Unimolecular Dissociation of the CH₃OCO Radical: An Intermediate in the CH₃O + CO Reaction

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This work investigates the unimolecular dissociation of the methoxycarbonyl, CH₃OCO, radical. Photolysis of methyl chloroformate at 193 nm produces nascent CH₃OCO radicals with a distribution of internal energies, determined by the velocities of the momentum-matched Cl atoms, that spans the theoretically predicted barriers to the CH₃O + CO and CH₃ + CO₂ product channels. Both electronic ground- and excited-state radicals undergo competitive dissociation to both product channels. The experimental product branching to CH₃ + CO₂ from the ground-state radical, about 70%, is orders of magnitude larger than Rice–Ramsperger–Kassel–Marcus (RRKM)-predicted branching, suggesting that previously calculated barriers to the CH₃OCO → CH₃ + CO₂ reaction are dramatically in error. Our electronic structure calculations reveal that the cis conformer of the transition state leading to the CH₃ + CO₂ product channel has a much lower barrier than the trans transition state. RRKM calculations using this cis transition state give product branching in agreement with the experimental branching. The data also suggest that our experiments produce a low-lying excited state of the CH₃OCO radical and give an upper limit to its adiabatic excitation energy of 55 kcal/mol.

Introduction

This paper investigates the dissociation dynamics of the methoxycarbonyl radical, CH₃OCO, produced by the 193 nm photolysis of methyl chloroformate. This radical serves as the intermediate along the reaction coordinate for the reaction of the methoxy radical with carbon monoxide, CH₃O + CO → CH₃ + CO₂. This reaction is important because of its relevance to the fate of methoxy radicals in atmospheric reactions and hydrocarbon combustion. Furthermore, the potential energy surface for this reaction is similar to that of the reaction HO + CO → H + CO₂, which proceeds via the analogous HOCO intermediate. While the HO + CO system has been the subject of numerous investigations, there are comparatively few studies on the CH₃O + CO system.

The kinetics of the CH₃O + CO reaction has been investigated previously. In the course of experiments on CH₃O + NO, Wiebe and Heicklen performed photolysis of methyl nitrate in the presence of N₂ and CO to verify if the reaction would produce CO₂. Indeed, they observed CO₂ formation, but could not accurately measure a rate constant, saying only that the removal rate of CH₃O by CO is approximately 5 × 10⁻⁴ slower than removal by NO in the temperature range 25–150 °C. They theorized that the principal products of CH₃O + CO could be (CH₃O)₂CO or (CH₃OCO)₂. Sanders et al. also principally studied the CH₃O + NO reaction but looked at the reaction of CH₃O with CO and found it too slow to measure the rate constant. They suggested an upper bound of log k = 6.7 M⁻¹ s⁻¹ for the reaction of CH₃O + CO. Lissi et al. used thermal decomposition of dimethyl peroxide in the presence of CO at 123–153 °C to measure the CH₃O + CO → CH₃ + CO₂ rate constant. Their results showed that Eₐ = 11.8 ± 1.5 kcal/mol for the reaction. Wantuck et al. measured removal of CH₃O by CO at 473–973 K and found that the rate could not be described by a simple Arrhenius expression. They expected CH₃ + CO₂ to be the major products but suggested that a minor HCO + H₂CO product channel may arise at high temperatures. Tsang and Hampson compiled the results of the above experiments in a kinetic database for combustion chemistry and recommended the value of Eₐ = 11.8 ± 1.5 kcal/mol found by Lissi et al. with an uncertainty factor of at least 5.

More recently, several theoretical studies have been published concerning the CH₃O + CO system. Francisco studied the CH₃O + CO reaction, considering only the CH₃ + CO₂ product channel via the CH₃OCO intermediate. His QCISD(T)/6-311++G(3df,3pd) calculations predicted an entrance channel barrier of 5.8 kcal/mol and a barrier of 38.2 kcal/mol for the CH₃OCO → CH₃ + CO₂ channel. Kang and Musgrave also calculated the CH₃OCO → CH₃ + CO₂ reaction barrier while testing their newly developed KMLYP hybrid density-functional method. Their value of 39.5 kcal/mol agreed with Francisco’s result.

Zhou et al. investigated the multichannel CH₃O + CO reaction at the B3LYP/6-311++G** level of theory. For dissociation of the CH₃OCO radical, they found the CH₃O + CO channel to have a 19.5 kcal/mol barrier and the CH₃ + CO₂ channel to have a 27.0 kcal/mol barrier. The other product channels examined were H₂CO + HCO and H₂CCO + OH, but both had higher barriers (38.9 and 35.0 kcal/mol, respectively) than the CH₃ + CO₂ channel. A direct abstraction
reaction of CH₃O + CO → H₂CO + HCO was also found, with a barrier of 17.16 kcal/mol relative to the reactants.

Wang et al. used the G2(B3LYP/MP2/CC) method to study the CH₃O + CO reaction and also completed multichannel Rice–Ramsperger–Kassel–Marcus (RRKM) calculations for a wide range of temperatures and pressures. They predicted a 6.39 kcal/mol barrier for the CH₃O + CO addition reaction leading to the CH₂OCO intermediate and a 32.3 kcal/mol barrier, measured from the zero point level of the radical intermediate, for the radical’s dissociation to CH₃ + CO₂. Examination of the transition state for this dissociation led them to assert that Francisco had misidentified the CH₃OCO → CH₃ + CO₂ transition state, making his barrier energy too high. Interestingly, they suggested strong CH₃ tunneling in the decomposition of CH₂OCO → CH₃ + CO₂, due to the transition state’s abnormally large imaginary frequency. In their calculations, they included the radical dissociation pathways to H₂CO + HCO and H₂CCO + OH as well as the direct reaction of CH₃O + CO → H₂CO + HCO. The RRKM results showed that under atmospheric conditions, the stabilization of the CH₂OCO radical would dominate. Under combustion conditions, the major products would be H₂O + HCO, from the direct abstraction channel. The same group later studied the mechanism of the H₂CCO + OH reaction. They predicted CO + CH₂OH to be the major products at lower temperatures, while H₂O + HCCO would dominate at higher temperatures. Referencing their previous work on CH₂O + CO, they showed that the CH₂OCO radical intermediate would play a very minor role in the H₂CCO + OH reaction.

The CH₂OCO radical could also serve as one of many possible intermediates in the vinyl + O₂ reaction. G2M(RCC, MP2) and multichannel RRKM calculations by Mebel et al. showed that the most favorable reaction pathway for this system leads to CHO + H₂CO. As part of a minor channel, the CH₂OCO radical can dissociate to make CH₃ + CO₂, but the CH₂O + CO products were not included in the analysis. The barrier for CH₂OCO → CH₃ + CO₂ at the B3LYP/6-311G(d,p) level of theory was found to be 27.1 kcal/mol, a result similar to that of Zhou et al.¹⁵

Figure 1 shows the energetics for the CH₂O + CO → CH₃ + CO₂ reaction at various levels of theory as calculated by Francisco,¹³ Wang et al.¹⁶ and Zhou et al.¹⁵ The calculated overall reaction enthalpies are in agreement, as well as the predicted barrier heights for CH₂OCO → CH₂O + CO. In contrast, the energies for the CH₂OCO → CH₃ + CO₂ transition state differ by up to 10 kcal/mol. The large discrepancy in the values calculated for the barrier to the CH₂O + CO₂ channel warrants more experimental efforts on the CH₂OCO radical. The original motivation for the experiments presented here was thus to measure a branching ratio between the two dissociation channels of the methoxycarbonyl radical and compare it to the RRKM-predicted branching ratios based on these published barrier heights.

The experiments described in this paper utilize methyl chloroformate, CH₃OC(O)Cl, as a photolytic precursor for the radical. This precursor and the photolysis wavelength of 193 nm were deliberately chosen to produce nascent CH₂OCO radicals with an internal energy range that spans the theoretically predicted dissociation barriers shown in Figure 1. Listed below are the reactions that are energetically possible for methyl chloroformate at 193 nm, with the dissociation pathways open to CH₂OCO radicals and other photolytic fragments indented (reactions 1–12). Reliable values for the enthalpies of reactions 6, 8, and 11 could not be found in the literature, so we calculated them by the G3/B3LYP method with Gaussian 98.¹⁹ For reaction 1, we used both G3/B3LYP and CCSD(T) as described in the Experimental Method section to calculate the C–Cl bond energy for both cis and trans conformers of methyl chloroformate. All the results are summarized in Table 1, while only the G3/B3LYP value for the most stable CH₂OCOCl and CH₃OCO conformers is shown in the list below.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH₀/kcal/mol</th>
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<tbody>
<tr>
<td>CH₃OC(O)Cl → CH₃OCO + Cl</td>
<td>ΔH₀ = 85.2 kcal/mol</td>
</tr>
<tr>
<td>CH₃OCO → CH₃O + CO</td>
<td>ΔH₀ = 15.0 kcal/mol¹⁶</td>
</tr>
<tr>
<td>CH₃OCO → CH₃ + CO₂</td>
<td>ΔH₀ = −22.54 kcal/mol¹⁶</td>
</tr>
<tr>
<td>CH₃OCO → H₂CO + HCO</td>
<td>ΔH₀ = 19.75 kcal/mol¹⁶</td>
</tr>
<tr>
<td>CH₃OCO → H₂CCO + OH</td>
<td>ΔH₀ = 35.84 kcal/mol¹⁶</td>
</tr>
<tr>
<td>CH₃OC(O)Cl → CH₃ + OC(O)Cl</td>
<td>ΔH₀ = 86.3 kcal/mol</td>
</tr>
<tr>
<td>OC(O)Cl → CO₂ + Cl</td>
<td>ΔH₀ = −37.4 kcal/mol²⁰</td>
</tr>
<tr>
<td>CH₃OC(O)Cl → H₂CO + HC(O)Cl</td>
<td>ΔH₀ = 24.4 kcal/mol</td>
</tr>
<tr>
<td>HC(O)Cl → HCl + CO</td>
<td>ΔH₀ = −10.8 kcal/mol²¹</td>
</tr>
<tr>
<td>H₂CO → H₂ + CO</td>
<td>ΔH₀ = 1.3 kcal/mol²²</td>
</tr>
<tr>
<td>CH₃OC(O)Cl → H₂CO + HOCCI</td>
<td>ΔH₀ = 71.2 kcal/mol</td>
</tr>
<tr>
<td>HOCCI → HCl + CO</td>
<td>ΔH₀ = −58.9 kcal/mol²³</td>
</tr>
</tbody>
</table>

In these experiments, photolysis of methyl chloroformate produces Cl atoms and momentum-matched CH₂OCO radicals that are dispersed by their recoil translational energy and thus by the radicals’ internal energy. Measurement of the recoil velocities of Cl atoms alone determines the total recoil translational energy distribution, and by energy conservation, the internal energy distribution of the momentum-matched

**TABLE 1: Theoretical D₆(CH₃OC(O)⁻Cl) at the G3//B3LYP and CCSD(T) Levels of Theory in kcal/mol**

<table>
<thead>
<tr>
<th>G3/B3LYP</th>
<th>CCSD(T)⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(cis-CH₃OC(O)⁻Cl)</td>
<td>85.4</td>
</tr>
<tr>
<td>D(trans-CH₃OC(O)⁻Cl)</td>
<td>81.3</td>
</tr>
</tbody>
</table>

⁶ The D₆ calculations correspond to reactions where cis- or trans-CH₃OC(O)Cl is dissociated into cis-CH₃-Cl + CO. The G3/B3LYP results in this table also refer to the cis-CH₃OC(O) radical for consistency, though the trans conformer is predicted to have the minimum energy at that level of theory. Note that cis-CH₃OC(O)Cl is approximately 4 kcal/mol lower in energy than the trans conformer.

Based on the CCSD(T)/6-311G(d,p) optimized geometries, single-point energies were calculated at the CCSD(T)/aug-cc-pV(Q+d)Z level of theory. Zero-potential vibrational energy correction and core-valence electronic correlations were included (see Experimental Method section).
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Figure 1. Energetics of the CH₃O + CO → CH₃ + CO₂ reaction. The numbers are computational results from refs 13, 15, and 16. JJ stands for QCISD(T)/6-311++G(3df,3pd) values (ref 13). ZZ stands for B3LYP/6-311+G** values (ref 15). BW stands for G2(B3LYP/MP2/CC) values (ref 16). Overlaid is the internal energy distribution of the nascent CH₃OCO radicals produced in the 193 nm photolysis of methyl chloroformate, as determined from the fitting of the data in Figure 3. The solid line is the distribution belonging to ground-state radicals, while the dashed line represents radicals assigned to an excited state. CH₃OCO radicals. These experiments also measure the velocity distributions of the products from dissociation of energetic CH₃OCO radicals, allowing us to probe the dissociation dynamics of the radicals and to measure a product branching ratio.

Experimental Method

A. Molecular Beam Scattering Experiments. The velocities of the primary photofragments and the products of the unimolecular dissociation of the CH₃OCO radicals were measured with the rotating-source crossed laser-molecular beam apparatus on the 21AI U9/Chemical Dynamics Beamline at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Details of the experimental apparatus have been described previously. A 10% methyl chloroformate-He molecular beam was created by bubbling He (800 Torr total backing pressure) through methyl chloroformate (97% purity, Aldrich) cooled to 16 °C and expanding it through an Even-Lavie (type E.L.-5-3-2000) pulsed valve with a 0.25 mm orifice operating at 40 Hz. The nozzle was heated to 107 °C to reduce cluster formation. The molecular beam of the parent molecule was characterized by directing the beam through a capper wheel along the detector axis. The measured number-density speed distribution of the methyl chloroformate molecular beam for the data presented here was typically peaked at 1.18 × 10⁸ cm/sec⁻¹ with a full width at half-maximum of 27%.

Photodissociation was accomplished with a Lambda Physik LPX 210i excimer laser operating at the 193.3 nm ArF transition. The laser ran at 40 Hz with a pulse energy between 80 and 150 mJ/pulse. The pulse energy varied over the course of our experiments, but a specific value was recorded for each individual spectrum. The laser beam was focused to an area of 2.1 mm wide by 8.9 mm high, intersecting the ~3 mm high molecular beam at a 90° angle in the interaction region. Photofragments recoiling in the direction of the detector traveled 10.05 cm to the ionizing region, where tunable VUV synchrotron radiation ionized a portion of the fragments. Photoionization energies were selected by tuning the gap of a U9 undulator, which generated the radiation. For example, Cl⁺ data were collected at m/e = 35 using a 14.8 eV photoionization energy, requiring a 34 mm undulator gap. Unwanted higher harmonics of VUV radiation were removed by a rare gas filter. The VUV beam was defined by a circular aperture of 7 mm diameter for a full-width at half-maximum of 0.27 eV, or 3%.

Ionized photofragments were mass-selected by an Extrel 1.7 MHz quadrupole mass spectrometer and then counted by a Dally detector. A multichannel scaler was used to record the total time of flight (TOF) of the photofragments from the interaction region to the detector. Recoil translational energy distributions were found by forward convolution fitting of the TOF spectra. The forward convolution fitting of the data takes into account the ion flight time, derived from the apparatus’ ion flight constant of 5.45 μs·amu⁻¹². The experimental data and fits shown in this paper have already subtracted the 1.6 μs delay between the trigger of the multichannel scaler and the arrival of the laser pulse at the interaction region.

The absorption spectrum of methyl chloroformate presented in this paper was collected on a Hewlett-Packard 8453 UV/visible spectrophotometer. The spectrum was taken on the vapor in the headspace above a liquid sample. The sample cuvette and spectrophotometer were flushed with nitrogen to prevent absorption of UV light by oxygen in the air.

B. Theoretical Calculations. The D₀(CH₃OC(O)−→Cl), the transition barrier heights involved in dissociation reactions (CH₃OCO → CH₃ + CO and CH₃OCO → CH₃ + CO₂), and the isomerization barrier between cis-CH₃OCO and trans-CH₃OCO were calculated by the G3/B3LYP method.25 We also evaluated the D₀ and transition/isomerization barrier heights at the coupled cluster level with single and double excitations plus a quasi-perturbative triple excitation [CCSD(T)]26–28 together with Dunning’s correlation consistent basis sets.29,30 Specifically, the geometries of cis-trans-CH₃OC(O)Cl, cis-trans-CH₃OC(O)CO, CH₃O, CH₃, CO₂, CO and the transition states were optimized at the CCSD(T)/6-311G(2df,p) level. Based on the optimized structures, single-point frozen core energy calculations were carried out at the CCSD(T)/aug-cc-pV(Q+d)Z level of theory. The calculations include a zero-point vibrational energy (ZPVE) correction at the minimum and transition state structures using the harmonic vibrational frequencies at the CCSD(T)/6-311G-(2df,p) level. The core-valence electron correlation (1s electrons on C and O, 2s/2p electrons on Cl) was obtained at the CCSD(T) level using the cc-pCVTZ basis set.31 The G3/B3LYP calculations were performed with the Gaussian 03 package of programs,32 with the exception of the enthalpies for reactions 6, 8, and 11, which were calculated separately in Gaussian 98. The CCSD(T) single-point energies and vibrational frequencies calculations were done with the program MOLPRO 2002.6.33 Transition state identities were confirmed by intrinsic reaction coordinate calculations.

Results and Analysis

The data showed that C−Cl bond fission is the major photodissociation channel of methyl chloroformate at 193 nm. Methyl chloroformate absorbs strongly at 193 nm, as shown in the absorption spectrum in Figure 2.

C−Cl fission was evidenced by a Cl⁺ time-of-flight (TOF) spectrum at m/e = 35 shown in Figure 3. The total recoil kinetic energy distribution P(Eᵣ) for C−Cl fission was determined by forward convolution fitting of the data. The total P(Eᵣ) is
the air-to-vacuum correction. A 193.3 nm photon, produced in our experiment, shown in Figure 4. The energy of a 193.3 nm photon, equals 14.8 eV for 15000 laser shots. The open circles represent experimental data points, while the bold solid line is the overall forward convolution fit to the data with the $P(E_T)$ shown in Figure 4. The thin solid line corresponds to chlorine atoms that are momentum-matched to CH$_3$OCO radicals formed in the ground state. The dashed line corresponds to chlorine atoms that are momentum-matched to CH$_3$OCO radicals assigned as being formed in an excited state. The dotted line shows a contribution near 60 $\mu$s from dissociation of OCOCl radicals, as reasoned in the fitting of the CH$_3$ and CO$_2$ data shown in Figures 11 and 15.

bimodal, with the low-energy component peaking at 1 kcal/mol. Our results suggest that the low kinetic energy C$\rightarrow$Cl bond fission channel produces CH$_2$OCO radicals in an excited electronic state. These data are marked by the dashed line in Figure 3 and have a $P(E_T)$ shown by the dashed line in Figure 4. The dominant, high kinetic energy, C$\rightarrow$Cl bond fission channel produces CH$_3$OCO radicals in the ground electronic state as shown by the solid lines in Figures 3 and 4. The dotted line fit in Figure 3 near 60 $\mu$s arrival time shows a contribution of Cl from dissociation of OCOCl radicals (reaction 7), as explained later in this section. The internal energy range of the nascent CH$_3$OCO radicals, although they all dissociate, is easily deduced from the momentum-matched Cl atom velocities using conservation of energy:

$$E_{\text{parent}} + h\nu = D_{ij}(C\rightarrow Cl) + E_{\text{int}} + E_{\text{Cl}} + E_T$$

This calculation was done for the entire distribution of $E_T$ produced in our experiment, shown in Figure 4. The energy of a 193.3 nm photon, $h\nu$, is equal to 147.8 kcal/mol, including the air-to-vacuum correction. $D_{ij}(C\rightarrow Cl)$ was calculated by G3//B3LYP and CCSD(T) methods, with the results shown in Table 1. We used the G3//B3LYP value for C$\rightarrow$Cl bond fission leading to the most stable (trans) conformer of the radical, $D_\theta = 85.2$ kcal/mol. $E_{\text{parent}}$ is the internal energy of the methyl chloroformate molecule; we estimated it by assuming that vibrational modes are not cooled by the nozzle expansion and have equilibrated to the nozzle temperature. Using vibrational modes calculated at the B3LYP/6-31G(d) level of theory, we determined the average vibrational energy of the methyl chloroformate molecule to be 2.8 kcal/mol at the 107 $^\circ$C nozzle temperature used in our experiments. $E_{\text{Cl}}$ refers to the energy of the spin–orbit state of the chlorine atoms. $E_{\text{Cl}}$ is 0 kcal/mol if Cl is produced in the $^2P_{3/2}$ state and 2.5 kcal/mol in the $^2P_{1/2}$ state. Our experiments cannot distinguish between the two spin–orbit states, but 235 nm photolysis of methyl chloroformate with resonance-enhanced multiphoton ionization detection in separate experiments revealed that both Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) are produced. The internal energy distribution of the radicals produced in our experiment is shown overlaid with the energetics of the CH$_3$OCO reaction in Figure 1.

Unimolecular dissociation of the nascent CH$_3$OCO radicals via reaction 2 was observed in the $m/e = 28$ (CO$^+$) TOF shown in Figure 5. The fit accounts for the velocity imparted to the CH$_3$OCO radical in the initial C$\rightarrow$Cl bond fission (reaction 1) as well as the velocity imparted during the recoil of CO from

Figure 2. Gas-phase absorption spectrum of methyl chloroformate. The absorption cross section is a lower bound, as we observed the magnitude of absorbance decreasing with time. This may be due to the molecules reacting with water vapor or the walls of the cuvette.

Figure 3. Time-of-flight (TOF) spectrum of $m/e = 35$ (Cl$^+$) taken at a source angle of 19.5$^\circ$ and ionization energy of 14.8 eV for 15000 laser shots. The open circles represent experimental data points, while the bold solid line is the overall forward convolution fit to the data with the $P(E_T)$ shown in Figure 4. The line fit in Figure 3 near 60 $\mu$s arrival time shows a contribution of Cl from dissociation of OCOCl radicals, as reasoned in the fitting of the CH$_3$ and CO$_2$ data shown in Figures 11 and 15.

Figure 4. Recoil kinetic energy distribution, $P(E_T)$, in C$\rightarrow$Cl bond fission derived from forward convolution fitting of the data in Figure 3. The solid gray line shows the total $P(E_T)$. The total $P(E_T)$ is divided into two subdistributions used in fitting of subsequent spectra. The black solid line corresponds to high $E_T$, low $E_{\text{int}}$ CH$_3$OCO radicals that are formed in the ground state. The dashed line corresponds to low $E_T$, high $E_{\text{int}}$ CH$_3$OCO radicals presumed to be in an excited state. Note that the relative contributions where they overlap are estimates only.

Figure 5. TOF spectrum of $m/e = 28$ (CO$^+$), 19.5$^\circ$ source angle, obtained from 100000 laser shots at an ionization energy of 15.4 eV. Open circles are experimental data, while the bold solid line is the overall fit to the data. The thin solid line shows CO produced by unimolecular dissociation of ground-state CH$_3$OCO radicals. This signal is fit as described in the text by the $P(E_T)$ distributions shown by the black solid lines in Figures 4 and 6. The dashed line shows CO produced by excited-state CH$_3$OCO radicals, fit by the dashed line $P(E_T)$s in Figures 4 and 7.
the methoxy radical in reaction 2. It was impossible to gain a satisfactory fit of the data by assigning one $P(E_T)$ for the dissociation of the total distribution of CH$_3$OCO radicals shown by the gray line in Figure 4. This led us to believe that the low $E_T$ CH$_3$OCO radicals, $\sim$15% of all the radical product, which are formed with high internal energy, are dissociating from an excited state and thus can exhibit different dissociation dynamics than the ground-state radicals. The thin solid line in Figure 5 shows CO produced from ground-state radical dissociation. These CO fragments recoil from methoxy radicals with a kinetic energy distribution shown by the solid line in Figure 6, and they originate from CH$_3$OCO radicals corresponding to the black solid line in Figure 4. Likewise, the dashed line in Figure 5 shows CO from dissociation of excited-state CH$_3$OCO radicals fit by the dashed lines of Figures 4 and 7. The dissociation of the excited-state CH$_3$OCO radicals to CH$_3$O + CO likely occurs via electronic predissociation by a repulsive excited-state potential surface, as much higher energies are partitioned to recoil kinetic energy than in ground-state dissociation.

Figure 8 shows a $m/e = 29$ (HCO$^+$) TOF spectrum. The majority of the signal is due to dissociative ionization of CH$_3$O fragments produced as partners to CO in reaction 2. The CH$_3$O$^+$ ion is known to predissociate to CHO$^+$ + H$_2$ even at the zero point level, so $m/e = 29$ is the value at which we detect CH$_3$O products. The data are momentum-matched to the CO$^+$ data in Figure 5 and are fit in an identical manner, with the thin solid line in Figure 8 showing CH$_3$O from dissociation of ground-state CH$_3$OCO and the dashed line showing CH$_3$O originating from excited-state radicals, fit by the corresponding $P(E_T)$s in Figures 4, 6 and 7. The dot-dashed line in Figure 8 shows HCO$^+$ signal from HCO and from dissociative ionization of H$_2$CO, assigned to reaction 4 for CH$_3$OCO radicals with high internal energy. This contribution is determined by the data in Figure 9, fit by the $P(E_T)$ in Figure 10. The dotted line shows a possible contribution from dissociative ionization of excited-state CH$_3$OCO radicals that may not dissociate before reaching the ionizer.

The presence of H$_2$CO was confirmed in a $m/e = 30$ (H$_2$CO$^+$) spectrum (Figure 9); and is assigned to the minor dissociation of CH$_3$OCO radicals to H$_2$CO + HCO (reaction 4). Note that the HCO and H$_2$CO products of reaction 4 would have essentially the same velocities as they differ by only one mass unit. The data are mostly fit by assignment to dissociation of excited-state radicals, as shown by the dot-dashed peak with an arrival time of 60–90 μs in Figure 9. An average of 15 kcal/mol is imparted in this step, as shown by the $P(E_T)$ in Figure 10.
determining the \( E_{\text{int}} \) of the two contributions. It is difficult to be accurate in
by the lower dot kcal/mol in recoil kinetic energy. This contribution is shown-
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10. The tail in the
m
Recoil translational energy distribution for CH\(_3\)OCO*
Figure 10.
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can also produce H\(_2\)CO, but the signal for its cofragment at
9 kcal/mol could provide a satisfactory fit. Reactions 8 and 11
ground-state radicals; an average recoil energy between 3 and
15 (CH\(_3\)Cl bond fission events imparting less than 25 kcal/mol in recoil kinetic energy. This contribution is shown-
by the lower dot—dashed line with arrival time extending to
150 \( \mu \)s in Figure 9, but is highly uncertain due to the overlap
of the two contributions. It is difficult to be accurate in
determining the \( P(E_T) \) describing the dissociation of these
ground-state radicals; an average recoil energy between 3 and
9 kcal/mol could provide a satisfactory fit. Reactions 8 and 11
can also produce H\(_2\)CO, but the signal for its cofragment at
\( m/e = 64 \) is comparatively low. For a \( m/e = 64 \) (HCOCl\(^+\)) TOF
spectrum taken at a source angle of 19.5\(^\circ\) and an ionization
energy of 14.8 eV for 75000 laser shots, the integrated signal
was 597 \pm 53 counts. Granted, it would be expected that a
significant portion of the nascent HCOCl or HOCCl fragments
would have sufficient internal energy to dissociate by reactions
9 or 12,\(^21\) but we observed virtually no HCl\(^+\) signal and no
obvious contribution to the CO\(^+\) TOF spectrum. Therefore, we
conclude that reactions 8 and 11 are negligible channels in the
precursor photodissociation.

Unimolecular dissociation of CH\(_3\)OCO radicals also produced
significant amounts of CH\(_3\) and CO\(_2\) via reaction 3. Figure 11
shows the \( m/e = 15 \) (CH\(_3\)^+) TOF spectrum taken at a 39.5\(^\circ\)
source angle and an ionization energy of 14.8 eV. The thin solid
line shows CH\(_3\) produced by the dissociation of ground-state
radicals. We first fit these data using the distribution of CH\(_3-
OCO\) radicals with internal energy above the G2(B3LYP/MP2/
CC) predicted dissociation barrier of 32.3 kcal/mol calculated
by Wang et al.\(^16\) (Later in this paper we refit the data as we
identified a second, lower transition state.) The fit accounts for
the velocity imparted to the CH\(_3\)OCO radical in the initial C—Cl
bond fission (reaction 1) as well as the velocity imparted during
the recoil of CH\(_3\) from CO\(_2\) in reaction 3. Figure 12 shows the
distribution of recoil kinetic energies imparted to the CH\(_3\) and
CO\(_2\) fragments. Excited-state CH\(_3\)OCO radicals can also
dissociate via reaction 3, as shown by the dashed line in Figure
11. The dissociation of these radicals is described by the \( P(E_T) \)
in Figure 13, which is used in conjunction with the dashed line
of Figure 4 to predict the TOF distribution in Figure 11. A
comparison of the CH\(_3\) TOF distribution to that of CO\(_2\) (Figure
15) revealed that the two signals are not completely momentum-
matched, as would be expected if reaction 3 were the only source
of CH\(_3\) and CO\(_2\). We concluded that there must be another
source of CH\(_3\)^+ signal. The dotted line in Figure 11 shows signal
from the initial photolysis of methyl chloroformate, reaction 6:

\[
\text{CH}_3\text{OC(O)Cl} \rightarrow \text{CH}_3 + \text{OC(O)Cl}.
\]

This signal is fit by the \( P(E_T) \) shown in Figure 11, where
the solid line is the total fit to the data. The thin solid line shows CH\(_3\)
produced by unimolecular dissociation of ground-state CH\(_3\)OCO radicals with
\( E_{\text{int}} \) \geq 32 kcal/mol, the predicted barrier to dissociation from ref 16.
This signal is fit by the \( P(E_T) \) distribution shown by the solid line in
Figure 12. The dashed line shows CH\(_3\) from excited-state CH\(_3\)OCO
radicals, fit by the dashed lines in Figures 4 and 13. The dotted line is
assigned to CH\(_3\) produced by reaction 6 and fit by the \( P(E_T) \) in Figure
14.

Unimolecular dissociation of CH\(_3\)OCO radicals also produced
significant amounts of CH\(_3\) and CO\(_2\) via reaction 3. Figure 11
shows the \( m/e = 15 \) (CH\(_3\)^+) TOF spectrum taken at a 39.5\(^\circ\)
source angle and 14.8 eV ionization energy for 50000 laser
shots. Open circles are experimental data points, and the bold solid line is the total fit to the data. The thin solid line shows CH\(_3\)
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14.
those of the CH$_3^+$ TOF in Figure 11 and are fit in an identical manner, using the $P(E_T)$s in Figures 4, 12 and 13. In the fitting of the CH$_3^+$ TOF, we also include a contribution from the CH$_3$-
OC(O)Cl $\rightarrow$ CH$_3$ + OC(O)Cl photolysis channel. The OC(O)-Cl radical has a predicted dissociation barrier of 2 kcal/mol. Thus, we can reasonably expect the full distribution of OC(O)-Cl to be unstable and produce CO$_2$ + Cl. We show this contribution to the CO$_2^+$ TOF by the dotted line and fit it using the $P(E_T)$ in Figure 16 in conjunction with that of Figure 14.

The magnitude of the observed CH$_3$ and CO$_2$ signal is surprising, given the high barrier of reaction 3 relative to reaction 2 predicted in the previous ab initio methods summarized in Figure 1. To investigate this phenomenon, we executed RRKM calculations to predict rate constants for the two dissociation channels of CH$_3$OCO for energies between 21 and 59 kcal/mol, which correspond to the internal energy range of ground-state radicals produced in our experiments. The calculations used vibrational frequencies and rotational constants for the radical and transition states taken from the G2//B3LYP results of Wang et al. The solid line shows $k_2/(k_2 + k_3)$ calculated using the frequencies, moments of inertia and transition state energies predicted by Wang et al. in ref 16. The dashed line shows $k_3/(k_2 + k_3)$ calculated using the parameters for the new, lower-energy transition state predicted in this work. The rate constants were calculated for the internal energy range of the ground-state radicals produced in our experiments.

The RRKM calculations, using the transition states of Wang et al., predicted a CO/CO$_2$ branching ratio of 280:1 for the dissociation of ground-state radicals in our experiment. Because the $E_{int}$ distribution of the radicals is broad, the branching ratio was calculated in the following way. For each internal energy, an energy-specific branching fraction was found. Each energy-specific branching fraction was multiplied by the fraction of radicals with that $E_{int}$ calculated by integrating the measured $P(E_T)$ in Figure 4 over the corresponding $E_T$ range at increments of 1 kcal/mol. The results were summed over the energies for ground-state radicals and then the ratio for CO/CO$_2$ was calculated.

An experimental branching ratio of 1:2.5 was determined by comparison of the signal attributed to dissociation of ground-state radicals in the CO and CO$_2$ TOF spectra. The spectra were taken under identical beam conditions, with the same source...
sections of room-temperature CO and CO$_2$ molecules while transition state for the CH$_3$O + CO reaction. The gray lines show the previously calculated energies for the trans conformer of the same transition state, which were also shown and referenced in Figure 1.

angle, ionization energy and number of laser shots. The experimental branching ratio $R$ was found as follows:

$$ R = \frac{\sigma_{\text{CH}_3 \text{O} + \text{CO}}}{\sigma_{\text{CH}_3 + \text{CO}_2}} = \frac{\text{CO}^+ \text{ signal}}{\text{CO}_2^+ \text{ signal}} \times \frac{\text{expected signal (CO)}}{\text{expected signal (CO$_2$)}} f_{\text{CO}^+ \rightarrow \text{CO}_2} \times f_{\text{CO}_2^+ \rightarrow \text{CO}} $$

$$ R = \frac{\sigma_{\text{CH}_3 \text{O} + \text{CO}}}{\sigma_{\text{CH}_3 + \text{CO}_2}} = \frac{6441 \text{ counts}}{4576 \text{ counts}} \frac{11258 \text{ counts}}{21098 \text{ counts}} \frac{12 \text{ Mb}}{2.5} = 1 $$

Here we integrate the spectra in the range 61.4–89.4 ns for the CO$^+$ data and 77.4–96.4 µs for the CO$_2^+$ data. The expected signals are the predicted integrated signals in the same TOF when it is assumed that the CO/CO$_2$ branching is 1:1, thus, they correct for the kinematic factors and Jacobians in the fitting of the data. The photoionization cross sections of the two products, $\sigma_{\text{ion}}$, are estimated by using the literature cross sections of room-temperature CO and CO$_2$ molecules while $f$ represents the percentage of the ionized product that is detected at its parent mass. In this case, $f = 1$ for both products because the photoionization energy used was below the appearance energies for daughter ions of both CO and CO$_2$.40

The large discrepancy in the theoretical (280:1) and experimental (1:2.5) product branching ratios led us to reevaluate the transition state for the CH$_3$ + CO$_2$ product channel. Our G3/B3LYP and CCSD(T) calculations revealed an additional transition state that is 18 kcal/mol lower than that predicted by Wang et al. The main difference lies in the geometry of the transition state. Wang et al. showed a transition state with trans geometry relative to the O–C bond. In fact, all of the published papers discussed thus far identified only the trans conformer of the transition state.13–18 Our predicted transition state with lower energy has a cis geometry. Figure 18 shows our calculated transition state energy, along with energetics and isomerization barriers for the CH$_3$O + CO reaction, on the same scale as previous theoretical predictions. Figure 19 shows the G3/B3LYP geometries of both the cis and trans transition state conformers. The critical implication of our results is that the lowest-energy barrier to dissociation of the CH$_3$OCO radical actually leads to CH$_3$ + CO$_2$, not CH$_3$O + CO. We executed RRKM calculations using the vibrational frequencies and moments of inertia in Table 2. The dashed line in Figure 17 shows that the CH$_3$O + CO channel is not dominant; rather, the CH$_3$ + CO$_2$ channel is favored for the range of $E_{\text{int}} = 21$ to 59 kcal/mol with our calculated transition states. We ignored the contribution of CH$_3$O + CO reaction. Bond lengths are in angstroms and angles are in degrees.

**Figure 18.** Energetics of the CH$_3$O + CO → CH$_3$ + CO$_2$ reaction calculated by G3/B3LYP and CCSD(T) methods in this work. Included is the isomerization barrier for the CH$_3$OCO radical and the energies for both the cis and trans conformers of the transition state for the CH$_3$ + CO$_2$ product channel. The gray lines show the previously calculated energies for the trans conformer of the same transition state, which were also shown and referenced in Figure 1.

**Figure 19.** G3/B3LYP geometries for the (a) cis and (b) trans conformations of the transition state for the CH$_3$OCO → CH$_3$ + CO$_2$ reaction. Bond lengths are in angstroms and angles are in degrees.

<table>
<thead>
<tr>
<th><strong>TABLE 2: Vibrational Frequencies and Moments of Inertia for Transition States Calculated at the B3LYP/6-311G(2df,p) Level of Theory</strong></th>
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<tbody>
<tr>
<td><strong>moments of inertia (amuÅ$^2$)</strong></td>
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<td>---------------------------------</td>
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<tr>
<td>trans-CH$_3$OCO</td>
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<td>TS1 (CH$_3$O + CO channel)</td>
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<td>TS2 (CH$_3$ + CO$_2$ channel)</td>
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<tr>
<th><strong>TABLE 3: Product Branching Ratios, $R$, Obtained from RRKM Predictions and Experimental Data</strong></th>
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<tr>
<td><strong>method</strong></td>
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<tr>
<td>RRKM using transition states from ref 16</td>
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<tr>
<td>RRKM using transition states from this work</td>
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<td>Experimental</td>
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Assuming our transition states are indeed correct, it is necessary to revise the fitting of our CH$_3$ and CO$_2$ TOF data. With the lower barrier to the CH$_3$ + CO$_2$ channel, the entire internal energy range of the nascent CH$_3$OCO radicals lies above the energy barriers to both reactions 2 and 3. Therefore, we ought to fit the CH$_3$ and CO$_2$ data using the full distribution of
The overall photolysis of methyl chloroformate is complex, with overlapping signal from several different channels making data analysis difficult. Performing these experiments with a longer photolysis wavelength would be advantageous in that the nascent CH₃OCO radicals would have lower internal energy, possibly avoiding formation of excited-state radicals. Such an experiment would also enable an experimental determination of the lowest barrier to dissociation of the CH₃OCO radical, which we predict as belonging to reaction 3. We did attempt these experiments using 248 nm photolysis of methyl chloroformate, but the absorption (Figure 2) is too low to yield sufficient signal. Preliminary velocity-map imaging experiments in our group showed that 235 nm photolysis produces CH₃OCO radicals with an internal energy range that spans both barriers to dissociation. If this photolysis wavelength is coupled with detection of stable CH₃OCO radicals, it would be possible to determine the lowest barrier to dissociation. This could be done by measuring the translational energy distribution for the stable radicals and comparing it to the full C−Cl bond fission P(E_f).

Both the CH₃ + CO₂ and CH₃O + CO channels are peculiar in that they could not be fit simply by the P(E_f) for initial C−Cl bond fission coupled with a single secondary P(E_f) for the kinetic recoil of the final product fragments. The data required two drastically different P(E_f) to describe the recoil products from the high- and low-internal energy CH₃OCO radicals, respectively. This suggests that there are two different mechanisms at work, leading us to assign low E_f, high E_int CH₃OCO radicals to an excited state. The experiments show that the excited state has an adiabatic excitation energy of at most 55 kcal/mol. There are currently no published theoretical studies that treat the low-lying excited states of the radical.

The experimental results presented here and the theoretical predictions summarized in Figure 18 offer insight into the CH₃O + CO bimolecular addition reaction. Although a handful of kinetics studies have been published for the CH₃O + CO reaction, the recommended study¹⁰ derives an Arrhenius expression from data over a narrow temperature range, so one cannot be assured the expression is in the high-pressure limit. There is, however, good agreement among various theoretical methods regarding the entrance channel barrier, but no experimental test. Now that our own calculations have revealed new features of the potential energy surface, it may be worthwhile to revisit CH₃O + CO kinetics experiments. One caution in applying the results of this paper to the CH₃O + CO bimolecular reaction is that our experiments can only reveal the portion of the dynamics that would proceed via the radical intermediate. Though the CH₃OCO intermediate has been consistently predicted by theory, a direct pathway to H₂CO + HCO has also been identified.¹⁵,¹⁶ The technique used in this paper cannot probe such direct reactions, nor would it easily lend itself to determination of the CH₃OCO → CH₃O + CO energy barrier as our results have shown that it is not the lowest barrier to dissociation of the radical. It could, however, prove useful for experimental verification of the CH₃OCO → CH₃O + CO₂ barrier.

After we submitted this paper and presented the work at national conferences, another recent paper concerning CH₃OCO was brought to our attention. Glaude et al. have studied the chemical kinetics of dimethyl carbonate (DMC), a compound of interest as an oxygenate additive for diesel fuel. The CH₃OCO radical is a key intermediate in the decomposition of DMC, so the ultimate fate of CH₃OCO radicals is important to the effectiveness of DMC as an oxygenate. Measurements of product mole fractions in an opposed-flow diffusion flame of...
DMC showed a majority of CO$_2$ and a minor amount of CO. The paper includes an estimate of the product branching using transition states for both reactions calculated with the CBS-Q method; they predicted the product branching for CH$_2$OCO decomposition to be 78% to CH$_3$ + CO$_2$ (14.7 kcal/mol barrier), and 22% to CH$_3$O + CO (22.7 kcal/mol barrier) at 1100 K. The Glaude paper also references previous work by Good and Francisco that includes a recalculation of the transition state for CH$_2$OCO → CH$_3$ + CO$_2$ with a barrier height of 14.7 kcal/mol and a cis-conformation in agreement with our results. This paper by Good and Francisco was not found in our initial literature searches nor referenced in other recent ab initio studies cited in the present work.

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References and Notes


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