Organic peroxy radicals (ROO) play an integral role in the chemistry of the troposphere. These radicals are formed as a result of OH-initiated oxidation of volatile organic compounds (RH) emitted from biogenic and anthropogenic sources; this process efficiently removes hydrocarbons from the atmosphere and serves as an important sink for the OH radical. Once formed, alkyl radicals (R) rapidly combine with O₂ via a three-body reaction to produce organic peroxy radicals.

\[
\text{RH} + \text{OH} \rightarrow \text{R} + \text{H₂O} \quad (1)
\]

\[
\text{R} + \text{O₂} + \text{M} \rightarrow \text{ROO} + \text{M} \quad (2)
\]

Peroxy radicals react with the NO_x and HO_x radical families. In urban areas, reactions with NO_x species dominate. By oxidizing NO to NO₂, peroxy radicals directly influence tropospheric ozone formation, since the photolysis of NO₂ forms O(3P), which rapidly reacts with O₂ to form O₃ in the sequence shown below.

\[
\text{ROO} + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad (3)
\]

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}(3\text{P}) \quad (4)
\]

\[
\text{O}(3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (5)
\]

In areas of low NO_x, organic peroxy radicals primarily react with other peroxy radicals (mainly HOO), propagating chain reactions that eventually lead to the removal of radicals from the atmosphere.

Keywords: acyl peroxy radical, acyl peroxide, peroxyacetyl radical, peroxyacetic acid, photoelectron spectroscopy, FA-SIFT, negative ion cycle, bond dissociation energy, atmospheric chemistry, peroxyacetyl nitrate
Due to their significance in atmospheric chemistry, the structure and thermochemistry of these radicals is of great interest. In particular, the peroxyacetyl radical \( \text{CH}_3\text{C(O)OO} \) is one of the most abundant peroxy radicals in the atmosphere. In polluted environments, this radical reacts with \( \text{NO}_2 \) to form peroxyacetyl nitrate [PAN].\(^6,7\)

\[
\text{CH}_3\text{C(O)OO} + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{C(O)OONO}_2 + \text{M} \tag{6}
\]

PAN is a key component in photochemical smog, it is a respiratory and eye irritant, and can damage vegetation. Due to its stability relative to other peroxynitrates, PAN acts as a temporary reservoir for \( \text{NO}_2 \) species and can undergo long-range transport from areas of high pollution to areas of low pollution, where subsequent thermal decomposition releases the reactive radicals.

The IR spectrum of the peroxyacetyl radical has been reported in a noble gas matrix from the flash thermolysis of PAN.\(^8\) The primary decomposition pathway of PAN was shown to occur by O–N bond fission regenerating the peroxyacetyl radical: \( \text{CH}_3\text{C(O)OOONO}_2 + \text{A} \rightarrow \text{CH}_3\text{C(O)OO} + \text{NO}_2 \). The resulting IR features were attributed to two stable conformers of the peroxyacetyl radical defined by the OCOO dihedral angle.

\[
\begin{array}{c}
\text{cis} \\
\text{trans}
\end{array}
\]

The \textit{trans}-structure is slightly more stable than the \textit{cis}-structure. Therefore, by changing the thermolysis temperature and, hence, the intensity ratio of the two sets of IR bands, spectral features corresponding to both the \textit{cis}- and \textit{trans}-conformers were assigned.

Several spectroscopic and kinetic studies have probed the strong UV \( \tilde{B} \rightarrow \tilde{X} \) transition in the peroxyacetyl radical.\(^9\text{-}13\) However, due to the repulsive nature of the \( \tilde{B} \) state, this transition is broad and featureless, providing few structural details.\(^2\) In contrast, the low-lying \( \tilde{A} \rightarrow \tilde{X} \) transition displays rotational and vibrational structure; however, due to its relatively small absorption cross-section, this transition requires use of sensitive spectroscopic techniques. Zalyubovsky \textit{et al.}\(^14\) recorded the gas-phase absorption spectrum of the peroxyacetyl radical produced from photolysis of \( \text{[COCl]}_2 \) in a \( \text{CH}_3\text{CHO} / \text{O}_2 / \text{N}_2 \) mixture using cavity ring-down spectroscopy. More recently, Hu \textit{et al.}\(^15,16\) employed near-IR/VUV ion enhancement spectroscopy to record the spectrum of peroxyacetyl radical produced from the thermal decomposition of PAN in a pyrolysis/supersonic pulsed nozzle. The results of these experiments are in excellent agreement with one another. The vibronic features were found to correspond to the \textit{trans}-conformer of the radicals, the \( \tilde{A} \rightarrow \tilde{X} \) term energy splitting was determined to be \( 5582.5 \pm 0.5 \text{ cm}^{-1} \) and several \( \tilde{A} \) state vibrational modes were identified.

Previously, we have employed negative ion spectroscopy and gas-phase ion–molecule reactivity studies to investigate several peroxy radicals,\(^17\text{-}24\) including \( \text{HOO}, \text{CH}_3\text{OH}, \text{CH}_2\text{CH}_2\text{OH}, \text{ICH}_2\text{I} \text{COO}, \) and most recently the peroxyformyl radical, \( \text{HCO} \text{O} \text{O} \). Negative ion spectroscopy provides thermodynamic information such as electron affinities (EA) and term energies \( (T_e) \), allows for the measurement of vibrational frequencies, and gives insight into the molecular structure of radical species as well as the corresponding anion. Gas-phase ion–molecule reactivity studies are used to determine the gas-phase acidity of the corresponding peroxy acid relative to that of a reference acid. These techniques are complementary, since the electron affinity of the radical can be combined with the gas-phase acidity to determine the bond dissociation energy using a negative ion thermochemical cycle.\(^25\text{-}28\)

Our recent study of the peroxyformyl radical\(^24\) is particularly relevant to the peroxyacetyl radical and highlights several important differences in the thermochemistry of acylperoxy [RC(O)OO] versus alkyperoxy [ROO] radicals. For example, the EA of peroxyformyl radical was found to be \( 2.493 \pm 0.006 \text{ eV} \), which is considerably higher than that of an alkyl peroxy radical, which ranges from 1.0–1.2 eV.\(^17,18,20\) The greater EA of the peroxyformyl radical is due to the electron withdrawing effects of the carbonyl group which stabilizes the corresponding anion. The photoelectron spectrum displays extended, partially resolved progressions in the O–O and C–OO stretching modes of the ground state of the \( \tilde{A} \)-radical, consistent with the delocalization of the negative charge in the anion across the OCOO backbone. Another important difference in the thermochemistry of the peroxyformyl radical is the significantly larger O–H bond dissociation energy of the corresponding acid; \( D_0(\text{cis-per oxy formic acid}) = 406 \pm 14 \text{ kJ mol}^{-1} \). Typically O–H bond dissociation energies of peroxy alcohols\(^17,18,20\) range from 350–364 kJ mol\(^{-1}\). This greater bond strength is attributed to two factors: (1) the strong intramolecular hydrogen bond that is formed between the acyl peroxy hydrogen atom and the carbonyl oxygen atom and (2) a reduction in the repulsive interaction between the O–H bonding orbital and lone pair of electrons on the neighboring oxygen atom through electron back-bonding effects.

In this work, we report the negative ion photoelectron spectrum of the peroxyacetate anion [CH\(_3\)C(O)OO\(^{−}\)]. This technique provides access to the two lowest electronic states of the peroxyacetyl radical through photodetachment of an electron from the corresponding anion. Analysis of the kinetic energy of the detached electron allows for the determination of the EA as well as the \( \tilde{A} \rightarrow \tilde{X} \) \( T_e \) of the peroxyacetyl radical. Additionally, the gas-phase acidity of peroxyacetic acid was measured using an ion–molecule bracketing technique and these measurements are used to determine the O–H bond dissociation energy. Electronic structure calculations provide additional insight into the structural and energetic aspects of the peroxy ion, the radical and the parent acid. The thermochemical values determined here are compared to those of the peroxyformyl radical and the atmospheric implications of these results are briefly discussed in relation to the thermochemistry of peroxyacetyl nitrate [PAN].
Experimental details

Negative ion photoelectron spectroscopy

These studies were carried out with an anion photoelectron spectrometer that has been described in detail elsewhere.\textsuperscript{20,29,30} The peroxyacetate anion, \( \text{CH}_3\text{C(O)OO}^- \), was generated in a flowing afterglow source\textsuperscript{20} through a series of ion–molecule reactions that occur downstream from a microwave discharge source forming \( 0^- \) anions.

\[
\text{O}^- + \text{H}_2\text{C} \rightarrow \text{H}_2\text{C} + \text{OH}^- \quad (7)
\]

\[
\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HOO}^- \quad (8)
\]

\[
\text{HOO}^- + \text{CH}_3\text{C(O)OR} \rightarrow \text{CH}_3\text{C(O)OR} + \text{OH}^- \quad (9)
\]

The final reaction step utilizes either methyl acetate \( [\text{CH}_3\text{C(O)}\text{OCH}_2\text{CF}_2\text{H}] \), ethyl acetate \( [\text{CH}_3\text{C(O)}\text{OCH}_2\text{CH}_3] \), or 2,2-difluoroethyl acetate \( [\text{CH}_3\text{C(O)}\text{OCH}_2\text{CH}_2\text{F}_2] \). Due to the large number of collisions in the source region \((0.5\text{torr}; \, 3\text{–}10\text{ms residence time})\), ions are prepared with an approximate 298K rotational and vibrational Maxwell–Boltzmann distribution. Negative ions are gently extracted from the source region and passed though a Wien filter for mass selection. The mass selected ion beam is then crossed with a 351.1 nm \((3.531\text{eV})\) line from a cw argon laser in an external build-up cavity producing roughly 100W of circulating power. Photoelectrons that are ejected perpendicular to the ion and photon beams into a small solid angle are analyzed by a hemispherical kinetic energy analyzer coupled to a position-sensitive detector. Spectra are obtained by measuring the photoelectron counts as a function of electron kinetic energy \( (\epsilon\text{KE}) \). The energy scale is converted to electron binding energy \( (\epsilon\text{BE}) \) by subtracting the electron kinetic energy from the photon energy.

The absolute energy scale is calibrated with the well-known electron affinity of the sulfur atom\textsuperscript{31} and a linear energy scale electron binding energy \( (\epsilon\text{BE}) \) by subtracting the electron energy resolution in these experiments is \( 12–15\text{meV} \); however, the electron binding energy corresponding to an isolated transition can easily be determined to an accuracy of \( \pm 5\text{meV} \). If that peak is associated with the transition from the ground state of the anion to the ground state of the neutral, the corresponding EA can be determined with similar accuracy. Although the presence of unresolved structure reduces the accuracy of the experimental result, Franck–Condon modeling of the full spectrum still allows quantitative assessments of the experimental error in the binding energy measurements.

Angular distribution measurements at a given electron kinetic energy were conducted by changing the angle \((\theta)\) between the electric field vector of the laser beam and the photoelectron collection axis. Photoelectrons have an angular distribution according to the expression,\textsuperscript{22}

\[
\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{peak}}}{4\pi} [1 + \beta (\epsilon\text{KE}) P_2 (\cos\theta)] \quad (10)
\]

where \( \sigma_{\text{peak}} \) is the total photodetachment cross section, \( \beta \) is the anisotropy parameter and \( P_2 (\cos\theta) \) is the second Legendre polynomial. Spectra collected at the magic angle \((\theta = 54.7^\circ)\) provide intensities that are free from angular dependence. Spectra collected at \( \theta = 0^\circ \) and \( \theta = 90^\circ \) allow for determination of the anisotropy parameter.\textsuperscript{30}

Flowing afterglow-selected ion flow tube (FA-SIFT) measurements

The gas-phase acidity \( (\Delta G_{298}) \) of peroxyacetic acid was determined using a tandem flowing afterglow-selected ion flow tube instrument, which has been described in detail previously.\textsuperscript{33} An ion–molecule bracketing technique\textsuperscript{34} was employed. In this method, the peroxyacetate ion is allowed to react with several reference acids \( (\text{AH}) \) of known acidity. If rapid proton transfer is observed, then the reference compound is a stronger acid than the peroxyacetic acid \( (\Delta G_{298}(\text{AH}) > \Delta G_{298}(\text{CH}_3\text{C(O)OOH})) \). If proton transfer is not observed then the reference compound is a weaker acid than the peroxyacetic acid \( (\Delta G_{298}(\text{AH}) < \Delta G_{298}(\text{CH}_3\text{C(O)OOH})) \). The occurrence or non-occurrence of proton transfer with a series of reference acids places an upper and lower bound on the acidity of the peroxyacetic acid. The gas-phase acidity is the free-energy change for heterolytic bond cleavage, \( \text{AH} \rightarrow \text{A}^- + \text{H}^+ \). Less energy is required to remove a proton from a stronger acid than from a weaker acid; thus, stronger acids have smaller free energy changes than do weaker acids. The enthalpy of deprotonation \( (\Delta H_{298}) \) can be found from Equation \((11)\) where \( \Delta S_{298} \), the entropy of deprotonation, is estimated from electronic structure calculations.

\[
\Delta H_{298}(\text{CH}_3\text{C(O)OOH}) = \Delta G_{298}(\text{CH}_3\text{C(O)OOH}) + \Delta S_{298}(\text{CH}_3\text{C(O)OOH}) \quad (11)
\]

The peroxyacetate anion was formed in a flowing afterglow source using the same synthesis scheme as in the above photodetachment study. Negative ions were extracted from the source region and focused into a quadrupole mass filter, which transmits one specific mass-to-charge ratio ion. The mass selected ion beam was injected into a reaction flow tube where the ions undergo multiple collisions with the He buffer gas \((0.5\text{torr} \, 10\text{ms residence time})\) resulting in an approximate 298K rotational and vibrational Maxwell–Boltzmann distribution. A measured flow of the neutral reference acid was introduced into the reaction flow tube at various distances through a manifold of inlets. The intensities of the reactant and product ions were measured using a triple quadrupole mass filter coupled to an electron multiplier as a function of reaction time. Neutral reactant flow rates were measured by monitoring the pressure change versus time in a calibrated volume system.

Despite injecting the peroxyacetate anions into the reaction flow tube with minimal energy, fragment ions due to collision-induced dissociation are also present in the reaction flow tube. Since the basicity of some of these fragment ions is greater than that of the peroxyacetate anion, the deprotonated reference acid was observed, even when it is a weaker acid than peroxyacetic acid. Additionally, depletion of the peroxyacetate
anion was also generally observed, since it reacts by neutral oxygen atom transfer. In order to determine whether proton transfer occurs between the peroxyacetate anion and the reference acid, the intensities of all ions were monitored as a function of time and the contribution from the fragment ions to the deprotonated reference acid signal was removed.

Electronic structure calculations
Two theoretical approaches, both provided in the Gaussian 03 suite of programs, were used to evaluate various structural and energetic aspects of the peroxyacetate anion as well as the corresponding radical and protonated species. Optimized geometries, harmonic vibrational frequencies (unscaled), and the rotational constants were calculated using the B3LYP/6-311++G(d,p) level of theory. This level of theory was chosen since it has been shown to produce reliable structures for this class of molecules. Two theoretical approaches, both provided in the Gaussian 03 suite of programs, were used to evaluate various structural and energetic aspects of the peroxyacetate anion as well as the corresponding radical and protonated species. Optimized geometries, harmonic vibrational frequencies (unscaled), and the rotational constants were calculated using the B3LYP/6-311++G(d,p) level of theory. This level of theory was chosen since it has been shown to produce reliable structures for this class of molecules. The G3MP2B3 composite technique was used to investigate various thermodynamic properties of these species. In this technique, geometries and zero point energies are calculated at the B3LYP/6-31G(d) level of theory followed by a series of well-defined \textit{ab initio} single-point energy calculations. This method has been tested on a variety of hydrocarbons, and the average deviation from experiment was reported to be 5 kJ mol\(^{-1}\). Independent evaluation of this method on a series of oxygenated species that are similar in structure to the peroxyacetyl radical suggest a slightly higher deviation of 6 kJ mol\(^{-1}\). Simulated photoelectron spectra were obtained by calculating the Franck–Condon (FC) factors at a vibrational temperature of 298 K using the PESCAL program. These simulations are based on the B3LYP/6-311++G(d,p) optimized geometries and normal modes for the anion and corresponding radical species, while electron binding energies are determined from the G3MP2B3 calculations.

Results and discussion
Photoelectron spectra of the peroxyacetate anion

Figure 1(a) shows the 351.1 nm magic angle photoelectron spectrum of the \(m/z\) 75 ion produced from the reaction of HOO\(^{-}\) with ethylacetate. The same spectral profile is observed when the \(m/z\) 75 ion is produced from the reaction of HOO\(^{-}\) with methylacetate and with 2,2-difluoroethylacetate. The anisotropy parameter \(\beta\) was measured and is negative across the entire spectrum, consistent with photodetachment from a \(\pi\)-type orbital. Since this ion is produced from an analogous set of reactions as was the peroxymate anion in our previous studies, it is likely that the \(m/z\) 75 ion is the peroxyacetate anion. However, because there is more than one acidic site in peroxyacetic acid, one must consider whether or not deprotonation can also occur at the methyl group to form the hydrogenperoxide ethylenolate anion [CH\(_2\)C(O\(^{-}\))OOH] as shown below. Although deprotonation at the OO–H-site is favored thermodynamically (by ~ 20 kJ mol\(^{-1}\)), such lack of selectivity has previously been reported in the deprotonation of acetic acid.\(^{41}\)
In order to confirm the identity of the observed spectrum, Franck–Condon simulations were performed. Analogous to the peroxyformate anion,26 there are two conformations of the peroxyacetate anion (see Table 1). While the trans-conformer is predicted to be 24 kJ mol\(^{-1}\) more stable than the cis-conformer, the two structures are separated by a significant isomerization barrier (70 kJ mol\(^{-1}\)), which could potentially trap some of the anion population in the higher energy cis-conformation. Thus, spectral simulations were performed for both the trans- and cis-conformations of the peroxyacetate ion as well as for the hydrogenperoxide ethyleneolate ion. These results are summarized in Figure 1(b)–1(d), where the individual vibronic transitions (sticks) are convoluted with a 13 meV FWHM Gaussian function [solid line], which represents the instrument resolution.

The simulated profile for the hydrogenperoxide ethyleneolate anion [Figure 1(d)] is inconsistent with the observed spectrum and, therefore, the formation of this isomer is excluded. As mentioned above, the trans-conformation is the lowest energy isomer of the peroxyacetate anion and indeed this simulation [Figure 1(b)] is in good agreement with the experiment, reproducing the lower binding energy portion (< 2.8 eV) of the spectrum quite well. The simulation for the cis-conformation of the peroxyacetate anion [Figure 1(c)] clearly does not agree with the experimental spectrum. However, since this profile is broad and featureless, it is difficult to exclude all contribution of this conformer from the observed spectrum and, in fact, the cis-anion may account for some of the intensity seen at lower binding energies to peak a (< 2.3 eV). However, if the cis-conformer is present, it is in minor amounts.

The simulation for the trans-peroxyacetate anion reproduces the lower binding energy portion of the observed spectrum quite well; however, it does not account for the sharp intense peaks at higher binding energy [shown as peaks b, c, and d in Figure 1(a)]. These peaks are likely due to photodetachment to the \(X^2A^+\) excited state of the trans-peroxyacetyl radical. To confirm this assignment, the Franck–Condon factors for the transition from the \(X^2A^+\) state of the trans-peroxyacetate radical to both the \(X^2A^+\) and \(X^2A^-\) states of the corresponding radical were computed and are shown in Figure 2. The sticks correspond to the individual vibronic transitions to the two states of the radical, while the lower trace results from convoluting those individual transitions with a 13 meV FWHM Gaussian function. The calculated electron affinities for both the ground and excited states of the radical have been slightly shifted (< 20 meV) and the intensities normalized to match the experimental spectrum. The excellent quality of the simulation is apparent, especially when one considers the multitude of transitions that contribute to the observed spectrum.

The \(EA\) of the trans-peroxyacetyl radical is determined to be 2.381 ± 0.007 eV, which corresponds to peak a in Figure 2. This assignment is in exact agreement with the G3MP2B3 calculated value. The broad features observed at higher binding energies represent excited vibrational levels of the \(X^2A^+\) state of the trans-peroxyacetyl radical. The presence of the methyl group at the carbonyl center leads to more complication and congestion in the ground state vibrionic features when compared to the rather simple peroxyformate anion spectrum, which is composed of extended, partially resolved progressions in the O–O and C–OO stretching modes.25 Five modes are activated upon electron photodetachment of the peroxyacetate anion: the O–O stretch \(\nu_{\perp}\), C–OO stretch \(\nu_{\parallel}\), CCOO backbone deformation \(\nu_{\parallel}\), OCO bend \(\nu_{\perp}\) and CCOO breathing motion \(\nu_{\perp}\). The frequencies of these modes have previously been determined using matrix isolation IR spectroscopy (see Table 2).8 Similar to the peroxyformyl radical, the frequencies of the O–O and C–OO stretches are within 130 cm\(^{-1}\) of each other and, therefore, are only partially resolvable with our instrument resolution. This, combined

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**Table 1.** Relative energies (kJ mol\(^{-1}\)) of the trans- and cis-conformers (going from the trans- to the cis-structure) calculated at the G3MP2B3 level of theory.

<table>
<thead>
<tr>
<th></th>
<th>(\Delta E)</th>
<th>(\Delta_{2p}GE)</th>
<th>(\Delta_{2p}GH)</th>
<th>(E^\dagger (E + E_{\text{esp}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)C(O)OOH</td>
<td>-21.9</td>
<td>-22.0</td>
<td>-22.9</td>
<td>35.8</td>
</tr>
<tr>
<td>CH(_3)C(O)OO~ (X^2A^+)</td>
<td>23.8</td>
<td>23.1</td>
<td>24.2</td>
<td>71.2</td>
</tr>
<tr>
<td>CH(_3)C(O)OO~ (X^2A^-)</td>
<td>2.9</td>
<td>1.2</td>
<td>3.4</td>
<td>24.5</td>
</tr>
</tbody>
</table>

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**Figure 2.** The 351.1 nm magic-angle photoelectron spectrum of the peroxyacetate anion reproduced from Figure 1(a) is shown as the upper trace. Franck–Condon factors are shown for transitions from \(X^2A^+\) peroxyacetate anion to \(X^2A^+\) (sticks) and \(X^2A^-\) (sticks at b, c and d) states of peroxyacetyl radical. The lower trace results from convoluting the stick spectra with a 13 meV FWHM Gaussian function. The energy scale for the simulation is shifted (< 20 meV) and intensities normalized to correspond to the experimental spectrum.
Photoelectron Spectroscopy and Thermochemistry of the Peroxyacetate Anion

with the extensive combination band progressions in the COO backbone deformation and O–O stretch, adds to the complexity of the spectrum.

The intense narrow peaks appearing at higher electron binding energies are due to photodetachment to the low-lying $A'_{2A'}$ electronic state of the radical. There have been two prior independent measurements of the $A'_{2A'} ← X'_{2A''}$ transition in the trans-CH$_3$C(O)OO radical; the splitting between the two states has been accurately determined to be $0.69214 ± 0.00006$ eV. This energy splitting, relative to peak $a$, corresponds to peak $b$, which is assigned as the $A'_{2A'}$ electronic band origin. Thus, the $A' ← X'$ transition is determined to be $0.691 ± 0.009$ eV, which is in good agreement with two previous measurements and with the G3MP2B3 calculated value of $0.70$ eV. The peaks at higher binding energies, peaks $c$ and $d$, are the fundamental and first overtone of the O–O stretch ($\nu_7$); the frequency of this mode is determined to be $916 ± 45$ cm$^{-1}$.

Gas-phase acidity measurements

Since the peroxyacetic acid reagent is not available in pure form, the gas-phase acidity of this compound was determined using an ion–molecule bracketing technique rather than a proton transfer equilibrium technique. This bracketing method allows for the determination of the gas-phase acidity of a compound through the examination of the occurrence, or non-occurrence, of proton transfer with several acids. In this manner, the acidity of the compound can be placed between two known acidity values with an error bar that spans the difference in values.

The gas-phase acidity of peroxyacetic acid was bracketed against five reference acids: formic acid ($1417 ± 2$ kJ mol$^{-1}$), acetic acid ($1428 ± 2$ kJ mol$^{-1}$), hydrogen sulfide ($1443.0 ± 0.1$ kJ mol$^{-1}$), tert-butylthiol ($1451 ± 2$ kJ mol$^{-1}$) and ethanethiol ($1461 ± 2$ kJ mol$^{-1}$). Proton transfer was not observed in the reactions of peroxyacetate anion with tert-butylthiol and ethanethiol; instead, these reactions proceed via neutral oxygen–atom loss to form the acetate anion. Proton transfer was observed in the reactions of formic acid and acetic acid. For the latter reaction, the occurrence of proton transfer was confirmed by evaluating the reaction with acetic acid-$d_3$, CD$_3$C(O)OH, where the formation of m/z 62, instead of m/z 59, is consistent with proton transfer. The reaction with hydrogen sulfide produces small amounts of the proton transfer product in addition to the oxygen–atom transfer product, suggesting that this reaction is slightly endothermic. Thus, the acidity of peroxyacetic acid is determined to be between that of acetic acid and tert-butylthiol at $\Delta aG_{298} = 1439 ± 14$ kJ mol$^{-1}$.

It has previously been shown using microwave spectroscopy that the lowest energy structure of peroxyacetic acid is
a cis-planar structure, where a strong intramolecular hydrogen bond exists between the peroxy hydrogen atom and the carbonyl oxygen atom.\(^{44}\) Rotation about the OCOO dihedral angle by 180° gives a higher energy trans-conformation, where the peroxy hydrogen atom points out of the plane of symmetry.

Using G3MP2B3 theory, we have calculated the relative energetics of these two conformers; these results are summarized in Table 1. At this level of theory, the trans-conformer is predicted to be approximately 23 kJ mol\(^{-1}\) higher in energy than the cis-conformer; a barrier of about 36 kJ mol\(^{-1}\) (trans to cis) separates the two structures. Although this isomerization barrier height is less than a typical ion–dipole complexation energy (60–80 kJ mol\(^{-1}\)),\(^{45}\) proton transfer is generally barrier-less and, therefore, proton transfer rather than isomerization is expected to occur. Since the anion exists in the trans-conformation, protonation initially forms the higher energy cis-conformer, where the peroxy hydrogen atom and the carbonyl oxygen atom is believed to be trapped in the higher energy trans-planar structure, where a strong intramolecular hydrogen bond exists between the peroxy hydrogen atom and the carbonyl oxygen atom.\(^{44}\) Rotation about the OCOO dihedral angle by 180° gives a higher energy trans-conformation, where the peroxy hydrogen atom points out of the plane of symmetry.

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Application of Equation (17) yields $\Delta H_{298}^{\circ}[\text{trans-CH}_2\text{Cl}(00)] = -158 \pm 14$ kJ mol$^{-1}$. Table 3 compares the thermochemical parameters for the peroxyacetyl radical and peroxyacetic acid determined in this study to our recently published values for the peroxyformyl radical and peroxyformic acid.24 The thermochemical parameters for these two peracids are similar to one another. While the $E_A$ of the peroxyacetyl radical is slightly lower than that of the peroxyformyl radical, the gas-phase acidities of peroxyacetic acid and peroxyformic acid are the same within our experimental error. Moreover, the O–H bond dissociation energies and heats of formation at 0 and 298 K for the cis- and trans-conformers of both peroxyacetic acid and peroxyformic acid are presented in Figure 3.

**Atmospheric and environmental implications**

The unexpected bond strengths of organic peracids, roughly 400 kJ mol$^{-1}$ [see Figure 3], sheds light on several problems in the atmospheric and environmental processing of aldehydes.

It is well known that samples of aldehydes that have been exposed to air are rapidly contaminated by carboxylic acids: RCHO + “air” $\rightarrow$ RC(O)OH. This is known to be a radical chain process in solution that is initiated by a radical abstraction from the aldehyde. A radical chain then ensues.

RCHO + radical $\rightarrow$ RC(O)I [18(a)]

RC(O)I + O$_2$ $\rightarrow$ RC(O)OO [18(b)]

RC(O)OO + RCHO $\rightarrow$ RC(O)OOH + RC(O) [18(c)]

Over time, the air oxidizes the aldehyde to a peracid. The peracid subsequently destroys the aldehyde via a Baeyer-Villiger oxidation:

\[
\text{RC(O)OO + H}_2\text{O} \rightarrow \text{RC(O)OH + O}_2
\]

The bond strength$^{26}$ of an aldehyde, $D_{298}[\text{RC(O)--H}]$, is about 370 kJ mol$^{-1}$ while that of a peroxyalcohol, $D_{298}[\text{ROO--H}]$, is approximately 350 kJ mol$^{-1}$. Consequently, step [18(c)] is roughly 20 kJ mol$^{-1}$ endothermic. However, the experimental bond energies in Figure 3 change the thermochemistry of [18(c)]. Our measured value for $D_{298}[\text{cis-CH}_2\text{Cl}(000)\rightarrow\text{trans-CH}_2\text{Cl}(000)\rightarrow\text{H}]$ of 408 $\pm$ 14 kJ mol$^{-1}$ now makes the H atom abstraction exothermic by about 38 kJ mol$^{-1}$.

In the atmosphere, a common fate of aldehydes is oxidation by OH radical to generate acyl radicals. These acyl radicals rapidly combine with oxygen to produce peroxyacetyl radicals.50,51

### Table 3. Thermochemical parameters.

<table>
<thead>
<tr>
<th>Peroxyacetyl radical and peroxyacetic acid</th>
<th>Peroxyformyl radical and peroxyformic acid$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_A[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$2.381 \pm 0.007$ eV</td>
</tr>
<tr>
<td>$T_e [\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$0.69214 \pm 0.00006$ eV</td>
</tr>
<tr>
<td>$\Delta G_{298}[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$1439 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta G_{298}[\text{cis-CH}_2\text{Cl}(00)]$</td>
<td>$1461 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H_{298}[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$1467 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H_{298}[\text{cis-CH}_2\text{Cl}(00)]$</td>
<td>$1490 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta_{298}[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$381 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta_{298}[\text{cis-CH}_2\text{Cl}(00)]$</td>
<td>$403 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta G_{298}[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$2.493 \pm 0.006$ eV</td>
</tr>
<tr>
<td>$T_e [\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$0.783 \pm 0.006$ eV</td>
</tr>
<tr>
<td>$\Delta G_{298}[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$1439 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta G_{298}[\text{cis-CH}_2\text{Cl}(00)]$</td>
<td>$1451 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H_{298}[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$1469 \pm 14$ kJ mol$^{-1}$</td>
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<tr>
<td>$\Delta H_{298}[\text{cis-CH}_2\text{Cl}(00)]$</td>
<td>$1483 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta_{298}[\text{trans-CH}_2\text{Cl}(00)]$</td>
<td>$393 \pm 14$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta_{298}[\text{cis-CH}_2\text{Cl}(00)]$</td>
<td>$406 \pm 14$ kJ mol$^{-1}$</td>
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</table>

$^a$All energy changes correspond to formation of the trans-conformation of the anion or radical, which are the most stable forms.24 Zalyubovsky 17,18,20,25 $T_e=0.691 \pm 0.009$ eV, this work; Bracketed between the acidity of acetic acid and tert-butylthiol; Determined from the acidity of trans-peroxy acid and the calculated energy difference between cis- and trans-conformers; Calculated from the corresponding $\Delta G_{298}$ and $\Delta S_{298}$. Calculated using the $E_A$, $\Delta H_{298}$, IE[H].24 Willano et al.24
In the case of formaldehyde, the resulting peroxyformyl radical is chemically-activated by 138 ± 14 kJ mol⁻¹; this exothermicity is determined as the difference in the heats of formation of the *trans*-peroxyformyl radical and the formyl radical.

Oxidation of acetaldehyde by OH / O₂ yields peroxyacetyl radicals that are chemically-activated as well. For *trans*-CH₃C(O)OO, the internal excitation can be calculated to be approximately 11,500 cm⁻¹ and can rearrange to CO + HOO. Therefore, the peroxyformyl radical is internally excited by approximately 11,500 cm⁻¹ and can rearrange to CO + HOO.

Figure 3. (a) Thermochemistry of peroxyacetic acid at 0 and 298 K. The heat of formation of peroxyacetic acid is calculated at the G3MP2B3 level of theory ([Equation (16)]). The bond dissociation energies are experimentally determined here ([Equation (14)]; a small energy correction is applied to the bond dissociation energy for cis-CH₃C(O)OOH → trans-CH₃C(O)OO + H and for cis-CH₃C(O)OOH → cis-CH₃C(O)OO + H (see text). The heat of formation of the peroxyacetyl radical is determined from the heat of formation of peroxyacetic acid and the corresponding bond dissociation energy ([Equation (17)]). (b) Thermochemistry of peroxyformic acid (Villano et al.²⁴) at 0 and 298 K.
The rate constants, $k_{23}$ and $k_{2-23}$, were measured to find $K_{aq}$.[23]. From the temperature dependence of the equilibrium constant, the enthalpy change is commonly determined by the van’t Hoff Equation. However because of the narrow temperature range, $\Delta_{\text{tr}} H_{298}[23]$, was determined by the third law method.[25] This approach uses a single value of the $K_{aq}$ and relies on equilibrium statistical mechanics to calculate the entropy change. Since the structural parameters of the reactants and products (vibrational frequencies and moments of inertia) can be estimated, their absolute entropy and the entropy of the reaction $\Delta_{\text{tr}} S_{298}$ were calculated. The enthalpy of reaction $^{54}$ was found to be $\Delta_{\text{tr}} H_{298}[23] = 118.8 \pm 4.0$ kJ mol$^{-1}$ and $\Delta_{\text{tr}} S_{298}[23] = 115.1 \pm 4.0$ kJ mol$^{-1}$.

We can use the thermochemistry of CH$_3$C(O)OO in Figure 3, together with known$^{46}$ properties of NO$_2$, NO$_3$, and CH$_3$C(O)O, to deduce the energetics of PAN.

$$\Delta_{\text{tr}} H_{298}[\text{CH}_3\text{C(O)OONO}_2] = \Delta_{\text{tr}} H_{298}[\text{trans-CH}_3\text{C(O)OO}] + \Delta_{\text{tr}} H_{298}[\text{NO}_2]$$

Evaluation of Equation (24) yields $\Delta_{298}[\text{CH}_3\text{C(O)O + NO}_3] = -243 \pm 15$ kJ mol$^{-1}$. The heat of formation of PAN can be used to find the threshold for the formation of the oxyacetyl and nitrate radicals.

$$\Delta_{\text{tr}} H_{298}[\text{CH}_3\text{C(O)OONO}_2] = -243 \pm 15$ kJ mol$^{-1}$

The $\Delta_{\text{tr}} H_{298}[25]$ is evaluated as ≤ 142 ± 15 kJ mol$^{-1}$ or 11,850 cm$^{-1}$. This would correspond to a photodissociation threshold of $\lambda_{\text{onset}} \approx 844$ nm.

It is instructive to compare these thermochemical results for PAN with those resulting from electronic structure calculations. Two important papers$^{8,53}$ use the CBS-Q and B3LYP/6-311G(d,p) methods to calculate the heats of formation of PAN as well as for the trans-CH$_3$C(O)OO and CH$_3$C(O)O radicals. These papers also calculate the reaction enthalpies for PAN. Table 4 presents a comparison of the experimental values with these computational values. It is important to recognize that this experimental study and the CBS-Q calculation of $\Delta_{\text{tr}} H_{298}[\text{trans-CH}_3\text{C(O)OO}]$ are anchored to the experimental value for this dissociation energy.$^{54}$ The experimental uncertainties are largely determined by the bracketing technique that was required to measure the $\Delta_{\text{tr}} H_{298}[\text{CH}_3\text{C(O)O + H}_2]$ values. Nevertheless the experimental findings in Table 4 suggest that the PAN decomposition route generating NO$_3$ is about 23 kJ mol$^{-1}$ lower than the pathway that generates NO$_2$. We should note that the calculation of the nitrate path, $\Delta_{\text{tr}} H_{298}[\text{trans-CH}_3\text{C(O)OO}]$, will be very difficult because NO$_3$ [(Fe$^{7+}$) is subject to Jahn–Teller distortion. Likewise the oxyacetyl radical, CH$_3$C(O), is metastable. All experimental evidence suggests that CH$_3$C(O)O instantly decomposes to CO$_2$ + CH$_3$. Indeed, this is the source of CO$_2$ in the matrix studies reported by von Ahsen et al.$^8$
Conclusions

The 351.1 nm photoelectron spectrum of the peroxy acetate anion was measured and is in good agreement with the calculated Franck–Condon factors for the $X^1A'$ state of the trans-conformer of the anion to the $X^2A''$ and $A^2A'$ states of the corresponding radical. The $\Delta A$ of the trans-CH$_3$C(O)OO is 2.381 ± 0.007 eV and the $T_a$ of the $A^2A'$ states is 0.691 ± 0.009 eV, which is in excellent agreement with two prior values.14–16 The gas-phase acidity of trans-peroxyacetic acid was bracketed between the acidity of acetic acid and tert-butylthiol at $\Delta aG_{298}[\text{trans-CH}_3\text{C(O)OOH}] = 1439 ± 14 \text{kJ mol}^{-1}$ and $\Delta aH_{298}[\text{trans-CH}_3\text{C(O)OOH}] = 1467 ± 14 \text{kJ mol}^{-1}$. The acidity of cis-CH$_3$C(O)OOH acid was found by adding a calculated energy correction to the acidity of the trans-conformer; $\Delta aG_{298}[\text{cis-CH}_3\text{C(O)OOH}] = 1461 ± 14 \text{kJ mol}^{-1}$ and $\Delta H_{298}[\text{cis-CH}_3\text{C(O)OOH}] = 1497 ± 14 \text{kJ mol}^{-1}$. The O–H bond dissociation energies for both conformers were determined using a negative ion thermodynamic cycle to be $D_{0}(\text{trans-CH}_3\text{C(O)OOH}) = 381 ± 14 \text{kJ mol}^{-1}$ and $D_{0}(\text{cis-CH}_3\text{C(O)OOH}) = 403 ± 14 \text{kJ mol}^{-1}$.

Acknowledgments

We are grateful to Professor John F. Stanton, Professor Kent M. Ervin and Professor Charles H. DePuy for helpful discussions and suggestions. Additionally, we acknowledge Ms Kristen M. Vogelhuber for assisting in the photoelectron spectroscopy experiments. This work is supported by the AFOSR [FA9550-09-1-0046]. WCL acknowledges support from the NSF (CHE0809391 and PHY0551010), VMB acknowledges support from the NSF (CHE-0647088) and GBE acknowledges support from the DOE (DE-FG02-93ER14364) and the NSF (CHE-0848606). The computational results are based upon work supported by the National Science Foundation under the following NSF programs: Partnerships for Advanced Computational Infrastructure, Distributed Terascale Facility (DTF) and Terascale Extensions: Enhancements to the Extensible Terascale Facility.

References

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<table>
<thead>
<tr>
<th>Process</th>
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<th>CBS-Q calc.</th>
<th>B3LYP/6-311G(d,p)</th>
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<tbody>
<tr>
<td>$\Delta H_{298}(\text{CH}_3\text{C(O)OO})$</td>
<td>-243 ± 14</td>
<td>-240 ± 7</td>
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<tr>
<td>$\Delta H_{298}(\text{trans CH}_3\text{C(O)OO})$</td>
<td>-158 ± 6</td>
<td>-154 ± 6</td>
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<td>$\Delta H_{298}(\text{CH}_3\text{CO}_2)$</td>
<td>-175 ± 6</td>
<td>-193 ± 6</td>
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<td>$\Delta G_{298}[\text{trans-CH}_3\text{C(O)OO + NO}_2]$</td>
<td>118.8 ± 4.0</td>
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<td>124 ± 8</td>
<td>122.4</td>
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</table>


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