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Review

Mass spectrometric study of simple main group molecules and ions important in atmospheric processes

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Abstract

Recent mass spectrometric studies of simple inorganic species (both charged and neutral) of main-group elements are reviewed, focusing attention on radicals and ions of interest to the chemistry of the atmosphere and its pollution. The examples illustrated concern the detection of HO_3, hydrogen trioxide, the O_2/O_3 isotope exchange and its charged intermediate O_5^+, the reactions promoted by ionization of ozone/halocarbon mixtures in atmospheric gases, the ion chemistry of NO_x oxides, and that of elemental chlorine and chlorine fluoride. Among the results of specific interest to gas-phase ion chemistry, the examples illustrated concern the intracluster ligand-switching reactions in ternary NO^+ complexes, the NO_2^+ reactivity towards ethylene and acetylene, the gas-phase basicity of Cl_2, the formation and characterization of Cl_2X^+ ions (X = Cl, F) and of $[H_3C\text{-}Cl\text{-}Cl]^+$, a new isomer of protonated dichloromethane. (Int J Mass Spectrom 194 (2000) 1–10) © 2000 Elsevier Science B.V.

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1. Introduction

In reviewing our recent activity in the mass spectrometric study of gaseous inorganic species we shall concentrate on a few topics selected for their impact on broad research areas of interdisciplinary relevance as well as for their intrinsic fundamental interest. As to the first aspect, a recurrent theme is the study of charged and neutral species of main-group elements of interest to the chemistry of the atmosphere and its pollution. In this line of research belong the gas-phase ion chemistry of ozone, that of nitrogen oxides and oxo acids, and that of halocarbon/ozone mixtures highly diluted in atmospheric gases. Representative examples of mass spectrometric studies devoted to fundamental aspects of gas-phase ion chemistry are the comparative analysis of the nitronium ion reactivity towards ethylene and acetylene, the positive ion chemistry of elemental chlorine and chlorine fluoride, the study of trihalogen cations and their reactions with simple molecules, such as methane, etc.

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The experimental approach followed in the above studies was generally based on the combination of chemical ionization (CI) for the preparation of the species of interest with instrumental techniques such as Fourier transform ion cyclotron resonance (FTICR) and especially mass-analyzed ion kinetic energy (MIKE), collision-activated dissociation (CAD), tandem mass spectrometry (MS/MS), and neutralization–reionization mass spectrometry (NRMS) for their structural characterization, the evaluation of their stability, and the survey of their reactivity. In most cases, the experimental approach was integrated by computational methods, implemented at high levels of theory, as allowed by the relatively simple nature of the systems investigated.

In the following, the most significant results from the study of a few representative systems will be concisely illustrated.

2. The long search of the elusive hydrogen trioxide, HO_3

HO_3 is a radical of great relevance to atmospheric chemistry, long postulated as a sink for OH radicals and a key intermediate in the $H + O_3$ reaction, the source of excited hydroxyl radicals whose emission is related to night-sky afterglow [1]. For all its attraction, HO_3 proved an extremely elusive species, defying a sustained experimental effort to demonstrate its very existence. This spurred a large number of theoretical studies, aimed at assessing the stability of HO_3 by increasingly sophisticated computational methods. Despite the deceptively simple nature of the trioxide, the results of a theoretical effort spanning almost three decades proved inconclusive and unusually inconsistent [2]. The summary of the theoretical analysis seems to be that hydrogen trioxide is thermodynamically unstable, or marginally stable, with respect to dissociation into HO and O_2, which of course does not settle the issue. The problem is compounded by the intrinsic limitation of purely thermochemical analyses, unable to assess the kinetic stability of species prone to energetically allowed dissociation. Based on the above considerations, it became plainly evident to us that direct experimental detection of HO_3 was the only way to demonstrate its existence and that NRMS showed considerable promise to this end. The first step of our project, namely the preparation of the required charged parent, was accomplished in 1994 [3], when we demonstrated the formation of protonated ozone from the process

$$AH^+ + O_3 \longrightarrow A + HO_3^+ \qquad (1)$$

$$(A = Kr, Xe, CH_4, NF_3, N_2O, CH_3F, SO_2, C_2H_2, \text{and } H_2O)$$

Whereas at the time much emphasis was given to the detection of the conjugate acid of ozone and to the evaluation of a fundamental property (the gas-phase basicity) of this important molecule, from our standpoint the most valuable asset was the availability of the ion required for NRMS. Alas, the elusive character of hydrogen trioxide manifested again, in that detection of the "recovery" ions from the sequence

$$HO_3^+ \xrightarrow{\text{Neutralization}} HO_3 \xrightarrow{\text{Reionization}} HO_3^+ \qquad (2)$$

proved beyond the capability of the instruments then available to us. It took five years before significant "recovery" peaks from sequence (2) could be recorded utilizing an improved instrument, a hybrid ZAB-Spec oa-TOF spectrometer. The results (Fig. 1) provided the long-sought demonstration that HO_3 does exist as an isolated species in the gas phase with a lifetime exceeding 1 μs, thus providing conclusive support for its postulated role in atmospheric chemistry [4].

3. Isotope exchange in ionized O_2/O_3 mixtures and the role of O_5^+

A problem that has puzzled atmospheric scientists for almost two decades is the unusually large enrichment in ^{17}O and ^{18}O of stratospheric and tropospheric ozone. Despite a sustained research effort, justified by the importance of ozone in atmospheric chemistry, a convincing explanation of the process responsible for

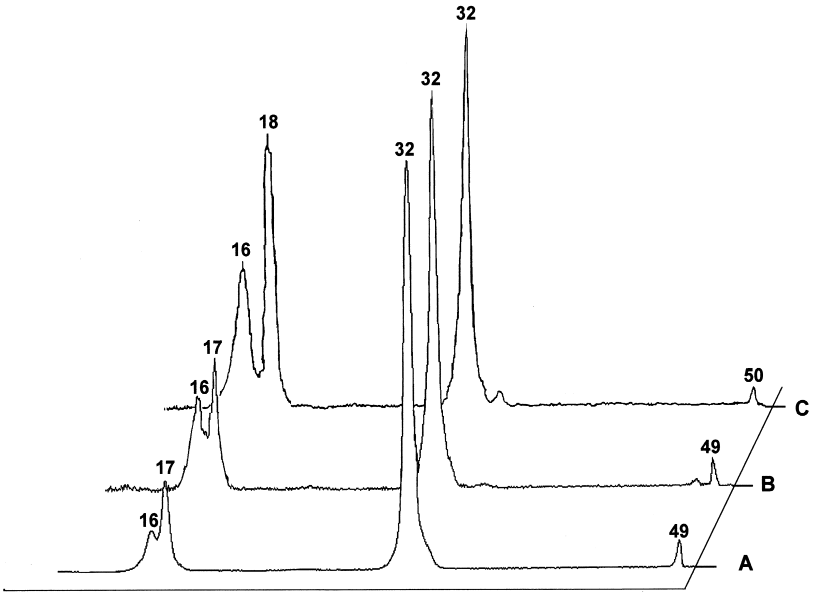
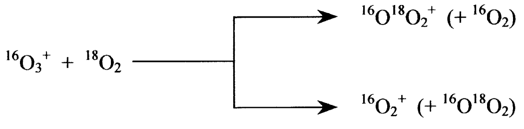


Fig. 1. A, NR^+ spectrum of HO_3^+ ion, *m/z* = 49. B, NR^- spectrum of the same ion. In both sets of experiments the kinetic energy was 4 kV; the neutralizing and reionizing gases were Xe and O_2, respectively. Note the "recovery" peak at *m/z* = 49. C, NR^+ spectrum of DO_3^+ ion, *m/z* = 50, conditions as in A and B, except the kinetic energy of 8 kV. Note the "recovery" peak at *m/z* = 50.

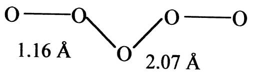
the enrichment is still missing; two alternative explanations are based on large, symmetry-related isotope effects [5] and on the kinetics of the collision processes yielding O_3 in a N_2/O_2 gas mixture [6]. Clearly, the input data required that accurate modeling studies take into account not only the measured enrichment, but also the effects of any O_2/O_3 isotopic mixing process occurring in the stratosphere. Here, ionic reactions are likely to play a significant role, in that O_n^+ clusters are present in air ionized by cosmic rays, short-wave UV radiations, lightning, radioactive emanation, etc. Investigation of the problem by FTICR and CI/CAD mass spectrometry [7] led us to the discovery of the isotope exchange occurring in ionized ozone/dioxygen mixtures. Kinetic measurements performed by FTICR spectrometry demonstrated that the processes



$$^{16}O_3^+ + {}^{18}O_2 \longrightarrow {}^{16}O^{18}O_2^+ \; (+ {}^{16}O_2) \quad (3)$$

$$^{16}O_3^+ + {}^{18}O_2 \longrightarrow {}^{16}O_2^+ \; (+ {}^{16}O^{18}O_2) \quad (4)$$

are relatively fast, e.g. the collisional efficiency of reaction (3) is ~10% at 298 K. The exchange intermediate is O_5^+, undetectable in the low-pressure FTICR experiments, but readily obtained from the CI of O_2/O_3 mixtures at several tenths of a Torr. The CAD spectrum of O_5^+ displays O_2^+ as the only significant fragment, and the spectra of ^{18}O-labeled ions denote extensive isotopic scrambling, e.g. the relative intensities of $^{16}O_2^+$, $^{16}O^{18}O^+$, and $^{18}O_2^+$ fragments from $^{16}O_3{}^{18}O_2^+$ are very close to those typical of a statistical distribution. The results of calculations performed at the CCSD(T)//B3LYP/6-311G(*d*) level of theory show that the most stable O_5^+ species has an open, symmetrical structure



whereby the central atom has lost memory of its former bonding in ozone, and the binding energy (BE) of the O_2–O_3 units is relatively small, 12.1 kcal mol^{-1} leading to $\Delta H_f^\circ (O_5^+) = 300.4$ kcal mol^{-1}, in excellent agreement with the value from earlier photoionization measurements. The theoretical and experimental results allow for a satisfactory interpretation of the isotope exchange mechanism. In the low-pressure FTICR experiments the O_5^+ complex undergoes prompt dissociation, allowing only the central atom to be exchanged between the O_2 and O_3 units. By contrast, the collisional stabilization of O_5^+ formed in the CI plasma makes the complex a long-lived species, where the O_2 and O_3 constituent units can undergo repeated association/dissociation processes without escaping from the potential energy well, leading to the observed isotopic randomization. The larger BE of O_2^+ to O_3 than to O_2 makes O_5^+ a species of interest to atmospheric ion chemistry, in that its formation from the reaction of O_3 with O_4^+ and larger O_n^+ clusters present in ionized air [8] is energetically allowed.

4. Ionization of ozone/chlorofluorocarbon mixtures in atmospheric gases

The tremendous interest in the atmospheric chemistry of halocarbons and its impact on ozone depletion has almost exclusively concerned neutral species. Yet, since the advent of rocket-born mass spectrometers [5] a rich ionic chemistry is known to occur in the atmosphere, which has stimulated the study of ionized halocarbons [9], as well as of the ionic chemistry of ozone (vide supra). In these studies the ion chemistry of ozone and halocarbons was examined separately, in contrast to the approach that proved so successful in the study of the corresponding neutral species. Recently we have undertaken the study of the ionic reactions in atmospheric gases (O_2, N_2) containing both ozone and halomethanes [10]. Among the many systems examined, ionization of O_2 containing O_3 and $CHCl_2F$ represents a suitable example. The salient feature of CI experiments is the formation of a charged adduct from the process

$$CHClF^+ + O_3 \rightarrow \underset{\mathbf{1}}{CHClFO_3^+} \tag{5}$$

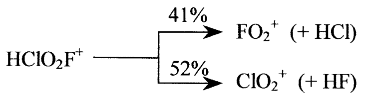
promoted by the product from the dissociative charge transfer

$$CHCl_2F + O_2^+ \rightarrow CHClF^+ + O_2 + Cl \tag{6}$$

Occurrence of reaction (6) was demonstrated by preliminary FTICR experiments performed in a pressure range (10^{-8}–10^{-7} Torr) where the adduct cannot be observed. At the higher pressures, up to 0.5 Torr, typical of O_2/CI experiments, the $CHClFO_3^+$ complex is collisionally stabilized, and hence detectable and amenable to mass spectrometric characterization. The MIKE spectrum is truly remarkable in that the major (80%) metastable transition

$$CHClFO_3^+ \rightarrow HClFO_2^+ \ (+\ CO) \tag{7}$$

denotes an exceptionally profound molecular reorganization characterized by the fission of all the bonds of the HCClF moiety. The CAD spectra of the charged fragment from Process (7), recorded in MS/MS experiments, demonstrated the following major dissociation channels



$$HClO_2F^+ \xrightarrow{41\%} FO_2^+ \ (+\ HCl) \tag{8}$$

$$HClO_2F^+ \xrightarrow{52\%} ClO_2^+ \ (+\ HF) \tag{9}$$

The mass spectrometric results were complemented by a computational study at the CCSD(T)//B3LYP/6-311G(*d*, *p*) level of theory that provided a satisfactory explanation for the experimental features. The product from reaction (5), **1**, is characterized as a species where a tetrahedral C atom is bound to H, F, and Cl atoms and to a slightly distorted ozone molecule (Fig. 2). Excited **1** can isomerize into **2**, in essence a formyl fluoride molecule linked, mainly electrostatically, to O_2Cl^+. This ion can rearrange into **3**, that contains a nearly linear COHF group linked to O_2Cl^+ and is liable to CO loss, yielding the $HFOOCl^+$ fragment **4**, that can either undergo HF loss, or isomerize into species **5**, liable to HCl loss. Significantly, the remarkable fragmentation sequence outlined by the above theoretical and experimental results is not peculiar of the $CHClFO_3^+$ ion, being instead a distinctive feature of the analogous com-

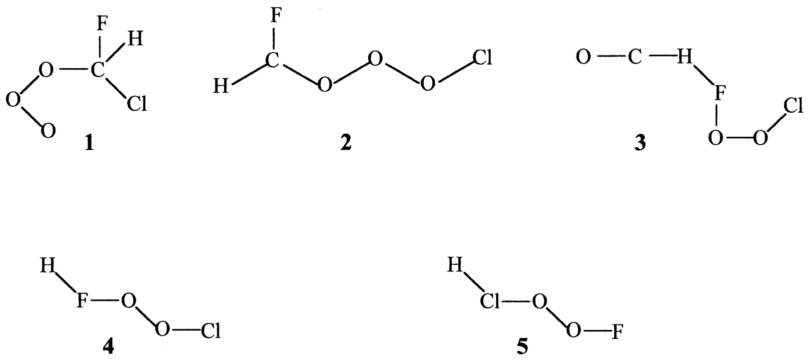


Fig. 2. Connectivity of relevant minima on the [C, H, Cl, F, O_3] energy surface (see text).

plexes formed upon ionization of CHX_3 (X = H, Cl, F)/ozone mixtures diluted in atmospheric gases.

5. Gas-phase NO^+ affinities

The interest in nitryl ion, NO^+, is highlighted by its extraordinary variety of roles in a multiplicity of fields. In atmospheric chemistry, the low recombination energy makes NO^+ an effective charge "sink", and the promoter of reaction chains eventually leading to hydrated-proton clusters, important in the chemistry of the ionospheric D region [11] and of the middle atmosphere [12]. The biochemical and physiological significance of NO^+ has received much attention, owing to the recognized impact on human health of compounds important for environmental or dietary reasons, including nitrates, nitrosoammines, NO_x species, etc. [13]. Nitryl ion, or some of its carriers, have been suggested to be involved in the neurotoxic and neuroprotective actions of NO [14, 15] an in the nitrous-acid promoted crosslinking of DNA [16].

A quantitative knowledge of the interactions of NO^+ with neutral ligands, spanning from H_2O to DNA bases, is central to the understanding and modeling of important problems in many research fields, and the value of constructing a scale of NO^+ binding energies was perceived almost two decades ago by Reents and Freiser [17]. In view of the upsurge of interest in nitryl ion, we decided to undertake a systematic study aimed at the extension and the revision of the NO^+ affinity scale, taking into account the changes undergone in the meantime by certain reference standards and the availability of new experimental and theoretical tools [18]. Accordingly, we constructed a ladder including 52 ligands (alkyl halides, alkyl nitrates, nitroalkanes, alcohols, nitriles, aldehydes, ketones, aromatic and heterocyclic compounds). In most cases the NO^+ BE differences were independently measured utilizing both the equilibrium and the kinetic method, whose agreement was generally excellent. The multiply interlaced relative BE ladder was converted into an absolute BE scale utilizing as the anchor the absolute NO^+ affinity of water, taken equal to 18.5 ± 1.5 kcal mol^{-1} based on

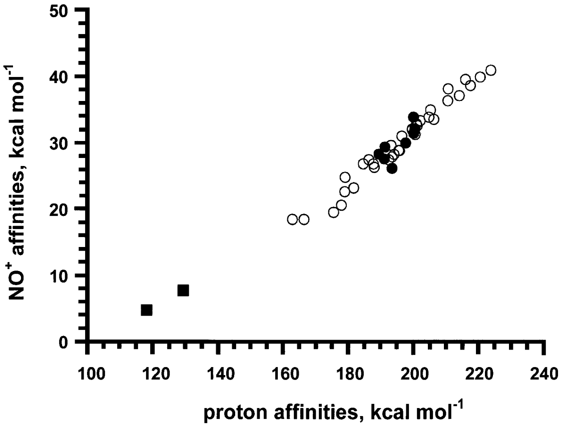


Fig. 3. Diagram of the correlation between NO^+ BEs and PAs values.

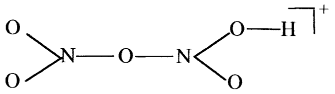
a direct measurement by pulsed high-pressure ion source mass spectrometry [19] in excellent agreement with the value from high level ab initio calculations [20]. Comparisons with the earlier results shows a satisfactory agreement as long as relative BE are concerned, whereas the absolute values differ considerably owing to the different choice of the absolute anchoring BE. As shown in Fig. 3, the NO^+ BEs fit a satisfactory linear correlation with the corresponding proton affinity (PAs), a result of interest in that it allows one to estimate within 1–2 kcal mol^{-1} the unknown NO^+ BE of a given ligand whose PA is included in the comprehensive compilations available at the present time.

6. The relative strength of the basic centers in the molecule of HNO_3 and its derivatives

The problem concerning the local PA of the basic centers in XNO_2 molecules dates back to 1990 with the discovery of two isometric forms, $H_2ONO_2^+$ and $HONO_2H^+$, of protonated nitric acid and the identification of $H_2ONO_2^+$ as the more stable one [21]. Subsequent mass spectrometric [22–25] and theoretical [26, 27] studies confirmed the above results and established that when $X = OH$ its PA exceeds that of the nitro group by as much as 20 kcal mol^{-1}, whereas the PA difference is reduced to ~5 kcal mol^{-1} when $X = CH_3O$, suggesting that the nitro group may become more basic in higher alkyl nitrates. To clarify this point we utilized mass spectrometric and ab initio methods to investigate the gas-phase protonation of C_2H_5-ONO_2 [28].

The results from FTICR, MIKE, and CAD spectrometry concur with those of calculations performed at the G2(MP2) level of theory in demonstrating the existence, and the equal stability of two protomers, the ion–dipole complex $C_2H_5OHNO_2^+$ and the covalently bound $C_2H_5ONO_2H^+$ species. Following a general procedure [29], the BE of NO_2^+ to C_2H_5OH was found by independent application of the equilibrium and the kinetic method to be 22.2 ± 2 kcal mol^{-1}, leading to a PA of 178.4 ± 2.6 kcal mol^{-1}, referring to the ether oxygen, in excellent agreement wit the theoretically estimated PA of 177 ± 2 kcal mol^{-1}, irrespective of the protonated site. The experimentally observed $C_2H_5ONO_2H^+ \rightarrow C_2H_5OHNO_2^+$ isomerization is also consistent with the theoretically computed ΔG°_{298} change of the process, -3 kcal mol^{-1}.

The results verify the hypothesis that the ΔPA difference between the RO and NO_2 groups in $RONO_2$ molecules decreases along the series R = H, CH_3, C_2H_5 and provide further support to the counterintuitive basicity order ($PA(HNO_3) > PA(CH_3ONO_2) \simeq PA(C_2H_5ONO_2)$). Another study relevant to the preferred protonation site in XNO_2 molecules concerns dinitrogen pentoxide ($X = NO_3$), a species of considerable atmospheric interest. Its gas-phase protonation was studied by a combination of experimental techniques, i.e. MIKE, CAD, and FTICR spectrometry and computational methods at the B3LYP 6-311++G(3*df*, 3*dp*)//6-311G (*d*,*p*) level of theory [30]. The results show that the most stable protomer is the adduct



in essence a complex where NO_2^+ is coordinated to the nitro group of nitric acid. The experimental PA (N_2O_5), 189.8 ± 2 kcal mol^{-1} compares with the theoretically calculated values ranging from 182–188 kcal mol^{-1}. Addition of NO_2^+ to XNO_2 molecules ($X = NH_2$, CH_3OH, C_2H_5OH) also yields adducts of the general structure $XNO_2NO_2^+$ where the nitronium ion is coordinated to the nitro group. Conversely, addition of the nitrylium ion, NO^+, to nitric acid gives as the most stable isomer an ion of the HO-NO_2NO^+ structure, whose conversion into the comparably stable HO-$NONO_2^+$ structure is characterized by a sizable barrier. The larger PA of N_2O_5 than that of HNO_3 and H_2O is relevant to atmospheric chemistry, supporting the model that identifies the first step of the destruction of N_2O_5 into ionic clusters and aerosols with its protonation by H_3O^+ and/or $H_2NO_3^+$.

7. Gas-phase reactivity of the nitronium ion

It has long been known that NO^+ ions form hydrated clusters in the D region of the ionosphere [8] and mixed clusters containing, in addition to H_2O, other neutral species present in the mesosphere and the stratosphere, such as HNO_3, NH_3, CH_3OH, etc. [31]. Studies aimed at examining the intracluster reactivity of nitric acid and dinitrogen pentoxide have emphasised the role of NO_2^+ in the chemistry of small clusters and hence in determing the steady-state ionic composition of the atmosphere [32–34]. Utilizing MIKE and FTICR spectrometry we recently demonstrated a novel intracluster reaction, namely a protonation induced ligand-switching process whose extent is critically affected by the nature of the ligands, in particular by the balance between their PA and NO_2^+ BE. Consider as a typical example the NO_2/CI experiments where association of nitric acid, methanol, and the nitronium ion gave a complex whose unimolecular dissociation was examined by MIKE spectometry

$$[CH_3OH(NO_2^+)HNO_3] \longrightarrow CH_3OH\ NO_2^+ + HNO_3 \qquad (10)$$

$$[CH_3OH(NO_2^+)HNO_3] \longrightarrow CH_3ONO_2NO_2^+ + H_2O \qquad (11)$$

Whereas fragmentation (10) is expected, reflecting the larger NO_2^+ BE of CH_3OH than of HNO_3, $\Delta(BE) = 3.2\ kcal\ mol^{-1}$ [29], fragmentation (11) denotes extensive intracomplex reorganization, yielding a molecule, H_2O, not preformed within the ternary cluster. Such behavior is not peculiar to the CH_3OH and HNO_3 ligands, as shown by a systematic study of different pairs of ligands, including HNO_3, H_2O, CH_3ONO_2, CH_3OH, C_2H_5OH, $C_2H_5ONO_2$, $H_2N\text{-}NO_2$, and NH_3. The general conclusion drawn from the analysis of the experimental trends is that the intracluster reorganization process is favored by (1) the larger local PA of the X site of any given XNO_2 ligand with respect to that of each X_1NO_2 counterpart, which drives the proton to X, and (2) the larger NO_2^+ BE of any given X_1NO_2 ligand with respect to that of each HX counterpart. In light of the previous considerations, the intracluster reorganization process appears to be of direct interest to ionic atmospheric chemistry [35].

Comparative studies of the gas-phase reactions of NO_2^+ with C_2H_4 [36] and C_2H_2 [37], prototypal examples of the electrophilic nitration of very simple π systems and useful starting points to model aromatic nitration, were performed utilizing a combination of mass spectometric and theoretical tools. The results of FTICR, MIKE, CAD, and N_fR/CA mass

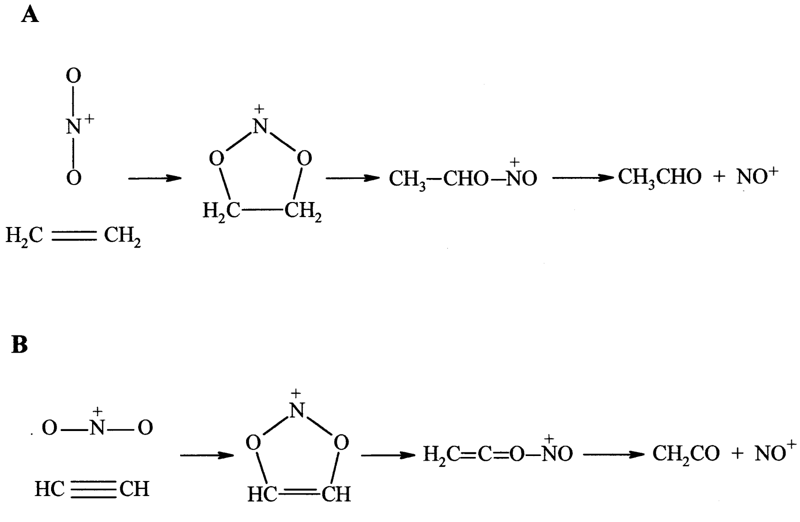


Fig. 4. Connectivity of the species involved in the reactions of nitronium ion with ethylene, A, and acetylene, B.

spectrometric experiments, complemented by calculations at the MP2/6-31+G* level of theory, showed that the reactions of NO_2^+ with ethylene and acetylene follow the same mechanism, i.e. 1–3 dipolar cycloaddition (Fig. 4), yielding, however, primary adducts of different stability. The $C_2H_2NO_2^+$ ion from acetylene has an aromatic character and is highly stabilized with respect to its $C_2H_4NO_2^+$ counterpart from ethylene. Both cycloadducts have a sufficiently large excess of internal energy to allow their rearrangement into O-nitrosated isomers, i.e. nitrosated acetaldehyde from C_2H_4 and nitrosated ketene from C_2H_2, whose identity was established by CAD spectrometry utilizing suitable models. Of particular interest was the utilization of N_fR/CAD mass spectrometry that allowed structural assignment of the neutral CH_3CHO and CH_2CO fragments from the dissociation of the corresponding nitrosated adduct, e.g. discrimination between acetaldehyde and ethylene oxide.

8. Ion chemistry of elemental chlorine and chlorine fluoride

Polyhalogen cations play a significant role in electrophilic halogenation and are extensively studied in solution and in the solid state. This contrasts with the scarcity of data on gaseous homo- and heteropolyhalogen cations, that consequently became the focus of our interest. Our study concentrated first on the most simple cation, Cl_2H^+, and was later extended to $FClH^+$, Cl_3^+, and Cl_2F^+.

Protonated elemental chlorine Cl_2H^+, the prototypal electrophile among the polychlorine cations, was obtained from two different reactions that mirror its twofold character of Brønsted and Lewis acid [38], namely protonation of chlorine

$$Cl_2 + BH^+ \rightarrow Cl_2H^+ + B \tag{12}$$

$(B = CO_2, HCl)$

and chlorination of HCl

$$HCl + XCl^+ \rightarrow Cl_2H^+ + X \tag{13}$$

$(X = FCl, Xe)$

$FClH^+$ and Cl_2F^+ are formed [38–40] upon fluorination of HCl and Cl_2 by XeF^+

$$XeF^+ + HCl(Cl_2) \rightarrow FClH^+ \ (Cl_2F^+) + Xe \tag{14}$$

whereas Cl_3^+ can easily be obtained [39,40] by chlorination of Cl_2

$$Cl_2H^+ + Cl_2 \rightarrow Cl_3^+ + HCl \tag{15}$$

Among the above ions, $FClH^+$ acts exclusively as a Brønsted acid, and Cl_3^+ and Cl_2F^+ act exclusively as chlorinating agents, whereas Cl_2H^+ displays both types of reactivity towards bases/nucleophiles. Despite the importance of elemental chlorine in fundamental and applied research, no experimental data on its PA and gas-phase basicity (GB) were available, thus stimulating their experimental and theoretical evaluation [38]. Different FTICR methods were utilized, including the “bracketing” technique, the equilibrium method, and the kinetic approach to equilibrium evaluation, based on the measurement of the forward and reverse rate coeffecients of the reaction. The best experimental estimated of the GB and PA of Cl_2 are 125.1 ± 1 kcal mol^{-1} and 131.4 ± 1 kcal mol^{-1}, respectively, the latter one in excellent agreement with the theoretical value of 132.0 kcal mol^{-1} computed at the CCSD(T) level of theory. The results concerning FCl were less accurate because its evaluated GB and PA, 103 and 110 kcal mol^{-1}, respectively, are affected by an uncertainty as large as 8 kcal mol^{-1}, which suggests adoption of the theoretical PA (121.0 kcal mol^{-1}) as the best available estimate, computed at the CCSD(T) level of theory.

The chlorinating ability of Cl_2H^+, Cl_3^+, and Cl_2F^+ ions toward several nucleophiles was examined in experiments whereby $NuCl^+$ ions, generated in the external source of a FTICR spectrometer (collisionally thermalized and mass selected) were allowed to react with another nucleophile, Nu_1

$$NuCl^+ + Nu_1 \rightarrow Nu_1Cl^+ + Nu \tag{16}$$

also performing mirror experiments that involved the reaction of Nu_1Cl^+ ions with neutral Nu [40]. The results allowed us to establish the following Cl^+ BE order

$$\mathrm{ClF} \leq \mathrm{HCl} \leq \mathrm{Xe} < \mathrm{Cl_2} < \mathrm{CO} < \mathrm{CH_3CN} < \mathrm{NH_3}$$

that incidentally explains the occurrence of formation reactions (13) and (15). Quantitative data were obtained for the compounds of interest: HCl, ClF, and Cl_2. In particular, utilizing the experimentally derived heat of formation of Cl_2H^+, the Cl^+ BE of HCl was estimated to be 71.6 ± 2 kcal mol^{-1}. Combining experimental and theoretical data, the Cl^+ BE of Cl_2 and of the chlorine atom of ClF were evaluated to be 76.5 ± 3 kcal mol^{-1} and 71.0 ± 3 kcal mol^{-1}, respectively. The observed reactivity pattern also provides evidence of the connectivity of gaseous Cl_2H^+, $FClH^+$, and Cl_2F^+ ions. The observation that Cl_2H^+ undergoes both H^+ and Cl^+ transfer supports the Cl–Cl–H connectivity, whereas the inability of $FClH^+$ to chlorinate molecules of large Cl^+ affinity such as CO, and its formation process involving fluorination of HCl, support the F–Cl–H connectivity. Likewise, formation of Cl_2F^+ from the fluorination of a molecule containing a preformed Cl–Cl bond, supports the asymmetric Cl–Cl–F connectivity.

Examination of the chlorinating reaction pattern displayed by Cl_2H^+, Cl_3^+, and Cl_2F^+ ions, revealed a peculiar behavior toward simple molecules such as H_2 and CH_4, whose chlorinated products, H_2Cl^+ and CH_4Cl^+, behave as pure Brønsted acids, devoid of chlorinating ability. Such evidence, together with the structural analysis accomplished by CAD spectrometry and consistent with the theoretical description of this chlorination reaction, leads to the $[H–Cl–H]^+$ and $[CH_3–Cl–H]^+$ connectivities, respectively [41]. The reactions of these cations proceed according to a mechanism whereby the terminal Cl atom inserts into a σ bond of the neutral molecule. In addition, the reaction of Cl_3^+ with methane gave a $[CH_3–Cl–Cl]^+$ ion, that behaves as a chlorinating and methylating agent. Its formation is the first example of dichlorodeprotonation, namely an electrophilic substitution whereby an H atom is replaced by the diatomic $[Cl\text{-}Cl]^+$ dichlorinium ion [42]. The mechanism suggested involves formation of a $[CH_3^+, HCl, Cl_2]$ complex that then evolves into $[CH_3–Cl–H]^+$ and/or $[CH_3–Cl–Cl]^+$ products. The energetics of these reaction pathways satisfactorily explains the failure of other chlorinating agents, such as Cl_2H^+ and Cl_2F^+, to undergo Cl_2^+ transfer to methane. A significant result is the first experimental and theoretical characterization of two $[C, H_3, Cl_2]^+$ isomers, having the $ClH_2C–Cl–H^+$ and the $CH_3–Cl–Cl^+$ connectivity, respectively. The first and more stable isomer behaves exclusively as a Brønsted acid, undergoing H^+ transfer to gaseous bases, and the PA of the conjugate base, $Cl–H_2C–Cl$, is estimated to amount to 150.2 ± 2 kcal mol^{-1}.

Acknowledgements

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