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Proton Affinity of Peroxyacetyl Nitrate Sampled by Membrane Introduction Mass Spectrometry

N. Srinivasan,[1] R. G. Cooks[1]* and P. B. Shepson[2]

[1]Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA
[2]Departments of Chemistry and Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907, USA

Peroxyacetyl nitrate (PAN) is a fragile, highly reactive molecule which has proven difficult to characterize by mass spectrometry. This study investigates the use of a membrane introduction system to sample PAN and demonstrates that the molecular ions $[M+H]^+$, $[M+H]^-$ and $M^{-\bullet}$ can be generated under chemical ionization conditions. Use of tandem mass spectrometry provides characteristic spectra. These capabilities are applied to generate adduct ions of PAN with reference compounds of known proton affinity. Collision induced dissociation of these ions gives, by application of the kinetic method relationship, an estimated value of 191 ± 3 kcal/mol (798 ± 12 kJ/mol) for the proton affinity of PAN.

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Peroxyacetyl nitrate (PAN) (**I**), first identified by Stephens *et al.*,[1] is a product of atmospheric oxidation of hydrocarbons in the presence of NO and NO_2 (NO_x). Thermal decomposition of PAN yields the peroxyacetyl radical and NO_2, (Eqn (1)) and kinetic data of Kenley and Hendry[2] show that while the lifetime of PAN (i.e. $1/k_f$) is about 30 minutes at 298 K, it is 2 months at −20°C. The NO_2 released upon thermal decomposition is a critical reagent in the production of tropospheric ozone. These facts led Singh and Hanst[3] to suggest that PAN is an important vehicle for the transport of tropospheric NO_x, thereby influencing the global distribution of ozone. PAN is also an important form of nitrogen in the middle troposphere[4] as well as having significant physiological effects.[5–7]

$$CH_3C(O)OONO_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CH_3C(O)OO^{\bullet} + NO_2 \qquad (1)$$

Measurements of PAN almost always use gas chromatography with electron capture detection.[8] However, the temporal and spatial variability of this pollutant make more rapid non-chromatographic analytical methods of interest. Facile thermal dissociation occurs using conventional methods of introduction of PAN into a mass spectrometer and the resulting mass spectra are dominated by ions which are not structurally diagnostic of PAN itself. In this study we report that it is possible to introduce PAN via a semi-permeable membrane. Furthermore, one can use this procedure to generate positively and negatively charged forms of intact ionized PAN.

The measurement of thermochemical quantities of PAN is of intrinsic interest and potentially important to the development of analytical techniques for detection of this species. Although some thermochemical properties of PAN have been estimated theoretically,[9] no information is available regarding the proton affinity (PA) of PAN. This study therefore aims also to utilize membrane introduction to estimate this quantity by application of the kinetic method.

*Correspondence to: R. G. Cooks, Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA.
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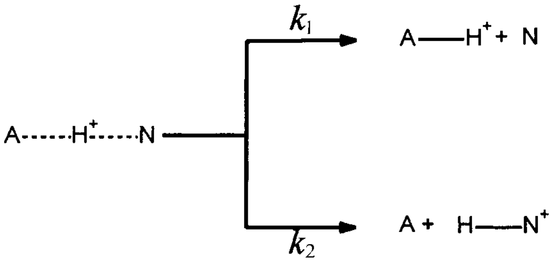
The kinetic method

The kinetic method, an approximate procedure for making thermochemical determinations, is based on the relative rates of competitive dissociations of mass-selected cluster ions.[10,11] Cluster ions bound by cations or anions are isolated and their dissociation (typically caused by collision-induced dissociation (CID)) is followed in an MS/MS experiment. In the case of proton affinity determinations, the fragmentation of the mass-selected proton-bound dimer to give the individual protonated bases, by competitive cleavage of the two hydrogen bonds, can be represented as shown in Eqn (2).

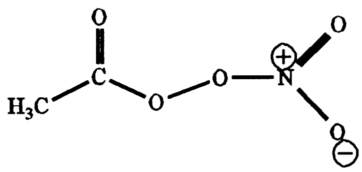


(2)

The ratio of the rates of the competitive dissociations of the proton-bound dimer can be simply expressed as the ratio of the abundances of the ions due to the individual protonated bases, viz. $\{[NH^+]/[AH^+]\}$. Theoretical treatments of the kinetic method[12–16] lead to the approximate expression:

$$\ln\left\{\frac{[NH^+]}{[AH^+]}\right\} \approx \frac{\Delta PA}{RT_{eff}} \qquad (3)$$

where $[NH^+]$ and $[AH^+]$ are the abundances of the two protonated bases, ΔPA is the proton affinity difference



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between the compounds A and N, and T_{eff} is the effective temperature of the activated dimer ion. When the effective temperature is known from examination of compounds of known PA, Eqn (3) can be used to provide proton affinity values for an unknown, A. Note that the method can be used to establish the relative order of proton affinities even in cases in which the fragmentation shown in Eqn (2) proceeds exclusively to give one set of products.

The kinetic method has been used for determining the gas-phase acidities and basicities of many classes of compounds.[13,14,17,18] It has also allowed the determination of other ion affinities, including ammonium ion,[19] metal ion,[20,21] chlorine cation,[22] cyanide cation[23] and carbonyl isocyanate[24] cation affinities. It is often sensitive to small thermochemical differences (well below 1 kcal/mol), and is applicable to polar and non-volatile samples, even when they are not available in pure form, as is the case in this study.[11] The method is best applied to chemically similar species, in which case entropy effects on reaction rates tend to cancel. In some cases[25] the dissociation of covalently bound ions is employed instead of the more desirable, weakly bound, clusters of cations and neutral molecules.

The present study employs chemical ionization to generate proton-bound dimers (or, less desirably, covalently bound complexes) between PAN and various reference compounds. These reference compounds, N, each of known PA, are used to establish a correlation based on Eqn (3) by plotting $1n[NH^+]/[AH^+]$ vs. the PAs of the reference compounds. Further, from Eqn (3), it follows that the slope of the straight line is equal to $1/RT_{eff}$ and the *x*-intercept corresponds to the PA of the unknown (PAN).

Membrane introduction mass spectrometry

The use of MIMS in process monitoring and environmental analysis is attractive because of the selectivity and sensitivity it provides. Membranes were first used in mass spectrometry for monitoring photosynthetic processes[26] and later the method was adapted to solution analysis, by examination of compounds that permeate through hollow fiber capillary membranes.[27] Since then, this area has grown[28–30] and MIMS has also been applied to such important areas such as biological waste water treatment,[31] chemical reaction monitoring,[32,33] bioreactor monitoring[34–38] and especially to the analysis of volatile and semi-volatile organic compounds.[29,39–41] Key to recent developments in MIMS has been the use of flow injection methods of sample handling[42,43] in which the solution is transported over the surface of the membrane, often located in a direct insertion membrane probe in the ion source. MIMS is particularly useful for ambient air sampling since it avoids the need for pre-concentration and yet allows separation of analytes from water vapor.

EXPERIMENTAL

Instrumentation

A Finnigan MAT, TSQ 700 triple quadrupole mass spectrometer (Finnigan Inc., San Jose, CA, USA) was used in all the experiments. The instrument was operated in either the electron ionization (EI) or chemical ionization (CI) mode to give either positively or negatively charged ions. Reference compounds of known PA were introduced into the ion source through the gas chromatography (GC) inlet via a Granville Phillips variable leak valve (Granville Phillips Co., Boulder, CO, USA) with heating as necessary to provide sufficient vapor pressure. Isobutane was used as the chemical ionization reagent gas for positive ion experiments and ammonia for negative ion experiments. The source temperature was maintained as low as possible (*ca.* 35 °C) and the direct insertion membrane probe was not heated; the sample simply was allowed to permeate through the membrane into the source under ambient conditions. The manifold temperature was held at 30 °C for all experiments, to minimize thermal decomposition of PAN. The typical scan range was 70–300 Da/charge and the scan rate was 0.5 s/scan. The production of adduct ions, including proton-bound dimers, is strongly dependent on the partial pressure of the constituent compounds and the ion source conditions were optimized to maximize the signal intensity of each proton-bound dimer.

Ions corresponding in mass-to-charge ratio to proton-bound dimers were generated in the ion source and mass-selected using the first quadrupole. These ions were excited and dissociated in the second quadrupole under very mild conditions, viz. nominal 2–4 eV collision energy, using a nominal argon pressure of 0.4 mtorr. A typical main beam attenuation was 10–20% (but see exceptions below). The abundances of the fragment ions were measured from the product ion mass spectra generated by scanning the third quadrupole. Each set of peak ratios was measured from an average of at least twenty individual scans. Collisional activation of all other ions, including protonated PAN, the hydride addition product and the anion radical, employed 30 eV collisions and the same nominal argon target pressure.

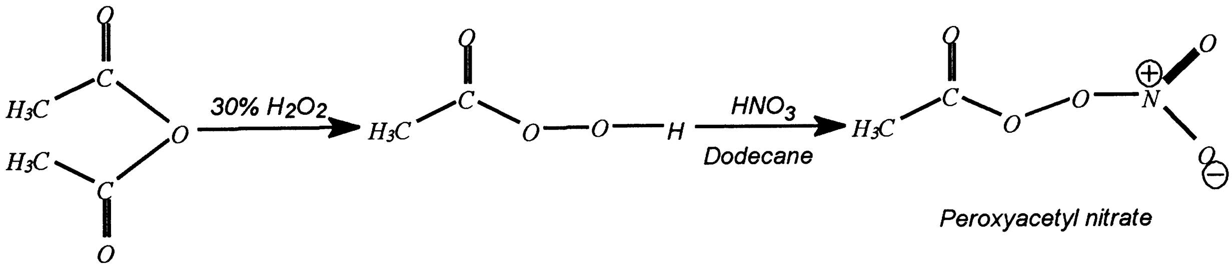
Membrane and sample inlet systems

A direct insertion membrane probe[43] was used to introduce PAN. The membrane probe utilized a silicone sheet membrane (Technical Products Inc., Decatur, GA, USA) with a thickness of 0.013 cm and surface area of approximately 30 mm^2. The membrane was sandwiched between a Teflon spacer and the end-ring of the probe.

Since neat PAN is an explosive liquid,[44] it was never isolated from *n*-dodecane, the solvent of choice during its synthesis. Instead, it was synthesized using a procedure very similar to that described by Nielsen *et al.*[45] (see Scheme 1). The solution-phase nitration was carried out in high molecular weight hydrocarbon solvent (dodecane) to take advantage of the lipophilicity of PAN.[46] The solution of PAN in dodecane was purged with nitrogen, allowing the volatile solute PAN to be transported to the membrane and into the mass spectrometer. A detailed description of the sample introduction system is given elsewhere.[47] During the PA measurement, the PAN impinger was kept in an ice bath and the sample was kept refrigerated between experiments.

RESULTS AND DISCUSSION

Figure 1 shows the total negative ion signal plotted against time when a membrane is used to sample the vapor from a PAN solution in *n*-dodecane. Ionization employed electron attachment under CI conditions (using NH_3 as reagent gas to mediate electron energies and so promote electron attachment). PAN permeates the dimethyl vinyl silicone polymer membrane very readily as shown by the rise time ($t_{10\%–90\%}$) of approximately 15 seconds. This time is comparable to the



Scheme 1.

rise times of many volatile organic compounds in MIMS using silicone membranes. However, the short time is noteworthy since the membrane probe was not heated to assist the transport of PAN through the membrane. The slight fall-off in signal at long times is probably due to small changes in membrane permeability; such effects are well known and do not affect quantitation performed using external standard solutions.

Under the conditions chosen for this experiment, PAN fragments extensively giving virtually no intact molecular radical anion. (Note, however, that the occurrence of ion/molecule reactions is strongly dependent on the reagent gas and experimental conditions chosen and $M^{-\cdot}$ ions were observable, see below.) As one would expect, the major fragments in the mass spectrum are the characteristic ions *m/z* 46 (NO_2^-), 30% relative abundance; *m/z* 62 (NO_3^-), 100%; *m/z* 59 ($CH_3CO_2^-$), 8%, and *m/z* 75 ($CH_3CO_3^-$ and/or $CHNO_3^-$), 22%. Scheme 2 illustrates some of the ions formed and suggests probable fragmentation pathways. There is a minor peak (5% relative abundance) at *m/z* 93, assigned to CO loss from the intact radical cation. This probably occurs after methyl rearrangement through a six-membered cyclic intermediate to an oxygen on nitrogen. Note although the fragments are assumed to arise from the anion radical, $M^{-\bullet}$, there may be contributions from the hydride addition product, $[M+H]^-$, *m/z* 122. Neither form of molecular ion is observed in spectra taken under conditions in which the partial pressure of PAN is low. Both are observed at higher PAN pressures (see below) and both are likely precursors to the nitrate ion at *m/z* 62.

Plots of the time profiles of the major fragment ions in the electron attachment mass spectrum of PAN are very similar to the total ion plot, as shown in Fig. 2. The identical forms of these plots confirm that these negatively charged fragment ions are all formed from the same compound. The data also demonstrate that the short rise times already noted (Fig. 1) are accompanied by equally remarkable short fall times. The data of Fig. 2 also serve to provide an indication of the repeatability of the measurements. Figure 3 shows a negative ion mass spectrum taken at a higher PAN partial pressure, under which conditions ion/molecule reactions are extensive. Note the abundant $[M+H]^-$ ion as well as the presence of many other adduct ions. Most of these are readily accounted for as the results of association of a fragment anion of PAN (HO^-, HO_2^-, $CH_3CO_2^-$, NO_2^-, NO_3^-, etc) with the neutral molecule. The peak assignments in this spectrum are based in part on tandem mass spectrometry results which are discussed below. The peak at *m/z* 93 is due to the methyl rearrangement process already discussed so it is interesting to note the presence of an ion, *m/z* 106, which corresponds formally to the methyl radical loss product. The base peak in the spectrum, *m/z* 119, corresponds formally to molecular hydrogen elmination from the anion, radical, although it is more likely to arise by fragmentation of one of the molecular adduct ions. There is evidence that the hydride adduct, $[M+H]^-$ undergoes loss of the elements of H_3: this is found in the fact that the negative ion CI mass spectra recorded using CCl_4 (Cl^- reagent) and CH_2Br_2 (Br^- reagent) display the halide addition products with PAN, i.e. $[M+X]^-$ as well as the remarkable ions $[M+X - H_3]^-$.

The mass spectrum of PAN, recorded under positive ion

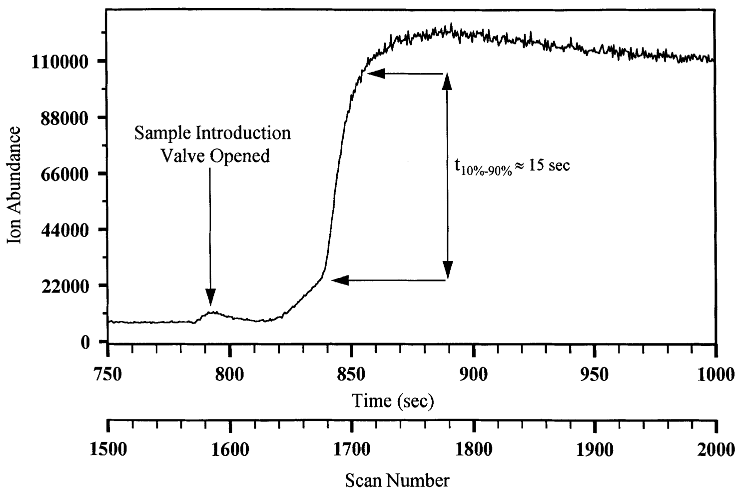


Figure 1. Total ion current vs. time for ions formed by electron attachment (NH_3 reagent gas) to PAN (*m/z* 121) showing permeability through a silicone membrane. The response time, $t_{10\%-90\%}$, is 15 s.

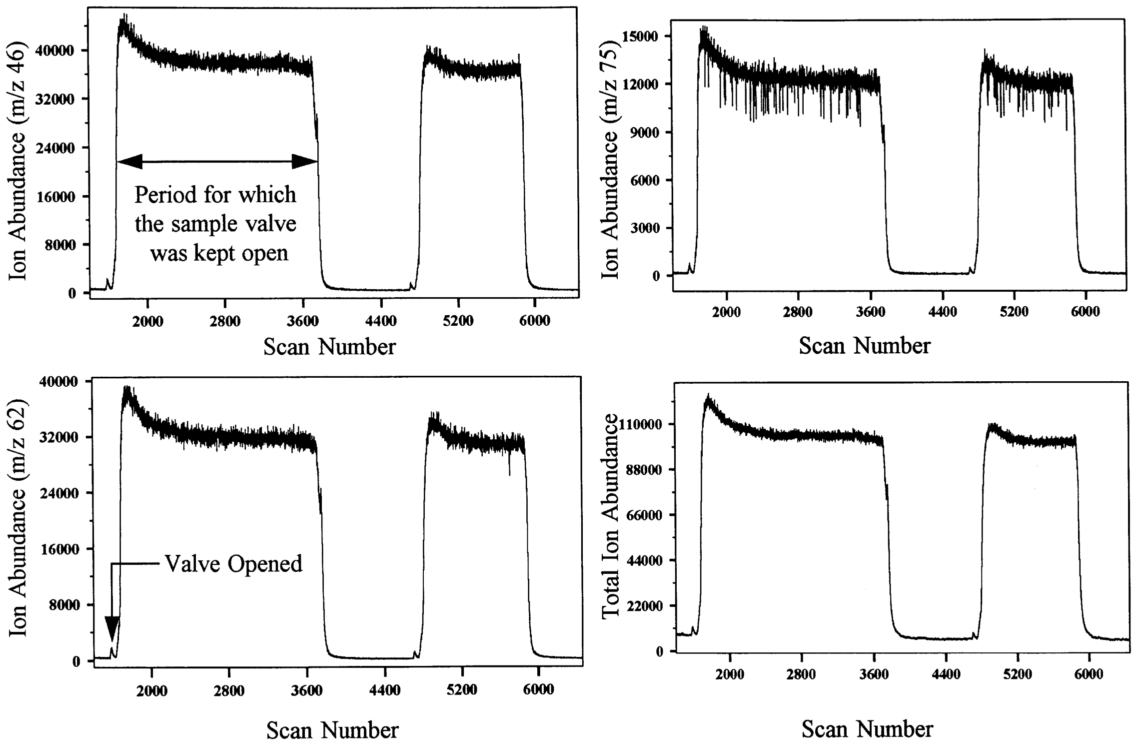
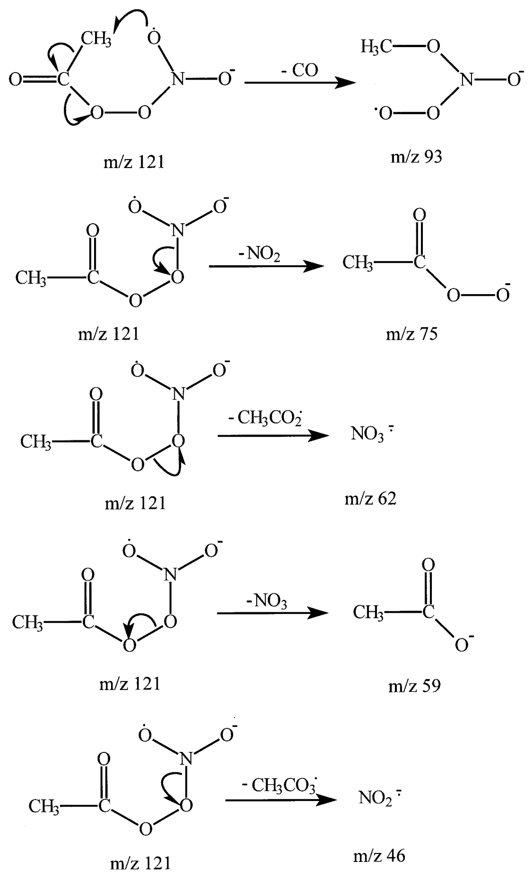


Figure 2. Ion current vs. time plots for individual ions and the total ion current for negative ions generated from PAN by electron attachment (NH_3 CI). Fragmentation is extensive, the molecular ion is very weak, and the major fragments include *m/z* 46, *m/z* 62, *m/z* 75 and *m/z* 93. The mass range was 70 to 250 Da/charge and the scan rate was 0.5 s/scan.



Scheme 2.

CI conditions using isobutane CI reagent gas, showed a characteristic protonated molecule as a major peak at *m/z* 122. However, unlike the negative ion spectra, it showed abundant ions due to the alkane solvent. It also showed low abundance adduct ions and fragments such as *m/z* 61, protonated acetic acid.

The complexity of the CI mass spectra is clearly a consequence of the ease with which PAN undergoes ion/molecule reactions in both the negative and positive ion modes. This makes tandem mass spectrometry (MS/MS) the method of choice for its determination, and data were recorded for two different forms of the molecular ion, $M^{-\bullet}$ and $[M+H]^{+}$. The collision-induced dissociation (CID) spectrum of the PAN anion radical (Fig. 4) shows the fragment ions already noted at *m/z* 75 (presumably formed

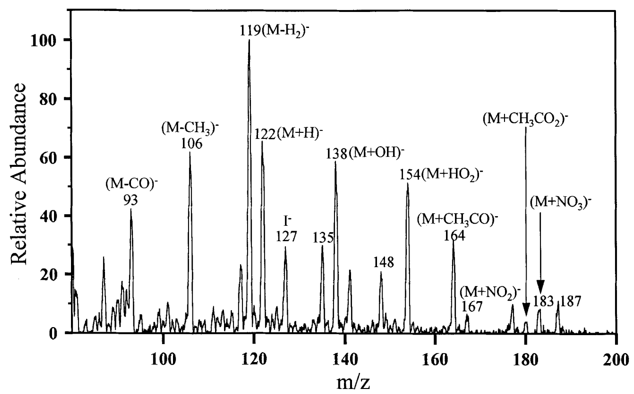


Figure 3. Ion/molecule chemistry of PAN under electron attachment conditions. The hydride addition product of PAN $[M+H]^{-}$, corresponds to *m/z* 122. Ammonia was used to mediate electron energies and so promote electron attachment.

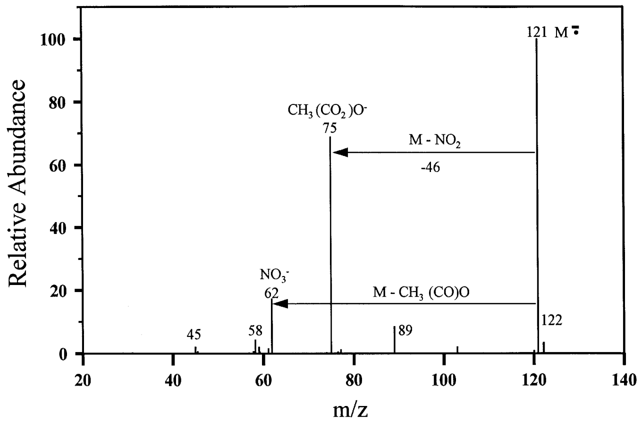


Figure 4. Collision-induced dissociation (MS/MS) spectrum of the PAN molecular radical anion $M^{-\bullet}$ (*m/z* 121). Argon was used as the collision gas and the collision energy was 24 eV.

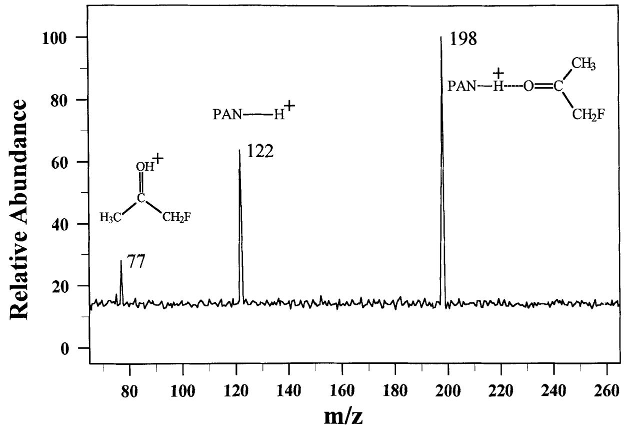


Figure 6. Collision-induced dissociation (MS/MS) spectrum of the proton-bound dimer of PAN and monofluoroacetone. Isobutane was used as the CI reagent gas. Activation was achieved with 2 eV collisions on an argon target at a nominal pressure of 0.4 mtorr.

by the loss of NO_2) and *m/z* 62 (presumably formed by the loss of CH_3CO_2 radical) while *m/z* 89 might be due to O_2 elimination. The CID spectrum of the $[M+H]^-$ ion, *m/z* 122, is also structurally diagnostic. The 30 eV argon collision gas spectrum shows *m/z* 62 (loss of acetic acid) as the dominant fragment ion. Interestingly, a parent ion scan for *m/z* 62 shows *m/z* 80 as well as the expected *m/z* 122. This suggests that acetic acid elimination may occur in two steps.

Tandem mass spectrometry is also the preferred method of examining PAN in the positive ion mode. The CID spectrum of protonated PAN generated under isobutane CI conditions (Fig. 5) shows one major fragment ion, corresponding to NO_3^+, *m/z* 62 and a minor ion, NO_2^+, *m/z* 46. The peak at *m/z* 62 corresponds to the elimination of acetic acid from $[M+H]^+$, and the peak at *m/z* 46 corresponds to the net elimination of peracetic acid. This CID spectrum demonstrates how readily and simply protonated PAN fragments.

Taken together, the results presented here demonstrate the possibility of rapid and selective PAN measurements by tandem mass spectrometry, either through fragmentation of $M^{-\bullet}$ followed by detection of *m/z* 75, or fragmentation of $[M+H]^+$, followed by detection of *m/z* 62. To maximize signal, care must be taken to control the ion/molecule reactions to which PAN is prone in both the negative ion mode and in the positive ion mode (compare Fig. 3).

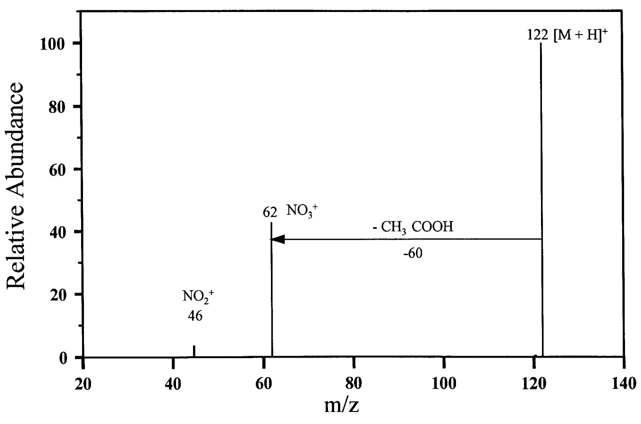


Figure 5. Collision-induced dissociation (MS/MS) spectrum of protonated PAN $[M+H]^+$ (*m/z* 122). Isobutane was used as the CI reagent gas. The collision gas used was argon and at a collision energy of 29 eV.

Proton affinity of PAN estimated by the kinetic method

In order to estimate the PA of PAN, proton-bound dimers with reference compounds of known PA were sought. Some were formed and they are readily recognized by their facile dissociation under mild CID conditions (nominal 0 to 4 eV collision energy) to give the protonated forms of the individual compounds. For example, the adduct ion generated by ionization of PAN using monofluoroacetone as the reference compound was mass-selected and dissociated by collision under very mild activation conditions. As is obvious from the product ion spectrum shown in Fig. 6 collision-induced dissociation of the cluster ion produces just two fragment ions, due to the two competing dissociation reactions shown in Eqn (2). These correspond to the protonated reference compound at *m/z* 77 and protonated PAN at *m/z* 122. This fragmentation behavior under mild activation conditions is evidence for the formation of the proton-bound dimer.[11] The fact that both monomers compete successfully for the proton requires that the PA of PAN be similar to that of monofluoroacetone.[48] This reference compound has a PA of 190.2 kcal/mol and hence the PA of PAN must be within 2 kcal/mol of this value. (Note that newly revised[48] PA values are used exclusively here.) This quantitative conclusion is based on prior measurements on many systems; if one assumes an effective temperature of 500 K (Eqn (3)) one calculates from the measured ion abundance ratio, a PA value for PAN of 191.5 kcal/mol. The PA value is better estimated from data for a number of different reference compounds. Unfortunately, only five compounds of 25 compounds (with various functional groups) studied gave proton-bound dimers with PAN. Others either failed to give adduct ions of the appropriate mass, or gave stable adducts which failed to undergo significant dissociation upon CID, or yielded covalent adducts which are discussed below. Data on the proton bound dimers and other adducts from which conclusions are drawn, are summarized in Table 1.

Acetone behaves analogously to fluoroacetone, but the higher PA of the reference compound meant that the only fragment observed upon dissociation was protonated acetone. This sets an upper limit for the PA of PAN at the value of the acetone PA, i.e. 194.1 kcal/mol. An upper limit is also provided by ethyl acetate at 199.7 kcal/mol. The 2,3-

Table 1. Product ions generated from the adducts of peroxyacetyl nitrate and various reference compounds

Reference	MW	PA[a] (kcal/mol)	Type of adduct	Diagnostic fragment ions[b]	PAN (PA)[c] (kcal/mol)
Fluoroacetone	76	190.2	PBD[d]	100%;[e] *m/z* 122 > *m/z* 77 (3.5:1)	191.5
Ethyl formate	74	191.3	PBD[f]	95%; *m/z* 75 > *m/z* 122 (10:1)	189.0
2,3-Butanedione	86	192.1	PBD[g]	30%; *m/z* 122 > *m/z* 87 (3:1)	193.2
Acetone	58	194.1	PBD	100%; *m/z* 59, no *m/z* 122	< 194.1
Ethyl acetate	86	199.7	PBD	100%; *m/z* 87, no *m/z* 122	< 199.7
Acetaldehyde	44	183.8	covalent[h]	10%; *m/z* 122 dominant[h]	> 183.8
Propionaldehyde	58	187.6	covalent	85%; *m/z* 59 ≈ *m/z* 122	≈ 187.6
Acrylonitrile	53	187.5	covalent	30%; *m/z* 122 dominant	> 187.5
Butyraldehyde	72	189.5	covalent	30%; *m/z* 73, no *m/z* 122	< 189.5
n-Butylbenzene	134	189.3	covalent	30%; *m/z* 135 > *m/z* 122	< 189.3
Nitrobenzene	123	191.1	covalent	5%; *m/z* 124> *m/z* 122 (4:3)	190.8
t-Butylalcohol	74	192.9	covalent	20%; *m/z* 75, no *m/z* 122	< 192.9
Butyronitrile	69	191.2	covalent	50%; *m/z* 70, no *m/z* 122	< 191.2
Valeronitrile	83	191.8	covalent	80%; *m/z* 84, no *m/z* 122	< 191.8
Dioxane	88	190.7	covalent	*m/z* 89 only, no *m/z* 122	< 190.7

[a] From Ref. 48.
[b] Protonated PAN and protonated reference are the diagnostic ions.
[c] Conclusion drawn from the individual measurement; uncertainty depends on the fraction of the fragment ion current in the diagnostic peak and other factors discussed in the text.
[d] PBD = proton-bound dimer.
[e] Diagnostic ions as a percentage of total fragment ions.
[f] In this case there is evidence for a contribution from a covalent isomer; there are minor ions at *m/z* 46 and 60 which make increasing contributions at higher energy.
[g] There is evidence of a contributing covalent ion.
[h] In the case of the covalent compounds, the nature and abundances of ions other than protonated PAN (*m/z* 122) and protonated reference [M+1], are not indicated explicitly.

butanedione case is interesting, since both fragments are observed and applying the 500 K assumption gives a PA for PAN of 193.2 kcal/mol. Ethyl formate also gave a proton-bound dimer, but in this case the ratio of fragment ion abundances was strongly dependent on the collision energy. The protonated ester peak had ten times the abundance of protonated PAN at 2eV and this translates to a PA for PAN of 189 kcal/mol, again making the same assumptions. Taken together, these data indicate that the PA of PAN is approximately 192 kcal/mol, with an uncertainty of about 2 kcal/mol.

In order to test this result, attempts were made to form proton-bound dimers with other compounds. Of those which gave adducts of the appropriate mass/charge ratio, ten were covalent complexes (or mixtures of loosely bound clusters and covalent complexes) which nevertheless yielded NH^+ and/or AH^+ (Eqn. (2)) on CID. The data for these compounds is included in Table 1. Note that the evidence that these were covalently bound adducts lies in the presence of other fragment ions. Figure 7 shows typical CID data for the adduct of protonated PAN and nitrobenzene, *m/z* 245. Fragmentation gives principally *m/z* 177, indicative of a covalently bound structure: however, the expected protonated monomers, *m/z* 122 and 124 are also present and are observed in low and similar abundances. This provides tentative evidence that the PA of PAN is similar to that of nitrobenzene (191.1 kcal/mol), a conclusion in agreement with the data on the proton-bound dimers. Note, however, that the abundance of the fragment ion at *m/z* 177 makes this result less reliable. In applications of the kinetic method, it is generally preferable to examine dissociations of loosely bound cluster ions.[11] The fact that many of the systems reported on in Table 1 are covalently bound is not unexpected in view of the high reactivity of protonated PAN. In other cases, strongly bound cluster ions have been used to estimate thermochemical values[25,49] and in the case of PAN they provide valuable confirmation of the estimated PA, since few proton-bound dimers could be formed. The data for these ten additional reference compounds set upper and lower limits for the PA of PAN which are consistent with the value of 191 obtained from the proton-bound dimers although the uncertainty is widened to ± 3 kcal/mol. Note that the individual measurements lead to the PAN PA values given in the last column of Table 1.

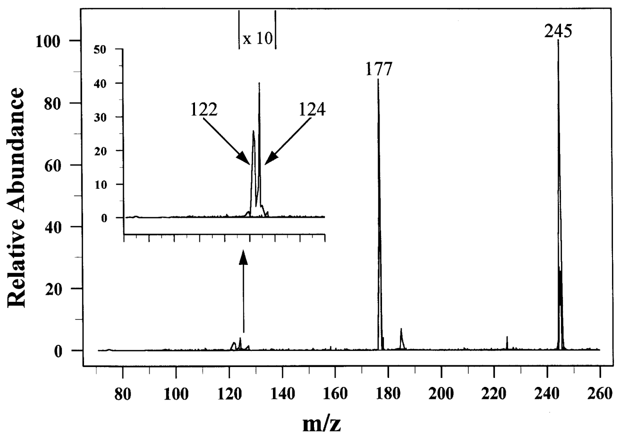
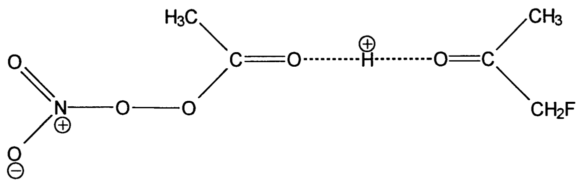


Figure 7. Collision-induced dissociation (MS/MS) spectrum of the mass-selected proton-bound dimer (*m/z* 245) of PAN and nitrobenzene. Activation was achieved with 2 eV collisions using an argon target at a nominal pressure of 0.4 mtorr.

The measurement is uncertain due to uncertainties in the literature PA values[48] (which are often 1–2 kcal/mol), the fact that reference compounds with a wide variety of functional groups were used, and because so many of the complexes were covalently bound. In other words, this is a particularly difficult case in which to apply the kinetic method. However, we have compensated for these difficulties by making measurements with a large number of reference compounds and are confident that the estimated PA is correct, within the estimated 3 kcal/mol uncertainty.

The estimated proton affinity for PAN is higher than the values reported in the literature for the esters of nitric acid[50] and related compounds[50,51] which are in the range 175–177 kcal/mol. On the other hand, it is similar to the values for carbonyl compounds such as formate esters. The most electronegative site in PAN is therefore probably the carbonyl oxygen. This makes it likely that the proton binds there. A possible structure of the proton-bound dimer is shown in the case of fluoroacetone as structure **II.** CID of the proton-bound dimer of PAN and ethyl acetate gives exclusively the protonated monomer of ethyl acetate (PA = 199.7 kcal/mol, see Table 1). This observation indirectly supports the assumption that **II** is a likely structure of the proton-bound dimer of PAN and monofluoroacetone. Structures in which binding is through the nitro group are possible but less likely given the low PA values for nitrate esters



II

This study has demonstrated that PAN can be monitored using positive or negative ion mass spectrometry with sample introduced by MIMS. This capability has been applied to the estimation of its PA. Future work will focus on the use of MIMS to perform trace analysis of PAN but no estimates on the sensitivity or detection limits of the MIMS method are yet available. However, the response times are appropriately short (less than 1 minute) for application to atmospheric monitoring and the method clearly provides very high specificity, especially if tandem mass spectrometry is used.

Acknowledgement

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