O− + Acetaldehyde Reaction Products: Search for Singlet Formylmethylene, a Wolff Rearrangement Intermediate

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ABSTRACT: The mass-resolved anionic products of the reaction of O− with acetaldehyde, H3CCHO, are studied using photoelectron imaging. The primary anionic products are vinoxide, H2CCHO−, formylmethylene anion, HCCHO−, and ketenylidene anion, CCO−. From photoelectron spectra of HCCHO−, the electron affinities of triplet (ground state) formylmethylene (1.87 ± 0.02 eV) and the vertical detachment energy corresponding to the first excited triplet state (3.05 eV) are determined, but no unambiguous assignment for singlet HCCHO could be made. The elusive singlet is a key intermediate in the Wolff rearrangement, resulting in formation of ketene. The fast rearrangement associated with a large geometry change upon photodetachment to the singlet surface may be responsible for the low intensity of the singlet compared to the triplet bands in the photoelectron spectrum. The title reaction also yields CCO−, whose formation from acetaldehyde is novel and intriguing, since it requires a multistep net-H4+ abstraction. A possible mechanism is proposed, involving an [H2CCO−]∗ intermediate. From the measured electron affinities of HCCHO (above), H3CCHO (1.82 ± 0.01 eV), and CCO (2.31 ± 0.01 eV), several new thermochemical properties are determined, including the C−H bond dissociation energies and heats of formation of several organic molecules and/or their anions. Overall, the reactivity of O− with organic molecules demonstrates the utility of this anion in the formation of a variety of reactive intermediates via a single process.

1. INTRODUCTION

The gas-phase reactivity of atomic oxygen radical anion (O−) with organic molecules is well documented.1−5 This anion primarily reacts with organics via H+, H*, or H2+ abstraction, as indicated by the respective reactions:

\[ O^- + RH \rightarrow OH^- + R^- \] (1)

\[ O^- + RH \rightarrow OH^- + R^+ \] (2)

\[ O^- + HRH \rightarrow H_2O + R^- \] (3)

These reactions are extremely useful, as they provide a convenient method for gas-phase synthesis of a number of important anion intermediates. These intermediates can be characterized by spectroscopy, reactivity, or fragmentation in order to obtain their thermochemical properties, as well as molecular and electronic structures. However, one disadvantage of O− as a reagent is that it is often unselective toward the site of deprotonation, resulting in a complex mixture of isomers. Thus, O− is most useful as a reagent when a limited number of H atoms are available.

The reaction of O− with acetaldehyde, H3CCHO, was examined previously by Grabowski and Melly using the flowing afterglow technique.5 The products observed were H2CCHO− (34%), HCCHO− (32%), OH− (9%), H3CCO2− (15%), and HCO− (10%). The primary products correspond to the reactions 1−3, while the minor products result from the addition of O−, followed by elimination.

Of the above products, particularly interesting is the formylmethylene anion, HCCHO−. Electron detachment from this anion yields formylmethylene, an important carbene intermediate in the Wolff rearrangement.6−9 This reaction is widely used in chemistry, especially in the synthesis of acids, ring contractions, and most importantly in the industrial process of photolithography.6 Although formylmethylene could be found in several low energy electronic states (triplet and singlet), it is the singlet that is involved in the Wolff rearrangement.

The general mechanism of the Wolff rearrangement via a formylmethylene intermediate is shown in Figure 1. Typically, HCCHO, I, is generated by pyrolysis or photolysis of a diazoketone. The carbene undergoes a 1,2-H atom shift to form ketene, H3CCO, 3. Isotopic labeling studies have shown the carbon atoms in H2CCO scramble, so an oxirene intermediate, 2, has been proposed to explain experimental observations.

Although Figure 1 provides a plausible mechanism for the Wolff rearrangement, several experiments have indicated the reaction is controlled by additional factors, such as precursor geometry.6−8 For example, photolysis of syn-α-diazoketones leads preferentially to the formation of ketenes, while photolysis of anti-α-diazoketones, such as 2,2,5,5-tetramethyl-4-diazo-3-hexanone does not always lead to significant yields of ketene products.9 Time-resolved studies have indicated there are at least

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two decay processes related to the starting geometry of the ketocarbene intermediate. A fast decay is consistent with a direct 1,2-H atom shift immediately upon photolysis. A slower component would imply the formation of a long-lived intermediate, such as oxirene or a ketocarbene. A recent study found evidence for nonstatistical behavior in the product ratio of the Wolff rearrangement due to a bifurcated potential energy surface. Thus, the mechanism in Figure 1 is too general for this reaction.

In this paper, we report a photoelectron imaging study of the products from the reaction of O with acetaldehyde. The primary purpose of the study was to investigate HCCHO via electron detachment of the formylmethylene anion. This approach provides an alternate pathway to generation of HCCHO, unlike the traditional decomposition of diazoketones. In addition, we investigate several other reactive intermediates formed in the O + H3CCHO reaction, including oxirene, H2CCHO−, and an apparent two-step reaction product, CCOO−. Both intermediates are characterized in comparison with previously recorded photoelectron spectra reported in refs 12–14 and refs 15 and 16, respectively.

2. EXPERIMENTAL AND THEORETICAL METHODS

The experiments were carried out using a pulsed negative-ion time-of-flight photoelectron imaging spectrometer described previously. A mixture of room-temperature acetaldehyde vapor in N2O carrier gas at a pressure of 30 psi was expanded into a vacuum chamber using a General Valve (series 99) pulsed supersonic nozzle. Anions were generated by collisions of 1 keV electrons from an electron gun, creating slow secondary electrons. The slow electrons undergo dissociative attachment to 1 keV electrons from an electron gun, creating slow secondary electrons. Anions were generated by collisions of 1 keV electrons from an electron gun, creating slow secondary electrons. The slow electrons were projected onto a microchannel-plate detector, coupled to a phosphor screen. The resulting images were recorded by a charge-coupled device camera. The images were accumulated for statistics and analyzed by inverse Abel transformation using the BASEX program. The transformed images yield intensities in radial and angular coordinates with respect to the image center, I(r,θ), where angle θ is defined relative to the laser polarization direction. Photoelectron spectra are obtained by integrating the transformed images with respect to the angular coordinate. The spectra were calibrated using the known photoelectron spectrum of O−. Photodetector angular distributions (PADs) were obtained by integration over r. The angular distributions were fit using the standard equation and characterized in terms of the anisotropy parameter β. Electronic structure calculations were carried out using the Gaussian 03 program. Unless stated otherwise, the geometry optimizations and frequency calculations reported in this work were performed at the B3LYP/aug-cc-pVDZ level of theory. Other basis sets, aug-cc-pVQZ and 6-311++G(3df,3pd), were also used, for comparison, but only small differences were found. For the HCCHO− and HCCCHO, we also employed the Moller–Plesset second-order perturbation theory (MP2), in order to compare the predictions of different methods. Frequency calculations were used to confirm that the optimized structures corresponded to local minima. Transition state structures were identified as structures with a single imaginary frequency.

3. EXPERIMENTAL RESULTS AND ANALYSIS

A representative mass spectrum of the ions formed by the reaction of O− with H3CCHO seeded in N2O is shown in Figure 2. The O− + H3CCHO reaction products are indicated with red arrows and labels. Similar to the high-pressure flow-tube results, we observe the oxirene anion, H2CCHO− (m/z = 43 amu) and the formylmethylene anion, HCCCHO− (m/z = 42 amu). In addition, we observe an m/z = 40 amu peak assigned to the ketenyldiene anion, CCOO−. The peaks marked with asterisks are different methods. Frequency calculations were used to confirm that the optimized structures corresponded to local minima. Transition state structures were identified as structures with a single imaginary frequency.
must be at least a two-step process, and a possible mechanism is proposed in section 4.2.

The product anions were characterized individually by photoelectron imaging. The HCCO$^+$ anion had not been previously studied by photoelectron spectroscopy, and we carried out both experiments, and only brief discussions of their photoelectron spectra are included in sections 3.2 and 3.3, respectively. These analyses are necessary not only for completeness of the present study but also because the resulting energetics are used in determining several thermochemical properties in section 4.3.

3.1. Formylmethylene Anion, HCCHO. The 532 and 355 nm photoelectron images and spectra of formylmethylene anion, HCCO$^+$ (m/z = 42 in Figure 2), are shown in Figure 3. The 532 nm image (a) shows a single feature assigned to the X$^1$A$^*$ ground state of HCCHO. To analyze the partially resolved vibrational structure, we performed a Fourier transform of the spectrum: $F(q) = F(eBE)$, where $q$ is signal frequency (in units of 1/eV), conjugate to electron binding energy (eBE). The result, $F(q)$, is plotted in Figure 4a. The high-$q$ part of the Fourier spectrum (red dotted line) corresponds to noise in the experimental data, while other dominant features of $F(q)$ (blue solid line) reflect the periodic components present in the original spectrum in Figure 3a. In particular, the peak at $q = 17.7$ eV$^{-1}$, marked in Figure 4a with an asterisk, corresponds to the dominant vibrational progression discerned in the photoelectron spectrum in Figure 3a. The features near $q = 0$ in Figure 4a define the overall envelope of the X$^1$A$^*$ spectral band in Figure 3a.
Figure 4b shows the same Fourier spectrum, but plotted as a function of $\omega$, defined as the periodic spectral interval corresponding to signal frequency $q$: $\rho_0 = 1/q, F(\omega)$ is obtained from $\tilde{F}(q) \sim 1/q F(\omega)$ corresponds to the low-$\omega$ part of $F(\omega)$, while the dominant vibrational peak at $q = 17.7\ eV^{-1}$ transforms into the corresponding peak, also marked with an asterisk, in Figure 4b. From the maximum position and width of this peak, we determine the average spacing of the partially resolved vibrational progression in Figure 3a as $456 \pm 28\ cm^{-1}$.

We further used the Fourier analysis as a low-pass filter for the 532 nm experimental spectrum shown in Figure 3a. Specifically, the high-$q$ (low-$\omega$) noise part of the Fourier spectrum was eliminated (replaced by zeros) and the resulting cleaned up spectrum, consisting only of the blue solid part in Figure 4, was used for inverse Fourier transform. This procedure yielded the filtered photoelectron spectrum shown as a solid red line in Figure 3a. The vibrational progression with the average spacing determined above is unmistakable in the filtered spectrum. Assigning the first peak of the filtered $X^2A''$ spectral band as the band origin yields the adiabatic electron affinity of HCCHO, $EA = 1.87 \pm 0.02\ eV$.

The 355 nm image in Figure 3b shows a second spectral feature, with a maximum around $3.05\ eV$. This feature is assigned to an excited state of HCCHO, $A^3A''$. Both bands, $X^2A''$ and $A^3A''$, have maximum intensities parallel to the laser polarization, corresponding to $\beta > 0$.  

### 3.2. Vinoxide Anion, $H_2CCHO^-$  

The vinoxide anion, $H_2CCHO^-$, has been the subject of several previous studies. Most recently, a high-resolution slow-electron velocity-map imaging (SEVI) study gave an adiabatic electron affinity $EA(H_2CCHO^-) = 1.8250 \pm 0.0012\ eV$. This result is compared to the EA values of $1.8248\ eV,^{31} 1.8171 \pm 0.023\ eV,^{28}$ and $1.8240 \pm 0.0050\ eV,^{35}$ obtained in earlier studies. A photoelectron image of $H_2CCHO^-$ has also been reported previously, giving an EA = $1.795 \pm 0.015\ eV$. Our results for this species are consistent with the previous studies and hence only a brief account is given here.

The 355 and 532 nm photoelectron images and spectra of $H_2CCHO^-$ (corresponding to $m/z = 43$ in Figure 2) are shown in Figure 5. The 355 nm image shows two major features, a low energy band assigned to the $X^2A''$ state of vinox with a higher energy feature assigned to the first excited state, $A^3A''$. The 532 nm spectrum shows a vibrational progression for the ground state only. Its onset allows for an unambiguous determination of adiabatic electron affinity, $EA(H_2CCHO^-) = 1.82 \pm 0.01\ eV (42.0 \pm 0.2\ kcal/mol)$, is in good agreement with the above SEVI experiment and other previous studies. It also agrees with the theoretical prediction of 1.84 $eV$ [B3LYP/6-311++G(3df,3pd)]. The 557 $\pm 70\ cm^{-1}$ spacing between the partially resolved peaks in the $X^2A''$ band (532 nm) is assigned to the CCO bending mode. Contributions from other modes (primarily due to CC and CO stretches) overlap with the main progression, resulting in additional structure and broadening of the bands in Figure 5.

The first excited state of $H_2CCHO^-$, $A^3A''$, also shows vibrational structure, with an onset at $2.80 \pm 0.01\ eV$ and an apparent spacing of about $1500\ cm^{-1}$. The band origin corresponds to a $0.98 \pm 0.02\ eV$ term energy for the $A^3A''$ excited state of vinox radical, in agreement with the SEVI result of $0.996 \pm 0.003\ eV$. The $\sim 1500\ cm^{-1}$ vibrational progression for the $A^3A''$ state at 355 nm (Figure 5) is in good agreement with the 1595 $cm^{-1}$ (unscaled) frequency of the CC stretch calculated at the B3LYP/6-311++G(3df,3pd) level. Several other modes, primarily the CO stretch, also contribute to the overall band shape. The $X^2A''$ transition exhibits perpendicular angular distributions at both wavelengths studied, corresponding to $\beta = -0.64(5)$ at 355 nm. The excited state has a parallel distribution, with $\beta = 0.51(5)$ determined for the first two vibrational features in the 355 nm image. Continetti and co-workers interpreted the photoelectron angular distributions in $H_2CCHO^-$ photodetachment using symmetry-based arguments. In the dominant electron configuration of $H_2CCHO^-$, [core](10a$^0$)(2a$^1$)HOMO, the 2a$^1$ HOMO is a nonbonding $\pi$ orbital, while the 10a$^0$ HOMO-1 is essentially an oxygen lone-pair with significant $s$ character in the plane of the molecule. Electron detachment from the 10a$^0$ orbital is expected to yield a predominantly parallel angular distribution, while detachment from 2a$^1$ should yield a perpendicular distribution. Thus, the perpendicular and parallel features seen in Figure 5 are consistent with the formation of $H_2CCHO$ in the $X^2A''$ and $A^3A''$ states, respectively.  

### 3.3. Ketenyldiene Anion, $CCO^+$.  

The 355 nm photoelectron image and photoelectron spectrum of $CCO^+$ ($m/z = 40$ in Figure 2) are shown in Figure 6. The results are in excellent agreement with previous findings for CCO$^+$ (not involving the title reaction), leaving no doubt about the identity of the observed species. All image features peak in the direction perpendicular to the laser polarization, corresponding to negative $\beta$ values, as expected for electron emission from a $d$-like $\pi^*$ HOMO of CCO$^+$. The spectrum shows a number of well-resolved vibrational peaks. The first set of peaks is assigned to the ground state of CCO, $X^2\Sigma^+$, and the origin yields $EA = 2.31 \pm 0.01\ eV$, in agreement with the previously reported values of $2.3207 \pm 0.0006\ eV$ (SEVI) and $2.310 \pm 0.012\ eV$ (photoelectron.
4. DISCUSSION

The major products formed from the reaction of O\(^-\) with H\(_2\)CCHO are CCO\(^-\), HCCCHO\(^-\), and H\(_2\)CCHO\(^-\). Of these, HCCCHO\(^-\) and H\(_2\)CCHO\(^-\) were observed previously, but CCO\(^-\) was not. Although HCCCHO\(^-\) was previously detected in the above reaction, it has not been studied by photoelectron spectroscopy. In section 4.1, we discuss our findings for HCCCHO\(^-\) and the corresponding neutral molecule. In section 4.2, a mechanism of CCO\(^-\) formation is proposed. Section 4.3 summarizes the thermochemical properties derived from our measurements.

4.1. Formylmethylene: Anion and Neutral Structures and the Wolff Rearrangement

The formation of HCCCHO\(^-\) in the O\(^-\) + H\(_2\)CCHO reaction was reported by Grabowski and Melly.\(^3\) The photodetachment of this anion gives formylmethylene, an intermediate in the Wolff rearrangement (see Figure 1).

The electronic structures of three lowest-energy electronic states of HCCCHO, the ground-state triplet (\(^3\)HCCHO), the singlet (\(^\text{1}\)HCCHO), and the excited-state triplet, are illustrated in Figure 7 for a planar molecular geometry with the H atoms in the cis configuration. In the ground state, the carbene structure has one electron in a \(\sigma\) and one in a \(\pi\) orbital. There is also a resonance structure with the unpaired \(\pi\) electron on the oxygen atom; this structure is best described as a \(\sigma,\pi\) biradical. Qualitative predictions suggest the carbene form is the primary resonance structure, so the biradical character of X\(^3\)A\(^\prime\) is usually ignored.

In the singlet carbene at a planar geometry (corresponding to the a\(^1\)A\(^\prime\) state), both electrons are paired in the carbon \(\sigma\) orbital, while the corresponding resonance structure with a C=O double bond is zwitterionic (Figure 7). However, the planar geometry is not the lowest energy structure of \(^1\)HCCHO. It twists around the C—C bond, forming the lower energy nonplanar structure. The nonplanarity is an important property of singlet formylmethylene.\(^34-36\)

The excited triplet state, \(^3\)A\(^\prime\)\(^\prime\), results from removal of an electron from the oxygen lone pair in the anion, producing a zwitterionic species best described as a \(\sigma,\pi\) biradical. In this state, there is an unpaired electron in the \(\pi\) system, which is resonance stabilized in a carbene zwitterionic structure. However, the \(\sigma,\pi\) biradical form is expected to be the primary resonance structure of the A\(^3\)A\(^\prime\) state.

The geometries of precursors are known to play a role in determining the rearrangement products of carbonyl-carbenes.\(^6,7\) In our investigation of HCCCHO\(^-\), both B3LYP and MP2 methods predict the nonplanar syn geometry of HCCCHO\(^-\) is the global minimum, while the anti geometry equilibrium is predicted to lie about 0.05 eV (1.1 kcal/mol) higher in energy.\(^15\) To guide our analysis, we performed an inexpensive, albeit admittedly crude, relaxed potential energy surface scan with respect to the H—C—(O)—H dihedral angle at the B3LYP/aug-cc-pVDZ level of theory. The result, plotted in Figure 8, shows a 0.15 eV (3.5 kcal/mol) barrier to interconversion. The dihedral angle corresponding to the minimum-energy structure is approximately 40°. On the basis of these findings, we expect the syn conformation of HCCCHO\(^-\) to be favored.

The ground state of neutral formylmethylene is a planar-geometry triplet. A similar potential energy surface scan (Figure 8) shows that the global minimum of HCCHO corresponds to a trans geometry, with the cis structure as a local minimum about 0.04 eV (1 kcal/mol) higher in energy. The barrier to cis—trans interconversion is predicted to be 0.30 eV (7 kcal/mol). Hence, we expect vertical electron detachment from the syn global minimum of the anion (VDE = 2.22 eV at the B3LYP/aug-cc-pVDZ level of theory) to yield the higher-energy cis-3HCCHO isomer with a calculated adiabatic electron affinity (relative to syn-HCCCHO\(^-\)) of about 1.93 eV. Vertical detachment from the slightly higher-energy anti anion (VDE = 2.18 eV at the B3LYP/aug-cc-pVDZ level of theory) would lead to the lower-energy trans-3HCCHO, with a calculated adiabatic electron affinity (relative to anti-HCCCHO\(^-\)) of about 1.83 eV.
The 532 nm photoelectron spectrum of HCCCHO\(^{-}\) in Figure 3a is congested, because of the overlap of many vibrational modes of \(^3\)HCCHO excited upon HCCCHO\(^{-}\) photodetachment. The electron affinity of \(^1\)HCCHO is determined to be 1.87 ± 0.02 eV, in good agreement with the calculated values for both the trans- and cis- forms of \(^3\)HCCHO (1.83 and 1.93 eV, respectively). The spectrum in Figure 3a does show a vibrational progression, with an average spacing of 456 ± 28 cm\(^{-1}\), as determined by the Fourier analysis described in section 3.1. The major geometry difference between the anion and neutral is the H−CC(O)−H dihedral angle, and so we expect the H−CC(O)−H out-of-plane bend to be the primary vibration excited upon photodetachment. The observed spectral interval is in good agreement with the fundamental frequency of this mode in cis-\(^1\)HCCHO, calculated to be 492 cm\(^{-1}\) (unscaled, B3LYP/aug-cc-pVQZ level of theory). This observation suggests the predominant presence of syn-HCCCHO\(^{-}\), consistent with the lower energy of the syn (compared to anti) conformation, as predicted by theory.

The same mode for the trans-\(^3\)HCCHO structure has a 626 cm\(^{-1}\) frequency, which is intriguingly close to the location of a secondary spectral feature at 608 ± 30 cm\(^{-1}\) in Figure 4b, just to the right of the main (\(^s\)) peak. Although the intensity of this secondary feature is too small to draw solid conclusions, we find that the integrated intensity ratio of the two peaks (\(\sim 20:1\)) is consistent with a statistical distribution of the syn- and anti-HCCCHO\(^{-}\) isomers, given the predicted energy difference (1.1 kcal/mol) and assuming an ion-beam (vibrational) temperature of \(\sim 200\) K.

The higher-energy feature in the 355 nm photoelectron spectrum of HCCCHO\(^+\) in Figure 3b is attributed to the excited triplet state, A\(^{3}\)A\(^{3}\), which arises from electron detachment of an oxygen lone-pair in HCCCHO\(^{-}\) (see Figure 7) with a calculated VDE of 3.00 eV (B3LYP/aug-cc-pVDZ). This prediction compares well with the band maximum observed at about 3.05 eV.

On the basis of various theoretical predictions, the HCCCHO\(^{-}\) \(\rightarrow\) \(^1\)HCCHO photodetachment transition is expected at eBE ≥ 2.60 eV, slightly higher in energy than \(^3\)HCCHO, but below the excited triplet, A\(^{3}\)A\(^{3}\). The photoelectron spectrum shows no clear evidence for \(^1\)HCCHO. The expected location of this transition, based on B3LYP/aug-cc-pVQZ, is indicated in Figure 3b by a dashed line. Although there is spectral intensity in this region, it is impossible to conclude if it is due to \(^1\)HCCHO or the X\(^{3}\)A\(^{3}\) band, or both.

Geometry optimization for \(^1\)HCCHO, starting from the global-minimum syn structure of HCCCHO\(^{-}\), at all levels of theory used in this study, leads to ketene, H\(_2\)C=O. This result is in accord with previous observations that syn-ketocarbenes preferentially form ketene products. It also agrees with the time-resolved studies\(^9\) that indicated a fast, direct rearrangement for syn-ketocarbenes. On the other hand, optimization of \(^1\)HCCHO geometry starting from the anti-HCCCHO\(^{-}\) structure yielded a stable minimum corresponding to anti-\(^1\)HCCHO, separated from ketene by a small barrier. Figure 9 summarizes the neutral product correlations for syn- and anti-HCCCHO\(^{-}\) photodetachment, including the anti-\(^1\)HCCHO \(\rightarrow\) H\(_2\)C=O transition state. At the B3LYP/aug-cc-pVQZ level of theory, vertical detachment of anti-HCCCHO\(^{-}\) yields \(^1\)HCCHO with an energy approximately equivalent to the transition state and the resulting neutral molecule is likely to undergo a 1,2-H atom shift to ketene. Overall, detachment to the singlet state is expected to result in a fast Wolff rearrangement to H\(_2\)C=O, regardless of the starting geometry of HCCCHO\(^{-}\). The transient nature of \(^1\)HCCHO contrasts that of \(^3\)HCCHO, which is a long-lived species, not subject to the Wolff rearrangement.

Although both HCCCHO\(^+\) and \(^1\)HCCHO are nonplanar at their respective equilibria, the geometry difference between the two is more significant than that of the anion and \(^1\)HCCHO (see Figure 9). Because of the large difference between the equilibrium geometries of HCCCHO\(^{-}\) and \(^1\)HCCHO (or H\(_2\)C=O), we expect these transitions to have poor Franck–Condon overlap and hence low intensity, compared to \(^1\)HCCHO. Photoelectron (transition-state) spectroscopy, is often a powerful tool for probing short-lived intermediates. For example, this utility is clearly born out in the studies of vinylidenes\(^39\) and oxayl\(^41\) However, to observe a short-lived intermediate, it must either be well separated in the photoelectron spectrum from other transitions or exhibit identifiable characteristic vibrational structure. In this study, the \(^1\)HCCHO transition is expected to have low intensity due to a poor Franck–Condon overlap, while lying in the same spectral range as the congested triplet band. For this reason, the photodetachment signal due to \(^1\)HCCHO is probably buried underneath the X\(^{3}\)A\(^{3}\) band, or both.

4.2. Ketenylidene Anion: Formation Mechanism. The photoelectron image and spectrum of the m/z = 40 anion presented in Figure 6 are in excellent agreement with previous results for CCO\(^{-}\)\(^{15,16,27,28}\) as discussed in section 3.3, leaving no doubt about the identity of the observed species. However, the formation of this anion in our ion source is both novel and interesting, because it must involve at least a two-step process that removes a net H\(_2\)^\(^+\) from H\(_3\)CCHO.

In Figure 10, we suggest a mechanism that assumes an initial H\(_2\)^\(^+\) abstraction to form either stable formylmethylene...
anion, HCCHO$^-$, via path a, or a metastable ketene anion [H$_2$CCO$^-$]$^*$, path b. Evidence that H$_2$CCO$^-$ is not stable is provided by the photoelectron spectra of the m/z = 42 ion (Figure 3), which does not show any low electron binding energy features expected for a weakly bound anion such as H$_2$CCO$^-$.

The [H$_2$CCO$^-$]$^*$ intermediate is expected to undergo rapid autodetachment to form H$_2$CCO + e$^-$. A second H$_2$$^+$ abstraction from the nascent H$_2$CCO by a second O$^-$ would yield then CCO$^-$, via step c in Figure 10.

We recognize that the evidence to support this proposal is scarce. Indeed, the electron/ion -- molecule chemistry in our ion source could conceivably involve alternative reactions, and the mechanism in Figure 10 is but one way to rationalize the formation of CCO$^-$ in our experiment. The principal weakness of the proposed explanation is the very low probability expected for a multistep process in a pulsed ion source. However, such processes are not unknown and the low intensity of the observed CCO$^-$ ions (see Figure 2) is consistent with a low-probability mechanism. In another example of such a process, vinoxide anion can be synthesized by the reaction of O$^-$ with ethanol$^{13,14,29}$, which requires a multistep mechanism that removes a net H$_3$$^+$ from CH$_3$CH$_2$OH. In the course of the present project, we confirmed this reaction by measuring photoelectron spectra of the m/z = 43 anion prepared from the reaction of O$^-$ and ethanol. The spectra were identical to those shown in Figure 5. In this case, the reaction probably proceeds via an initial H$_2$$^*$ abstraction from ethanol that produces a metastable acetaldehyde anion, [H$_3$CCHO$^-$]$^*$, which decays via electron emission to H$_3$CCHO. A secondary proton abstraction by O$^-$ then gives the vinoxide anion, H$_2$CCHO$^-$.

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**Figure 9.** Schematic correlation diagram for HCCHO$^-$ photodetachment at the B3LYP/aug-cc-pVDZ level of theory. Detachment of HCCHO$^-$ from either syn or anti geometries leads to the Wolff rearrangement product H$_2$CCO.

**Figure 10.** Proposed mechanism for the formation of CCO$^-$ in the reaction of O$^-$ with acetaldehyde, H$_3$CCHO, via a two-step process involving the ketene anion intermediate, [H$_2$CCO$^-$]$^*$. 

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Table 1. Thermochemical Quantities Either Used or Obtained in This Work (all values in kcal/mol)

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<tr>
<td>XIII</td>
<td>$\Delta$EA(HCCO)</td>
<td>53.3 ± 0.2</td>
<td>this work: experiment (Figure 6)</td>
</tr>
<tr>
<td>XIV</td>
<td>$\Delta$IP(H)</td>
<td>313.6</td>
<td>refs 46,50,51</td>
</tr>
<tr>
<td>XV</td>
<td>$\Delta$acidH$_{298}$ (H$_2$CCCHO)</td>
<td>365.9 ± 2.2</td>
<td>ref 52</td>
</tr>
<tr>
<td>XVI</td>
<td>$\Delta$acidH$_{298}$ (HCCO$^\circ$)</td>
<td>360.2 ± 3.6</td>
<td>ref 53</td>
</tr>
<tr>
<td>XVII</td>
<td>BDE(H−CH$_2$CHO)</td>
<td>94.3 ± 2.2</td>
<td>this work: eq 7, XI, XIV, XV</td>
</tr>
<tr>
<td>XVIII</td>
<td>BDE(H$_2$CC(O)−H)</td>
<td>39.3 ± 2.2</td>
<td>this work: eq 8, I, III, IV</td>
</tr>
<tr>
<td>XIX</td>
<td>BDE(H−CCO$^\circ$)</td>
<td>99.9 ± 3.6</td>
<td>this work eq 7, XIII, XIV, XVI</td>
</tr>
</tbody>
</table>

$^a$Recommended value. $^b$Presently reported on NIST Web site$^{46}$ (not recommended).

4.3. Thermochemistry. The electron affinities determined in this study can be used to calculate thermodynamic properties of the corresponding anions and radicals. Of primary interest are heats of formation ($\Delta$H$_{298}$) and bond dissociation energies (denoted here as BDE, but also commonly referred to as $\Delta$H$_{298}$).

The R−H BDEs are calculated using the acidity/electron affinity cycle:$^{44,45}$

$$\text{BDE(R−H)} = \Delta_{\text{acid}}H_{298}(\text{RH}) + \text{EA}(\text{R}) - \text{IP}(\text{H}) + \text{[thermal correction]} \quad (7)$$

where IP(H) is the ionization potential of the hydrogen atom. The [thermal correction] term arises from integrated (0 to 298 K) differential heat capacities (ΔC$_p$) of the reactants and products. This term is small, typically about 0.3 kcal/mol. It is absorbed by other, larger uncertainties involved in the calculations and, therefore, disregarded from this point on. The thermochemical parameters used in our calculations and the results are summarized in Table 1. The source column either gives references for the previously known values or specifies how the new values were determined. Although multiple paths to a given quantity are possible within the self-consistent framework of thermodynamics, only a selected one or two are identified in each case.

For example, from the experimentally determined EA(H$_2$CCCHO) = 1.82 ± 0.01 eV = 42.0 ± 0.2 kcal/mol (line XI in Table 1), we calculate, using eq 7, the C−H bond dissociation energy on the methyl group of acetaldehyde, BDE(H−CH$_2$CHO) = 94.3 ± 2.2 kcal/mol (line XVII). From the same calculation using the more precise SEVI value for the electron affinity (1.8250 ± 0.0012 eV),$^{12}$ we obtain a BDE = 94.4 ± 2.2 kcal/mol, which is indistinguishable from our value. This comparison is, nonetheless, quite instructive, as it serves to emphasize that the main contribution to the uncertainty comes from the measured acidity of acetaldehyde, $\Delta_{\text{acid}}H_{298}$ (H$_2$CCCHO) (line XV in Table 1), and not the spectroscopic determination of electron affinity of the corresponding radical.

Bond dissociation energies and gas-phase acidities are related to the corresponding heats of formation:

$$\Delta_tH_{298}(R) = \text{BDE}(R−H) + \Delta_tH_{298}(\text{RH}) - \Delta_tH_{298}(H) \quad (8)$$

$$\Delta_tH_{298}(R^-) = \Delta_{\text{acid}}H_{298}(\text{RH}) + \Delta_tH_{298}(\text{RH}) - \Delta_tH_{298}(H^+) \quad (9)$$

Substituting the above result, BDE(H−CH$_2$CHO) = 94.3 ± 2.2 kcal/mol in eq 8, we obtain the formation enthalpy of the vinoxy radical, $\Delta_tH_{298}$(H$_2$CCCHO$^+$) = 1.4 ± 2.2 kcal/mol (line IV).

The first C−H bond dissociation energy on the methyl group of acetaldehyde (94.3 kcal/mol, as determined above) is slightly smaller than many typical C−H BDEs. For comparison, in propane, the H−CH$_2$CH$_2$CH$_3$ BDE is calculated to be 100.4 ± 3.4 kcal/mol.$^{44}$ The small difference can be partially attributed to resonance stabilization of the unpaired electron in the vinoxy radical resulting from acetaldehyde dissociation.

Vinoxy radical has a planar structure, with the unpaired electron on the carbon radical center stabilized by resonance with the π electrons in the carbonyl bond. This radical can be regarded as an allyl radical (H$_2$CCHCH$_2$) with one of the methylene groups replaced by an oxygen atom. Allyl radical is formed by methyl C−H cleavage in propene (CH$_3$CHCH$_2$) and the corresponding BDE(H−CH$_2$CH(CH$_3$)$_2$) = 88.8 ± 0.4 kcal/mol$^{45}$ is distinctly lower than the BDE(H−CH$_2$CHO) = 94.3 ± 2.2 kcal/mol obtained above. Allyl radical has two equivalent
resonance structures, with the radical site located on either of the terminal methylene groups. The double-resonance stabilization is reflected in the low BDE of propene. In vinyloxy radical, on the other hand, the resonance structures are not equivalent: the configuration with a π bond on the more electronegative oxygen atom is dominant, while the structure with a π bond connecting the carbon atoms has a smaller contribution. As a result of the decreased resonance stabilization of the unpaired electron, acetaldehyde has a larger BDE, compared to propene.

In contrast, BDE(H₂C(O)−H), i.e., the C−H BDE of H₂CCHO° on the central carbon, to give H₂CCO, is determined to be only 39.3 ± 2.2 kcal/mol (line XVIII in Table 1). This is less than half the energy of a C−H bond on the methylene and reflects the stability of ketene, in which the two unpaired electrons couple to form a CC π bond.

The thermochemistry of ketenylidene is obtained from the EA of CCO. Using our experimental EA(CCO), eq 7, and the thermochemical values in Table 1, we calculate BDE(H−CCO°) = 99.9 ± 3.6 kcal/mol (line XIX). The bond energy calculated using the SEVI value15 for EA(CCO) is 100.1 ± 3.6 kcal/mol, which is, again, indistinguishable from our value (within the uncertainly limits). We also obtained ΔH₂⁹⁸(CCO) = 90.2 ± 4.2 kcal/mol (line VIII). This result is in agreement with the previously reported value ΔH₂⁹⁸(CCO) = 92.0 ± 4.6 kcal/mol,25 although the agreement could be expected due to the use of similar thermochemical cycles. However, both of these values differ significantly from the value presently reported in the NIST Chemistry WebBook database, ΔH₂⁹⁸(CCO) = 68.499 kcal/mol (line IX).46

The correct value ΔH₂⁹⁸(CCO) is important both in itself and as a parameter used in calculating the thermodynamic properties of other species. In order to examine the above discrepancy, we used B3LYP/6-31+G(d) to estimate BDE(H−CCO) and BDE(C−CO) and compared the results with the corresponding BDE values obtained from eq 9 using ΔH₂⁹⁸(CCO) = 90.2 kcal/mol (this work) and 68.499 kcal/mol (NIST Chemistry WebBook).16

Substituting ΔH₂⁹⁸(CCO) = 90.2 kcal/mol in eq 9, we obtain BDE(H−CCO) = 99.9 kcal/mol (Table 1, line XIX), in excellent agreement with the DFT prediction of 98 kcal/mol. Using eq 8 with ΔH₂⁹⁸(CCO) = 68.499 kcal/mol,46 on the other hand, gives a much lower BDE(H−CCO) value of 78 kcal/mol. Theory also predicts BDE(C−CO) = 60 kcal/mol, in good agreement with the BDE(C−CO) of 54.7 kcal/mol, obtained using ΔH₂⁹⁸(CCO) = 90.2 ± 4.2 kcal/mol (this work) and the standard heats of formation of C and CO, 171.30 and −26.41 kcal/mol, respectively. The same calculation using ΔH₂⁹⁸(CCO) = 68.499 kcal/mol predicts a C−CO bond energy of 76.4 kcal/mol, which differs significantly from the DFT prediction. While DFT BDEs are not indisputable, the calculations support the findings based on our experimental measurements. Therefore, we recommend ΔH₂⁹⁸(CCO) = 90.2 ± 4.2 kcal/mol.

5. CONCLUSIONS

We used photoelectron imaging spectroscopy to characterize the HCCHO°, H₂CCHO, and CCO° products of the reaction of O° with H₂CCHO. From photoelectron spectra of the formylmethylenie anion, the electron affinity of HCCHO (1.87 ± 0.02 eV) and the detachment energies for two triplet bands are determined, but no unambiguous assignment for the singlet state of HCCHO could be made. This is attributed to the singlet being an intermediate in the Wolff rearrangement, which results in formation of ketene; we therefore expect large geometry change (thus, poor Franck-Condon overlap) and fast rearrangement upon photodetachment to the singlet surface. The title reaction also provides a unique method for synthesizing CCO°−, whose formation in our ion source is both novel and intriguing. A possible two-step mechanism for CCO°− formation is suggested, involving an [H₂CCO°−]· intermediate. From the measured electron affinities of HCCCHO, H₂CCHO, and CCO, several new thermochemical properties have been determined, such as the C−H bond dissociation energies and heats of formation of some organic molecules and/or their anion. In particular, we determine the heat of formation of CCO, ΔH₂⁹⁸(CCO) = 90.2 ± 4.2 kcal/mol, and recommend revising the presently accepted value. Overall, the high reactivity of O° with organic molecules demonstrates the utility of this reagent in the formation of a variety of reactive intermediates via a single process.

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