



Thermochemistry of halogen-containing organic compounds with influence on atmospheric chemistry



Juan Z. Dávalos*, Rafael Notario, Carlos A. Cuevas, Josep M. Oliva, Alfonso Saiz-Lopez

Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain

ARTICLE INFO

Article history:

Received 11 October 2016

Received in revised form 4 November 2016

Accepted 7 November 2016

Available online 9 November 2016

Keywords:

Atmospheric halogenated-species

Isodesmic-reactions

Enthalpy

Atomization

G3-G4-QCISD

ABSTRACT

We report a study on the thermochemical properties of a wide variety of halogen-containing organic compounds with relevance on several atmospheric chemical processes, such as catalytic ozone destruction. In particular, we have computationally determined the standard molar enthalpies of formation, $\Delta_f H_m^\circ(\text{g})$, and the carbon-halogen bond dissociation enthalpies, *BDE*, in the gas phase at 298.15 K. A reliable estimation of these thermodynamic magnitudes was deduced, using atomization and isodesmic reactions methodologies, from *ab initio* computational methods. The enthalpies of formation of the radicals formed through bond dissociations have also been computed.

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1. Introduction

Halogenated organic species are emitted into the atmosphere from a variety of sources of both natural and anthropogenic origin. The lifetime of these species ranges from less than 6 months for Very-Short Lived species (VSLs), to several years for Long-lived (LL) species [1]. The natural source of halogenated hydrocarbons, e.g. bromoform (CHBr_3), has been found to be marine phytoplankton [2] and seaweed [3], while anthropogenic sources arise from chemical products widely used in many industrial and domestic applications [4].

The breakdown products (i.e. halogen atoms and oxides) of VSL and LL species can alter the oxidative capacity of the atmosphere through several processes [5,6]: (i) ozone destruction involving catalytic cycles; (ii) changes in the partitioning of HO_x and NO_x ; (iii) the oxidation of dimethyl sulphide (DMS) and iv) the oxidation of elemental mercury ($\text{Hg}^0 \rightarrow \text{Hg}^{\text{II}}$). Of special significance is the stratospheric ozone destruction caused by both anthropogenic emissions of LL sources such as halons [7], and oceanic emissions of VSLs [8].

Modeling of the atmospheric chemistry of halogenated hydrocarbons requires also reliable thermochemical data, such as enthalpies of formation, $\Delta_f H_m^\circ(\text{g})$ and bond dissociation enthalpies, *BDE*. Calorimetry, kinetic, photoelectron spectroscopy and photoionization mass spectrometry, e.g. photoion-photoelectron coincidence

PEPICO techniques, are well established tools for thermochemical measurements of radical, neutral and ionic species. The development of different PEPICO versions, *Threshold* [9], *Imaging* [10] or *Pulsed Field Radiation* [11], has allowed the unambiguous determination of thermochemical parameters of a wide variety of species including those with atmospheric relevance. Though several databases, including NIST [12], Pedley [13], JPL [14], Luo [15], Kurdchaker and Kurdchaker [16] and Gurvich et al. [17], containing the relevant thermochemical data, many discrepancies exist and numerous data have considerably large error bars or are based on inaccurate experimental information. Moreover the scarcity of experimental data is particularly severe for bromine and iodine containing species. In this context, the theoretical determination of thermochemical properties of halogenated organic compounds is of importance. Models using methodologies such as atomization [18] and isodesmic reaction schemes are widely applied in predicting molecular energetic parameters [19–22]. The *ab initio* Gaussian-*n* (*Gn*) family of approaches of Pople et al. [23] is one of so-called model chemistries widely used in thermochemistry and it serves as a template for several other models, e.g. those of very high level accuracy based on Coupled Cluster CC-theory [24].

The present work has the following objectives:

- (i) To confirm the reliability of $\Delta_f H_m^\circ(\text{g})$ and carbon-halogen *BDE* available data for a set of halogenated organic compounds with atmospheric relevance.
- (ii) To reproduce the best experimental available values by means of atomization and isodesmic reaction methods using *ab initio* calculations.

* Corresponding author.

E-mail address: jdavalos@iqfr.csic.es (J.Z. Dávalos).

- (iii) To determine the intrinsic accuracy of our methodology for predicting thermochemical properties of halogenated organic compounds of atmospheric interest.
- (iv) To expand the existing database of thermochemical properties of halogenated organic species, so that the inclusion of the obtained parameters in atmospheric models helps to further improve our understanding of the atmospheric impacts of these species.

The set of the studied halogenated organic species includes CHBr_3 , CH_2Br_2 , CH_3Br , CH_2BrCl , CHCl_2Br , CHBr_2Cl , CH_2Cl_2 , CH_3Cl , $\text{Cl}_2\text{C}=\text{CCl}_2$, $\text{ClCH}=\text{CCl}_2$, CHCl_3 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, $\text{Cl}_2\text{C}=\text{O}$, $\text{ClHC}=\text{O}$, CH_3I , CH_2I_2 , CH_2ICl , CHI_2Br . These species, and their breakdown products, contribute to ozone destruction in both troposphere and stratosphere [1], and may be a link between climate change and tropospheric ozone [25].

2. Computational methods

Standard *ab initio* molecular orbital calculations [26] were performed with the Gaussian 09 series of programs [27]. The energies of the compounds studied were computed using two different theoretical model chemistry Gaussian-*n* methods, at the G3 [28] and G4 [29] levels. Note that G3 theoretical procedure modifies and corrects many of the deficiencies of the *Gn* ($n = 1, 2$) theories and in turn, G4 improves G3 mainly in the geometry optimizations and zero-point energy corrections. Energies at 0 K and enthalpies at 298.15 K for the compounds studied in this work are collected in Table S1 of the Supporting Information.

G3 and G4 methods are available for chlorine and bromine, but not for iodine. For this reason, the energy of iodine-containing compounds has been computed using two different methods. Optimization and frequency calculations have been carried out at the MP2 level of theory with QZVP basis set [30,31]. Additionally, QCISD(T)/QZVP single point calculations have been carried out on the MP2/QZVP optimized geometries.

3. Results and discussion

3.1. Enthalpies of formation $\Delta_f H_m^\circ(\text{g})$ of neutrals

3.1.1. Experimental values

Table 1 lists the available experimental values of $\Delta_f H_m^\circ(\text{g})$ for the set of halogen-containing compounds studied in this work. We also present those collected in reviews and evaluations. The most reliable values of $\Delta_f H_m^\circ(\text{g})$ are written in bold.

In the case of dihalomethanes, there is a good agreement among known experimental $\Delta_f H_m^\circ(\text{g})$ values of CH_2Cl_2 , which were obtained from combustion, vaporization and reaction calorimetric measurements [12,13]. Lago et al. [32], taking the recommended $\Delta_f H_m^\circ(\text{g})$ of this compound and TPEPICO (Threshold Photoelectron-Photoion Coincidence Spectroscopy) results, derived reliable experimental $\Delta_f H_m^\circ(\text{g})$ values for five neutral dihalomethanes (CH_2Br_2 , CH_2BrCl , CH_2I_2 , CH_2IBr and CH_2ICl) with a precision better than $3 \text{ kJ}\cdot\text{mol}^{-1}$. The self consistency of them, in particular of $\text{CH}_2\text{Br}_x\text{I}_{2-x}$ dihalomethanes, has been checked and confirmed by other results [33], although Baer et al. [34] proposed to revise the $\Delta_f H_m^\circ(\text{g})$ of CH_2I_2 , changing to $113.5 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$, on the basis of both experimental (TPEPICO) and theoretical *ab initio* grounds in order to obtain a good consistency of their results on iodine-loss processes of $\text{C}_2\text{H}_4\text{I}_2^+$ cations.

For CH_3Br , we have recommended the $\Delta_f H_m^\circ(\text{g})$ consigned by Kudchadker-Kudchadker [35] which considers the values reported by Pedley [13], Cox-Pilcher [36] and in NIST [12]. For CH_3Cl , CHCl_3 , $\text{Cl}_2\text{C}=\text{CCl}_2$, $\text{ClCH}=\text{CCl}_2$ and $\text{ClCH}_2\text{CH}_2\text{Cl}$, according to Manion [37]

criteria, we recommend values of NIST [12]. For CH_3I , we consider reliable and updated the $\Delta_f H_m^\circ(\text{g})$ deduced by Bodi et al. [38] from iPEPICO (Imaging-Photoelectron-Photoion Coincidence Spectroscopy) results.

To our knowledge, for two of the species, CHCl_2Br and CHBr_2Cl there are no experimental $\Delta_f H_m^\circ(\text{g})$ values available in the literature. In the case of $\text{ClHC}=\text{O}$, Gurvich et al. [17] reported an estimated $\Delta_f H_m^\circ(\text{g})$ with high uncertainty ($\pm 20 \text{ kJ}\cdot\text{mol}^{-1}$), which is excluded as a reliable experimental datum. Therefore, the $\Delta_f H_m^\circ(\text{g})$ of the three compounds described above have been computed.

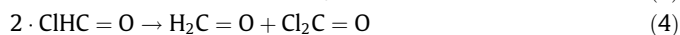
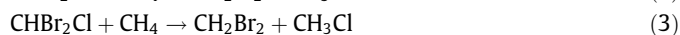
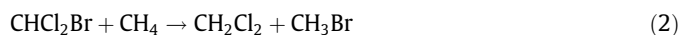
3.1.2. Computed values

$\Delta_f H_m^\circ(\text{g})$ of only chloro- and/or bromo-containing compounds have been evaluated using the G3 and G4 model chemistries. The standard procedure to obtain $\Delta_f H_m^\circ(\text{g})$ in Gaussian-*n* theories is through atomization reactions [39].

Several authors [40–42] have shown that more accurate $\Delta_f H_m^\circ(\text{g})$ can be derived using isodesmic or homodesmotic [43] reactions rather than atomization energies. The cancellation of errors for such cases involving similar chemical bonds improves the agreement with the experiment. Ragavachari et al. [44] proposed to use a standard set of isodesmic reactions, the “bond separation (BS) reactions”, to derive the theoretical $\Delta_f H_m^\circ(\text{g})$. BS reactions are those where all formal bonds between non-hydrogen atoms are separated into the simplest parent molecules containing these same types of linkages. Thus, for example, the BS reaction for CHCl_2Br is:



For three compounds, additional isodesmic reactions have been used, reactions (2)–(4) for CHCl_2Br , CHBr_2Cl and $\text{ClHC}=\text{O}$, respectively:



$\Delta_f H_m^\circ(\text{g})$ of the studied compounds, computed using atomization and isodesmic reactions (at *Gn* level) are collected in Table 1. As shown, except for CHBr_3 , there is a very good agreement between recommended experimental and computed values, particularly using G4 methodology where the deviations between theoretical and experimental data are less than $3 \text{ kJ}\cdot\text{mol}^{-1}$. These values are also consistent with those reported in the literature and obtained from e.g. CCSD calculations (see Table 1). For CHBr_3 the deviations among experimental and computed *Gn* values can be up to $14 \text{ kJ}\cdot\text{mol}^{-1}$. It is noteworthy that the $\Delta_f H_m^\circ(\text{g})$ of this compound estimated by Burcat et al. [45], using the DK-CCSD(T) method, is the closest to the experimental recommended value.

As shown in Fig. 1, $\Delta_f H_m^\circ(\text{g})$ computed from *Gn* methodologies using both atomization (atom) and bond separation (BS) reactions schemes correlate very well with the corresponding experimental values, as shown by Eqs. (5)–(8), being the best correlations those using G4 methods.

$$\Delta_f H_m^\circ(\text{exp}) = 1.0248 \cdot \Delta_f H_m^\circ(\text{G3, atom}) + 3.78; \quad n = 11, \\ R = 0.9985, \quad \text{sd} = 4.35 \text{ kJ}\cdot\text{mol}^{-1} \quad (5)$$

$$\Delta_f H_m^\circ(\text{exp}) = 1.0074 \cdot \Delta_f H_m^\circ(\text{G3, BS}) + 4.08; \quad n = 9, \\ R = 0.9992, \quad \text{sd} = 3.47 \text{ kJ}\cdot\text{mol}^{-1} \quad (6)$$

$$\Delta_f H_m^\circ(\text{exp}) = 1.0059 \cdot \Delta_f H_m^\circ(\text{G4, atom}) + 0.16; \quad n = 11, \\ R = 0.9994, \quad \text{sd} = 2.70 \text{ kJ}\cdot\text{mol}^{-1} \quad (7)$$

$$\Delta_f H_m^\circ(\text{exp}) = 1.0159 \cdot \Delta_f H_m^\circ(\text{G4, BS}) + 1.87; \quad n = 9, \\ R = 0.9995, \quad \text{sd} = 2.70 \text{ kJ}\cdot\text{mol}^{-1} \quad (8)$$

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