

A photoionization study of the COOH species

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A photoionization mass spectrometric study has been performed on the products of the $F + \text{HCOOH}$, $F + \text{DCOOH}$, and $F + \text{HCOOD}$ reactions. Hydrogen/deuterium abstraction on the carbon site yields the COOH/COOD radical which can be photoionized and detected. Abstraction on the oxygen site also occurs, but does not yield a detectable isomeric HCOO/DCOO product. Instead, CO_2 is readily observed, implying that HCOO/DCOO is unstable to decomposition under the conditions of this experiment. The detection of COOH is believed to be the first experimental evidence for the stability of this species in the gas phase. An adiabatic ionization potential of 8.486 ± 0.012 eV is obtained. Combined with the recently obtained $\Delta H_{f,0}^\circ(\text{COOH}^+) = 143.2 \pm 0.5$ kcal/mol, this ionization potential leads to $\Delta H_{f,0}^\circ(\text{COOH}) = -52.5 \pm 0.6$ kcal/mol. Hence, COOH is stable with respect to the lowest energy dissociation products ($\text{H} + \text{CO}_2$) by 10.2 ± 0.6 kcal/mol.

I. INTRODUCTION

The subject of the present study is the neutral COOH/HCOO species. The goal is to determine the heat of formation of one, or both of these species. To our knowledge, they have not previously been identified by experimental techniques in the gas phase, although they have been inferred. The method we have adopted was to generate COOH/HCOO by the $F + \text{HCOOH}$ reaction, and thence to measure the adiabatic ionization potential of the free radical species by photoionization mass spectrometry. In this fashion, with a known value for $\Delta H_{f,0}^\circ(\text{COOH}^+)$ —which we report in the previous article¹—we can arrive at $\Delta H_{f,0}^\circ(\text{COOH})$. In addition to the question of energetics, detailed knowledge about the variation of the photoionization cross section with photon energy provides, in principle, information about the change in geometrical structure between the neutral species (which is not known, except from *ab initio* calculations and estimates from matrix isolation frequencies) and the cation (which is now known fairly well). Prior studies impacting on the stability and structure of the COOH/HCOO species are summarized below.

The reaction



is the dominant source of CO_2 in the oxidation of hydrocarbons,² is important in the chemistry of the upper atmosphere,³ and the formation of chemical smog.⁴ The heats of formation of the constituent species are well known;⁵ the reaction is exothermic by 24.39 kcal/mol at 0 K. The reaction has been the subject of numerous investigations.⁶⁻¹⁰ They can be summarized as follows:

- although exothermic, the reaction has an activation barrier,
- the Arrhenius plot is nonlinear,
- there is a pressure effect.

The reaction has been modelled⁸ to proceed through a collision complex COOH^* , which can be stabilized to COOH by a third body. Milligan and Jacox¹¹ observed in-

frared absorption spectra upon vacuum ultraviolet photolysis of H_2O in a CO matrix at 14 K, which they were able to assign to *cis* and *trans* stereoisomers of COOH, presumably formed by the reaction of OH with the CO matrix.

Harding¹² reported preliminary results of an *ab initio* examination of the potential surface on which this reaction proceeds. Briefly, his calculation predicts that OH adds to CO with perhaps a very small barrier to form the *trans* isomer of COOH. The *trans* isomer converts readily to the *cis* form, a low barrier existing between the two. Product formation is predicted to take place exclusively from the *cis* form. The energetics displayed in his schematic diagram (Fig. 1) clearly show that stable *trans* and *cis* forms should exist, lying ~ 25 kcal/mol below the $\text{OH} + \text{CO}$ asymptote, and even a few kcal/mol below the $\text{H} + \text{CO}_2$ asymptote. There are implications in this report that there may even be local minima for HCOO entities.

Shortly thereafter, McLean and Ellinger¹³ performed a series of CI calculations and found the *trans* isomer to be 3.3 ± 0.5 kcal/mol lower in energy than the *cis* form. Their best estimated geometry for the *trans* form is shown in Fig. 2(a). The assumed *trans* geometry employed by Milligan and Jacox¹¹ (using "borrowed" distances and angles from HCOOH and HONO) which they employed to calculate vibrational frequencies is shown in Fig. 2(b). The agreement is quite good. Unfortunately, McLean and Ellinger¹³ did not calculate the energies of the $\text{OH} + \text{CO}$ and $\text{H} + \text{CO}_2$ asymptotes relative to COOH. Hence, unlike the *ab initio* calculation of COOH^+ by Frisch *et al.*,¹⁴ which was able to predict a proton affinity of CO_2 [and hence $\Delta H_f(\text{COOH}^+)$] in good agreement with available experimental data, the calculation of McLean and Ellinger¹³ did not attempt to predict the thermochemical stability of COOH.

However, this missing information from *ab initio* calculations has been provided recently by Aoyagi and Kato.¹⁵ They calculate a stability of 16.9 kcal/mol for the *trans* form of COOH (and 15.5 kcal/mol for the *cis* form), relative to $\text{OH} + \text{CO}$. They provide evidence that their calculation un-

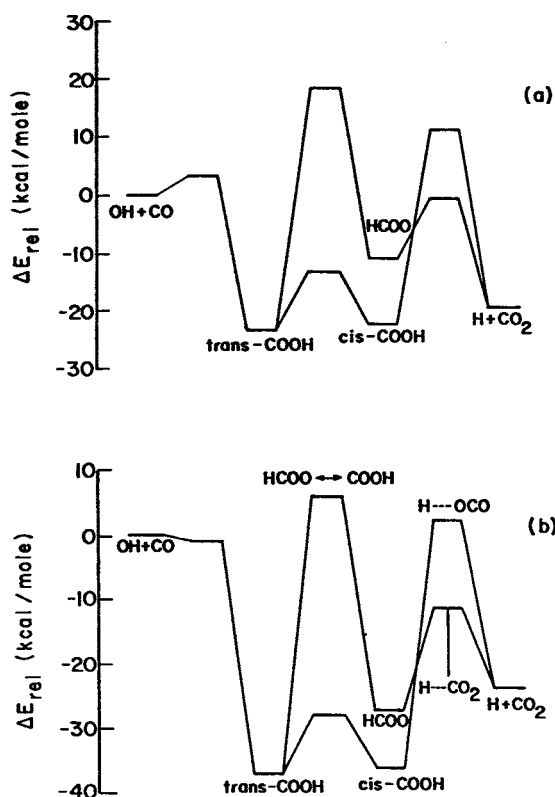


FIG. 1. (a) Schematic diagram of the calculated potential energy surface for the reaction $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$, from Ref. 12. (b) A similar, but more recent energy level diagram in which the minima and saddle-point energies were taken from "best estimates" including experimental selections, but connectivity of the reaction paths was based on *ab initio* results. From Ref. 29.

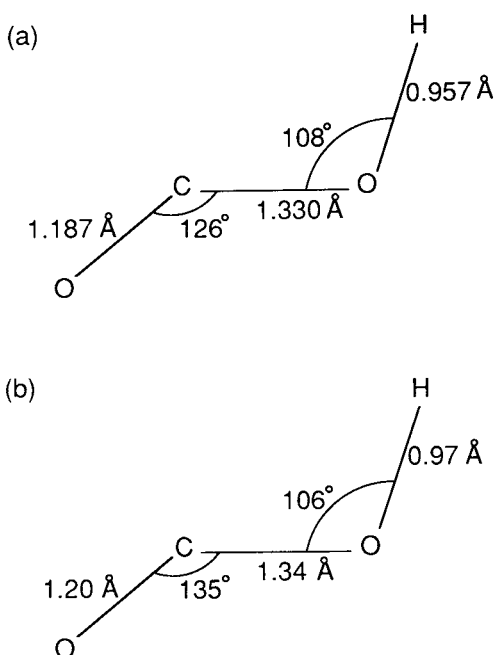


FIG. 2. (a) The geometrical structure of the trans form of COOH, that is, the more stable form of the ground state, as calculated by McLean and Ellinger (Ref. 13). (b) The assumed geometry of trans-COOH used by Milligan and Jacox (Ref. 11) to calculate infrared frequencies in good agreement with their observations.

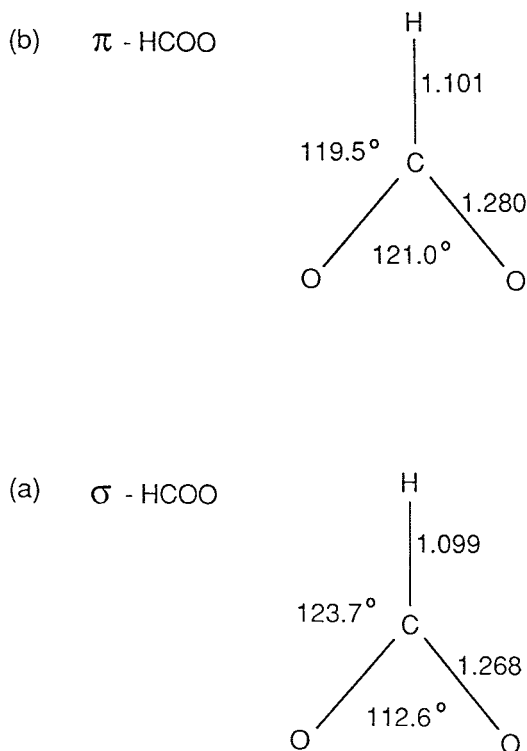


FIG. 3. The geometrical structure of HCOO, described as an optimized MRCI structure, by McLean *et al.* (Ref. 16). (a) The lower σ state. (b) The upper π state, excited by 9.2 kcal/mol.

derestimates the stabilization energy of COOH by 9.0 kcal/mol, and hence their final estimate is that trans COOH is stable by 25.9 kcal/mol with respect to OH + CO. This result presumably applies to a D_e value, i.e., referred to the bottoms of the respective potential wells.

McLean *et al.*¹⁶ also calculated the structure of an HCOO isomer. Their optimized multireference configuration interaction (MRCI) structure is shown in Fig. 3. It consists of a lower σ state and an upper π state, both having similar C_{2v} symmetry, and separated by 9.2 kcal/mol. Unfortunately, the relative stabilities of HCOO and COOH cannot be assessed from these calculations, since they were performed at different levels of *ab initio* calculations.

However, a slightly earlier multiconfiguration self-consistent-field (MCSCF) calculation of HCOO performed by Feller *et al.*¹⁷ reached the conclusion that HCOO is approximately 2 kcal/mol lower in energy than $\text{CO}_2 + \text{H}$, at the CI level of theory. This result also presumably does not include the effect of zero point energies.

In summary, the geometrical structures of COOH and HCOO appear to be fairly well established, primarily on the basis of *ab initio* calculations. For the COOH isomer, there is some experimental support from the infrared spectra of species observed in a matrix isolation experiment.

From the *ab initio* calculation of Aoyagi and Kato,¹⁵ we can infer $\Delta H_{f_0}^{\circ}(\text{COOH})_{\text{trans}} \sim -40$ kcal/mol, assuming that their stabilization energy with respect to OH + CO is a D_e value. Similarly, the value of $\Delta H_{f_0}^{\circ}(\text{HCOO})$ based on the calculation of Feller *et al.*¹⁷ is ~ -38 kcal/mol, assuming

that their stabilization energy is also a D_e value. With the inclusion of zero point energies, both of these species would be predicted to be unstable with respect to $H + CO_2$, which has a summed heat of formation of -42.331 kcal/mol.

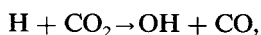
A. Electron impact mass spectrometry

Bernecker and Long¹⁸ obtained ΔH_{f^0} (COOH) = -39 kcal/mol from the appearance potential (AP) of $C_2H_5^+$ from propanoic acid. Later, Haney and Franklin¹⁹ measured the AP of CH_3^+ from CH_3COOH , and inferred ΔH_{f^0} (COOH) = -58 ± 4 kcal/mol. Both results can be criticized, the latter because it does not refer to the lowest energy process. Haney and Franklin¹⁹ also inferred ΔH_{f^0} (HCOO) ≥ -46 kcal/mol, by measuring the threshold for CH_3^+ from methyl formate. In this case as well, the desired fragment does not result from the lowest energy process, thereby raising the possibility of a kinetic shift. If the errors inherent in the experiments of Haney and Franklin are assumed to approximately cancel, the implication is that COOH is more stable than HCOO by at least 12 kcal/mol.

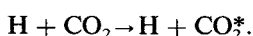
B. Other methods

Benson²⁰ has listed $\Delta H_{f_{298}^0}$ (COOH) = -51 ± 3 kcal/mol and $\Delta H_{f_{298}^0}$ (HCOO) = -36 ± 4 kcal/mol in 1968; in 1976,²¹ these have changed slightly to $\Delta H_{f_{298}^0}$ (COOH) = -50 ± 1 kcal/mol and $\Delta H_{f_{298}^0}$ (HCOO) = -36 ± 2 kcal/mol. O'Neal and Benson²² have experimentally inferred $\Delta H_{f_{298}^0}$ (COOH) = -53 kcal/mol. The more recent tabulation of Benson²¹ presumably takes this, as well as previous measurements into account, and hence the values quoted therein are considered his best current estimates. They imply that COOH is *stable* with respect to the lowest energy products ($H + CO_2$) by 8 kcal/mol, whereas HCOO is *unstable* with respect to these products by 6 kcal/mol. The compilation of Glushko *et al.*²³ selects $\Delta H_{f_{298}^0}$ (COOH) = -51 ± 3 kcal/mol (Benson's 1968 value) and leads to $\Delta H_{f_0^0}$ (COOH) = -50.2 ± 3 kcal/mol. With this choice, and the aforementioned values of ΔH_{f^0} (COOH), the adiabatic IP of COOH should be ~ 8.4 eV.

The reverse reaction,



has also received a great deal of attention since the early work of Oldershaw and Porter.²⁴ The inelastic scattering process,



is equally important, from the viewpoint of collisional cross sections, and an understanding of the reaction surface. These reactions are obviously endothermic. Both types of studies (inelastic and reactive scattering) have been well summarized in a recent review article by Flynn and Weston.²⁵ This review article includes the elegant studies of Wittig and co-workers^{26,27} who prepare a van der Waals complex such as

$HBr \cdot CO_2$, then photodissociate the HBr moiety, thus imposing an orientational constraint on the $H + CO_2$ reaction. The most recent degree of sophistication in this type of study has been the application of femtosecond laser techniques by Zewail and co-workers²⁸ to monitor the evolution of OH + CO products.

Schatz *et al.*²⁹ have made the most recent effort to provide a theoretical rationalization of these latter observations. They have developed a composite potential surface using some experimental information, and used quasiclassical trajectory methods to predict the probability of inelastic and reactive scattering into various channels. Their schematic energy level diagram [Fig. 1(b)] while qualitatively similar to that used by Harding¹² in calculating the OH + CO reaction, differs quantitatively in some significant points.

(a) In their chosen surface, HCOO is stable with respect to $H + CO_2$ by 3.5 kcal/mol. In the diagram displayed by Harding, HCOO is unstable with respect to $H + CO_2$ by ~ 8 kcal/mol.

(b) Schatz *et al.* use a stability of *trans*-COOH relative to $H + CO_2$ of 13.6 kcal/mol, whereas Harding's diagram indicates a corresponding stability of ~ 4 kcal/mol. In general, the potential energy surface used by Schatz *et al.*, displays lower barriers, and deeper potential wells, than the corresponding features of Harding's surface by ~ 10 – 15 kcal/mol. The difference can be attributed to the fact that Harding's surface is based on *ab initio* calculations, whereas Schatz *et al.* try to incorporate both *ab initio* and experimental values into a fitted surface.

As we have shown, the experimental potential well for COOH, and the possible one for HCOO, are not firmly established. A primary goal of the present research is to provide independent experimental values for the stabilities of COOH and HCOO. MacDonald and Sloan³⁰ have previously studied the reactions of F atoms with HCOOH and DCOOH for the purpose of establishing the microscopic reaction dynamics of these systems. Their method of diagnosis was to monitor the infrared chemiluminescence of the vibrationally excited HF (DF) products. Their conclusion with respect to the F + DCOOH reaction was that both DF and HF products were observed, and in fact, that the HF product (+ DCOO) was twice as abundant as the DF product (+ COOH). However, in the latter reaction a large amount (50%–80%) of the reaction exoergicity was channelled into vibrational energy of DF which therefore displayed an inverted vibrational energy distribution and left behind a relatively cold COOH, whereas the former reaction yielded a very low average HF vibrational excitation, but a distribution which "shows population to the highest energy allowed by thermochemistry." This implies that in most, though not all of the encounters producing HF + DCOO, the DCOO can be expected to acquire a large fraction of the available exoergicity. If, as anticipated from the earlier discussion, the DCOO/HCOO is at best marginally stable with respect to $H + CO_2$, the prospects for observing a stable HCOO will be diminished significantly if it is formed with internal excitation. The experiments of MacDonald and Sloan were not designed to detect either COOH or HCOO, and hence could not provide direct evidence for the stability of either species.

II. EXPERIMENTAL ARRANGEMENT

The basic photoionization mass spectrometric apparatus has been described previously.³¹ For the generation of COOH species by the reaction of F atoms with HCOOH, a flow tube and reaction cup were employed, essentially identical to that used in earlier F + SiH₄³² or F + C₂H₄³³ studies. F atoms were produced in a microwave discharge through pure F₂. They entered a cup through a small orifice, and HCOOH, DCOOH, or HCOOD also flowed into this reaction chamber. The reaction products effused into and through an "open" ionization chamber. This crude molecular beam was crossed by a wavelength-selected photon beam emanating from the exit slit of a 3 m vacuum ultraviolet monochromator. The fast-flowing fluorine was trapped for the duration of the experiments by a helium cryopump.

HCOOH, DCOOH, and HCOOD were obtained from commercial sources^{34,35} and were used without further purification. The primary light source utilized in these experiments was the many-lined emission from a discharge through molecular hydrogen. The nominal wavelength resolution was 0.28 Å [full width at half-maximum (FWHM)], but for these free radical studies, measurements were confined to the peaks in the light spectrum.

III. EXPERIMENTAL RESULTS

A. The F + HCOOH reaction

In this experiment, we succeeded in detecting $m/e = 45$ ions well below the threshold for COOH⁺ (HCOOH), which occurs at 1011.0 ± 0.3 Å,¹ and therefore, this signal is attributable to photoionization of the free radical(s) COOH and/or HCOO. This is the first direct measurement, to our knowledge, of this (these) species. A photoion yield curve of

the radical is shown in Fig. 4. We note a rather steep descent in relative photoionization cross section from ~ 1200 to ~ 1290 Å, and then a more gradual decline, clearly visible above the background level until ~ 1460 Å. In addition, there appears to be evidence for rounded step structure. The gradual decline toward threshold is indicative of a substantial geometry change occurring between the neutral radical and the cation. Before attempting an analysis, we sought to establish which of the two isomeric forms of the free radical are produced and ionized, and toward this end, we performed similar experiments, but with DCOOH and HCOOD as the reagents.

B. The F + DCOOH and F + HCOOD reactions

The presumption in this experiment was that deuterium abstraction from DCOOH would form COOH, while hydrogen abstraction would form DCOO. Conversely, deuterium abstraction from HCOOD would produce HCOO, and hydrogen abstraction would lead to COOD. If both isomers survived and could be photoionized, they could be distinguished by mass analysis. In the DCOOH experiment, only the $m/e = 45$ signal (corresponding to COOH) could be clearly distinguished in the 1200–1400 region. Similarly, in the HCOOD experiment, only $m/e = 46$ (COOD) signal was present. Instead of the HCOO/DCOO species, in both experiments molecular CO₂ could readily be identified in the chemical reaction products, since it has strong, characteristic autoionization peaks. In addition, HF and DF were detected as reaction products, providing further verification that abstraction occurs on both the carbon and oxygen sites. Upon reinspection of the F + HCOOH experiment, we verified that, besides COOH, significant amounts of nascent CO₂ are present there also.

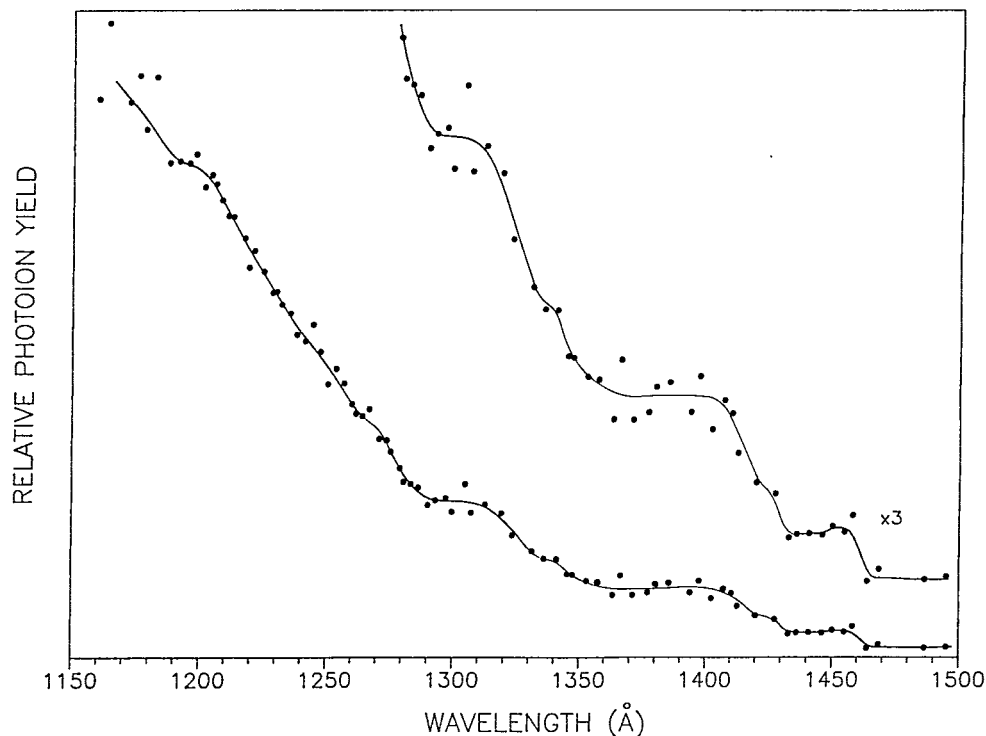


FIG. 4. The photoion yield curve of $m/e = 45$ obtained from the reaction of F atoms with HCOOH. The threshold region has been amplified, and is shown as an inset. The analysis (see the text) leads to the conclusion that the free radical formed in the hydrogen abstraction reaction has the COOH structure. The HCOO structure is either inherently unstable with respect to H + CO₂, or is formed with sufficient internal energy to decompose to these products.

These observations, and the inferences that follow, could plausibly be expected from the conclusions of MacDonald and Sloan.³⁰ It will be recalled that these authors found that in the reaction



most of the exoergicity (50%–80%) is detected as vibrational energy of the DF product, and therefore, a relatively cool COOH is generated. By contrast, the reaction



yields a very low *average* HF vibrational excitation, even though the HF vibrational population includes some very high levels. The average DCOO internal energy is therefore substantial, and decomposition of the DCOO prior to collisional relaxation could readily occur. Hence, while our experiment provides strong support for the stability of COOH against decomposition, it does not prove that “cold” HCOO would be unstable. A different type of experiment (see Discussion section, below) could shed more light on this question.

Now, let us turn to an analysis of Fig. 4. It seems clear from the evidence presented above that we are dealing with an ionizing transition from a COOH structure (Fig. 2, and possibly the *cis* form as well) to a COOH⁺ structure (Fig. 5). The gradual decline in the photoion yield curve of Fig. 4 from ~1290 Å to longer wavelength is the type of behavior to be expected for a substantial change in geometry. The most significant changes are

- a decrease in the C–O distance, from 1.330 to 1.216 Å,
- a decrease in the C=O distance, from 1.167 to 1.130 Å,
- a large increase in the OCO bond angle from 126° to 174°.

Schaefer³⁶ has computed the *L* matrix, relating the internal coordinates to the normal coordinates for the COOH⁺ structure corresponding to Fig. 5. Of the 6 normal modes, the O–H stretching frequency at 3475 cm⁻¹ (calculated) has almost no coupling to other internal coordinates. To a large extent, this is also true for the COH bending mode (1033 cm⁻¹) and because of symmetry, it is totally the case for the O–C–O–H torsion mode (573 cm⁻¹). This leaves the OCO in-plane bending mode (525 cm⁻¹) and the two C–O stretching modes (1245 cm⁻¹ and 2435 cm⁻¹), as potentially active frequencies in the Franck–Condon transition.

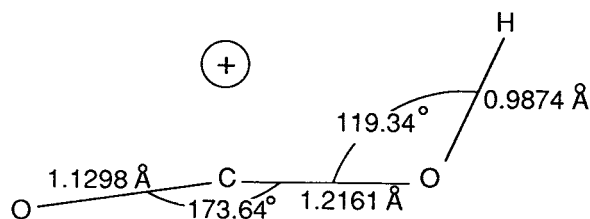


FIG. 5. The geometrical structure of the ground state of COOH⁺, as calculated by Frisch *et al.* (Ref. 14).

(These frequencies are rather similar to the three frequencies of CO₂, $\nu_2 = 667$ cm⁻¹, $\nu_1 = 1388$ cm⁻¹, and $\nu_3 = 2349$ cm⁻¹). In the present case, there is fairly strong coupling between the two CO₂ stretching modes, and some coupling between the OCO bend and the COH bend.

The experimental data (Fig. 4) show evidence for onsets of rounded steps at ~1430, ~1415, ~1365, and possibly ~1330 Å, which seems to very roughly correspond to three consecutive quanta of ~2300 cm⁻¹ and one quantum of 1500 cm⁻¹. These could be identified with a progression in the higher frequency asymmetric C–O stretch, and a single quantum excitation of the lower frequency symmetric C–O stretch. The much lower OCO bending frequency would be much more difficult to observe, given the scatter in the data. Clearly, a more definitive interpretation of the data would need to be based on a rather involved calculation of the Franck–Condon factors active in this transition, and their relative intensities.

The first clear departure from the background level, which we identify with the adiabatic ionization potential, is 1461 ± 2 Å = 8.486 ± 0.012 eV. This “first step” is unlikely to be a hot band, because of its intensity. If it were a hot band, it would require a temperature of 2000–3000 K, while in our experience the method of production (H abstraction) and the opportunity for collisional relaxation in our apparatus tends to yield vibrationally thermalized radicals at ~300 K. When this value is combined with the recently obtained¹ ΔH_f° (COOH⁺) = 143.2 ± 0.5 kcal/mol, the result is ΔH_f° (COOH) = -52.5 ± 0.6 kcal/mol. Hence, COOH is stable with respect to the dissociation products H + CO₂ by 10.2 ± 0.6 kcal/mol.

IV. DISCUSSION AND CONCLUSIONS

(A) The reaction of F atoms with HCOOH produces free radicals (COOH and/or HCOO) which are stable enough to be photoionized and detected as the corresponding parent ions.

(B) The reaction of F atoms with DCOOH produces free radicals which, upon photoionization, yield *m/e* = 45 parent ions (identified as COOH⁺ resulting from COOH), but *not* *m/e* = 46 parent ions, which might have provided evidence for a stable DCOO species. An analogous conclusion can be reached by reacting F atoms with HCOOD. To our knowledge, this establishes the stability of gaseous COOH for the first time. There are various possible explanations for the failure to detect HCOO⁺/DCOO⁺ ions in this experiment, including

- (1) the inherent lack of stability of HCOO relative to H + CO₂,
- (2) the formation of hot HCOO in the chemical reaction, which would accelerate the decomposition of an HCOO entity,
- (3) the very low probability of photoionization of an HCOO entity, since the lowest energy ionization path would be to a COOH⁺ structure, with a much higher energy required to reach an HCOO⁺ structure.

The fact that nascent CO₂ was observed in abundance in

these measurements argues strongly for (1) or (2) as the likely causes.

(C) The photoion yield curve of COOH^+ (COOH) displays a gradual approach to the adiabatic onset, implying a significant change of geometry between neutral radical and cation. This is consistent with recent *ab initio* calculations of these structures.

(D) There is evidence for a vibrational progression in the photoion yield curve of COOH^+ (COOH), with a vibrational interval of about 2300 cm^{-1} , and perhaps a single quantum excitation of a frequency of about 1500 cm^{-1} .

(E) The adiabatic ionization potential of COOH is $8.486 \pm 0.012\text{ eV}$. Together with $\Delta H_f^\circ(\text{COOH}^+) = 143.2 \pm 0.5\text{ kcal/mol}$, this value leads to $\Delta H_f^\circ(\text{COOH}) = -52.5 \pm 0.6\text{ kcal/mol}$. Hence, COOH is stable with respect to the lowest energy dissociation products ($\text{H} + \text{CO}_2$) by $10.2 \pm 0.6\text{ kcal/mol}$. The C–H bond energy in HCOOH is $89.3 \pm 0.6\text{ kcal/mol}$ at 298 K (87.9 at 0 K). This value is rather close to the C–H bond energy in CH_2O^{23} , $88.1 \pm 1.2\text{ kcal/mol}$, and slightly lower than that in $\text{CH}_3\text{OH}^{23}$, $95.3 \pm 2.4\text{ kcal/mol}$, at 298 K .

(F) The prevailing evidence is that COOH^+ is much more stable than HCOO^+ —by perhaps 105 – 115 kcal/mol . For the neutral species, indirect evidence suggests that COOH is more stable than HCOO by only $\sim 15\text{ kcal/mol}$. For the corresponding negative ions, HCOO^- (the formate ion) appears to be the more stable species.³⁷ This successive change in relative stability of these isomeric species with addition of an electron appears to be an interesting topic for theoretical interpretation. It also offers an alternative approach to establishing the stability of HCOO , by measuring the photodetachment spectrum of HCOO^- .

(G) The results of the present experiments provide some firmer limits to the parameters of the potential energy surface used for the modeling of the $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ reaction and the reverse reaction.

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