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Infrared absorption of gaseous c-CICOOH and t-CICOOH recorded with a step-scan Fourier-transform spectrometer

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Two conformers of CICOOH were produced upon irradiation at 355 nm of a gaseous flowing mixture of Cl2, HCOOH, and N2. A step-scan Fourier-transform infrared spectrometer coupled with a multipass absorption cell was utilized to monitor the transient spectra of CICOOH. Absorption bands with origins at 1808.0 and 1328.5 cm−1 are attributed to the C=O stretching and COH bending modes of t-CICOOH, respectively; those at 1883.0 and 1284.9 cm−1 are assigned as the C=O stretching and COH bending modes of c-CICOOH, respectively. These observed vibrational wavenumbers agree with corresponding values for t-CICOOH and c-CICOOH predicted with B3LYP/aug-cc-pVTZ density-functional theory and the observed rotational contours agree satisfactorily with simulated bands based on predicted rotational parameters. The observed relative intensities indicate that t-CICOOH is more stable than c-CICOOH by ~3 kJ mol−1. A simple kinetic model is employed to account for the production and decay of CICOOH.

I. INTRODUCTION

The hydrocarboxyl radical (HOCO) is an important intermediate in the reaction of OH with CO, which is the major reaction responsible for the oxidation of CO to CO2 in the atmosphere and in combustion systems.1−4 HOCO is also produced in other reactions. The reaction of OH with formic acid (HCOOH), the most abundant carboxylic acid in the troposphere,5 is not only a source of HOCO but also a major sink for HCOOH.6 Another important source of HOCO in the atmosphere is the reaction of Cl with HCOOH. In the laboratory, this reaction also serves as a source to produce HOCO.7

West and Rollefson reported that CO2 and HCl were produced upon irradiation of a mixture of Cl2 and HCOOH; they proposed that HOCO and CICOOH are reaction intermediates.8 Li et al., irradiated mixtures of Cl2, O2, HCOOH, and He with a Xe flash lamp to investigate the bimolecular rate coefficients of reactions (2) and (4) based on the following mechanism:

Cl2 + hν → 2Cl

Cl + HCOOH → HCl + HOCO

HOCO + O2 → CO2 + HO2

Cl + HOCO → HCl + CO2. (4)

Values of \( k_2 = (1.83 \pm 0.12) \times 10^{-13} \) and \( k_4 = (4.8 \pm 1.0) \times 10^{-11} \) cm3 molecule−1 s−1 were derived on fitting the temporal profile of CO2 probed with the P(4) line in the \( \nu_3 \) band of CO2 with a simplified equation of exponential rise and a literature value of \( k_3 = 1.9 \times 10^{-12} \) cm3 molecule−1 s−1.9 By comparison of the decay rates of the reactant and a reference compound determined with infrared (IR) absorption, Wallington et al.10 evaluated \( k_2 = (2.00 \pm 0.25) \times 10^{-13} \) cm3 molecule−1 s−1 under 700 Torr of N2 or synthetic air.

The experiment on reaction of Cl with monodeuterated formic acid HCOOD indicated that reaction (2) proceeds predominantly via abstraction of the H-atom on the carbon to form HOCO rather than abstraction of the hydroxyl hydrogen to form HCO2.7 This finding is consistent with the results of Tyndall et al.11 who reported a yield of 96 ± 5% for CO2 from the reaction of Cl with HCOOH in 700 Torr of air based on their measurements with Fourier-transform infrared (FTIR) spectra; CO2 was presumably produced from reactions (3) and (4).

Li et al. proposed that reaction (4) might proceed via direct abstraction of a H-atom, formation of a CICOOH complex, or a short-lived intermediate in which the C–Cl bond is rapidly formed and the H atom is rapidly abstracted.9 In contrast, West and Rollefson postulated the formation of transient chlorofomeric acid (CICOOH) that decomposes readily to HCl and CO2 via the cis configuration (c-CICOOH). For convenience, the trans and cis notations in this paper follow the same nomenclature as for HCOOH.12 therefore c-CICOOH has its H atom cis to the Cl atom with respect to the C–O bond.

Herr and Pimentel13 photolyzed a mixture of Cl2 and HCOOH with a flash lamp and monitored reaction intermediates with a rapid-scan IR spectrometer; a transient band at
768 cm$^{-1}$ was observed and assigned as the C–Cl stretching mode of CICOOH. Jensen and Pimentel$^{14}$ further studied the unimolecular decomposition

$$\text{CICOOH} \rightarrow \text{HCl} + \text{CO}_2$$

(5)

over the temperature range 288–343 K by monitoring the decay of this 768 cm$^{-1}$ band and derived a rate coefficient of $k_s = 5 \times 10^{13} \text{exp}(-7050/T)$ s$^{-1}$. They proposed that the rate-determining step for reaction (5) is the conversion from $t$-CICOOH to $c$-CICOOH with a barrier about $58 \pm 7$ kJ mol$^{-1}$. No distinction of absorption between conformers of CICOOH was discussed, nor was any other IR absorption band of CICOOH reported.

Several quantum-chemical calculations on $c$-CICOOH and $t$-CICOOH have been performed.$^{15–19}$ The conformation notation employed in this paper is consistent with that used in Refs. 17 and 18, but is the reverse of that in Refs. 14–16 and 19. Conformer $t$-CICOOH is predicted to be more stable than $c$-CICOOH by $4–11$ kJ mol$^{-1}$ and the barrier to convert from trans to cis conformers is $41–50$ kJ mol$^{-1}$, depending on the methods of calculation.$^{15,17,19}$ Stephenson et al.$^{17}$ argued that because of the disagreement between the vibrational wavenumber (768 cm$^{-1}$) of the only band observed by Pimentel and coworkers$^{13,14}$ and the value (725 cm$^{-1}$) predicted quantum chemically, a search for the carbonyl absorption in the 1800–1880 cm$^{-1}$ region would provide crucial evidence whether CICOOH was indeed observed previously.

We have demonstrated that by coupling a multipass absorption cell with a step-scan FTIR spectrometer, time-resolved IR absorption spectra of transient intermediates in gaseous reactions can be recorded.$^{20–23}$ Here such an application is further demonstrated by our observation of transient IR absorption spectra of $c$-CICOOH and $t$-CICOOH upon photolysis of a gaseous mixture of Cl$_2$/HCOOH/N$_2$ at 363 K.

II. EXPERIMENTS

The sample compartment of a step-scan Fourier-transform spectrometer (Thermo Nicolet, Nexus 870) contains a flow reactor inside which a set of White cell mirrors with a base path length of 20 cm and an effective path length of 6.4 m was installed.$^{21,22}$ The flow reactor has a volume of $\sim 1.6$ L and accommodates two rectangular quartz windows ($3 \times 12$ cm$^2$) to pass the photolysis beam that propagates perpendicularly to multiply passed IR beams. The beam from a frequency-tripled Nd:YAG (yttrium aluminum garnet) laser (LOTIS TII, LS-2137/20, 11 Hz, 74 mJ pulse$^{-1}$, beam dimension 0.5 cm$^2$) emitting at 355 nm passed through these quartz windows and was reflected eight times with a pair of external laser mirrors to photodissociate a flowing mixture of Cl$_2$/HCOOH/N$_2$. We obtained temporally resolved difference absorption spectra from interferograms recorded simultaneously with ac- and dc-coupled signals of a mercury cadmium telluride detector (20 MHz response bandwidth).$^{21,26}$ The ac-coupled signal was further amplified (Stanford Research Systems, Model SR560, bandwidth 100 Hz–1 MHz) 20 times before being transferred to an external 14-bit digitizer (Gage Applied Technology, CompuScope 14100, 10$^8$ sample s$^{-1}$), whereas the dc-coupled signal was sent directly to the internal 16-bit digitizer (2 $\times 10^5$ sample s$^{-1}$) of the spectrometer. Typically, 500 data points were acquired at 1 $\mu$s integrated intervals (100 dwells at 10 ns gate width) to cover a period of 500 $\mu$s after photolysis; these signals were typically averaged over 40 laser shots at each scan step. With appropriate optical filters to define a narrow spectral region, we performed undersampling to decrease the size of the interferogram, hence the duration of data acquisition. For spectra in the range 1055–2100 cm$^{-1}$, 1192 scan steps at a resolution of 2.0 cm$^{-1}$ were completed within $\sim 1.5$ h. For spectra in the range 1000–3150 cm$^{-1}$ at a resolution of 5.0 cm$^{-1}$, 1472 scan steps were completed within $\sim 2$ h. Experimental conditions were as follows: flow rates $F_{\text{HCOOH}} \approx 0.25 – 1.05$, $F_{\text{Cl}_2} \approx 2.1$, and $F_{\text{N}_2} \approx 26.1$ STP cm$^3$ s$^{-1}$ (STP denotes standard temperature 273.15 K and pressure 1 atm); total pressure $\approx 58$ Torr. To minimize the formation of dimeric formic acid, the flow reactor was heated to $T = 363$ K with heated water circulated from a thermostat bath through the jacket of the reactor. Based on the equilibrium constant between monomeric and dimeric HCOOH, the fraction of (HCOOH)$_2$ is less than 10% under our experimental conditions.$^{27}$

The efficiency of photolysis of Cl$_2$ is estimated to be $\sim 4$% based on the absorption cross section of $\sim 1.6 \times 10^{-19}$ cm$^2$ molecule$^{-1}$ at 355 nm (Ref. 28) and the laser fluence of $\sim 2.6 \times 10^{10}$ photons cm$^{-2}$, HCOOH (99%, Riedel-de Haën), Cl$_2$ (99.99%, AGA Specialty Gases), and N$_2$ (99.995%, AGA Specialty Gases) were used without further purification.

III. QUANTUM-CHEMICAL CALCULATIONS

The equilibrium geometry, vibrational wavenumbers, and IR intensities of $c$-HCOOH, $t$-HCOOH, $c$-HOCO, $t$-HOCO, $c$-CICOOH, and $t$-CICOOH were calculated with the B3LYP density-functional theory using the GAUSSIAN 03 program.$^{29}$ The B3LYP method uses Becke’s$^{30}$ three-parameter hybrid exchange functional with a correlation functional of Lee et al.$^{31}$ Dunning’s correlation-consistent polarized-valence triple-zeta basis set, augmented with $s$, $p$, $d$, and $f$ functions (aug-cc-pVTZ) was applied in these calculations.$^{32,33}$ Analytic first derivatives were utilized in geometry optimization, and vibrational wavenumbers were calculated analytically at each stationary point. Rotational parameters of $c$-HOCO, $t$-HOCO, $c$-CICOOH, and $t$-CICOOH in their vibrational ground and excited ($\nu = 1$) states were also calculated with B3LYP/aug-cc-pVTZ for spectral simulation.

IV. RESULTS

A. Absorption spectra recorded upon photolysis of a mixture of HCOOH/Cl$_2$/N$_2$

The absorption spectrum of a static gaseous mixture of HCOOH/Cl$_2$/N$_2$ (1/0.6/10.7 at 54.3 Torr) at 363 K was recorded with a conventional FTIR technique. The characteristic bands of $t$-HCOOH at 2943, 2196, 1770, 1387, 1229, and 1105 cm$^{-1}$ are consistent with literature values.$^{34}$ Upon
Four new bands diminished in intensity afterward and became nearly undetectable ~500 μs after laser irradiation.

B. Quantum-chemical calculations

Geometries of c-CICOOH and t-CICOOH predicted with B3LYP/aug-cc-pVTZ are shown in Fig. 2. For comparison, results from MP2/6-311G** (Ref. 17) and CCSD(T)/aug-cc-pVTZ (Ref. 19) are listed in parentheses and brackets, respectively; the deviations among these results are within 2% for both conformers.

The conformer t-CICOOH is more stable than c-CICOOH; the zero-point-energy corrected energy of t-CICOOH is smaller than c-CICOOH by 2 kJ mol−1 at the B3LYP/aug-cc-pVTZ level of theory, slightly smaller than values ~8 kJ mol−1 reported by Francisco and Ghoul15 using the UMP2/6-311G** method and by Stephenson et al.17 using MP2/6-311G**, but similar to a value of 4 kJ mol−1 reported by Yu et al.19 using the high-level CCSD(T)/aug-cc-pVTZ method.

The isomerization barrier from t-CICOOH to c-CICOOH was calculated to be 41−50 kJ mol−1 using various methods,15,17,19 as compared to the experimental value of 58±7 kJ mol−1 determined by Jensen and Pimentel14 from the temperature dependence of the decay of the 768 cm−1 band assigned to CICOOH; they assumed that the rate-determining step is the trans-cis isomerization of CICOOH before its rapid decomposition to HCl and CO2.

The harmonic vibrational wavenumbers and IR intensities of t-CICOOH and c-CICOOH predicted with the B3LYP/aug-cc-pVTZ method are listed in Table I. Values predicted previously with MP2/6-311G** (Ref. 17) and HF/3-21G (Ref. 15), including the fundamental (ν=0→ν=1) vibrational wavenumbers reported for t-CICOOH,17 are listed also for comparison. For t-CICOOH, the most intense absorption bands are predicted to be at 1844, 1127, and 706 cm−1, cor-

---

**Figure 1:** Three-dimensional plot of time-resolved difference absorption spectra upon laser photolysis of HCOOH/Cl2/N2 (1/9/103 at 58 Torr) at 563 K; spectral resolution 5.0 cm−1. (a) Spectra integrated over 50 μs intervals: downward features are due to consumption of HCOOH (the saturation near 1750 cm−1 is truncated), whereas upward features A1 and A2 correspond to formation of c-CICOOH and features B1 and B2 correspond to formation of t-CICOOH. The band near 2350 cm−1 is due to CO2.

**Figure 2:** Geometries predicted with the B3LYP/aug-cc-pVTZ method for c-CICOOH and t-CICOOH. Bond lengths are in Å and bond angles in degrees. The values in parentheses are derived with MP2/6-311G** (Ref. 17) and the values in brackets are derived with CCSD(T)/aug-cc-pVTZ (Ref. 19).
responding approximately to C=O stretching, C–O stretching, and the C–Cl stretching mixed with OCO bending modes, respectively. Intense absorption bands of c-CICOOH are predicted to occur at 1919, 1286, and 1131 cm⁻¹, attributable to C=O stretching, COH bending, and C–O stretching modes, respectively. The values predicted for t-CICOOH are within 5.2% of the harmonic wavenumbers and 3.5% of the fundamental vibrational wavenumbers predicted previously with MP2/6-311G**.17 Similarly, the values predicted for c-CICOOH are within 7.0% of the harmonic wavenumbers predicted previously with MP2/6-311G**.17

The predicted molecular axes, vibrational displacements (thin arrows), and their corresponding dipole derivatives (thick dashed arrows) for the C=O stretching and COH bending modes of c-CICOOH and t-CICOOH are shown in Fig. 3. The projection vectors of the dipole derivative onto the molecular axes represent the weighting of the transition types. The C=O stretching band of t-CICOOH is a hybrid type with a ratio of a-type/b-type=1/2, whereas the COH bending band of t-CICOOH is a hybrid type with a ratio of a-type/b-type=3/1. For c-CICOOH, the C=O stretching band has a ratio of a-type/b-type=43/57, whereas the COH bending band has a ratio of a-type/b-type=1/1.

Rotational parameters for the equilibrium geometry, the vibrational ground state, and excited states (v_j=1) of each vibrational mode of c-CICOOH and t-CICOOH were calculated with the B3LYP/aug-cc-pVTZ method. These parameters and the ratios of A'/A'', B'/B'', and C'/C'', in which the prime and double prime indicate the excited and ground states, respectively, for the C=O stretching and COH bending modes of these two conformers of CICOOH are listed in Table II.

The HOCO radical has been well characterized with quantum-chemical calculations.35–42 We performed calculations on HOCO at the same level as for CICOOH mainly for comparison purposes. Vibrational wavenumbers (in cm⁻¹) and IR intensities (in km mol⁻¹) for c-HOCO are 3562 (16),

![Fig. 3. Displacement vectors (thin solid arrows) and vectors of dipole derivatives (thick dashed arrows) predicted with the B3LYP/aug-cc-pVTZ method for the COH bending and C=O stretching modes of (a) t-CICOOH and (b) c-CICOOH. Molecular axes a and b are shown in the plane; the axis c points out of the plane perpendicularly.](image-url)
TABLE II. Comparison of rotational parameters of c-CICOOH and t-CICOOH in ground and vibrationally excited states predicted with B3LYP/aug-cc-pVTZ.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>( \nu=0 )</th>
<th>( \nu=1 )</th>
<th>( \nu=1/\nu=0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-CICOOH C=O stretch</td>
<td>0.401 508</td>
<td>0.398 943</td>
<td>0.397 497</td>
</tr>
</tbody>
</table>

| COH bend | 0.400 508 | 0.398 943 | 0.398 600 | 0.397 497 | 0.397 793 | 0.170 474 | 0.169 698 | 0.169 617 |

| c-CICOOH C=O stretch | 0.390 067 | 0.387 953 | 0.386 525 | 0.386 793 | 0.387 793 | 0.170 474 | 0.169 698 | 0.169 617 |

| COH bend | 0.390 067 | 0.387 953 | 0.387 793 | 0.387 793 | 0.387 793 | 0.170 474 | 0.169 698 | 0.169 617 |

1860 (339), 1293 (1), 1067 (165), 598 (31), and 588 (105); corresponding values for t-HOCO are 3786 (125), 1897 (246), 1239 (238), 1079 (79), 620 (4), and 550 (85). For c-HOCO, the most intense absorption bands are at 1860 and 1067 cm\(^{-1}\), corresponding approximately to the C-O stretching and C-O stretching modes, respectively, whereas the most intense bands of t-HOCO are at 1897 and 1239 cm\(^{-1}\), corresponding to the C-O stretching and COH bending modes, respectively. The COH bending mode of c-HOCO at 1293 cm\(^{-1}\) has a very small intensity, as indicated above.

V. DISCUSSION

A. Assignments of c-CICOOH and t-CICOOH

At 363 K, negligible dimeric formic acid is present; therefore only the reactions of Cl atom with HCOOH need to be considered. Based on theoretical calculations, the reaction might involve two reaction intermediates, HOCO and CICOOH.\(^{19}\) The \( \nu_1 \) (3636 cm\(^{-1}\)) and \( \nu_2 \) bands (~1853 cm\(^{-1}\)) of gaseous t-HOCO have been characterized previously.\(^{43,45}\) Most vibrational bands of t-HOCO isolated in CO,\(^{46}\) Ar,\(^{47}\) Ne matrices,\(^{48}\) and c-HOCO isolated in a CO matrix have been reported.\(^{46}\) Only one band, the C=Cl stretching \( (\nu_8) \) mode near 768 cm\(^{-1}\), of gaseous CICOOH (presumably due to \textit{trans} configuration) was reported.\(^{13,14}\)

Upon excitation of a flowing mixture of HCOOH/Cl\(_2\)/N\(_2\), four transient bands near 1285, 1883, 1329, and 1808 cm\(^{-1}\), showed as A1, A2, B1, and B2 in Fig. 1(b), were observed. Bands A1 and A2 correlate well in intensity under various experimental conditions; bands B1 and B2 also correlate with each other, even though we cannot positively rule out the possibility that other combinations of these features are correlated.

The possibility that these bands are due to t-HOCO is eliminated because the C=O stretching band of t-HOCO reported by Sears \textit{et al}.\(^{44}\) lies at 1852.567 cm\(^{-1}\), at least 32 cm\(^{-1}\) separated from the observed bands. Furthermore, the \( \nu_3 \) mode of t-HOCO isolated in Ar or Ne was observed to absorb at ~1210 cm\(^{-1}\),\(^{47,48}\) 74 cm\(^{-1}\) from the observed A1 band.

According to the only report on IR absorption of c-HOCO, an intense band at 1797 cm\(^{-1}\) and a weaker one at 1261 cm\(^{-1}\) were assigned to absorption of the C=O stretching and COH bending modes of c-HOCO isolated in solid CO.\(^{46}\) Observed wavenumbers of the B2 (1808 cm\(^{-1}\)) and A1 (1285 cm\(^{-1}\)) bands in this work fit satisfactorily with these reported values. However, according to quantum-chemical calculations, two most intense absorption bands of c-HOCO are at 1860 and 1067 cm\(^{-1}\), the latter corresponds to approximately the C=O stretching mode. The intensity of the COH bending mode (predicted to be 1293 cm\(^{-1}\)) at B3LYP/aug-cc-pVTZ) has an IR intensity 1/340 that of the C=O stretching band of c-HOCO isolated in solid CO.\(^{46}\)
previously observed for c-HOCO and t-HOCO are also indicated with dashed lines and marked with $m$ for matrix and $g$ for gaseous experiments. The spectrum of HCOOH is also shown in Fig. 4(b) to indicate the regions (1730–1810 and 1000–1140 cm$^{-1}$, with gray color) that are unusable because of saturated absorption of the parent. If we assume small corrections to derive expected vibrational wavenumbers from calculated harmonic vibrational wavenumbers of CICOOH, similar to those indicated in frames (c) and (d) of Fig. 4 for HOCO, the expected vibrational wavenumbers and relative IR intensities of t-CICOOH and c-CICOOH (Table I) fit well with observed (B1, B2) and (A1, A2) groups of bands, respectively. If bands A1 and A2 are assigned to the COH bending and C=O stretching modes of c-CICOOH, the experimental values deviate only about 2% and 3%, respectively, from our calculated harmonic wavenumbers. Similarly, if bands B1 and B2 are attributed to the COH bending and C=O stretching modes of t-CICOOH, the deviations are 2% and 1%, respectively.

As a derivation of rotational parameters from observed spectra is unlikely to be practicable with the present spectral resolution, we simulated the band contour using the molecular parameters predicted with B3LYP/aug-cc-pVTZ for comparison with observed spectra. With the SPECVIEW program$^{49}$ we simulated the spectrum of each band using predicted rotational parameters $A^\prime$, $A^\prime\prime$, $B^\prime$, $B^\prime\prime$, $C^\prime$, and $C^\prime\prime$ (Table II), $J_{\text{max}}=120$, $T=363$ K, and a Doppler width (full width at half maximum) of 2.0 cm$^{-1}$. The resultant rotational contours simulated for these four bands with $a$-type/$b$-type ratios calculated quantum chemically (Sec. IV B) are shown in frames (a) and (b) of Fig. 5 for t-CICOOH and c-CICOOH, respectively. A comparison of the observed transient spectrum averaged over 100–150 $\mu$s (with open circle marks) with the combined simulated contour (solid lines) of these four bands is shown in Fig. 5(c). The missing data for the P branch of the B2 band in the 1750–1810 cm$^{-1}$ region are due to interference from saturated absorption of HCOOH. For this simulation, A1 band has $v_0=1284.9$ cm$^{-1}$ with $a$-type/$b$-type =1/1, A2 band has $v_0=1838.0$ cm$^{-1}$ with $a$-type/$b$-type =43/57, B1 band has $v_0=1328.5$ cm$^{-1}$ with $a$-type/$b$-type =3/1, and B2 band has $v_0=1808.0$ cm$^{-1}$ with $a$-type/$b$-type =1/2; values of $v_0$ are listed in Table I for comparison with calculations. Observed integrated intensity ratios of C=O stretching to COH bending modes are $\sim 6.5$ and $\sim 1.1$, respectively, for t-CICOOH and c-CICOOH, which are consistent with the quantum-chemically predicted values of 7.2 and 1.1, respectively.

When the quantum-chemically predicted IR intensities are used, the population ratios of t-CICOOH to c-CICOOH can be estimated to be $\sim 2.5 \pm 0.3$ based on the observed integrated intensities of B1 and A1 bands; the error limits reflect errors only in simulation, not the errors in the predicted IR intensities. If we assume that the simulation of the B2 band is reliable even though only part of the band was observed, the observed population ratio is $\sim 2.6 \pm 0.3$ based on the integrated intensities of simulated B2 and A2 bands, consistent with the result derived from B1 and A1 bands. A concentration of t-CICOOH greater than that of c-CICOOH is consistent with the quantum-chemically predicted result that t-CICOOH is slightly more stable than c-CICOOH. Assuming a Boltzmann population at 363 K, we derive from the observed intensity ratio an energy difference of $2.8 \pm 0.3$ kJ mol$^{-1}$ between these two configurations. If an error of a factor of 2 is assumed for the predicted IR intensity, then $\Delta E=2.8 \pm 1.9$ kJ mol$^{-1}$. This value is consistent with values of 2 kJ mol$^{-1}$ calculated with B3LYP/aug-cc-pV TZ in this work and 4 kJ mol$^{-1}$ reported by Yu et al.$^{19}$ using the CCSD(T)/aug-cc-pVTZ method, but slightly smaller than values $\sim 8$ kJ mol$^{-1}$ reported by Francisco and Ghoul$^{15}$ using UMP2/6-311G** and by Stephenson et al.$^{11}$ using MP2/6-311G**; the latter two methods used a smaller basis set and are expected to be less accurate.

Considering possible chemical reactions, vibrational wavenumbers, rotational contours, relative IR intensities, and relative concentrations, we are confident of the assignments of the four transient features A1, A2, B1, and B2 observed near 1285, 1883, 1329, and 1808 cm$^{-1}$ to the COH bending and C=O stretching modes of c-CICOOH, COH bending, and C=O stretching modes of t-CICOOH, respectively. According to quantum-chemical calculations, the C–Cl stretching (691 cm$^{-1}$) and C–O stretching (1131 cm$^{-1}$) modes of c-CICOOH are expected to have intensities $\sim 0.25$ those of the A1 and A2 bands, and the C–Cl stretching (706 cm$^{-1}$) and C–O stretching (1127 cm$^{-1}$) modes of t-CICOOH are expected to have intensities slightly smaller than that of the B2 bands. The C–Cl stretching mode is beyond our detection range (950–7000 cm$^{-1}$), whereas the C–O stretching mode of CICOOH is severely overlapped by the intense absorption of HCOOH (Fig. 4). The 768 cm$^{-1}$ band observed by Pitmentel and coworkers$^{13,14}$ does not match the predicted wavenumber for the C–Cl stretching mode of c-CICOOH or t-CICOOH.

According to literature values, t-HOCO absorbs at 1852.6 (Ref. 44) and $\sim 1210$ cm$^{-1}$. The 1852.6 cm$^{-1}$ band might be buried between the B2 and A2 bands, but we
observed no discernible feature in the 1200–1250 cm\(^{-1}\) region near the A1 band. It is likely that \(t\)-HOCO was not produced directly from reaction (2) because \(t\)-HCOOH is the dominant conformer and the Cl atom only abstracts the hydrogen on the C atom. Conformer \(c\)-HOCO was observed only in a CO matrix,\(^{40}\) with two intense lines at 1797 and 1088 cm\(^{-1}\); the 1261 cm\(^{-1}\) line is expected to have a small intensity according to calculations with the B3LYP/aug-cc-pVTZ method. Both absorption regions (~1800 and 1090 cm\(^{-1}\)) for \(c\)-HOCO were inaccessible in this work because of the intense absorption of HCOOH.

B. Possible mechanism of the Cl+HCOOH reaction

The reaction of Cl with HCOOH is believed to proceed via reaction (2).

\[
\text{Cl} + \text{HCOOH} \rightarrow \text{HCl} + \text{HOCO}.
\]  

(2)

Tyndall et al.\(^{11}\) determined a yield of 96 ± 5% for CO\(_2\) and suggested that the other channel

\[
\text{Cl} + \text{HCOOH} \rightarrow \text{HCl} + \text{HCO}_2.
\]  

(6)

is unimportant. Miyoshi et al.\(^{7}\) also showed that reaction (6) is unimportant by deuterium experiments. Yu et al.\(^{40}\) employed UQCISD(T, full)/6-311+G(3df, 2p)//UMP2 (full)/6-311+G(d, p) and reported that reactions (2) and (6) have barriers of 3.7 and 68 kJ mol\(^{-1}\), respectively. They concluded that the C-site hydrogen abstraction of \(t\)-HCOOH to form \(c\)-HOCO dominates, consistent with experimental observations. Rate coefficient \(k_2 = (1.83 ± 0.12) \times 10^{-13}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) near 298 K was reported by Li et al.,\(^9\) similar to \(k_2 = (2.00 ± 0.25) \times 10^{-13}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) reported by Wallington et al.\(^{10}\)

Further reaction of HOCO with Cl\(_2\) is unimportant because this reaction is expected to have a large barrier. In contrast, reaction of Cl with HOCO to form HCl and CO\(_2\) is expected to be rapid,

\[
\text{Cl} + \text{HOCO} \rightarrow \text{HCl} + \text{CO}_2
\]  

(4)

and the rate coefficient was determined to be \(k_4 = (4.8 ± 1.0) \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) near 298 K, \(\sim 250\) times greater than \(k_2\).\(^9\) Yu et al.\(^{19}\) employed CCSD(T) theory to investigate reaction (4) and found that the reaction occurs via a CICOOH intermediate that is formed through the barrierless addition reaction of Cl to the carbon atom in HOCO. The CICOOH intermediate dissociate into HCl and CO\(_2\) through a four-center (Cl–C–O–H) transition state that lies \(\sim 234\) kJ mol\(^{-1}\) below the asymptotic reactant channel. They derived a thermal rate coefficient of \(k_4 = 3.0 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), consistent with experimental results. They also employed a direct MP2/6-31G(d) molecular dynamics method to find reactive trajectories of two kinds, both of which proceed through CICOOH with lifetimes \(\sim 0.31\) and 1.9 ps, respectively. They suggested that the long-lived CICOOH might be stabilized with a third collision partner, consistent with our experimental observation of both conformers of CICOOH upon photolysis of a mixture of Cl\(_2\) and HCOOH under 58 Torr of N\(_2\).

We employ a simple mechanism to describe the reactions in our system,

\[
\text{Cl} + \text{HCOOH} \rightarrow \text{HCl} + \text{HOCO}
\]  

(2)

\[
\text{Cl} + \text{HOCO} \rightarrow \text{CICOOH}
\]  

(7)

\[
\text{CICOOH} \rightarrow \text{HCl} + \text{CO}_2
\]  

(5)

in which \(k_7\) is expected to be much larger than \(k_4\), as supported by reported values of \(k_4 \approx 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) near 298 K.\(^9,10\) The rate-determining step for formation of CICOOH is reaction (2). Under such conditions, [HOCO] is expected to be in the steady state and

\[
[\text{HOCO}] = k_2[\text{HCOOH}]/k_7.
\]  

(8)

By solving the differential equations of

\[
\frac{d[\text{Cl}]c}{dt} = k_2[\text{Cl}][\text{HCOOH}] - k_5[\text{Cl}][\text{CICOOH}],
\]  

(9)

\[
\frac{d[\text{Cl}]t}{dt} = -2k_4[\text{Cl}][\text{HOCO}],
\]  

(10)

we derived the concentration of CICOOH as

\[
[\text{CICOOH}] = [\text{Cl}]_0 \frac{k_4[\text{HCOOH}]}{2k_2[\text{HCOOH}] - k_5} \times [\exp(-k_7t) - \exp(-2k_4[\text{HCOOH}]t)].
\]  

(11)

The temporal profile of the absorbance integrated over the 1350–1250 cm\(^{-1}\) region, including absorption of both \(c\)-CICOOH and \(t\)-CICOOH, upon photodissociation at 355 nm of a flowing mixture of HCOOH/Cl\(_2\)/N\(_2\) (1/9/103 at 58 Torr) is shown in Fig. 6. When we fitted this profile to Eq. (11), we derived first-order rate coefficients as \(k_4[\text{HCOOH}] = (2.7 ± 0.7) \times 10^3\) s\(^{-1}\) and \(k_5 = (9.2 ± 2.7) \times 10^3\) s\(^{-1}\), respectively. Using the initial concentrations of [HCOOH] = 1.5 \times 10^{16} molecule cm\(^{-3}\) and assuming that reaction (2) is rate-determining for the formation of CICOOH, we estimated a bimolecular reaction rate coefficient of \(k_2 = (1.8 ± 0.5) \times 10^{-13}\) at 363 K, consistent with the literature value of \(2 \times 10^{-13}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 298 K.\(^9,10\) The \(k_5\) value at 363 K derived in this work is about one twentieth of the
value, \(1.8 \times 10^5\) s\(^{-1}\), derived from the rate equation reported by Jensen and Pimentel.\(^6\) This also indicates that the 768 cm\(^{-1}\) band observed by them might not be due to CICOOH.

VI. CONCLUSION

Four IR absorption bands of two conformers of CICOOH were observed with a step-scan Fourier-transform spectrometer upon irradiation at 355 nm of a flowing gaseous mixture of Cl\(_2\) and HCOOH in N\(_2\). By considering possible chemical reactions, vibrational wavenumbers, rotational contours, relative IR intensities, and relative concentrations predicted with quantum-chemical calculations, we attributed absorption bands with origins at 1808.0 and 1328.5 cm\(^{-1}\) to the C=O stretching and COH bending modes of \(t\)-CICOOH, respectively. Similarly, band origins at 1883.0 and 1284.9 cm\(^{-1}\) are assigned as the C=O stretching and COH bending modes of \(c\)-CICOOH, respectively. From the observed and predicted relative intensities, we estimate that \(t\)-CICOOH is more stable than \(c\)-CICOOH by \(\sim 3 \pm 2\) kJ mol\(^{-1}\), consistent with quantum-chemical calculations.

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