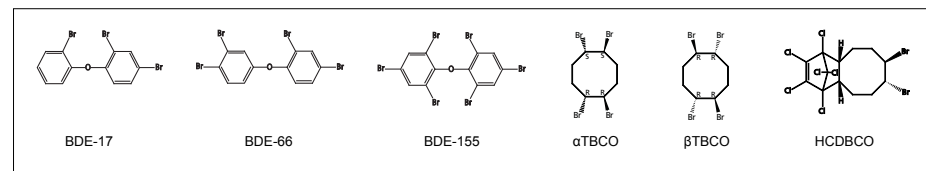


Figure 2: The structures of the compounds that did not display [M+I]⁻ clusters

There are certain geometrical demands that must be met before a halogen bond can be formed between an iodide ion and a brominated flame retardant. In order for an $n \rightarrow \sigma^*$ electron donation to occur from the iodide anion to a bromine atom, the C-Br...I atoms must be roughly linear.^{2,3} Also, the Br-I-Br angle is typically approximately 70°, 120°, or 180°.^{4,6}

Based on these criteria, it is not surprising that no iodo-adducts were observed for any of the Brominated Diphenyl Ethers (BDEs) investigated (see Figure 2). Achieving a C-Br...I bond angle of 180° for two C-Br moieties simultaneously is impossible in a substituted ring system such as that of the BDEs.

However, this method was successfully applied to both α - and γ -HBCD (see Figure 3). In both of these isomers, the flexibility of the cyclododecane ring facilitates the configuration required for the formation of the bridging iodo-adduct. Based on this preliminary data, it appears that this method may be limited to aliphatic or cycloaliphatic brominated flame retardants.

The selectivity of the intramolecular halogen bond was further exemplified by the observation that although α -TBCO, β -TBCO, and HCDBCO are cycloaliphatic compounds (see Figure 2), their configurations were found to be unsuitable for adduct formation. These are particularly interesting cases as they support the conclusion drawn in the γ -/ δ -TBECH example that bridging does not occur between adjacent bromine atoms. If this were the case, one would expect to observe [M+I]⁻ clusters for the TBCO isomers and HCDBCO as well.

This principle could be applied to other brominated flame retardants and related compounds where only certain isomers have a structural configuration amenable to forming this type of iodo-adduct. Chromatographic separation of isomeric mixtures coupled with iodo-adduct formation could be a unique tool for obtaining structural clues about an isomer and assisting in the deconvolution of complex mixtures.

References

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Contact Information

- ^a Wellington Laboratories Inc., Research Division, Guelph, Ontario, N1G 3M5, Canada
^b Chemistry Dept., University of Guelph, Guelph, Ontario, N1G 2W1, Canada

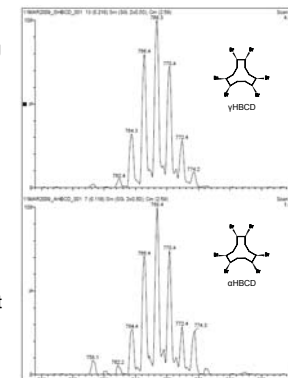


Figure 3: A mass spectra of alpha and gamma HBCD showing the iodo-adduct clusters.