Mechanisms of photodissociative ionization of HCOOH: The heat of formation of $COOH^+$

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The dissociative ionization of HCOOH to form $COOH^+ + H + e$ has been reinvestigated. Experiments with DCOOH and HCOOD demonstrate that rearrangement competes with direct bond cleavage in this dissociation, even near threshold. Extrapolation of the photoion yield curve of $COOH^+$ to the background level is ambiguous. A photoelectron–photoion coincidence experiment was thereupon performed, to obtain a breakdown diagram. From the 0 K cross over energy of 12.30 ± 0.02 eV, we infer $\Delta H_{f_0^0}$ $(COOH^+) = 143.2 \pm 0.5$ kcal/mol, and proton affinity (PA) $(CO_2) = 129.2 \pm 0.5$ kcal/mol. Some possible mechanisms for the rearrangement process are explored, but the calculated barriers are too high to explain the observation.

I. INTRODUCTION

The free radical COOH and its cation, $COOH^+$, have both been the subjects of extensive investigation, but these studies have been almost completely disconnected from one another. The goal of the present article is to reexamine the heat of formation of $COOH^+$, by photodissociative ionization of HCOOH. In the accompanying article,[1] we generate the neutral COOH and produce the cation by photoionization. The adiabatic ionization potential is, of course, the link between the heats of formation of COOH and $COOH^+$. Prior studies related to $\Delta H_f^0(COOH^+)$ are summarized below.

Pritchard *et al.*,[2] studied formic-*d* acid (DCOOH) by electron impact, and found an appearance potential of 12.4 eV for $m/e = 46$ $(DCOO^+)$ and 12.8 eV for $m/e = 45$ $(COOH^+)$, implying that $DCOO^+$ is the structure which is more stable. We shall return to this process in the present study, using photoionization, and demonstrate that in all likelihood a rearrangement occurs, so that the lower energy process corresponds to $COOD^+$. More recently, Burgers *et al.*,[3] have offered evidence that $HCOO^+$ may be stable enough to survive at least 10 μs before rearranging to $COOH^+$. A precise value of the heat of formation of $COOH^+$ implies an accurate value for the proton affinity of CO_2. The structural question then can be rephrased—is the proton affinity greater at the C or the O site?

It is known from laboratory studies that a $COOH^+$ entity is formed in the proton transfer reaction between H_3^+ and CO_2. Ion–molecule reactions are thought to play an important role in the formation of interstellar molecules.[4] $COOH^+$ is one of the key ions which are assumed as intermediates in a variety of gas phase reactions in interstellar clouds. In 1981, Thaddeus *et al.*,[5] detected some interstellar lines in the 85 GHz region which they tentatively assigned to $HOCO^+$ or HOCN. (Here, $HOCO^+$ is synonymous with $COOH^+$.) Shortly thereafter, Bogey *et al.*,[6,7] obtained the submillimeter wave spectrum of $COOH^+$ in the laboratory, leading to the conclusion that three interstellar lines were indeed due to $COOH^+$. Just after the initial observations of Bogey *et al.*,[6] Amano and Tanaka[8,9] observed the ν_1 fundamental band of $COOH^+$ in laboratory investigations in the infrared, providing independent confirmation, and also detailed spectroscopic information from which a structure could be deduced.

Some *ab initio* calculations were reported at about the same time as these spectroscopic observations. Frisch *et al.*,[10] and later Yu *et al.*[11] calculated the geometric structures and stabilities of $COOH^+$ and HCO_2^+. The two calculations agree rather well with one another. Their calculated structures and frequencies appear to be close to the experimental values of Amano and Tanaka.[12] According to these calculations, HCO_2^+ appears to be much less stable than $COOH^+$, lying 105.8–108.7 kcal/mol higher according to Frisch *et al.*,[10] and 115.4 kcal/mol higher from the Yu *et al.*[11] results. Furthermore, the barrier to rearrangement $(HCO_2^+ \rightarrow COOH^+)$ is small: 0.4–9.5 kcal/mol,[10] or 8.47 kcal/mol.[11] These calculations (see below) appear to be in fairly good agreement with experimental values for the proton affinity of CO_2. If the calculated barrier to rearrangement is as accurate, the implication is that HCO_2^+ may be able to survive briefly, if prepared in a narrow energy range near its local minimum.

The most direct approach to the determination of the heat of formation of $COOH^+$ [and hence proton affinity (PA) (CO_2)] is by measuring the dissociative ionization threshold from HCOOH by photoionization. It is the lowest energy fragmentation path. We are aware of three such measurements. Warneck[13] reported 1009 ± 3 Å $\equiv 12.29 \pm 0.03$ eV for this threshold. Villem *et al.*[14] obtained 12.26 ± 0.02 eV as a photodissociative ionization threshold, and later Golovin *et al.*,[15] reported 12.36 ± 0.1 eV. Apart from the small variation in threshold determination, there are two factors that neither Warneck nor the Russian workers appear to have taken into account in determining ΔH_f $(COOH^+)$. The value for ΔH_f (HCOOH) used by Warneck is -3.919 eV $\equiv -90.37$ kcal/mol, that by the Russian workers is -90.58 kcal/mol. Both appear to be values for $\Delta H_{f_{298}^0}$ (HCOOH), which is given in the NBS compilation[16] as -90.45 kcal/mol. The corresponding value at 0 K is

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-88.79 kcal/mol.[17] Furthermore, there is no indication that either group considered the influence of the internal energy of HCOOH on the dissociative ionization threshold; the inference is that they performed a simple linear extrapolation. Such an onset should be shifted to higher energy by the internal thermal energy of HCOOH at 298 K, which amounts to 1.125 kcal/mol. These corrections are additive in determining $\Delta H_{f_0^0}(COOH^+)$. When taken into account, they yield 143.4 ± 0.5 kcal/mol[14] 144.1 ± 0.7 kcal/mol[13] and 145.7 ± 2.3 kcal/mol.[15] The corresponding proton affinities of CO_2 at 0 K are 127.9, 127.2, and 125.6 kcal/mol. Proton affinities are generally evaluated at 298 K, for which the above values become 129.0 ± 0.5, 128.3 ± 0.7, and 126.7 ± 2.3 kcal/mol, respectively. Frisch *et al.*,[10] obtained 130.7 kcal/mol for this quantity, using their *ab initio* energies and empirically correlated frequencies, in good agreement with these experimental values.

II. EXPERIMENTAL ARRANGEMENT

The basic photoionization mass spectrometric apparatus has been described previously.[18] Two different target chambers were employed. The experiment performed directly on HCOOH, HCOOD, DCOOH, and DCOOD utilized a conventional, more enclosed ionization chamber. As we shall illustrate below, there were some ambiguities in the threshold determinations from these species, which motivated us to measure a coincidence spectrum involving mass analyzed photoions and threshold photoelectrons. For this latter experiment, the target chamber contained a collimated hole structure on one side (for selecting near zero energy electrons) and a wire mesh opposite this side. The collimated hole structure is sometimes referred to as a steradiancy analyzer, and has been described previously.[19] A field of 6–8 V/cm was applied across this region, directing the near zero energy electrons through the collimated hole structure to a channeltron multiplier. The same field accelerated the ions through the wire mesh and into the focusing lens system, quadrupole mass filter, and a dynode multiplier. For these coincidence experiments, a detected photoelectron provided a start pulse, while the detected photoion provided the stop pulse. The coincidence measurements were performed on HCOOH and DCOOD, in the energy region where the first fragmentation occurs. Corresponding threshold photoelectron spectra were also obtained in this energy region. The HCOOH sample was from K&K Laboratories (99%), while HCOOD, DCOOH, and DCOOD (all declared as 98% D) were obtained from Cambridge Isotope Laboratories. The samples were used without further purification, although the experiments with HCOOD and DCOOD required prolonged deuteration of the inlet line.

The primary light source utilized in these experiments was the many-lined emission from a discharge through molecular hydrogen. The wavelength resolution was 0.28 Å [full width at half-maximum (FWHM)].

III. EXPERIMENTAL RESULTS

A. Photodissociative ionization of HCOOH and DCOOH

In order to establish more precisely the heat of formation of $COOH^+$, and to examine the possibility of detecting $HCOO^+$, we reexamined the photodissociative onset for $COOH^+$ from formic acid.

1. HCOOH—the threshold for formation of $COOH^+$/$HCOO^+$

The photoion yield curve for formation of ions with $m/e = 45$ from HCOOH in the threshold region is shown in Fig. 1. Unlike the normal photoion yield curve of a fragment ion, which typically displays a linear postthreshold behavior, this fragmentation threshold curve has a tail ($\sim$1015–1010 Å), followed by a linear ascent ($\sim$1010–1003 Å), then a brief, steeper increase ($\sim$1003–1001 Å) followed by a plateau ($\sim$1000–992 Å) and another steep increase ($\sim$992–990 Å), almost like step function behavior.

It is known that formic acid (HCOOH) exists in *cis* and *trans* forms, differing in energy by about 4 kcal/mol.[20] One possible explanation for the step-like behavior is production of $HCOO^+/COOH^+$ from each of these isomeric species, the difference in onsets representing the difference in energy between *cis* and *trans* forms. However, Boltzmann population arguments based on the energy gap between *cis* and *trans* forms of formic acid, enable us to conclude that the isomeric composition of formic acid vapor does not play a relevant role in these threshold measurements (the population of the higher energy *cis* form is too small to be significant). Another possible source of confusion is the presence of hydrogen-bonded dimers of formic acid in the vapor. Thomas[21] has examined this effect in the photoelectron spectrum of formic acid at several temperatures. At 300 K and 10 mTorr pressure, he calculates a trivial (nominally zero) dimer: monomer ratio, and our target pressure is $\sim$2 orders of magnitude lower. Hence, dimer effects can be safely excluded in our experiment. A third possibility, which seems extremely unlikely in view of the information concerning the relative stabilities of $COOH^+/HCOO^+$ discussed in Sec. I, is that the two onsets are related to the thresholds for forma-

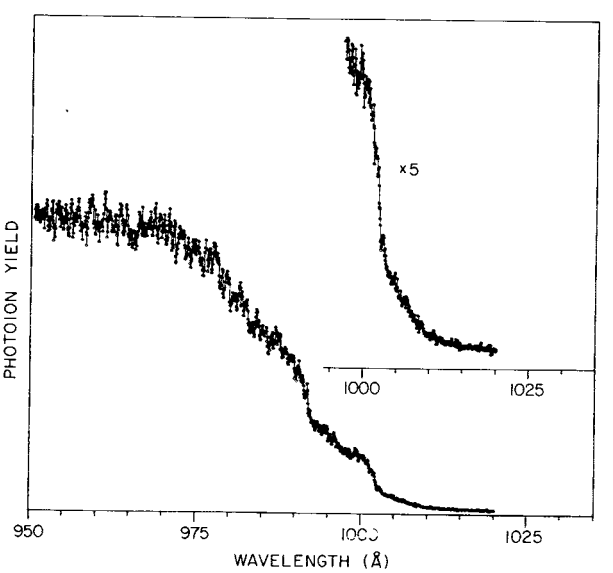


FIG. 1. The photoion yield curve of $m/e = 45$ from HCOOH. This turns out to be the structure $COOH^+$, as established in the DCOOH experiment.

tion of these respective isomeric fragments. Finally, a possible explanation involves the excitation function, or probability of ionization, of the parent ion prior to dissociation. This total ionization cross section displays vibrational steps near the two aforementioned steep onsets.[14] As we shall see later, the two steep increases very nearly correspond to the formation of $v'=0$ ($\sim$1001.4 Å) and $v'=1$ ($\sim$991.2 Å) in the first excited state of $HCOOH^+$. Thus, we can tentatively extract a threshold for the formation of the fragment with $m/e=45$ by extrapolating the initial linear ascent ($\sim$1010–1003 Å), rather than the steeper increase corresponding to the vibrational step. This procedure yields a value of 1011.0 ± 0.3 Å $\equiv 12.264$ eV.

In order to further clarify the isomeric possibilities and to arrive at a more unambiguous explanation, we decided to examine the photodissociative ionization behavior of DCOOH.

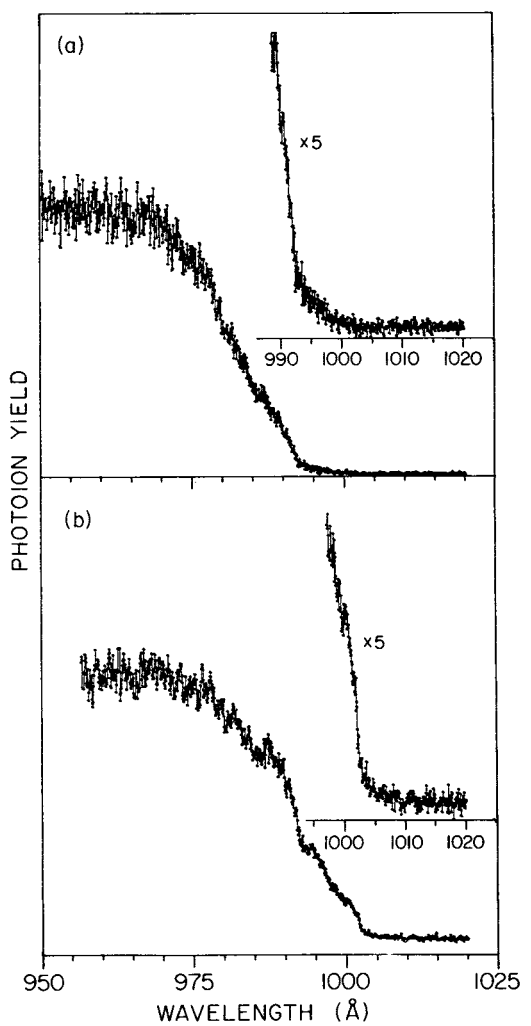


FIG. 2. (a) The photoion yield curve of $m/e=45$ from DCOOH. [The isotopic impurity HCOOH was 2%; the $COOH^+$ (HCOOH) contribution has been subtracted.] (b) The photoion yield curve of $m/e=46$ from DCOOH.

2. DCOOH—the thresholds for formation of $m/e=45$ and 46

The photoion yield curves for formation of ions with $m/e=45$ and $m/e=46$ are shown in Figs. 2(a) and 2(b), respectively. It is immediately apparent that the threshold region for $m/e=45$ does not display the two step onset, whereas $m/e=46$ does. The linearly extrapolated onset for $m/e=45$ to the background level occurs at $\sim$993.5 Å $\equiv$ 12.480 eV, whereas the corresponding extrapolated onset for $m/e=46$ occurs at $\sim$1003.0 Å $\equiv$ 12.361 eV. (It should be noted that, unlike $m/e=45$ in HCOOH, the $m/e=46$ fragment in DCOOH does not display a brief linear portion before the steep onset which corresponds to the first step.) The fact that the sharp, step-like increases are observed in the $m/e=46$ curve, but not in the $m/e=45$ curve, appears to be simply a consequence of the appearance energies of these fragments. The higher appearance energy of $m/e=45$ occurs at or beyond the second step.

If $m/e=46$ corresponded to a $DCOO^+$ structure formed by simple bond rupture of the O–H bond, and $COOH^+$ ($m/e=45$) resulted from simple bond rupture of the C–D bond in $DCOOH^+$, then we would be left with the conclusion that $DCOO^+$, having the lower threshold, is more stable than $COOH^+$. This conclusion seems extremely unlikely, in view of the extensive discussion on this point in Sec. I. It will be recalled, however, that these experimental observations are somewhat similar to those of Pritchard *et al.*[2] which led them to draw just such a conclusion. The *ab initio* calculations of Frisch *et al.*,[10] which compared so favorably with the newly found geometrical structure of $COOH^+$ as well as the proton affinity of CO_2, and which predict that $HCOO^+$ is less stable than $COOH^+$ by 4.59–4.71 eV, and also the calculations of Yu *et al.*,[11] which find that $HCOO^+$ is 4.99 eV less stable than $COOH^+$, appear to make this view untenable. Instead, our inference is that simple bond cleavage does not occur to form $DCOO^+$. Rather, rearrangement occurs in the dissociative ionization process, so that the $m/e=46$ ion appears at or near the threshold for $COOD^+$.

If thermochemistry alone governs the appearance potentials of $COOD^+$ and $COOH^+$, then one can estimate the difference in appearance potentials from the respective zero-point energies. In the absence of secondary isotope effects, we can formally write

$$\mathrm{AP}\ (\mathrm{COOD}^+) = \Delta_e - \mathrm{zpe}(\mathrm{DCOOH}) + \mathrm{zpe}(\mathrm{COOD}^+), \tag{1}$$

$$\mathrm{AP}\ (\mathrm{COOH}^+) = \Delta_e - \mathrm{zpe}(\mathrm{DCOOH}) + \mathrm{zpe}(\mathrm{COOH}^+), \tag{2}$$

where AP stands for the appearance potential, Δ_e is the energy from the bottom of the DCOOH potential energy surface to the bottom of the dissociative potential energy surface, and zpe refers to the respective zero point energies. Subtracting Eq. (1) from Eq. (2), we obtain

$$\mathrm{AP}(\mathrm{COOH}^+) = \mathrm{AP}(\mathrm{COOD}^+) + \mathrm{zpe}(\mathrm{COOH}^+) - \mathrm{zpe}(\mathrm{COOD}^+). \tag{3}$$

The *ab initio* calculations of Frisch *et al.*[10] provide us with

the vibrational frequencies of both $COOH^+$ and $COOD^+$. Thus, zpe $(COOH^+) = 4643$ cm^{-1}, zpe $(COOD^+) = 4034.5$ cm^{-1}, and their difference is 608.5 $cm^{-1} \equiv 0.075$ eV, which is close to the experimentally determined difference, 0.118 eV, with the $COOD^+$ fragment appearing at the lower energy. This result implies that there is very little activation energy involved in the rearrangement.

Similarly, we can write

$$\mathrm{AP}\ (COOH^+) = \Delta_e - \mathrm{zpe}(HCOOH) + \mathrm{zpe}(COOH^+). \quad (4)$$

Now substracting Eq. (1) from Eq. (4), we obtain

$$\mathrm{AP}\ (COOH^+/HCOOH) - \mathrm{AP}\ (COOD^+/DCOOH) = \mathrm{zpe}(DCOOH) - \mathrm{zpe}(HCOOH) + \mathrm{zpe}(COOH^+) - \mathrm{zpe}(COOD^+).$$

The vibrational frequencies of HCOOH and DCOOH are fairly well established experimentally.[22] The corresponding zpes are 7161.5 and 6508.5 cm^{-1}, and their difference, 653 cm^{-1}, very nearly cancels the difference in zpes between $COOH^+$ and $COOD^+$, 608 cm^{-1}. Thus, AP $(COOH^+/HCOOH)$ should be very nearly the same as AP $(COOD^+/DCOOH)$, i.e., within 0.5 Å. This is not quite the case, as can be noted by comparing the threshold value in Fig. 1 with that in Fig. 2(b). These thresholds are also listed in Table I. The extrapolated threshold in Fig. 1 is 12.264 eV, that in Fig. 2(b) is 12.361 eV, a difference of almost 0.1 eV. Admittedly, this calculation combines experimental frequencies for the parent neutral species with *ab initio* calculated frequencies for the cation fragments, but the latter have been shown to be rather close to experimental values, where available, and the nature of the calculation allows for cancellation of errors. A plausible explanation is that the appearance of $COOD^+$ from DCOOH is very slightly ($\sim$0.1 eV) retarded by the barrier to rearrangment.

These preliminary experiments provided us with an approximate value for the dissociative ionization threshold, but forced us to focus on two problems which needed to be solved before a more accurate appearance potential could be obtained.

(1) There appear to be two mechanisms, simple bond cleavage and rearrangement, contributing to the fragment intensity near the ionization threshold. Can the superposition of the fragment intensities from these two processes confuse the extrapolation procedure used in determining the onset of fragmentation in HCOOH?

(2) In those instances where a "step behavior" is observed in the threshold region, the true fragmentation threshold occurs at lower energy than the steps, in a Frank–Condon gap. The intensity of the fragment ion is weak in this region, and the ion yield curve displays curvature, making a linear extrapolation uncertain.

In order to clarify the effects of total ionization probability, rearrangement and possible kinetic shift effects, additional experiments were performed.

B. Photodissociative ionization of HCOOD and DCOOD

1. HCOOD

Our first approach was to examine the fragmentation thresholds for the remaining isotopic forms (HCOOD and DCOOD), and to use analogous zero point energy analyses, in the hope that a consistent appearance potential would emerge.

The photoion yield curves of $CCOH^+$ (HCOOD) and $COOD^+$ (HCOOD) are displayed in Figs. 3(a) and 3(b), respectively. In Figure 3(a) (extrapolated onset = 993.2 $\pm$ 0.6 Å $\equiv$ 12.483 $\pm$ 0.008 eV), there is no step structure, just a linear postthreshold increase. In Fig. 3(b), one sees the two steps, and below them a short linear region with an extrapolated onset of 1011.0 $\pm$ 1.0 Å $\equiv$ 12.264 $\pm$ 0.012 eV. As in Figs. 2(a) and 2(b), the $COOD^+$ appears at lower energy than the $COOH^+$, although in the DCOOH case it requires a rearrangement, whereas in the HCOOD case it could occur by simple bond cleavage. The appearance of step structure for the $m/e = 46$ fragment, and its absence in the $m/e = 45$ fragment, is again a consequence of the location of steps in the total ion yield. In the $m/e = 45$ figures, the onset occurs beyond (at higher energy than) the steps in the total ion yield, and hence is absent.

TABLE I. Appearance energies and Δ_e values for dissociative ionization of isotopic formic acid species.

Process	Appearance wavelength, (Å)	0 K appearance energy (eV)[a]	Δ_e (eV)[a,b]
$HCOOH \rightarrow COOH^+ + H + e$	1011.0 $\pm$ 0.3	12.312 $\pm$ 0.004	12.624 $\pm$ 0.004
$DCOOH \rightarrow COOD^+ + H + e$	1003.0 $\pm$ 0.3	12.411 $\pm$ 0.004	12.718 $\pm$ 0.004
$DCOOH \rightarrow COOH^+ + D + e$	993.5 $\pm$ 0.3	12.529 $\pm$ 0.004	12.760 $\pm$ 0.004
$HCOOD \rightarrow COOD^+ + H + e$	1011.0 $\pm$ 1.0	12.315 $\pm$ 0.012	12.623 $\pm$ 0.012
$HCOOD \rightarrow COOH^+ + D + e$	993.2 $\pm$ 0.6	12.535 $\pm$ 0.008	12.767 $\pm$ 0.008
$DCOOD \rightarrow COOD^+ + D + e$	1003.7 $\pm$ 0.3	12.406 $\pm$ 0.004	12.637 $\pm$ 0.004

[a] Vibrational frequencies for computation of zero point energies and internal thermal energy corrections of isotopic formic acid species taken from Ref. 22; vibrational frequencies of $COOH^+$ and $COOD^+$ for computation of zero point energies taken from Ref. 10. The appearance wavelengths are corrected to 0 K as described by P. M. Guyon and J. Berkowitz, J. Chem. Phys. **54**, 1814 (1971).

[b] Δ_e (analogous to D_e) is the difference in electronic energy from the minimum of the initial formic acid species to the minimum of the products.

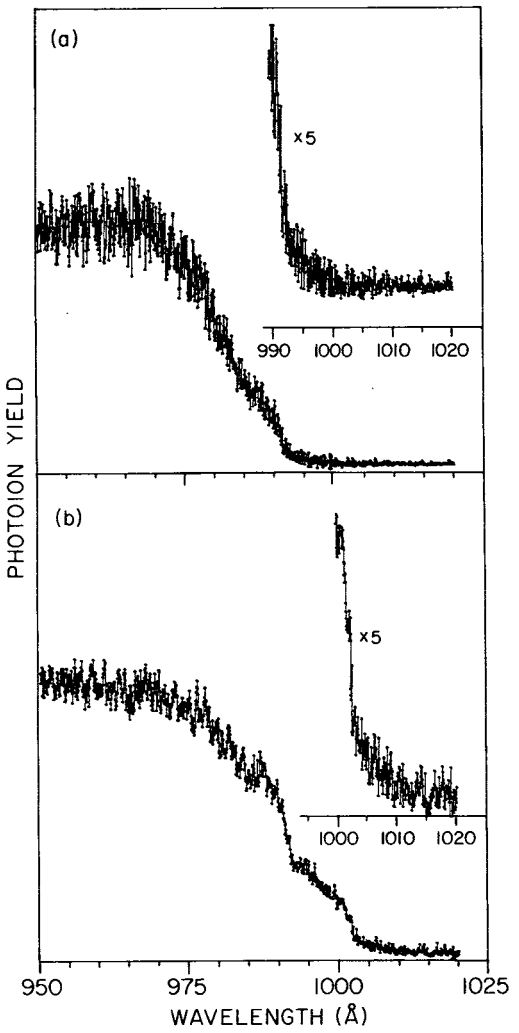


FIG. 3. (a) The photoion yield curve of $m/e = 45$ from HCOOD. [The isotopic impurity HCOOH was 6.5%; the $COOH^+$ (HCOOH) contribution has been subtracted.] (b) The photoion yield curve of $m/e = 46$ from HCOOD. [A background at $m/e = 46$ due to $HCOOH^+$ (HCOOH) from the isotopic impurity is suppressed in this figure.]

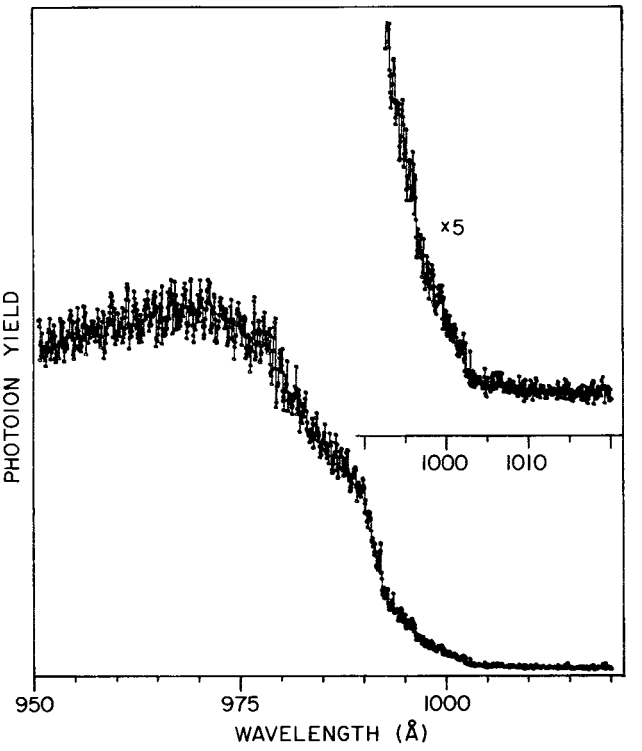


FIG. 4. The photoion yield curve of $m/e = 46$ from DCOOD.

2. DCOOD

The photoion yield curve of $COOD^+$ (DCOOD) appears in Fig. 4. Between ~1010–992 Å, one observes a somewhat curved ascent; between ~992–990 Å there is a steeper increase, and below 990 Å, a more gradual and linear portion. Prior to the present work, we were unaware of any photoelectron spectrum of DCOOD. We shall show below that the steep increase between ~992–990 Å corresponds to the formation of $v' = 1$ in the first excited state of $DCOOD^+$. It is interesting, and we believe significant, that no steep increase appears at the $v' = 0$ position. We shall return to this point in the next section. The extrapolation of the photoion yield curve to the background level yields an appearance potential of 1003.7 ± 0.3 Å $\equiv 12.353 \pm 0.004$ eV.

All of the appearance potentials mentioned above have subsequently been corrected for internal thermal energy of the neutral species, and are summarized in Table I. Also listed there are the values of Δ_e obtained from each threshold. If each of these thresholds were thermochemically significant, the various Δ_e values should be the same, apart from secondary isotope effects. The observed values can be placed into two categories. The lowest thresholds [$COOH^+$ (HCOOH), $COOD^+$ (HCOOD), and $COOD^+$ (DCOOD)] have Δ_e (avg) $= 12.628 \pm 0.013$ eV; each is the lowest energy fragment, and can be produced by simple bond cleavage. The other three processes, with $\Delta_e > 12.718$ eV, involve either rearrangememt [$COOD^+$ (DCOOH)] or correspond to a thermochemically higher energy process [$COOH^+$ (DCOOH)], or both [$COOH^+$ (HCOOD)].

C. Photoion–photoelectron coincidence studies

The next approach was the photoelectron–photoion coincidence experiment. In this study, the number of true coincidences between near zero energy photoelectrons and parent photoions are recorded at a selected photon energy, and the process repeated for photoelectrons and fragment ions. The fraction of total coincidences for parent and fragment ions is plotted as a function of photon energy, producing a breakdown diagram. The cross-over point, where half the coincidences occur for parent ions and the other half for fragment ions, should be close to the 0 K appearance energy. Corrections (usually small) need to be made to take into account the initial thermal energy of the molecule, the transmission function of the steradiancy analyzer, and the energy deposition function, in this case the threshold photoelectron spectrum. In Figs. 5(c) and 6(c), the breakdown diagrams are displayed for HCOOH and DCOOD. Above each breakdown diagram is the corresponding photoion yield curve,

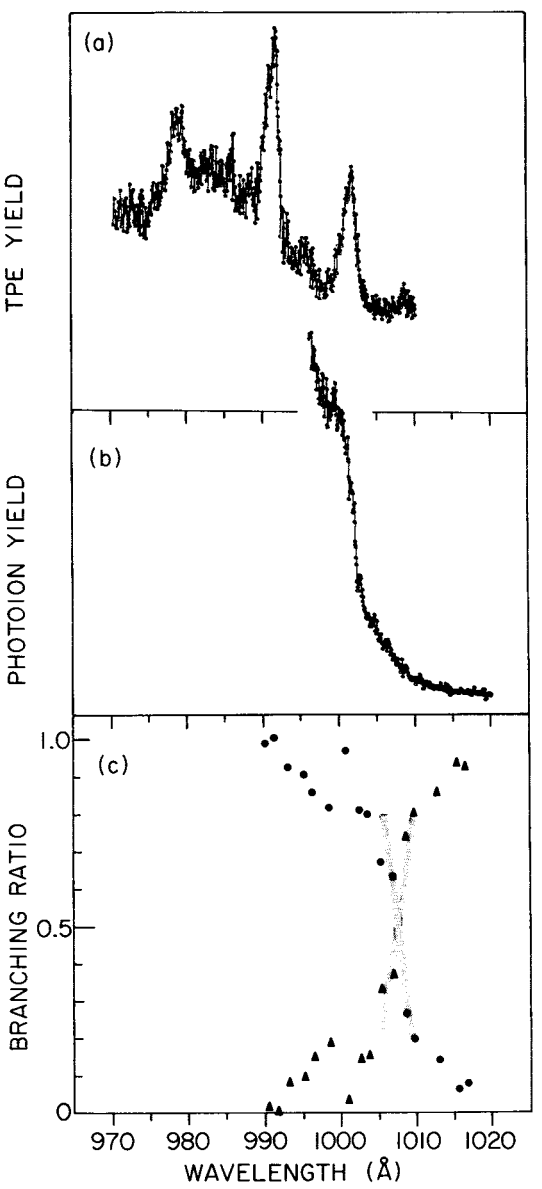


FIG. 5. (a) Threshold photoelectron spectrum of HCOOH. (b) Expanded photoion yield curve of $COOH^+$ (HCOOH). (c) The breakdown diagram for the process $HCOOH^+ \rightarrow COOH^+ + H$. ● fraction of coincidences with $COOH^+$ ($m/e = 45$). ▲ fraction of coincidences with $HCOOH^+$ ($m/e = 46$).

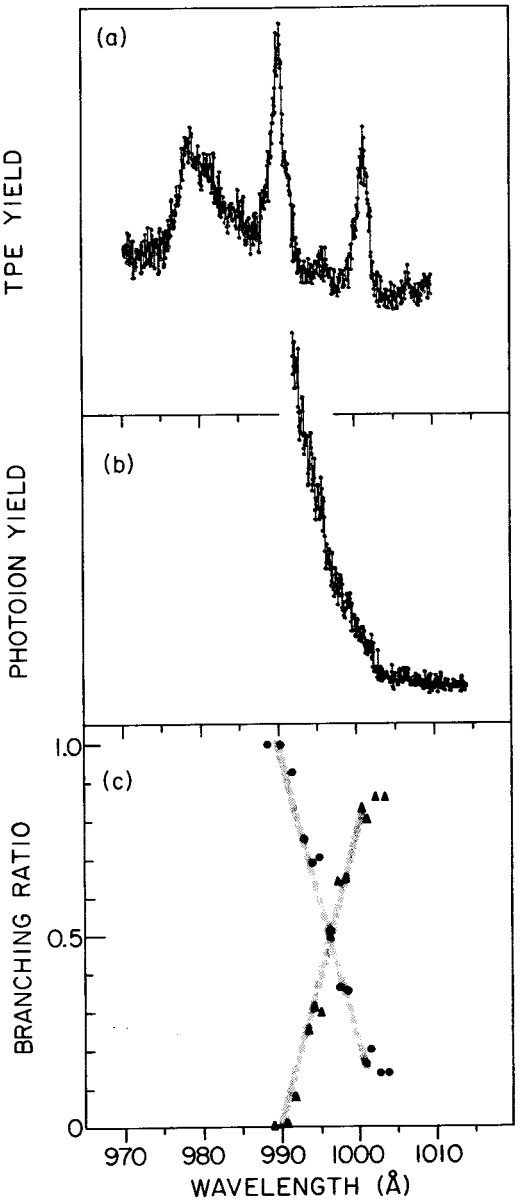


FIG. 6. (a) Threshold photoelectron spectrum of DCOOD. (b) Expanded photoion yield curve of $COOD^+$ (DCOOD). (c) The breakdown diagram for the process $DCOOD^+ \rightarrow COOD^+ + D$. ● fraction of coincidences with $COOD^+$ ($m/e = 46$). ▲ fraction of coincidences with $DCOOD^+$ ($m/e = 48$).

i.e., $COOH^+$ (HCOOH) in Fig. 5(b) and $COOD^+$ (DCOOD) in Fig. 6(b). In the upper panels [Fig. 5(a) and 6(a)] are the corresponding threshold photoelectron spectra (TPES). The TPES are quite similar to one another, and also similar to the He I PES of HCOOH (the second photoelectron band) given by Turner *et al.*[23] However, the resolution of the TPES spectra is about 18 meV, while that of Turner *et al.* is about 35 meV. Some splitting can be seen at the higher resolution, and a weak hot band is observed.

The difference in cross over wavelengths between HCOOH (~1008 Å) and DCOOH (~996.5 Å) is about 11.5 Å. The cross over wavelength for HCOOH is very nearly equal to the 0 K threshold for this process listed in Table I. For DCOOD, however, the cross over wavelength is about 3.3 Å lower than the corresponding 0 K threshold. On the basis of zero point energy differences, the cross over wavelengths should differ by about 7 Å. Thus, $COOD^+$ (DCOOD) appears to have a delayed onset of about 3.3–4.5 Å.

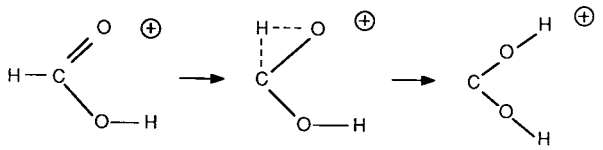
By comparing Fig. 5(a) and Fig. 1, it becomes apparent that $v' = 0$ (~1001.4 Å) and $v' = 1$ (~991.2 Å) in the TPES of HCOOH coincide with the two step-like features in the photoion yield curve of $COOH^+$.

In Fig. 6(a), one sees both the $v' = 0$ (~1001.1 Å) and $v' = 1$ (~990.4 Å) peaks in the TPES of DCOOD. As noted earlier, the steep increase in Fig. 6(b) correlates with the position of the $v' = 1$ state, but no increase occurs at the

wavelength corresponding to formation of $v' = 0$. This can be rationalized if we recognize that this wavelength (1001 Å) is in the thermal tail of the threshold. Hypothetically, an experiment carried out at 0 K would have a threshold at 12.402 eV≡999.8 Å, i. e., at higher energy than this peak. Most of the molecules with internal thermal energy (primarily rotational energy) cannot derive sufficient energy from the $v' = 0$ peak to dissociate.

IV. INTERPRETATION OF RESULTS

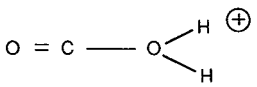
In the photodissociative ionization of both HCOOH and DCOOD, we are presumably observing the sum of two processes—bond cleavage and rearrangement. In these two cases the processes are indistinguishable by mass. The bond cleavage normally is discussed as proceeding through a loose complex, with no significant activation energy. The rearrangement process, on the other hand, likely proceeds through a tight complex. A plausible sequence of events for rearrangement is



I II III

where structrure III can produce $COOH^+$ in two equivalent ways. This scheme is reminiscent of the keto–enol transition, which has been found to be exothermic and facile in recent studies of acetic acid[24] and acetone.[25] Curtiss[26] has calculated that structure III is ~2 kcal/mol less stable than structure I, using a small basis set. Structure II corresponds to the transition state, and presents the barrier to rearrangement. The minimum energy necessary to form $COOH^+$ from $HCOOH^+$ is about 22 kcal/mol. If the barrier to rearrangement is $\gtrsim$22 kcal/mol, and if H permeates this barrier more readily than D, then a composite of bond cleavage and rearrangement might conceivably explain the delayed cross over energy for DCOOD relative to HCOOH.

The preliminary calculations of Curtiss[26] indicate that structure II lies about 67 kcal/mol higher than structure I (6-31 G* level), drops to 49 kcal/mol above structure I with correlation (MP4 SDQ/6-31 G* level), to 47 kcal/mol with inclusion of triples, and 40 kcal/mol with a larger basis set. Zero point energy effects should lower this quantity by ~4.5 kcal/mol. This is still about 13 kcal/mol above the dissociation threshold, which is approximately the onset of the rearrangement process. It might be argued that the first excited state of $HCOOH^+$ is more favorable for the formation of the transition state, since it corresponds to the ejection of an electron from the carbonyl π bond, and the observed dissociation onset occurs very nearly at the adiabatic onset for the excited state. However, Curtiss' calculations result in a substantial barrier to formation of structure II from this first excited state, both in plane and perpendicular to the plane. Other rearrangement schemes for arriving at a symmetric structure analogous to III, e.g.



were also explored, but the barrier to these structures was even higher. Hence, although the rearrangement process occurs readily within 0.09 eV of the thermochemical threshold, the mechanism for this facile rearrangement requires more extensive investigation.

Our goal in the present experiments was to establish the appearance potential of $COOH^+$ (HCOOH). Since any appearance potential measurement represents an upper limit, and the $COOH^+$ (HCOOH) threshold is lower than that for $COOD^+$ (DCOOD), including zero point energy effects, we select the 1008 Å≡12.300 eV cross over energy of $COOH^+$ (HCOOH) as the 0 K threshold. Oliveira *et al.*[27] have shown that the correction for thermal energy, steradiancy analyzer function and the photoelectron spectrum is particularly small when the position of the dissociation onset is in the Franck–Condon valley between states, which corresponds to the present situation. In addition, the thermal energy of HCOOH is less than that of bromobutane and iodobutane studied by Oliveria *et al.*, and our steradiancy analyzer has better resolution. Hence, the correction of the cross over energy to 0 K should be less than 0.02 eV.

With auxiliary thermochemical data ($\Delta H_{f_0^\circ}$ (HCOOH)[17] = −88.79 kcal/mol and $\Delta H_{f_0^\circ}(H)$[28] = 51.634 kcal/mol) we compute $\Delta H_{f_0^\circ}$ ($COOH^+$) = 143.2 ± 0.5 kcal/mol. This value corresponds to a proton affinity for CO_2 at 0 K of 128.0 ± 0.5 kcal/mol, or more conventionally, $PA(CO_2)_{298\,K}$ = 129.2 ± 0.5 kcal/mol, using the stationary electron convention.

Of the previous photoionization studies on $COOH^+$ from HCOOH, the value reported by Villem *et al.*,[14] when corrected for internal thermal energy, is virtually identical with the present result, whereas the other investigations yield higher energy thresholds. We believe that this is fortuitous, since the more extensive investigation undertaken here, involving various isotopic species, indicates that the extrapolation to the base line is somewhat arbitrary and uncertain in this molecule.

The value chosen for the proton affinity of CO_2 in the NBS compilations[29,30] is 130.9 kcal/mol, which happens to coincide with the number based on Warneck's result. However, Adams *et al.*[31] have recently obtained PA (CO_2) = 128.5 ± 1 kcal/mol, based on relative proton affinities of CF_4, CO_2, NO, CH_4, and HCl. Their result is in rather good agreement with the present one, and indicates that the values in the NBS scale of proton affinities based on PA (CO_2) should be lowered by ≈2 kcal/mol. The PA (CO_2) obtained in the *ab initio* calculations of Frisch *et al.*[10] (130.7 kcal/mol) is also a bit high, but within the error limit of modern calculations (± 2 kcal/mol).

The mechanism of the rearrangement process observed in the present study clearly warrants a more careful analysis of the $HCOOH^+$ potential energy surface by more extensive *ab initio* methods.

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