International Journal of Mass Spectrometry 354–355 (2013) 62–69

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Halide adducts of 1,3,5-trinitrobenzene: Vibrational signatures and role of anion–π interactions

Barbara Chiavarino[a,1], Maria Elisa Crestoni[a,1], Philippe Maître[b], Simonetta Fornarini[a,*]

[a] Dipartimento di Chimica e Tecnologie del Farmaco, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy
[b] Université Paris Sud, Laboratoire de Chimie Physique, UMR8000 CNRS Faculté des Sciences, Bâtiment 350, 91405 Orsay Cedex, France

ARTICLE INFO

Article history:
Received 11 March 2013
Accepted 13 May 2013
Available online 21 May 2013

Dedicated to the memory of Prof. Detlef Schroeder, honoring his contributions to gas phase ion chemistry and his committed zest for science.

Keywords:
Anion–arene adducts
Mass spectrometry
IRMPD spectroscopy
Photodissociation
Structure elucidation

ABSTRACT

The fluoride and chloride complexes with 1,3,5-trinitrobenzene (TNB–F$^-$ and TNB–Cl$^-$) are obtained as gaseous species by electrospray ionization and are assayed by IR multiple photon dissociation spectroscopy along with quantum chemical calculations. The stable structure is quite different for the two complexes. A strongly covalent σ-complex (Meisenheimer complex) holding fluorine on a tetrahedral carbon at a formerly unsubstituted ring position is the stable form of TNB–F$^-$ while a σ-complex with fluorine bound to a nitro-substituted carbon is 78 kJ/mol higher in energy. The TNB–Cl$^-$ complex presents an off-center binding of chlorine placed above a CH group of a scantily perturbed TNB unit. This structure conforms to a weak σ-binding motif. The observed vibrational features support two diverse binding motifs and previous findings about TNB–I$^-$ and TNB–Br$^-$ show the transition to occur between the fluoride and chloride adducts while both I$^-$ and Br$^-$ complexes are consistent with a weak σ-binding motif. Implication of these results is expected in the design of halide ion transporters.

1. Introduction

Anion recognition and transport have attracted a lot of attention because of their importance in biological as well as in artificial chemical systems [1]. A large number of enzyme substrates are anionic at physiological pH and malfunctions of anion-channels can lead to diseases, so-called channelopathies, like cystic fibrosis [2]. Various kinds of interactions, namely ion–dipole interactions, hydrogen bonding, halogen bonding, coordination to metal ions and hydrophobic effects, are exploited in the design of synthetic anion receptors [2–4]. In this context, anion–π interactions have come into the focus of attention as documented by numerous recent reviews [5–12]. This important weak force established between an anion and an electron-deficient arene has indeed experienced a rapidly growing interest. Features of these interactions have been described in crystallographic studies [13,14] and in theoretical [15–21] and experimental [22–28] reports.

Pioneering work on the gas phase interaction of anions with electron deficient aromatics is due to Kebarle, Hiraoka and coworkers [29,30]. The clustering reactions between gaseous anions and hexafluorobenzene have been described and suggested to involve covalent bonding by fluoride ion and mainly electrostatic bonding by chloride, bromide and iodide [31].

The halide ion series is now examined in the negatively charged adduct ions with 1,3,5-trinitrobenzene (TNB) aiming to gain an insight into the anion interaction with a representative π-acidic aromatic ring. The nature of the anion is known to play a major role in determining the binding motif [5,12]. Highly nucleophilic anions such as RO$^-$ (R = H, CH_3, C_2H_5) form covalent, anionic σ-complexes with TNB which have been characterized as naked species by infrared multiple photon dissociation (IRMPD) spectroscopy [32,33]. In this way the existence of anionic σ-complexes (also named Jackson–Meisenheimer complexes, well known intermediates in nucleophilic aromatic substitution reactions [34]) has been ascertained in the gas phase, a result that met interest and appreciation by Detlef Schroeder. IRMPD spectroscopy exploiting the high fluence and ample tunability of IR free electron lasers (FELs) has emerged as a powerful tool for elucidating the structural and electronic features of ionic species in the gas phase [35–39]. Detlef Schroeder has clearly foreseen the bright perspectives for establishing correlations between solution chemistry and the gas phase brought about by the recent progress in the spectroscopy of gaseous ions and by IRMPD spectroscopy in particular [40]. To name a few examples from our own work about ionic species interrogated by IRMPD spectroscopy at the CLIO (Centre Laser Infrarouge

---

* Corresponding author. Tel.: +39 06 4991 3510; fax: +39 06 4991 3602.
E-mail address: Simonetta.fornarini@uniroma1.it (S. Fornarini).
[1] Fax: +39 06 4991 3602.

1387-3806/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ijms.2013.05.014

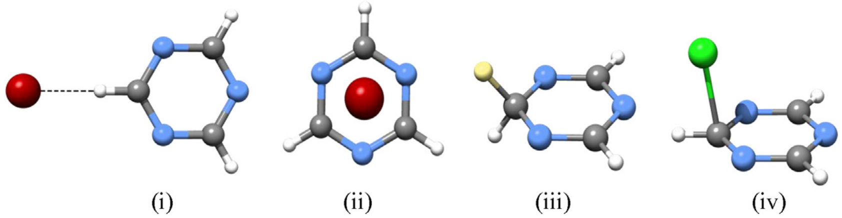

Fig. 1. Binding modes between an anion and an electron-deficient aromatic ring (halide ion and 1,3,5-triazine in this example): (i) hydrogen bonding, (ii) anion–π bonding, (iii) strongly covalent σ interaction, (iv) weakly covalent σ interaction.

d'Orsay) FEL beamline, we may mention the cationic intermediates from protonation of aromatic molecules [41–48] and metal complexes exerting biological functions [49–52] and synthetic, native and post-translationally modified amino acids [53–57]. Negatively charged species have been tackled less frequently. However, two recent studies have addressed the negative ions from exemplary nitroarenes, the nitrobenzene radical anion [58] and deprotonated 2,4-dinitrotoluene [59]. Both species gain their stability from the contribution of resonance structures allowing the negative charge to be distributed over the oxygen atoms of the nitrogroups. The same effect is expected to affect the structure and electronic features of the TNB–halide ion adducts. The binding motifs, however, may vary over a range of different structures that have been systematically explored by computational tools [5,10,12,15–21,60–64]. Fig. 1 shows four distinct modes of contact between a halide ion and an electron deficient aromatic ring, here exemplified by 1,3,5-triazine [10,12], (i) hydrogen bonding, (ii) anion–π bonding, where the anion is located above the center of the aromatic ring, and (iii) σ interaction, yielding a Meisenheimer complex. Furthermore, a weakly covalent σ interaction has been identified where the anion is placed above or outside the periphery of the π system. In the first IR spectroscopic study of the bromide and iodide complexes with TNB, the sampled adducts displayed vibrational features consistent with a weakly covalent σ-complex [33] (depicted as (iv) in Fig. 1). A transition to a strongly covalent σ interaction is expected, moving to halide ions of higher nucleophilicity, namely chloride and fluoride, and is the subject of the present investigation.

2. Experimental methods

2.1. Mass spectrometry and IRMPD spectroscopy

Both TNB–Cl^- and TNB–F^- complexes have been obtained as gaseous species by electrospray ionization (ESI) of a methanol solution containing TNB (0.01 mM) and either NH_4Cl (0.1 mM) or NH_4F (0.2 mM), respectively. The chemicals used were obtained from Sigma–Aldrich s.r.l. (Milan, Italy). In a preliminary study the ions have been assayed by tandem mass spectrometry using a commercial hybrid triple quadrupole linear ion trap mass spectrometer ($Q1q2Q_{LIT}$) (2000 QTrap from Applied Biosystems). Typical ESI conditions were a flow rate of 5–10 μl/min, ion-spray voltage at −4.5 kV, declustering potential at −5 V and entrance potential at −1 V. When the methanol solution of TNB and NH_4Cl is subjected to ESI in the negative-ion mode, the TNB–Cl^- adduct is the major ionic species observed. In contrast, the TNB/NH_4F solution gives deprotonated TNB as abundant species in 1:1 ratio with TNB–F^-. The ion of interest was mass selected using Q1. CID experiments were performed in the quadrupole collision cell q2 at variable collision energies (E_{lab} = 5–50 eV) with N_2 as collision gas at a nominal pressure of 3.5×10^{-5} mbar. The dissociation product pattern was monitored by scanning Q_{LIT} in mass analyzing quadrupole configuration.

IRMPD spectroscopy in the mid-IR range was performed at CLIO with the FEL beamline coupled with a modified a modified Paul-ion trap mass spectrometer (Bruker Esquire 3000+) [65]. The FEL was operated at 44 MeV and a fairly stable power around 800–900 mW was obtained. The laser beam delivered pulsed radiation in 8 μs long macropulses at the repetition rate of 25 Hz and ions were typically irradiated by 1–2 macropulses. Mass spectra were obtained by accumulation of seven sequences and averaged over four at each photon energy, which was increased in steps of 4–5 cm^{-1}.

2.2. Computational details

Molecular geometry optimization and energy calculations were performed using the Spartan'10 version 1.1.0 program package with density functional theory at the B3LYP/6-311 + G(d,p) level. Vibrational frequency analysis, carried out at the same level, allowed to verify whether the opimized structures correspond to minima. Harmonic frequencies allowed also to obtain calculated IR spectra and zero point energies (ZPVEs). No frequency scaling factor has been applied, due to the observed fair agreement between calculated and experimental positions of the most intense band. For comparison, calculations for structures, energies, and IR spectra were also carried out at B3LYP/aug-cc-p-VDZ level and at MP2/aug-cc-p-VDZ level leading to similar results. Hence, only the results obtained at B3LYP/6-311 + G(d,p) level are reported.

Computed IR absorption spectra are plotted by assuming that the IR bands have a Gaussian shape with a full width at half maximum (fwhm) of 15 cm^{-1}. Relative energies at 0 K were obtained from electronic energies and include ZPVE contributions. The charge distribution was determined using the natural population analysis method.

3. Results and discussion

3.1. Dissociation paths of TNB–Cl^-/F^- complexes

IRMPD spectroscopy largely relies on revealing the fragmentation processes activated by heating the sampled ion through the absorption of multiple photons resonant with an active vibrational mode. In a preliminary survey the dissociation of TNB–Cl^-/F^- complexes has been investigated by collision induced dissociation (CID) at variable energy. As frequently observed, the typical protofragmentation processes observed under IRMPD conditions occur along the lowest energy paths observed by CID. When TNB–$^{35}Cl^-$ complexes at m/z 248 are mass selected in the first quadrupole of the QTrap instrument and allowed to undergo dissociation in the second quadrupole, two fragmentation products are observed at m/z 35 and m/z 46 (Eq. (1)). The ions are ascribed to $^{35}Cl^-$ and NO_2^-. The breakdown curves reported in Fig. 1S suggest a lower critical energy for Cl^- loss relative to NO_2^- loss. The gas phase acidity (ΔH°_{acid}) of their conjugate acids, HCl and HNO_2, is equal to 1395 and 1424 kJ/mol [66], respectively, and the CID results suggest that the ΔH°_{acid} value of TNB is higher [67]. The TNB–F^- complex displays a somewhat different CID behavior, yielding ions at m/z 46 (NO_2^-) and at m/z 212 ($[TNB-H]^-$), albeit to minor extent (Eq. (2)).