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Modeling the Competitive Dissociation of Protonated 2,3-Butanedione. The Enthalpy of Formation of Methylhydroxycarbene

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The enthalpy of formation of methylhydroxycarbene, CH_3COH, has been determined from measurements of the threshold energy for collision-induced dissociation of protonated 2,3-butanedione in a flowing afterglow-triple quadrupole mass spectrometer and found to be 16 ± 4 kcal/mol, 57 ± 4 kcal/mol higher than that of acetaldehyde. From the measured enthalpy of formation, the difference between the first and second C−H BDEs in ethanol is found to be 17 kcal/mol, which implies a singlet−triplet splitting of 28 kcal/mol in the carbene. The activation energies for loss of ketene and carbon monoxide from protonated butanedione are found to be 60 ± 4 and 50 ± 4 kcal/mol, respectively. On the basis of experimental and computational results, the loss of carbon monoxide is proposed to proceed through a tight transition state. Although calculations also suggest a tight transition state for loss of ketene, the experimental data indicate that it occurs via a loose transition state, possibly forming by proton transfer along the direct dissociation pathway.

Introduction

As reaction transient intermediates, carbenes have played an important role in many fields including synthesis, photochemistry, and combustion chemistry.[1−3] As a result, numerous experimental and theoretical studies[1−6] have been carried out to elucidate the role that substitution has on carbene properties and reactivity. The most important effect of a substituent is on the relative energies of the spin states of the carbenes. Whereas methylene and carbenes with electron withdrawing groups tend to have triplet ground states, carbenes with strong electron donating groups tend to be ground-state singlets.[4,5] With the exception of methylene,[7−9] phenyl- and vinylcarbene,[9] and some halocarbenes,[10,11] however, reliable experimental thermochemical data for carbenes are scarce, although these data are fundamentally important for understanding the nature and reactivity of carbene intermediates.

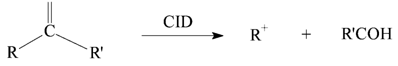
A hydroxy substituent is a π-electron donor and would be expected to favor the singlet states of carbenes. Unsubstituted hydroxycarbene was suggested as an intermediate in the photochemistry of formaldehyde,[12] and the reactions of atomic carbon with water[13] and oxygen with methane.[14] Therefore, hydroxycarbenes potentially play an important role in some organic reactions and in combustion processes. Given the potential importance of hydroxycarbenes in these areas, it is important to understand their structural and thermochemical properties. The only hydroxycarbene for which thermochemical properties are known is hydroxymethylene, HCOH. In 1982, Pau and Hehre reported the enthalpy of formation of hydroxymethylene, measured by using proton affinity bracketing measurements with D_2COH^+.[15] They found that the proton affinity of hydroxycarbene to be between those of ethylisopropylamine and dimethylisopropylamine. A comparison of their proton affinities with that for formaldehyde[16] indicates an energy difference of 60 ± 2 kcal/mol between the two neutral precursors.[17] Theoretical values for the energy difference are lower and generally range from 50 to 55 kcal/mol.[18,19]

The homologue of hydroxycarbene, methylhydroxycarbene, may be a product of the photodissociation[20] and pyrolysis[21−23] of pyruvic acid, and the reaction of acetic acid with atomic carbon.[24] Further, experimental studies of the rearrangement of CH_3COH to acetaldehyde were carried out.[21,22,25] Computational studies of the isomerization reaction were also reported[20,22,26,27] and examined, inter alia, the energy difference between the carbene and acetaldehyde and the barriers for the unimolecular rearrangement.[28]

Recently, we reported the determination of the enthalpy of formation of isonitrile, HNC, using collision-induced dissociation (CID) threshold measurements with protonated nitriles, $RCNH^+$ (eq 1, where R = methyl, ethyl, *tert*-butyl, phenyl, and vinyl).[29] Given the excellent results for

$$RCNH^+ \rightarrow R^+ + HNC \qquad (1)$$

these experiments, we sought to use the same approach to measure the enthalpies of formation of hydroxycarbenes, which are isoelectronic with isonitriles. By comparison with the reaction shown in eq 2, the enthalpies of formation of hydroxycarbenes could be obtained by using CID of protonated aldehydes or ketones, as shown in eq 2. Unfortunately, although



$$RC(={}^+OH)R' \xrightarrow{CID} R^+ + R'COH \qquad (2)$$

protonated aldehydes do dissociate to form hydroxycarbenes, numerous other pathways are available. For example, CID of protonated acetaldehyde results in the formation of at least six ionic products at energies lower than that required for formation of methyl cation.[30] Moreover, deuterium labeling and qualitative comparisons of energy-resolved mass spectra indicate that some of the methyl cation produced is formed via rearrangement

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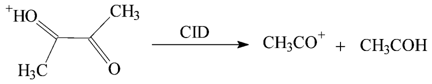
processes.[30] Therefore, to determine the thermochemical properties of hydroxycarbenes using CID of protonated acetaldehyde, it would be necessary to fully characterize the structures of at least seven products and the mechanisms by which they are formed. Similar complications have been encountered with other alkyl-substituted aldehydes.[30]

Unlike what was found with simple aldehydes, dissociation of protonated 2,3-butanedione, **1H**$^+$, is relatively simple with only three ionic products observed. At high energies, formation of methylhydroxycarbene, CH_3COH, and acetyl cation, is the major pathway. In this paper, we report the determination of the enthalpy of formation of putative methylhydroxycarbene, generated by CID of protonated 2,3-butanedione, **1H**$^+$ (eq 3).



(3)

1H$^+$

By modeling the data obtained from energy-resolved CID measurements, the threshold energy for acetyl cation is determined, from which the enthalpy of formation of the carbene can be calculated. The enthalpy of formation of methylhydroxycarbene then can be used to derive additional thermochemical properties, including the second C−H bond dissociation energy in ethanol. Using these properties, the singlet−triplet splitting energy of methylhydroxycarbene can be estimated empirically. Our thermochemical results are consistent with those expected for a singlet carbene. Details are presented in the results and discussion section.

Experimental Section

Most experiments were carried out at room temperature in a flowing afterglow triple-quadrupole instrument that was described previously.[31] The pressure of the helium buffer gas in the flow tube was typically 0.4 Torr, with a flow rate of ca. 200 std cc/s. Protonated water, H_3O^+, was formed in the ion source region using electron ionization of water. Protonated 2,3-butanedione, **1H**$^+$, was usually generated by the proton-transfer reaction between H_3O^+ ($PA(H_2O) = 165.5$ kcal/mol)[16] and 2,3-butanedione vapors (PA(**1**) = 191.7 kcal/mol)[16] added to the flow tube reactor through a gas inlet located at least 30 cm from the ion source. The relative yields of the CID products were the same when H_3O^+, CH_5^+ ($PA(CH_4 = 129.9$ kcal/mol),[16] or $CH_3OH_2^+$ ($PA(CH_3OH) = 180.3$ kcal/mol)[16] was used as the CI reagent, providing evidence that the products were formed from a common reactant ion structure. Ions in the flow tube were thermalized by ca. 10^5 collisions with the helium buffer gas prior to analysis.

Ions generated in the flow tube were extracted through a 1 mm orifice into a differentially pumped region and then focused into the triple quadrupole mass spectrometer. Following mass-selection of the desired reactant ion with the first quadrupole (Q1) mass filter, ions were injected into the second quadrupole (Q2), which was operated as rf only and served as a reaction chamber. The product ions formed in CID were then analyzed by the third quadrupole analyzer (Q3). The ion axial kinetic energy in Q2 was determined by the second quadrupole rod offset voltage, and the CID collision energy in the center-of-mass frame was calculated by $E_{cm} = E_{lab}[m/(m + M)]$, where m is the mass of the neutral target (argon), M is the mass of the reactant ion (**1H**$^+$), and E_{lab} is the nominal lab energy that corresponds to the ion axial kinetic energy. The ion energy origin and distribution were determined using retarding potential analysis. Ion distributions were typically Gaussian in shape, with a full-width at half-maximum of 1.0−1.5 eV. Absolute cross sections for the dissociation, σ_p, were calculated by $\sigma_p = I_p/Inl$, where I_p is the intensity of the product, I is the intensity of the reactant, l is the path length for the reaction (24 ± 4 cm),[31] and n is the number density of the target. The results reported in this work were obtained using argon as the collision gas. Experiments carried out with xenon gave indistinguishable results. Single collision cross sections were obtained by measuring the data at four different pressures and linearly extrapolating to $P = 0$. The reported results are the average of five independent data sets.

Mass-analyzed ion kinetic energy (MIKE) experiments were also carried out, using a triple-sector Kratos MS-50 TA mass spectrometer (Kratos Analytical, Ramsey, NJ) with EBE geometry.[32]

Data Analysis and Modeling

The data analysis and modeling procedures used for extracting CID thresholds from energy-dependent cross section data were described in detail previously[29,33−35] and are only discussed briefly here. The threshold energy for dissociation is determined by fitting the measured product ion cross sections with the model threshold law given by eq 4, where E is the center-of-mass

$$\sigma(E) = \sigma_0 \sum_i P_i g_i (E + E_i - E_0)^n / E \qquad (4)$$

collision energy, E_i is the internal energy of the reactant ion, E_0 is the threshold dissociation energy at 0 K, σ_0 is a scaling factor, n is an adjustable parameter, and P_i is the probability for the dissociation of the ion, where i represents the reactant ion vibrational states with internal energy E_i and population g_i ($\sum g_i = 1$). The internal energy distributions are estimated from vibrational frequencies and rotational constants, calculated at B3LYP/6-31+G* level of theory.[36,37] Vibrational frequencies are scaled by a factor of 0.965 to account for anharmonicities. Dissociation probabilities, P_i, are calculated from the RRKM dissociation rate constants and assume a constant time window for dissociation, ca. 30 μs. The transition state for the dissociation is characterized by the activation entropy, $\Delta S^\ddagger$, calculated by using $\Delta S^\ddagger = k_B \ln Q^\ddagger/Q + (E_v^\ddagger - E_v)/T$, where $Q^\ddagger$ and Q are the partition functions of the transition state and the activated complex, respectively, and $E_v^\ddagger$ and E_v are the corresponding average vibrational energies. By convention, activation entropies are evaluated at 1000 K.

The experimental cross sections are fit by varying σ_0, n, and E_0 so as to minimize the deviations between the experimental data and calculated cross sections in the steeply rising region directly above the threshold. The CID threshold energy obtained in this manner corresponds to the bond dissociation energy at 0 K. The dissociation enthalpy at 298 K is calculated by using the integrated heat capacities of the dissociation products and reactant. The CRUNCH program written by Armentrout and co-workers[33,38−40] was used to carry out all the data analysis and modeling.

Results and Discussion

Collision-induced dissociation of protonated 2,3-butanedione, **1H**$^+$, over the energy range of 0−9.5 eV (c.m.) results in the formation of three observed products, m/z 43, 45, and 59. The product at m/z 43 is likely the acetyl cation, CH_3CO^+, whereas the ions of m/z 45 and 59 probably correspond to the protonated acetaldehyde and protonated acetone ions, respectively, that result from rearrangement and loss of ketene or carbon

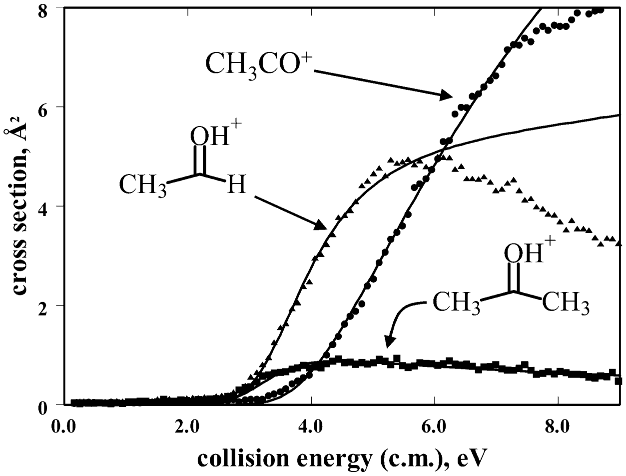
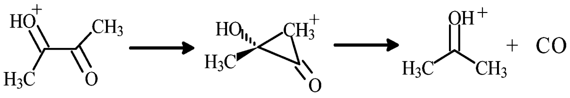


Figure 1. Cross sections for fomation of the acetyl cation, CH_3CO^+ (●), protonated acetaldehyde, CH_3CHOH^+ (▲), and protonated acetone, $CH_3COHCH_3^+$ (■). The solid lines are optimized fits to the data, obtained by using the transition state parameters shown in Table 3.

monoxide. Upon dissociation of the deuterated ion, **1D**$^+$, prepared by the reaction of **1** with D_3O^+, the product with *m*/*z* 43 is still observed, but the other products shift one unit higher in mass, consistent with the proposed structures of the products. The CID cross sections for the products obtained from **1H**$^+$ as a function of the collision energy (Figure 1) show that the *m*/*z* 45 and 59 products have the lower apparent onsets, but at energies above 6.3 eV the CH_3CO^+ ion is most abundant. Formation of *m*/*z* 43 ion by secondary fragmentation of either protonated product can be ruled out. First, the acetyl ion is not a product in the CID of protonated acetaldehyde,[30] ruling out its formation from the *m*/*z* 45 product. Second, although protonated acetone does lose acetyl cation upon CID, secondary fragmentation of protonated acetone would be indicated by the formation of formyl cation, HCO^+, with *m*/*z* 29. This ion is a major product in the CID spectrum of protonated acetone but is not observed over most of the energy range shown in Figure 1. Upon diligent searching, the *m*/*z* 29 ion is found to be formed as a very minor product at energies greater than ca. 8 eV, but with a maximum cross section that is less than 0.5% of that for acetyl cation. The 8 eV onset is consistent with what is expected for formation of the ion by secondary fragmentation of the protonated acetone product, and the small cross section for the reaction indicates that it is not a significant process. Similarly, the onset for formation of *m*/*z* 43 is likely too low to be the result of sequential dissociation. The appearance energy for the dissociation of protonated acetone to give acetyl cation in our instrument is greater than 2 eV,[41] such that any *m*/*z* 43 formed by secondary fragmentation of protonated acetone should have an onset of ca. 5 eV, 1 eV higher than that observed upon CID of **1H**$^+$. Given these observations, we conclude that all three products are formed as primary products from the CID of **1H**$^+$.

Given that the proton affinity of 2,3-butanedione is known,[16] the enthalpy of formation of CH_3COH can be determined from the threshold energy for the formation of CH_3CO^+, which can obtained from the energy-resolved cross sections by using the modeling procedures described above. However, the presence of the alternate dissociation channels makes the analysis more challenging because these channels can lead to "competitive shifts" in the onsets of product formation.[40] Therefore, we modeled the data by assuming statistical dissociation of **1H**$^+$ to give the observed products. The analysis procedure was described in detail by Rodgers and Armentrout[40] and involves incorporating the statistical branching ratio into the probability term in the model equation shown in eq 4. This approach has been used successfully to determine bond dissociation energies of alkali cation bound dimers,[42,43] trihalide ions,[34] protonated nitriles,[29] and pentavalent siliconate ions.[44]

The dissociation branching ratios incorporated into the modeling are calculated using RRKM theory, which requires transition state structures for each reaction pathway. The formation of CH_3COH by direct cleavage is assumed to have a loose, product-like transition state (the phase-space limit) as described by Rodgers et al.[40] Support for this assumption is found in the MIKE experiments, discussed at the end of this section. Formation of the *m*/*z* 45 and *m*/*z* 59 ions at low energy by loss of CH_2CO and CO, respectively, likely occurs via rearrangement of the ion during dissociation. Initial predictions of the transition states for these processes were obtained from electronic structure calculations.[37] Qualitative transition state structures for loss of CO and CH_2CO, calculated at the HF/6-31+G* level of theory, are shown in eqs 5 and 6, respectively. Loss of CO requires transfer of a methyl group and can be envisioned as occurring through a protonated cyclopropanone-like transition state (eq 5). Similarly, loss of CH_2CO requires hydrogen atom migration, and a 4-centered transition state was calculated for this process (eq 6). Transition state structures calculated at the B3LYP/6-31+G* and MP2/6-31+G* levels of theory are similar to those obtained from the HF calculations. Moreover, at each level of theory the structures have a single imaginary frequency, indicating that they are saddle-points on the potential energy surfaces.



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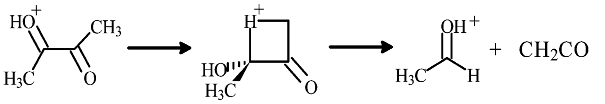

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Attempts to model the data using the transition states described above gave mixed results. Whereas we were able to accurately reproduce the cross sections for formation of the *m*/*z* 43 and 59 ions, we could not find any combination of fitting parameters that gave a reasonable fit for the *m*/*z* 45 ion data. When the parameters for the four-membered transition state described above are used, the predicted relative intensity of the CH_2CO loss is too low by a factor of ca. 100, indicating that the assumed transition state for this process is too "tight". The excellent fits obtained for the other two reaction channels indicate that the relative transition states assumed for these processes are reasonable.

Fortunately, the properties of the transition state for ketene and carbon monoxide loss do not need to be known a priori to model the data but can be determined by manually adjusting the transition state properties to optimize the fits to the data.[44] Full fitting of the data requires eight parameters: transition state entropies and threshold energies for each of the three reaction channels, the exponential parameter n, and the scaling parameter σ. We know, however, from the experiments the energy onsets for each channel, the absolute cross sections for all three channels, and the shapes of the curves. If the formation of CH_3CO^+ is assumed to occur by a loose transition state, then there are seven experimentally known parameters and seven unknowns to solve, and the properties of the transition states for CO and CH_2CO loss can be determined by fitting the experi-

TABLE 1: Supplemental Thermochemical Values

R	$\Delta H_{f,298}$(R), kcal/mol[a]	PA(R), kcal/mol[b]
2,3-butanedione, **1**	−78.1	191.7
acetaldehyde (CH_3CHO)	−40.8	183.7
acetone	−52.2	194.0
ketene (CH_2CO)	−11.4	197.3
carbon monoxide (CO)	−26.4	
methane (CH_4)	−17.9	
water (H_2O)	−57.8	

[a] Values taken from ref 49; uncertainties are ±1 kcal/mol or less. [b] Values taken from ref 16; absolute uncertainties are ±2 kcal/mol.

TABLE 2: Fitting Parameters for a Representative Data Set as a Function of Transition State Properties

$\Delta S^‡$ (ketene loss)[a]	ΔH_{298}(43)[b]	ΔH_{298}(45)[b]	ΔH_{298}(59)[b]	n[c]	χ^2 [d]
3.01R	3.18	2.37	2.12	1.23	4.42
3.59R	3.18	2.41	2.13	1.20	3.85
4.03R	3.17	2.43	2.13	1.18	3.49
4.64R	3.16	2.46	2.13	1.17	3.28
5.11R	3.15	2.48	2.13	1.16	3.23
5.43R	3.14	2.49	2.13	1.16	3.33
5.75R	3.13	2.50	2.12	1.17	3.53

[a] Activation entropy for formation of the *m/z* 45 ion; the transition state frequencies correspond to the frequencies of the reactant ion, minus a reaction coordinate, scaled by an appropriate factor. [b] Dissociation enthalpy for the formation of the corresponding ion obtained from the modeling; in eV. [c] Optimized exponential factor, eq 4. [d] Arbitrary units.

mental data. Therefore, in addition to optimizing the standard fitting parameters (E_0, n, σ), we manually vary the transition states to reproduce best the relative cross sections of the three reaction channels.

We fit the data by optimizing the E_0 values for each channel, n, and σ over a given energy range for each data set as the transition states for loss of CH_2CO and CO are systematically varied. The energy range for the fit is 3−6 eV, covering the steeply rising regions of the *m/z* 43 and *m/z* 45 channels, and a flat region of the cross sections for formation of *m/z* 59. Initially, the transition state for loss of CO was restricted to that obtained from the B3LYP calculations. The frequencies for the transition state for formation of the *m/z* 45 ion were taken to be the same as those for the reactant ion, minus a reaction coordinate, and then scaled. The optimized fitting parameters for a representative data set as a function of the $\Delta S^‡$ value for the *m/z* 45 channel are listed in Table 2. There are small differences in the χ^2 values obtained from the different fits, with the best results obtained for a transition state with $\Delta S^‡ = 5.11$ eu. This is significantly looser than the calculated transition state, which has $\Delta S^‡ = -3.52$ eu. After finding the best transition state for CH_2CO loss, the transition state for carbon monoxide loss was optimized in a similar fashion, by fixing the $\Delta S^‡(m/z\ 45) = 5.11$ eu and adjusting the B3LYP frequencies. The iterative process was repeated until a minimum value for χ^2 was obtained. After all the data sets were fit, the average transition states for the two channels were determined, and all the data sets were fit again using common transition states for all data sets. The reported values are the averages obtained using the same transition states for all the data sets. The average 298 K dissociation enthalpies for formation of CH_3CO^+, $CH_3C(OH)H^+$, and $CH_3C(OH)CH_3^+$ are listed in Table 3, along with the optimized fitting parameters. Calculated cross sections are shown as solid lines in Figure 1.

The uncertainties assigned to the dissociation energies include the standard deviations of the results, a 0.15 eV (lab frame) contribution due to uncertainty in the absolute energy scale, and a contribution due to uncertainties in the transition states. The contribution due to choice of transition state was estimated by comparing the measured threshold values with those obtained when one of the transition state entropies was varied while the others were held at their optimized values. The net contribution to the uncertainties is the root-square-sum of the differences between the dissociation energies obtained when the entropies of the three transition states were varied by ±4 eu and those reported in Table 3. Thus, the dissociation energy for formation of the acetyl cation changes by at most 0.013, 0.004, and 0.006 eV when the transition state entropies for formation of *m/z* 43, *m/z* 45, and *m/z* 59 ions, respectively, are changed by ±4 eu. The combination of these components leads to an overall uncertainty of 0.3 kcal/mol in the measured dissociation energy due to the choice of the transition states. A similar exercise was carried out for the other two channels. The ±4 eu uncertainty chosen for the transition state entropy corresponds to at least twice the standard deviations of the optimal activation entropies for the rearrangement channels.

TABLE 3: Average Fitting Parameters for the Dissociation of Protonated Butadiene

channel	*m/z* 43	*m/z* 45	*m/z* 59
ΔH_{298}, kcal/mol	77 ± 3	60 ± 4	50 ± 4
$\Delta S^‡$, eu	+19 ± 4	+7 ± 4	−11 ± 4
n		1.1 ± 0.2	

Given the dissociation energy for formation of CH_3CO^+, only the reaction channels shown in eq 7 are thermochemically accessible. Included in eq 7 are the enthalpies for formation of those neutral products from protonated butanedione, where available.

$$\mathbf{1H}^+ \rightarrow CH_3CO^+ + CO + CH_4 \qquad \Delta H = 17\ \text{kcal/mol} \quad (7a)$$

$$CH_3CO^+ + CH_2CO + H_2 \qquad \Delta H = 40\ \text{kcal/mol} \quad (7b)$$

$$CH_3CO^+ + HCCH + H_2O \qquad \Delta H = 57\ \text{kcal/mol} \quad (7c)$$

$$CH_3CO^+ + CH_3CHO \qquad \Delta H = 20\ \text{kcal/mol} \quad (7d)$$

$$CH_3CO^+ + CH_3COH \quad (7e)$$

Although the neutral products of the dissociation cannot be detected in this experiment, evidence suggests that it is the carbene that is formed along with CH_3CO^+ (eq 7e). The predominance of CH_3CO^+ at high energies, despite the higher energy onset, indicates that formation of this product has a looser transition state than those for formation of the other ions.[34] This is consistent with a direct cleavage mechanism, which would give methylhydroxycarbene, CH_3COH. Additional support for the direct cleavage mechanism comes from deuterium labeling studies. As noted above, CID of deuterated 2,3-butanedione, $\mathbf{1D}^+$ (eq 3), leads to formation of CH_3CO^+ without deuterium incorporation. Previous studies[29,30] have shown that isomerization to the corresponding aldehyde as in eq 7d is often accompanied by deuterium incorporation into the cation fragment. However, whereas these observations are evidence against the formation of acetaldehyde, they do not rule it out and, moreover, do not rule out the other possible reaction channels shown in eq 7. The most important evidence supporting the formation of CH_3COH in the dissociation of protonated butanedione comes from the MIKE experiments. Most importantly, the formation of acetyl cation from metastable ion fragmentation of $\mathbf{1H}^+$ formed by proton transfer from H_3O^+, investigated using MIKE experiments, gives a narrow, essentially Gaussian-shaped peak, consistent with formation by simple bond cleavage[45] with small kinetic energy release. A small $T_{1/2}$ value of 0.07 eV is found, as expected for a simple direct cleavage.[45,46]

The small measured kinetic energy release puts limits on the range of parameters that can be used to model the data. For example, if it is assumed that the neutral products accompanying loss of the acetyl cation are acetylene and water, then the activation energy for formation of the *m*/*z* 43 ion needs to be about 57 kcal/mol to have a small kinetic energy release. A dissociation energy of 57 kcal/mol can be obtained by assuming a very tight transition state for formation of acetyl cation ($\Delta S^{\ddagger} = -11$ eu), which would be consistent with what would be expected for a complicated rearrangement process. Under this assumption, the barriers for loss of CH_2CO and CO are 49 and 39 kcal/mol, respectively. Both values are higher than the adiabatic dissociation energies and, therefore, would correspond to activation barriers for the reactions. However, the validity of these results can be ruled out for two reasons. First, modeling the data with the tight transition state for formation of acetyl requires using unrealistically tight transition states for the loss of ketene or CO. The optimal fit has the activation entropy for loss of ketene of −16 eu, much lower than the calculated value of −3.5 eu for this process. To produce this transition state, it was necessary to increase all the frequencies of the transition state to at least 500 cm^{-1}. The affect on the CO loss channel is even more dramatic, as the best fit to the data required an activation entropy of −30 eu. To obtain a transition state this tight, all the vibrational frequencies below 1100 cm^{-1} had to be increased to that level. Therefore, if the dissociation occurs to form acetylene and water, then the transition state for loss of CO cannot have any frequencies below 1000 cm^{-1}, a highly unlikely scenario. The effects on the modeling parameters are even larger when the data are modeled by assuming the formation of more energetically favorable products shown in eq 7.

A second argument against the formation of rearrangement products is that the small kinetic energy shift rules out a significant barrier for the reverse reaction. In other words, if the dissociation occurs to form neutral products by rearrangement, then that requires the reverse process, the formation of protonated butanedione, to occur without a barrier. This would require that, for example, the termolecular reaction of acetyl cation with acetylene and water would give $\mathbf{1H}^+$ without an enthalpy barrier, an unlikely scenario. On the other hand, singlet carbenes are strong nucleophiles and react readily with electrophilic substrates,[2] including acids.[47,48] For example, at the B3LYP/aug-cc-pVDZ level of theory, the protonation of singlet methylene is predicted to occur without an energy barrier,[41] providing support for the supposition that the carbene can be formed without a reverse activation barrier. Therefore, formation of the carbene by direct dissociation is consistent with a small kinetic energy release. It should be noted that the small kinetic energy release for the *m*/*z* 43 ion is inconsistent with the ion being formed by dissociative rearrangement of the *m*/*z* 59 product. Given the measured kinetic energy release results and its implications, the most reasonable assumption is that the formation of acetyl cation occurs by direct dissociation to form the methylhydroxycarbene as the neutral product.

Thermochemical Results. Given that CH_3CO^+ is formed by direct dissociation without a barrier in excess of the endothermicity, then the enthalpy of formation of methylhydroxycarbene can be calculated from eq 8, where $\Delta H_{298}(CH_3CO^+{-}CH_3COH)$ is the enthalpy of the acetyl cation−methylhydroxycarbene bond, obtained from the energy-resolved CID experiments. Using $\Delta H_{f,298}(\mathbf{1}) = -78.1 \pm 1.0$ kcal/mol[49] and $PA(CH_2CO) - PA(\mathbf{1}) = 5.6 \pm 1.4$ kcal/mol (see Table 1),[16,50] the enthalpy of formation of CH_3COH is calculated to be 16 ± 4 kcal/mol, where the uncertainty is the root-square-sum of the component uncertainties.

$$\Delta H_{f,298}(CH_3COH) = \Delta H_{298}(CH_3CO^+{-}CH_3COH) + PA(CH_2CO) - PA(\mathbf{1}) - \Delta H_{f,298}(CH_2CO) + \Delta H_{f,298}(\mathbf{1}) \quad (8)$$

The measured enthalpy of formation of methylhydroxycarbene is 57 ± 4 kcal/mol higher than that of acetaldehyde (Table 1). The result is in good agreement with the calculated values for the energy difference between methylhydroxycarbene and acetaldehyde, which range from 51 kcal/mol at the G1 level of theory to 62 kcal/mol obtained by using CISD/3-21G approach.[22,26,27] At the G2[51] and CBS-Q[52] levels of theory, the isomerization energy is calculated to be 50.9 and 51.3 kcal/mol, respectively. Although the measured energy difference between the carbene and the aldehyde is higher than that calculated at high levels of theory, it is only slightly less than that measured for HCOH, 60.4 kcal/mol.[17] Therefore, methyl substitution does not have a large effect on the energy for the carbene−aldehyde isomerization reaction.

The enthalpy of formation of methylhydroxycarbene can be used to derive additional thermochemical properties, including the second C−H bond dissociation energy (BDE) in ethanol. A reliable value for the α-C−H BDE in ethanol can be obtained from electronic structure calculations. At the CBS-Q level of theory,[52] the 298 K enthalpy for the reaction in eq 9 is calculated

$$CH_3CH_2OH + CH_2OH \rightarrow CH_3CHOH + CH_3OH \quad (9)$$

to be −1.4 kcal/mol, which corresponds to the difference in the α-C−H BDE in ethanol and the C−H BDE in methanol. Using $\Delta H_{298}(HOCH_2{-}H) = 98.1 \pm 1.0$ kcal/mol[49] gives an α BDE in ethanol of 96.7 kcal/mol, which leads to a BDE of 80 kcal/mol for the α C−H bond in methylhydroxy radical.[16,53,54] Poutsma et al.[11] noted a remarkable relationship between the difference in the first and second C−H BDEs (the "Divalent State Stabilization Energy", DSSE) and the singlet−triplet energy splitting (ΔE_{ST}) in carbenes. For a series of halogen-substituted carbenes, ΔE_{ST} is related to the DSSE by the relationship shown in eq 10 (values in kcal/mol), with a correlation coefficient $r^2 = 0.9995$.

$$\Delta E_{ST} = 1.33{*}DSSE + 6.11 \quad (10)$$

Moreover, comparison with theoretical calculations suggests that the relationship holds for a wide variety of singlet carbenes, including those with hydroxy substituents. By using the relationship shown in eq 10 with the estimated DSSE for the formation of methylhydroxycarbene, a singlet−triplet splitting of ∼28 kcal/mol is obtained. This is slightly higher than the value of 23.0 predicted by Yadav and Goddard[26] but is in reasonable agreement with a value of 30.5 kcal/mol obtained at the CBS-Q level of theory. A value of 33.0 kcal/mol is obtained with the G2 approach. A summary of the energies for many of the decomposition processes of ethanol is shown in Figure 2.

Methylhydroxycarbene is a potential product of the reaction of carbon atom with methanol. From the measured enthalpy of formation, insertion of ^3P carbon into the C−O bond of methanol is exothermic by 107 ± 4 kcal/mol.[13] To put this result into context, it will be necessary to measure the energies for methoxy- and hydroxymethylcarbenes, which result from insertion into the O−H and C−H bonds, respectively. These experiments are currently in progress.

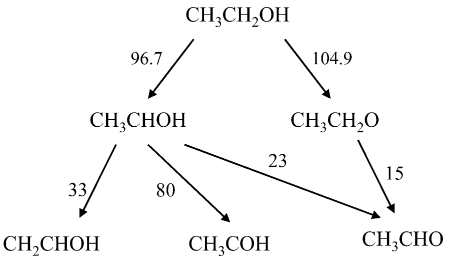

Figure 2. Experimental C−H bond dissociation energies (in kcal/mol) for the decomposition of ethanol.

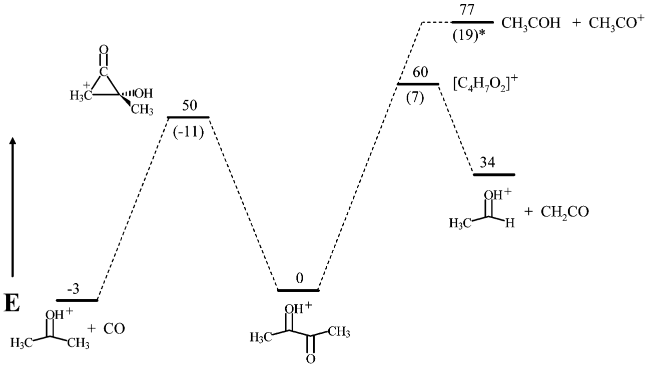

Figure 3. Experimentally determined thermochemical parameters for dissociation of protonated butanedione. Activation energies (in kcal/mol) and activation entropies (in eu, indicated in parentheses) were determined by modeling the energy-resolved CID data. Reaction energies for formation of protonated acetaldehyde and protonated acetone were calculated from literature data.[16] The activation entropy for formation of acetyl cation and the carbene (marked with ∗) corresponds to the value for the orbiting transition state calculated by using phase space theory. The structure of the transition state for ketene loss is not known; see text for discussion.

Other Products. The dissociation enthalpies measured for ketene and carbon monoxide loss are higher than the thermodynamic limits for these reactions by 26 and 53 kcal/mol, respectively, and likely correspond to the energies of the rearrangement transition states. A potential energy surface showing the dissociation processes of protonated butanedione is shown in Figure 3. In the MIKE experiments, the peak of *m*/*z* 59 corresponding to the loss of carbon monoxide is about 3 times the width of the *m*/*z* 43 peak and dish-shaped, indicating a substantial kinetic energy release (KER) into the ion, consistent with a reverse activation energy associated with the dissociation reaction. The $T_{1/2}$ value obtained from the *m*/*z* 59 peak is 1.21 eV, much greater than the value of 0.07 eV found for formation of the ion with *m*/*z* 43. The reverse energy barrier is expected because the formation of protonated acetone and carbon monoxide from $\mathbf{1H}^+$ is slightly exothermic, 52.6 kcal/mol lower than the measured activation energy. At the B3LYP/6-31+G* level of theory, the transition state for carbon monoxide loss is calculated to be 1.5 eV lower in energy than acetyl cation + methylhydroxycarbene, in fair agreement with the observed energy difference of 1.2 eV. Therefore, both the activation entropy and the energy of the calculated transition state agree with the experimentally determined parameters.

Given that the measured activation entropy of the transition state for the loss of ketene channel is significantly different from that for the calculated structure, it is not surprising that the measured energy of the transition state, 60 ± 4 kcal/mol, is significantly lower than that for the calculated structure, ~76 kcal/mol. The lower measured energy for this process along with the loose transition state suggest that the transition state for ketene loss is more product-like than that obtained from the calculations. However, a product-like transition state for formation of $CH_3C(OH)H^+$ and ketene is found to be too loose and does not give a good fit of the data. Therefore, although the transition state is significantly looser than that calculated, it is not a simple product-like transition state in the phase space limit. It is likely that for this process, the transition state would correspond to the point where the proton transfer occurs. Because this will occur along the simple bond cleavage reaction pathway, the transition state will be very loose, similar to the transition state for simple cleavage. Attempts to calculate the transition state corresponding to this dissociation pathway have been unsuccessful. The MIKE experiments indicate a $T_{1/2}$ value of 0.32 eV for formation of the *m*/*z* 45 ion, smaller than that for the *m*/*z* 59 ion, but still consistent with the formation by a rearrangement process. The smaller KER in the protonated acetaldehyde product compared to the protonated acetone is likely because the energy difference between the barrier and the products, 26 kcal/mol, is only half as large as that for the CO loss channel.

Conclusions. Collision-induced dissociation of protonated butanedione occurs by three reaction pathways. Two are rearrangement pathways that lead to the formation of protonated carbonyl compounds, whereas the third is direct dissociation resulting in the formation of acetyl cation and methylhydroxycarbene. From the measured threshold for the direct dissociation, the enthalpy of formation of methylhydroxycarbene is found to be 16 ± 4 kcal/mol, and the energy required for isomerization to acetaldehyde is 57 ± 4 kcal/mol. The difference between the first and second C−H bond dissociation energies in ethanol, obtained in this work, implies a singlet−triplet splitting of 28 kcal/mol.

Activation energies for the rearrangement processes have also been obtained and are found to be 60 ± 4 and 50 ± 4 kcal/mol for the loss of ketene and carbon monoxide, respectively. Unlike most of the previous studies of competitive CID involving rearrangements, the entropies of the transition states for these channels were obtained empirically, by finding the values that gave the best fits to the data, as opposed to using a calculated structure. The energy and entropy of the transition state for carbon monoxide loss are in good agreement with those predicted for a tight transition state at the B3LYP/6-31+G* level of theory. However, the measured transition state parameters for ketene loss do not agree with those obtained computationally and suggest that the products are formed by a different mechanism, through a significantly looser transition state.

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Supporting Information Available: Metastable kinetic energy spectrum for the decomposition of $\mathbf{1H}^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The enthalpy of formation of 60.4 kcal/mol for HCOH used in this work is higher than the original value of 54.2 kcal/mol reported by Pau and Hehre.[15] The difference is due to revision of the proton affinity scale that has occurred since the original report.[16]

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