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GAS PHASE ANION REACTIONS AT ATMOSPHERIC PRESSURE

ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETRIC STUDIES RELATED TO THE ELECTRON-CAPTURE DETECTOR

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SUMMARY

Negative ion atmospheric pressure ionization mass spectrometry has been used to investigate the gas phase atmospheric pressure anion chemistry of $N_2O_2H^-$ and HSO_3^-. $N_2O_2H^-$ has been shown to be a stronger base than HSO_3^-. Specific types of reaction (*e.g.* proton abstraction, and dehydration) have been identified for each of these anions. Although the analytical significance of these reactions has not yet been demonstrated, certain compounds such as alcohols which do not readily attach electrons directly can easily be detected by observing a specific anion reaction product. The technique appears to provide an additional dimension to established gas chromatographic–mass spectrometric analyses.

INTRODUCTION

For many years, our group has been interested in the rates and mechanisms of thermal electron attachment to gas phase molecules[1–3]. Our study of these phenomena has been based on an analysis of the changes in response (gas phase electrical conductance) of a conventional gas chromatographic electron-capture detector produced by changes in temperature, gas concentration, and electron collecting pulse parameters. Although this technique has provided fundamental information about electron attachment processes[4–5], it is incapable of providing much information about the gas phase chemistry which pertains at atmospheric pressure.

Atmospheric pressure ionization mass spectrometry (APIMS) provides an obvious method for studying this chemistry. In APIMS, ions are produced at atmospheric pressure in a gas sample obtained from the effluent of a gas chromatograph or from some other source and are then extracted from the ionization region and mass analyzed. Although techniques for APIMS have been available for some time[6] and some analytical applications have been made[7–9], very little has been done to explore the chemistry of gas phase anions at or near atmospheric pressure.

Since the development of negative chemical ionization mass spectrometry (NCIMS)[10] has led to the elucidation of a rather extensive body of moderate pressure (*ca.* 1 Torr) gas phase anion chemistry[11-13] and to the development of useful analytical techniques based on this chemistry[14-15], we see reason to expect similar results from the study of anion chemistry at higher pressures.

This paper presents our initial work toward this objective. In particular, we have studied one chemical system which has been proposed as responsible for producing an enhancement in the response of the standard electron-capture detector[16-17], and several other systems which have not as yet been applied analytically. Specific differences between anion chemistry at low pressure (*ca.* 1 Torr) and at higher pressure (*ca.* 1 atm) have been observed.

EXPERIMENTAL

The mass spectrometer used in these experiments was an Extranuclear SpectrEL quadrupole (Extranuclear Labs., Pittsburgh, PA, U.S.A.) having a nominal mass range of from 2 to 400 a.m.u. It was modified to allow analysis of either positive or negative ions from an external high-pressure ionization source. The standard ion source region block and filament holder were removed and replaced with a cylindrical stainless steel wire mesh accelerating lens. The standard electronics were modified so as to allow the polarity of the potentials applied to all four ion focussing lenses and to the electron multiplier to be switched either positive or negative depending on the charge of the ions under investigation. The entire vacuum chamber enclosing the mass spectrometer was pumped simultaneously by two oil diffusion pumps, the stan-
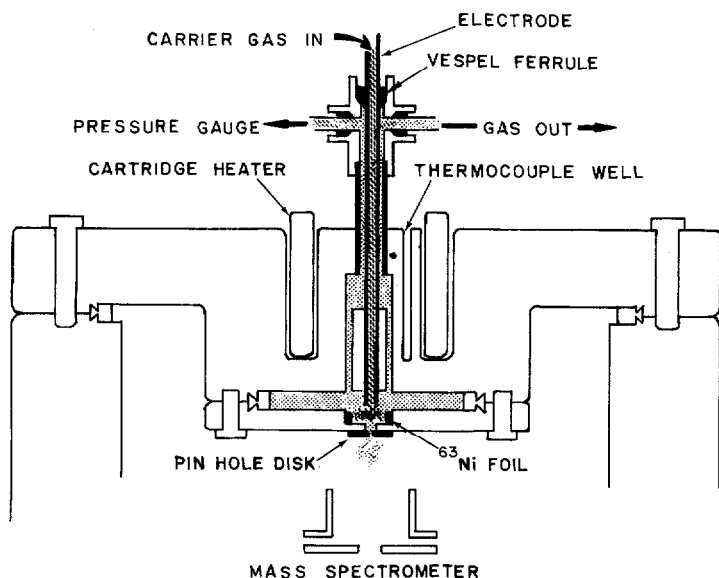

Fig. 1. High-pressure ionization source. Source is built into a stainless-steel flange which mounts directly to vacuum chamber of a quadrupole mass spectrometer. Analytes are added to carrier gas through a gas chromatograph.

dard 680 l/s pump and a supplemental 280 l/s pump and maintained at a pressure $< 8 \cdot 10^{-5}$ Torr during all analyses.

The external ion source, constructed in-house, resembled in its essential features a standard electron-capture detector for gas chromatography (GC) and is shown schematically in Fig. 1. It is built into a stainless-steel flange which mounts directly above the first (accelerating) lens of the mass spectrometer. Its cylindrical chamber (3/8 in. I.D.) is concentric with the central axis of the lens stack and quadrupoles. This chamber is separated from the mass spectrometer vacuum chamber by a 0.001-in. thick stainless-steel disk (Optimation, Windham, NH, U.S.A.) containing a pinhole aperture (nominally 15 μm diameter). The entire ion source, including the pinhole disk, is at ground potential. Ions effuse from the source and are then electrostatically accelerated by the first lens inside the mass spectrometer vacuum chamber.

Ions and thermalized electrons are produced from the carrier gas within the source chamber by beta particles emitted from a ^{63}Ni foil which is formed into a cylinder and positioned against the chamber wall just above the pinhole disk. Carrier gas enters the source chamber through a 1/8 in. O.D. stainless-steel tube positioned along the chamber axis, and is directed through the ionization region and directly at the pinhole aperture. The carrier gas exits the source through a needle valve directly to the atmosphere or to a vacuum manifold. In this way, the total source pressure can be varied from 0.5 to about 5 atmospheres. The gas inlet tube is electrically isolated from the source chamber and can serve as an electrode for collecting free electrons as in a standard electron-capture detector. All experiments reported herein were done without application of an electron collecting pulse to this electrode. The entire ion source can be heated to temperatures ranging from ambient to 600 K. Carrier gas flow-rates were generally within the range 125–175 cm^3/min, so that the residence time for gas within the ionization region was < 0.5 s.

The carrier gases used in these experiments were nitrogen (ultra-high purity), argon (zero grade), and a mixture of argon plus 10% methane (zero grade) all from Big 3 Industries, Houston, TX, U.S.A. In each case, the negative-ion mass spectrum obtained when only the carrier gas was present in the ion source included only a few ions in relatively low abundance. Typically this background consisted of the Cl$^-$ ion and one or two of its hydrate clusters formed from a residual chlorocompound and water contamination which proved impossible to remove completely even with extensive baking and flushing. These were generally ignored.

In a typical experiment, a reagent gas (e.g., N$_2$O, O$_2$, or SO$_2$) or vapor was mixed with the carrier prior to entry into the source. This was done in one of two ways. Reagents which were permanent gases were frequently added to the carrier directly from a pressurized tank through a flow controller. Alternatively, reagents were encapsulated in a permeation tube[18] and the carrier gas passed over the tube at a precisely controlled temperature. This latter method was particularly convenient for adding reagents which were volatile solids or liquids. The negative ion spectrum obtained from the carrier gas plus reagent mixture always contained one or two ions typical of the reagent in abundances considerably greater than the background ions present in the pure carrier gas spectrum. It is the reaction of these reagent gas ions with specific analytes and/or the competition of the analyte electron attachment rate with the reagent electron attachment rate which we have studied in the present work.

Since analytes (*e.g.* alcohols, aromatics, chlorocompounds, etc.) were hardly ever obtainable with absolute purity, they were always introduced into the carrier–reagent mixture through a gas chromatograph. A portion of the GC column effluent (1/4 of the total 3 cm^3/min flow) was split off and monitored with an appropriate detector, usually a flame ionization detector. The remainder (3/4 of the total flow) was added to the carrier–reagent mixture prior to entry into the ion source. In this way negative ion mass spectra could be obtained from the analyte–carrier–reagent mixture during elution of the major peak in the chromatogram of the analyte. Experience has shown that this is imperative in studying analytes which attach electrons slowly or which undergo slow ion–molecule reactions with the reagent ion. In such cases, very small concentrations of impurities in the analyte which capture electrons rapidly or which undergo rapid ion–molecule reaction with the reagent ion can cause serious problems in interpretation. In extreme cases, terminal ions resulting from the impurity can completely dominate the resulting mass spectrum. For example, in studying the reaction of the reagent $N_2O_2H^-$ ion with various aliphatic alcohols, we found that a small concentration of an aliphatic acid impurity in the alcohol completely eliminated the negative ion product of the alcohol–$N_2O_2H^-$ reaction.

In a typical experiment complete negative-ion mass spectra are obtained for both the carrier–reagent mixture and for the analyte–carrier–reagent mixture and compared. The range for the mass spectra is determined by the molecular weights of the analyte and reagent and by the maximum masses of plausible product ions including higher mass clusters. Ions associated only with the carrier–reagent mixture and ions associated with the analyte–carrier–reagent mixture are thus identified.
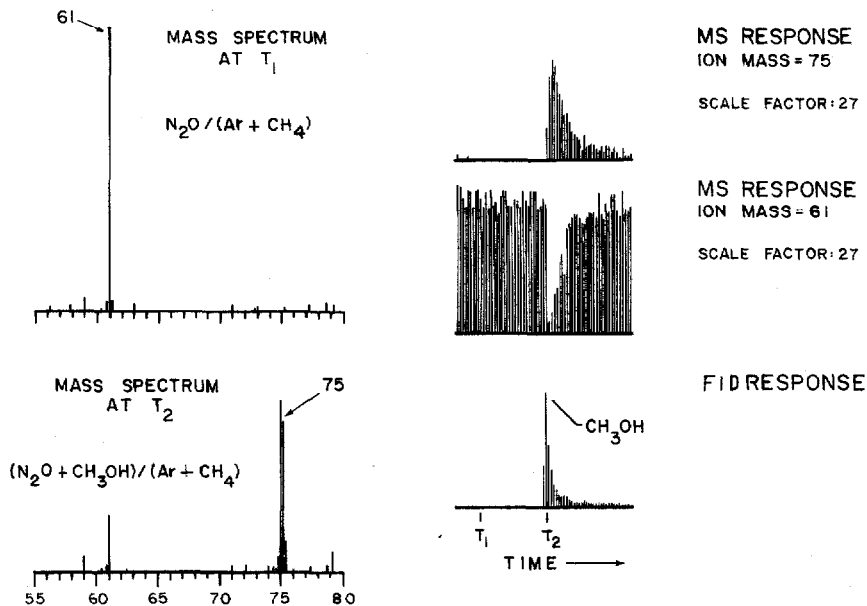

Fig. 2. Typical set of experimental data for reaction of a reagent negative ion ($N_2O_2H^-$, m/e 61) with an analyte (CH_3OH) to form an anion characteristic of the analyte (CH_3ONNO^-, m/e 75). Reaction occurs in a carrier gas mixture (Ar + CH_4) containing the reagent as the analyte elutes from a GC column into the ion source.

These ions were then studied further using the technique of selected ion monitoring. In this technique, only the intensities of selected ions are monitored before, during, and after introduction of the analyte into the ion source. In general, one observes a decrease in ions associated with the reagent and an increase in ions produced by reaction with the analyte as the analyte passes through the ion source. In principle, the decrease in reagent ion intensity should precisely complement an increase in analyte ion intensity and the shapes of the selected ion intensity curves should reflect the GC detector response as the analyte elutes. A typical set of data is shown in Fig. 2.

To facilitate the collection of data during the short duration of a GC peak (typically 5–15 s for capillary columns), a computer-based system has been developed. An Apple IIe computer has been interfaced to the mass spectrometer mass scan control through a 12 bit D/A converter (Adalab Data Acquisition/Control Card, from Interactive Microware, State College, PA, U.S.A.) and to the mass spectrometer ion signal output through a 12 bit A/D converter (AI13 Analog Input Card, from Interactive Structures, Bala Cynwyd, PA, U.S.A.). The computer has been programmed in machine language using the LISA V2.6 assembler (Lazer's Interactive Symbolic Assembler, from Lazerware, Corona, CA, U.S.A.). Assembly of the program directly into machine language results in an object code which executes rapidly and can collect sufficient data for true signal averaging. This has proved to be essential since the negative-ion intensities available in our system (small aperture, low analyte and reagent concentration) are relatively low. In the signal-averaging mode of data collection, the intensity at each m/e setting is repeatedly sampled and summed. In this way even intensities with an inherent signal-to-nose ratio of < 1 can be measured. This can be used to particular advantage in the study of electron attachment or negative-ion reactions at thermal energies, since generally only a few ions are involved. In such cases the intensity at these selected masses can be sampled many times producing a very large enhancement of the signal-to-noise ratio. We have found that although the computer system can scan the mass setting voltage at the rate of 20 μs per setting, inherent response characteristics in the mass spectrometer limit the scanning rate to 2 ms per voltage setting. This means for example that a mass spectrum can be scanned from 2 to 202 a.m.u. in 0.2 a.m.u. intervals (1000 voltage settings) once every 2 s. If the spectrum is scanned only at whole mass intervals (200 voltage settings), a single scan requires only 0.4 s. Obviously, the number of scans which can be averaged within the duration of a GC peak depends on the width of the peak, on the mass interval scanned, and on the mass resolution required. Typically we average 100 scans per GC peak.

Initiation and termination of data collection are done manually at the computer keyboard. The GC chromatogram is monitored on a separate recorder. To obtain the complete negative-ion mass spectrum associated with elution of a given analyte, data collection is initiated when the GC detector response reaches half its maximum value, and is terminated when the response drops to half its maximum. Data collection for selected-ion monitoring is initiated prior to elution of the analyte and continued throughout its elution. In this mode, the GC detector response is also measured with the computer data system and plotted along with the selected-ion chromatograms for correlation.

In the present experiments the ion source was maintained at a temperature > 545 K. At this temperature association ions or clusters, such as hydrates or alcoholates, generally are not observed.

The GC column used was a fused-silica bonded phase capillary column (30 m × 0.32 mm) coated with DB5 Durabond (1.0 μm thick) from J & W Scientific, Rancho Cordova, CA, U.S.A. Since the liquid phase is bonded directly to the silica surface, column bleed is minimal and does not contribute significantly to the observed mass spectra.

The analytes were all reagent grade obtained from Baker Chemical, Fisher Scientific, or Aldrich Chemical and were used as received. Methanol-d_4 (99.5% isotopic purity) was used as received from Stohler Isotope Chemicals, and isotopically labeled $^{15}N_2O$ was used as received from Cambridge Isotope Laboratory.

The reagents used were SO_2 from a permeation tube (VICI Metronics, Santa Clara, CA, U.S.A.) and N_2O at a concentration of 0.103% premixed with argon in a pressurized tank (Union Carbide, Linde Division, Somerset, NJ, U.S.A.).

RESULTS AND DISCUSSION

In order to detect compounds such as alkanes which do not rapidly attach electrons, the carrier gas used in a conventional electron-capture detector has been intensionally doped with N_2O. This has been shown to significantly increase the detector response for such compounds and a mechanism based on the anion chemistry of N_2O has been proposed[16-17].

In the absence of any proton-containing species, the proposed mechanism involves the following equilibrium with thermal electrons:

$$N_2O + e^- \rightarrow O^- + N_2 \tag{1}$$

$$O^- + N_2O \rightarrow NO^- + NO \tag{2}$$

$$NO^- + M \rightarrow NO + M + e^- \tag{3}$$

where M is some third body. Reactions of O^- or NO^- with an analyte molecule result in a net electron loss and produce a corresponding sensitized detector response. It has been shown[19] that under some conditions O^- will react with hydrogen containing molecules such as H_2 or CH_4 to form OH^- by hydrogen atom abstraction:

$$O^- + RH \rightarrow OH^- + R \tag{4}$$

Further, hydroxide ion derived from N_2O has been observed and used as a reactant ion in NCIMS analyses of carboxylic acids, amino acids, alcohols, ketones, and esters[13], cyclic diols[20], steroids[21], essential oils[22], and acyl chlorides[12].

However, a major difference between NCIMS analyses and ECD analyses is that the former are done at a relatively low pressure (10^{-2}–1 Torr) while the latter are done at atmospheric pressure. Parkes has studied ion–molecule reactions in N_2O using a drift tube and a mass filter[23], and pointed out that reactions 1–3 are low-pressure reactions. At higher pressures of N_2O some higher order reactions such as
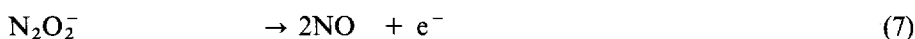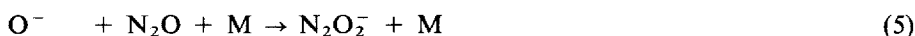
$$O^- + 2N_2O \rightarrow N_2O_2^- + N_2O \tag{5}$$

$$NO^- + 2N_2O \rightarrow N_3O_2^- + N_2O \tag{6}$$

become predominant. Moruzzi and Dakin[24] have observed ions having m/e 60

($N_2O_2^-$) and m/e 74 ($N_3O_2^-$), and found that these ions dominate at pressures above 1 Torr. These observations suggest that the anion chemistry of N_2O in the electron-capture detector at atmospheric pressure may be somewhat more complicated than represented by reactions 1–4.

The $N_2O_2^-$ ion
    When N_2O (0.012%) was mixed with equal amounts of Ar and N_2 at an ion source pressure of 1.2 atmospheres, we observed only a single negative ion at m/e 60 at temperatures ranging from 275 to 600 K. This mass corresponds to the $N_2O_2^-$ ion. Two reaction mechanisms are suggested for the production of this ion:

$$N_2O \quad + \; e^- \qquad \rightarrow O^- \quad + \; N_2 \qquad\qquad\qquad (1)$$

$$O^- \quad + \; N_2O + M \rightarrow N_2O_2^- + M \qquad\qquad\qquad (5)$$

$$N_2O_2^- \qquad\qquad\quad \rightarrow 2NO \; + \; e^- \qquad\qquad\qquad (7)$$

or

$$2N_2O \; + \; e^- \rightarrow N_2O_2^- + \; N_2 \qquad\qquad\qquad (8)$$

$$N_2O_2^- \qquad\qquad \rightarrow 2NO \; + \; e^- \qquad\qquad\qquad (7)$$

Either mechanism would be consistent with our results. When the source pressure is increased from 1.2 to 2.36 atm at 575 K, the intensity of the m/e 60 ion is increased by a factor of 8 indicating that formation of this ion involves a high order reaction.
    Of course these studies do not reveal any information about the structure of the m/e 60 ion but two possible structures are: $O–N–N–O^-$ and $NO^- \cdots NO$, the latter being considered an ion–molecule complex or cluster. We favor the first structure since it parallels that considered for hyponitrous acid and the hyponitrite ion, as will be discussed later. Also we would not expect an $NO^-(NO)$ complex to be stable enough to survive the higher temperatures.
    A reviewer suggested varying the partial pressure of NO in the system to see if it affects the m/e 60 peak. This study should shed light on the structure of $N_2O_2^-$ as a discrete ion or as a cluster $NO^-(NO)$. Unfortunately the addition of NO to the Ar + CH_4 + N_2O reaction mixture gave an ion at m/e 46, presumably NO_2^-. Apparently the NO used was contaminated by NO_2 or was oxidized by the N_2O or by an O_2 impurity to NO_2. The m/e 60 peak was diminished in lieu of the m/e 46 peak and other ions thought to be derived from NO_2^-. In the ensuing discussion, we will write the formula for the m/e 60 peak as an empirical formula $N_2O_2^-$ with no intention of designating the structure.
    Also, at higher pressures a second ion having m/e 42 appears at relatively low intensity. Field and co-workers[11–13] have also observed an ion having m/e 42 in their NCIMS studies and proposed that it was either CNO^- or N_3^-. The possible formation of CNO^- was ascribed to pyrolysis of CH_4 by the hot filament in their ion source. The formation of CNO^- is unlikely in our experiments since there was no obvious source of carbon atoms and since temperature was insufficient for pyrolysis. We suggest that the ion is N_3^- produced by the following sequence of reactions:

$$NO^- + N_2O + M \rightarrow N_3O_2^- + M \qquad (6)$$

$$N_3O_2^- \qquad\qquad \rightarrow N_3^- + O_2 \qquad (8)$$
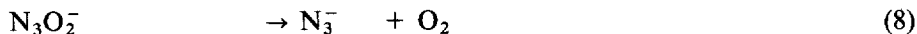
In no case did we observe any of the intermediate ions $(O^-, NO^-, \text{ or } N_3O_2^-)$ involved in the reaction mechanisms proposed above. In general, it was possible to avoid the formation of N_3^- by keeping the source pressure at about 1 atmosphere.

If N_3^- is produced by reactions 6 and 8, as previously suggested, the structure of $N_3O_2^-$ most likely involves three nitrogen atoms bonded together, $ONNNO^-$ or $NNNOO^-$. The formation of the former structure would involve the least amount of rearrangement in reaction 6 but would require a more complicated closure of an intermediate ring to form O_2. The structure could also be a complex: $NO^-(N_2O)$ as suggested by a reviewer. Again, it should be emphasized that the information from these experiments sheds no direct evidence on the structure of these ions.

The $N_2O_2H^-$ ion

When either methane or *n*-hexane was mixed with N_2O and Ar in our ionization source (pressure 1.2 atm, temperature 300°C), only one negative ion having m/e 61 was observed. We suggest this is $N_2O_2H^-$ produced either by the reaction:

$$OH^- + N_2O \rightarrow N_2O_2H^- \qquad (9)$$

where OH^- comes from reactions 1 and 4 or by the reaction:

$$N_2O_2^- + RH \rightarrow N_2O_2H^- + R \qquad (10)$$

where $N_2O_2^-$ comes from reactions 1, 5, and 7 or from reactions 8 and 7.

Another possible species having m/e 61 is HCO_3^- (or $CO_2 \cdot OH^-$). In order to show that the ion at m/e 61 is $N_2O_2H^-$ rather than HCO_3^-, three experiments were done. First, CO_2 was added to the reaction mixture. This did not increase the intensity of the m/e 61 ion. Second, isotopically labelled $^{15}N_2O$ was added to the reaction mixture. This produced an ion having m/e 63, apparently $^{15}N_2O_2H^-$, and a corresponding decrease in the intensity of the m/e 61 ion. Third, a mixture of N_2O and CO_2 were added to the carrier gas through a GC (6 ft. × 1/8 in. column, packed with Haysep Q). At room temperature, N_2O and CO_2 were separated as shown in Fig. 3. Selected-ion monitoring at m/e 61 showed no evidence for the formation of an ion with this mass as CO_2 eluted into the ion source, but did show definite evidence for formation of such an ion as the N_2O eluted. Most likely the H atom abstraction occurs directly by $N_2O_2^-$ and this would not be expected if the structure of m/e 60 were $NO^-(NO)$. At no time did we observe either of the intermediate ions $(O^-,$ or $OH^-)$ in this reaction mixture.

There are at least two possible structures for the ion $N_2O_2H^-$: $(O-N=N-OH)^-$ or $(N=N-O\cdots HO)^-$. Based on the observation that the m/e 61 ion shows correlations with ion source temperature and N_2O concentration similar to those observed for $N_2O_2^-$ (discussed above) the structure should be molecular $^-O-N=N-OH$ rather than the less stable $N_2O \cdot OH^-$. Furthermore, the $^-O-N=N-OH$ structure is the anion of hyponitrous acid, $HO-N=N-OH$, which is known to exist[25,26] in the gas phase and in solution.
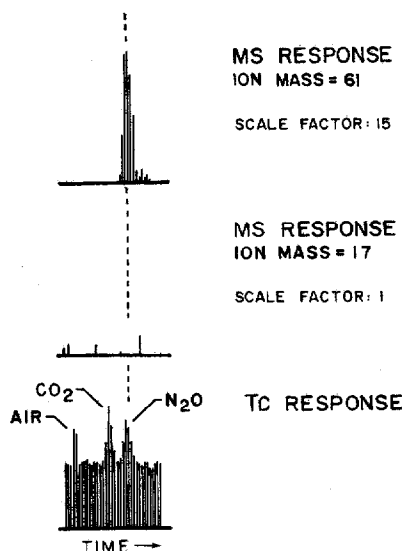
Fig. 3. Gas chromatogram and selected-ion (m/e 17, and m/e 61) chromatograms obtained when a mixture of CO_2 and N_2O was added to argon + methane carrier gas.

Some hydrogen-containing compounds do not produce $N_2O_2H^-$ when mixed with N_2O and Ar. The addition of aromatic hydrocarbons such as benzene or toluene decreased the intensity of the $N_2O_2^-$ ion but no ion with m/e 61 was observed.

$N_2O_2H^-$ reaction with acids (proton abstraction)

Since $N_2O_2H^-$ is the anion of the weak hyponitrous acid ($N_2O_2H_2$), it would logically be expected to undergo gas phase acid–base reactions:

$$AH + N_2O_2H^- \rightarrow N_2O_2H_2 + A^- \tag{11}$$

For example, when acetic acid (mol.wt. = 60) is eluted from the GC column into an N_2O–(Ar + CH_4) mixture in our ionization source, we observe a decrease in the $N_2O_2H^-$ (m/e 61) reagent ion intensity and a corresponding increase in intensity of an ion having m/e 59 (CH_3COO^-). Analogous results have been observed for at least six analyte acids. These results are being used to establish the relative base strength of $N_2O_2H^-$ and will be published elsewhere.

$N_2O_2H^-$ reaction with aliphatic alcohols (dehydration)

Aliphatic alcohols are very weak acids. Generally they did not react by proton transfer to $N_2O_2H^-$ as did the stronger acids. Instead, we found that they reacted to give the anion of an ester.

$$ROH + HONNO^- \rightarrow RONNO^- + H_2O \tag{12}$$

(M) (m/e = 61) (m/e = M + 61 − 18)
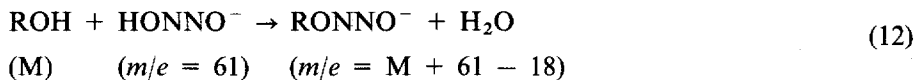
For example, when methanol (mol.wt. = 32) is eluted from the GC column into an $N_2O-(Ar + CH_4)$ mixture in our ionization source, we observe a decrease in the $N_2O_2H^-$ (*m/e* 61) ion intensity and a corresponding increase in intensity of an ion having *m/e* 75 (CH_3ONNO^-).

We have verified reaction 12 using isotopically labelled compounds. When $C^2H_3O^2H$ is eluted into an $N_2O-(Ar + CH_4)$ mixture, the intensity of the $N_2O_2H^-$ ion decreases and the intensity of the expected product, $C^2H_3ONNO^-$ (*m/e* 78), increases. This confirms that the methyl group in the product comes from the alcohol reactant rather than from the methane in the carrier gas mixture. When reaction 12 was observed with $^{15}N_2O$ in the carrier gas mixture, the product ion $CH_3O^{15}N^{15}NO^-$ (*m/e* 77) was observed as expected. Analogous reactions have been observed with at least 14 other C_2-C_6 aliphatic alcohol analytes including ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *tert.*-butyl alcohol, 1-pentanol, 2-pentanol, cyclopentanol, 1-hexanol, 3-hexanol, and cyclohexanol.

$N_2O_2H^-$ reactions with $CH_3-C=$ or $CH_3-C\equiv$

The reaction of $N_2O_2^-$ with compounds which contain a methyl group adjacent to a double or triple bond but which are only weakly acidic (*e.g.*, aliphatic nitriles, aldehydes, ketones and methyl-substituted aromatics) consistently resulted in the formation of one or two conjugated anions and the elimination of water. In general, the second anion is much less abundant than the first. For example:

$$^-ONNOH + CH_3C\equiv N \rightarrow [HONNC(H)CN]^- + H_2O \qquad (13)$$

$$[HONNC(H)CN]^- \rightarrow [NNCCN]^- + H_2O \qquad (14)$$

The SO_2^- ion

When SO_2 is mixed with the argon and methane carrier gas at 530 K, a single negative ion is observed at *m/e* 64 (SO_2^-). Significant reactions of SO_2^- with compounds which have a low electron-capture detector response have not been identified as yet.

The HSO_3^- ion

When both SO_2 and N_2O are mixed with the argon plus methane carrier gas two negative ions are observed; one at *m/e* 64 (SO_2^-) and a more abundant ion at *m/e* 81 (HSO_3^-). Using selected ion monitoring, we have been able to identify some reactions of HSO_3^- which are analogous to those of $N_2O_2H^-$.

HSO_3^- reactions with acids (proton abstraction)

The HSO_3^- ion is the anion of H_2SO_3 which has a pK_a of about 2 in aqueous solution. HSO_3^- does not abstract a proton from acetic acid while $N_2O_2H^-$ does. This indicates that $N_2O_2H^-$ is a stronger base than HSO_3^-.

### HSO_3^- reactions with alcohols (dehydration)

Aliphatic alcohols react with HSO_3^- to form the anion of an ester.

$$ROH + HSO_3^- \rightarrow ROSO_2^- + H_2O$$

$$M \qquad (m/e = 81)\ (m/e = M + 81 - 18)$$

(15)
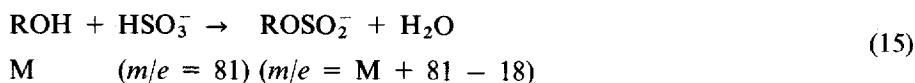
For example, when ethanol (M = 46) is eluted from the GC column into an N_2O–SO_2–(Ar + CH_4) mixture in the API ionization source, a decrease is observed in the HSO_3^- (m/e 81) ion intensity and a corresponding increase is observed in the $CH_3CH_2OSO_3^-$ (m/e 109) intensity. These reactions are analogous to those observed for $N_2O_2H^-$.

HSO_3^- reactions with $CH_3-C=$ or $CH_3-C\equiv$

The reaction of HSO_3^- with compounds which contain a methyl group adjacent to a double or triple bond but which are only weakly acidic (*e.g.* aliphatic nitriles, aldehydes, and ketones, and methyl-substituted aromatics) consistently results in the formation of only one conjugated anion and the elimination of water. For example:

$$HSO_3^- + C_6H_5-CH_3 \rightarrow C_6H_5-CH_2-SO_2^- + H_2O$$

(16)
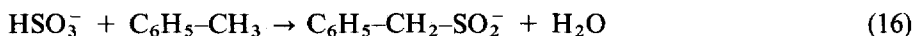
In the case of the reaction with nitromethane, the dehydration reaction takes place in preference to the proton abstraction reaction. The terminal anion is CNO^- (m/e 42) which is formed from the intermediate by loss of a molecule of H_2O and SO_2. This is different from the reaction of nitromethane with $N_2O_2H^-$ where proton abstraction occurs, giving a stable $CH_2NO_2^-$ (m/e 60). This observation further supports the previously discussed conclusion that $N_2O_2H^-$ is a stronger base than HSO_3^-.

CONCLUSIONS

All of these conclusions refer to the API–ECD–MS source where ionization is initiated by soft beta particles from a ^{63}Ni foil.

(1) The ion $N_2O_2^-$ or $NO(NO^-)$ is the predominant anion observed from a mixture of N_2O and Ar.

(2) The ion $N_2O_2H^-$ or $N_2O(OH^-)$ is the predominant anion observed from a mixture of N_2O and Ar + CH_4.

(3) $N_2O_2H^-$ is basic and reacts with acidic compounds by proton abstraction.

(4) $N_2O_2H^-$ reacts with a variety of alcohols to produce a characteristic anion and water.

(5) $N_2O_2H^-$ reacts with compounds containing a $CH_3-C=$ or $CH_3-C\equiv$ group to produce a characteristic anion and water.

(6) The ion SO_2^- is the predominant anion observed from a mixture of SO_2 and Ar plus methane.

(7) The ion HSO_3^- is the predominant anion observed from a mixture of SO_2, N_2O and Ar plus methane.

(8) HSO_3^- is a weaker base than $N_2O_2H^-$, but will react with some acidic compounds by proton abstraction.

(9) HSO_3^- reacts with a variety of alcohols to produce a characteristic anion and water.

(10) HSO_3^- reacts with compounds containing a $CH_3-C=$ or $CH_3-C\equiv$ group to produce a characteristic anion and water.

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