

# Unimolecular Dissociation of the CH<sub>3</sub>OCO Radical: An Intermediate in the CH<sub>3</sub>O + CO Reaction<sup>†</sup>

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This work investigates the unimolecular dissociation of the methoxycarbonyl, CH<sub>3</sub>OCO, radical. Photolysis of methyl chloroformate at 193 nm produces nascent CH<sub>3</sub>OCO 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 CH<sub>3</sub>O + CO and CH<sub>3</sub> + CO<sub>2</sub> product channels. Both electronic ground- and excited-state radicals undergo competitive dissociation to both product channels. The experimental product branching to CH<sub>3</sub> + CO<sub>2</sub> 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 CH<sub>3</sub>OCO → CH<sub>3</sub> + CO<sub>2</sub> reaction are dramatically in error. Our electronic structure calculations reveal that the *cis* conformer of the transition state leading to the CH<sub>3</sub> + CO<sub>2</sub> 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 CH<sub>3</sub>OCO 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, CH<sub>3</sub>OCO, 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, CH<sub>3</sub>O + CO → CH<sub>3</sub> + CO<sub>2</sub>. This reaction is important because of its relevance to the fate of methoxy radicals in atmospheric reactions and hydrocarbon combustion.<sup>1,2</sup> Furthermore, the potential energy surface for this reaction is similar to that of the reaction HO + CO → H + CO<sub>2</sub>, which proceeds via the analogous HOCO intermediate. While the HO + CO system has been the subject of numerous investigations,<sup>3–7</sup> there are comparatively few studies on the CH<sub>3</sub>O + CO system.

The kinetics of the CH<sub>3</sub>O + CO reaction has been investigated previously. In the course of experiments on CH<sub>3</sub>O + NO, Wiebe and Heicklen performed photolysis of methyl nitrate in the presence of N<sub>2</sub> and CO to verify if the reaction would produce CO<sub>2</sub>.<sup>8</sup> Indeed, they did observe CO<sub>2</sub> formation, but could not accurately measure a rate constant, saying only that the removal rate of CH<sub>3</sub>O by CO is approximately 5 × 10<sup>−4</sup> slower than removal by NO in the temperature range 25–150 °C. They theorized that the principal products of CH<sub>3</sub>O + CO could be (CH<sub>3</sub>O)<sub>2</sub>CO or (CH<sub>3</sub>OCO)<sub>2</sub>. Sanders et al. also principally studied the CH<sub>3</sub>O + NO reaction but looked at the reaction of CH<sub>3</sub>O with CO and found it too slow to measure the rate constant.<sup>9</sup> They suggested an upper bound of log *k* = 6.7 M<sup>−1</sup> s<sup>−1</sup> for the reaction of CH<sub>3</sub>O + CO. Lissi et al. used

thermal decomposition of dimethyl peroxide in the presence of CO at 123–153 °C to measure the CH<sub>3</sub>O + CO → CH<sub>3</sub> + CO<sub>2</sub> rate constant.<sup>10</sup> Their results showed that *E*<sub>a</sub> = 11.8 ± 1.5 kcal/mol for the reaction. Wantuck et al. measured removal of CH<sub>3</sub>O by CO at 473–973 K and found that the rate could not be described by a simple Arrhenius expression.<sup>11</sup> They expected CH<sub>3</sub> + CO<sub>2</sub> to be the major products but suggested that a minor HCO + H<sub>2</sub>CO 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 *E*<sub>a</sub> = 11.8 ± 1.5 kcal/mol found by Lissi et al. with an uncertainty factor of at least 5.<sup>12</sup>

More recently, several theoretical studies have been published concerning the CH<sub>3</sub>O + CO system. Francisco studied the CH<sub>3</sub>O + CO reaction, considering only the CH<sub>3</sub> + CO<sub>2</sub> product channel via the CH<sub>3</sub>OCO intermediate.<sup>13</sup> 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 CH<sub>3</sub>OCO → CH<sub>3</sub> + CO<sub>2</sub> channel. Kang and Musgrave also calculated the CH<sub>3</sub>OCO → CH<sub>3</sub> + CO<sub>2</sub> reaction barrier while testing their newly developed KMLYP hybrid density-functional method.<sup>14</sup> Their value of 39.5 kcal/mol agreed with Francisco's result.

Zhou et al. investigated the multichannel CH<sub>3</sub>O + CO reaction at the B3LYP/6-311++G\*\* level of theory.<sup>15</sup> For dissociation of the CH<sub>3</sub>OCO radical, they found the CH<sub>3</sub>O + CO channel to have a 19.5 kcal/mol barrier and the CH<sub>3</sub> + CO<sub>2</sub> channel to have a 27.0 kcal/mol barrier. The other product channels examined were H<sub>2</sub>CO + HCO and H<sub>2</sub>CCO + OH, but both had higher barriers (38.9 and 35.0 kcal/mol, respectively) than the CH<sub>3</sub> + CO<sub>2</sub> channel. A direct abstraction

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reaction of  $\text{CH}_3\text{O} + \text{CO} \rightarrow \text{H}_2\text{CO} + \text{HCO}$  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  $\text{CH}_3\text{O} + \text{CO}$  reaction and also completed multichannel Rice–Ramsperger–Kassel–Marcus (RRKM) calculations for a wide range of temperatures and pressures.<sup>16</sup> They predicted a 6.39 kcal/mol barrier for the  $\text{CH}_3\text{O} + \text{CO}$  addition reaction leading to the  $\text{CH}_3\text{OCO}$  intermediate and a 32.3 kcal/mol barrier, measured from the zero point level of the radical intermediate, for the radical’s dissociation to  $\text{CH}_3 + \text{CO}_2$ . Examination of the transition state for this dissociation led them to assert that Francisco had misidentified the  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3 + \text{CO}_2$  transition state, making his barrier energy too high. Interestingly, they suggested strong  $\text{CH}_3$  tunneling in the decomposition of  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3 + \text{CO}_2$ , due to the transition state’s abnormally large imaginary frequency. In their calculations, they included the radical dissociation pathways to  $\text{H}_2\text{CO} + \text{HCO}$  and  $\text{H}_2\text{CCO} + \text{OH}$  as well as the direct reaction of  $\text{CH}_3\text{O} + \text{CO} \rightarrow \text{H}_2\text{CO} + \text{HCO}$ . The RRKM results showed that under atmospheric conditions, the stabilization of the  $\text{CH}_3\text{OCO}$  radical would dominate. Under combustion conditions, the major products would be  $\text{H}_2\text{CO} + \text{HCO}$ , from the direct abstraction channel. The same group later studied the mechanism of the  $\text{H}_2\text{CCO} + \text{OH}$  reaction.<sup>17</sup> They predicted  $\text{CO} + \text{CH}_2\text{OH}$  to be the major products at lower temperatures, while  $\text{H}_2\text{O} + \text{HCCO}$  would dominate at higher temperatures. Referencing their previous work on  $\text{CH}_3\text{O} + \text{CO}$ , they showed that the  $\text{CH}_3\text{OCO}$  radical intermediate would play a very minor role in the  $\text{H}_2\text{CCO} + \text{OH}$  reaction.

The  $\text{CH}_3\text{OCO}$  radical could also serve as one of many possible intermediates in the vinyl +  $\text{O}_2$  reaction. G2M(RCC, MP2) and multichannel RRKM calculations by Mebel et al. showed that the most favorable reaction pathway for this system leads to  $\text{CHO} + \text{H}_2\text{CO}$ .<sup>18</sup> As part of a minor channel, the  $\text{CH}_3\text{-OCO}$  radical can dissociate to make  $\text{CH}_3 + \text{CO}_2$ , but the  $\text{CH}_3\text{O} + \text{CO}$  products were not included in the analysis. The barrier for  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3 + \text{CO}_2$  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.<sup>15</sup>

Figure 1 shows the energetics for the  $\text{CH}_3\text{O} + \text{CO} \rightarrow \text{CH}_3 + \text{CO}_2$  reaction at various levels of theory as calculated by Francisco,<sup>13</sup> Wang et al.<sup>16</sup> and Zhou et al.<sup>15</sup> The calculated overall reaction enthalpies are in agreement, as well as the predicted barrier heights for  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3\text{O} + \text{CO}$ . In contrast, the energies for the  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3 + \text{CO}_2$  transition state differ by up to 10 kcal/mol. The large discrepancy in the values calculated for the barrier to the  $\text{CH}_3\text{O} + \text{CO}_2$  channel warrants more experimental efforts on the  $\text{CH}_3\text{OCO}$  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.

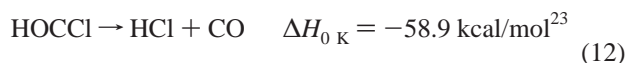
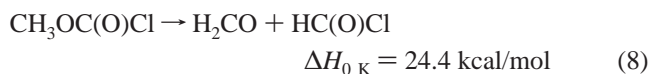
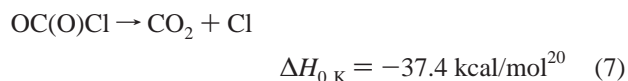
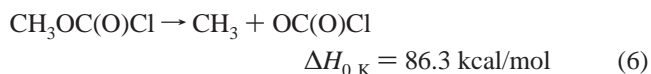
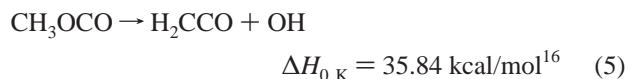
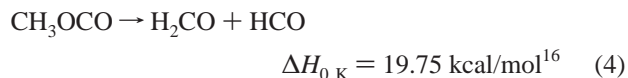
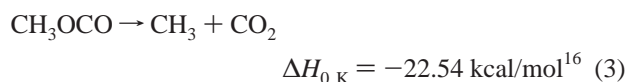
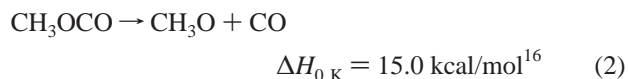
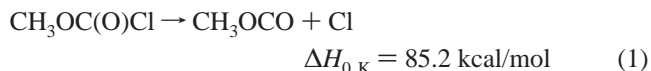
The experiments described in this paper utilize methyl chloroformate,  $\text{CH}_3\text{OC(O)Cl}$ , as a photolytic precursor for the radical. This precursor and the photolysis wavelength of 193 nm were deliberately chosen to produce nascent  $\text{CH}_3\text{OCO}$  radicals with an internal energy 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  $\text{CH}_3\text{OCO}$  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

**TABLE 1: Theoretical  $D_0(\text{CH}_3\text{OC(O)Cl}$ ) at the G3//B3LYP and CCSD(T) Levels of Theory in kcal/mol<sup>a</sup>**

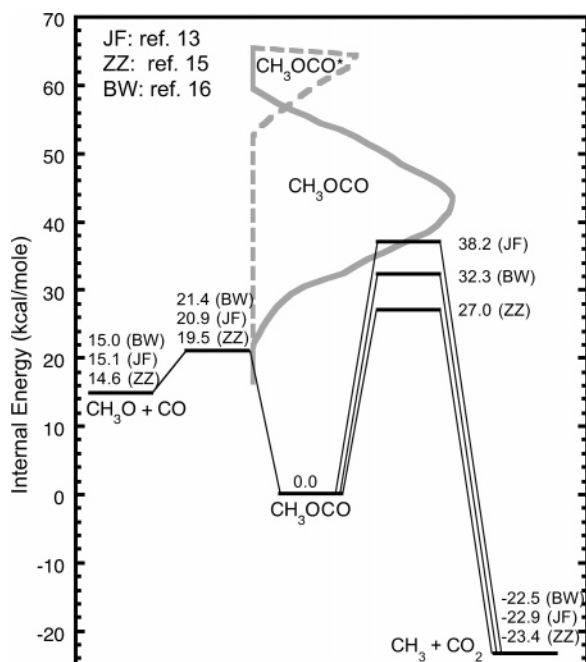
	G3//B3LYP	CCSD(T) <sup>b</sup>
$D_0(\text{cis-CH}_3\text{OC(O)Cl})$	85.4	84.6
$D_0(\text{trans-CH}_3\text{OC(O)Cl})$	81.3	80.3

<sup>a</sup> The  $D_0$  calculations correspond to reactions where *cis*- or *trans*- $\text{CH}_3\text{OC(O)Cl}$  is dissociated into *cis*- $\text{CH}_3\text{OCO} + \text{Cl}$ . The G3//B3LYP results in this table also refer to the *cis*- $\text{CH}_3\text{OCO}$  radical intermediate for consistency, though the *trans* conformer is predicted to have the minimum energy at that level of theory. Note that *cis*- $\text{CH}_3\text{OC(O)Cl}$  is approximately 4 kcal/mol lower in energy than the *trans* conformer. <sup>b</sup> Based on the CCSD(T)/6-311G(2df,p) optimized geometries, single-point energies were calculated at the CCSD(T)/aug-cc-pV(Q+d)Z level of theory. Zero-point vibrational energy correction and core-valence electronic correlations were included (see Experimental Method section).

them by the G3//B3LYP method with Gaussian 98.<sup>19</sup> 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  $\text{CH}_3\text{OC(O)Cl}$  and  $\text{CH}_3\text{-OCO}$  conformers is shown in the list below.



In these experiments, photolysis of methyl chloroformate produces Cl atoms and momentum-matched  $\text{CH}_3\text{OCO}$  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



**Figure 1.** Energetics of the CH<sub>3</sub>O + CO → CH<sub>3</sub> + CO<sub>2</sub> reaction. The numbers are computational results from refs 13, 15, and 16. JF 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 CH<sub>3</sub>OCO 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. CH<sub>3</sub>OCO radicals. These experiments also measure the velocity distributions of the products from dissociation of energetic CH<sub>3</sub>OCO 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 CH<sub>3</sub>OCO radicals were measured with the rotating-source crossed laser-molecular beam apparatus on the 21A1 U9/Chemical Dynamics Beamline at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Details of the experimental apparatus have been described previously.<sup>24</sup> 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 chopper 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  $1.18 \times 10^5$  cm<sup>3</sup>sec<sup>-1</sup> 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<sup>+</sup> 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 Daly 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  $5.45 \mu\text{s}\cdot\text{amu}^{-1/2}$ . 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.

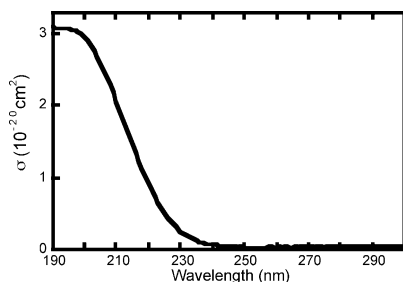
**B. Theoretical Calculations.** The  $D_0(\text{CH}_3\text{OC}(\text{O})\cdots\text{Cl})$ , the transition barrier heights involved in dissociation reactions (CH<sub>3</sub>OCO → CH<sub>3</sub>O + CO and CH<sub>3</sub>OCO → CH<sub>3</sub> + CO<sub>2</sub>), and the isomerization barrier between *cis*-CH<sub>3</sub>OCO and *trans*-CH<sub>3</sub>OCO were calculated by the G3//B3LYP method.<sup>25</sup> We also evaluated the  $D_0$  and transition/isomerization barrier heights at the coupled cluster level with single and double excitations plus a quasi-perturbative triple excitation [CCSD(T)]<sup>26–28</sup> together with Dunning's correlation consistent basis sets.<sup>29,30</sup> Specifically, the geometries of *cis*-/*trans*-CH<sub>3</sub>OC(O)Cl, *cis*-/*trans*-CH<sub>3</sub>OCO, CH<sub>3</sub>O, CH<sub>3</sub>, CO<sub>2</sub>, 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-pwCVTZ basis set.<sup>31</sup> The G3//B3LYP calculations were performed with the Gaussian 03 package of programs,<sup>32</sup> 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.<sup>33</sup> Transition state identities were confirmed by intrinsic reaction coordinate calculations.

## Results and Analysis

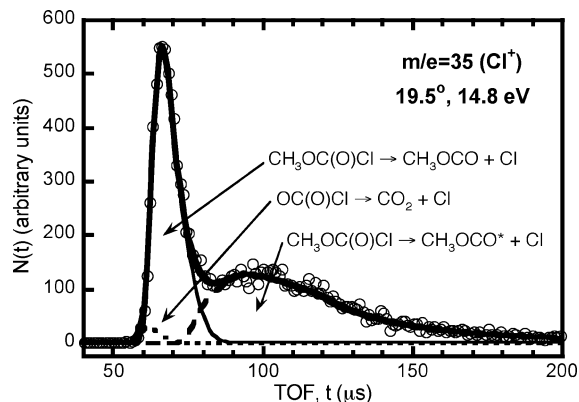
The data showed that C–Cl bond fission is the major photodissociation channel of methyl chloroformate at 193 nm. Methyl chloroformate absorbs strongly at 193 nm, as shown in the absorption spectrum in Figure 2.

C–Cl fission was evidenced by a Cl<sup>+</sup> time-of-flight (TOF) spectrum at  $m/e = 35$  shown in Figure 3. The total recoil kinetic energy distribution  $P(E_T)$  for C–Cl fission was determined by forward convolution fitting of the data. The total  $P(E_T)$  is





**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.



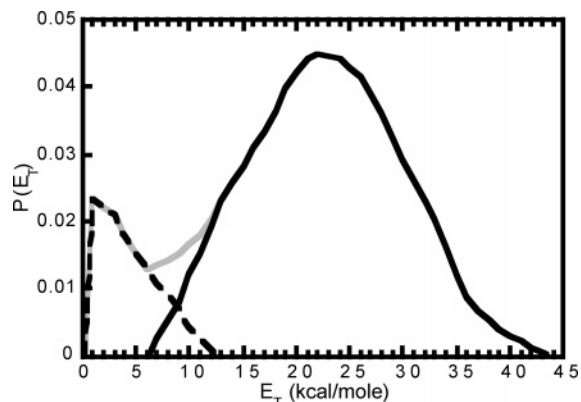
**Figure 3.** Time-of-flight (TOF) spectrum of  $m/e = 35$  ( $\text{Cl}^+$ ) taken at a source angle of  $19.5^\circ$  and ionization energy of  $14.8$  eV for 15000 laser shots. The open circles represent experimental data points, while the bold solid line is the overall forward convolution fit to the data with the  $P(E_T)$  shown in Figure 4. The thin solid line corresponds to chlorine atoms that are momentum-matched to  $\text{CH}_3\text{OCO}$  radicals formed in the ground state. The dashed line corresponds to chlorine atoms that are momentum-matched to  $\text{CH}_3\text{OCO}$  radicals assigned as being formed in an excited state. The dotted line shows a contribution near  $60 \mu\text{s}$  from dissociation of  $\text{OCOCl}$  radicals, as reasoned in the fitting of the  $\text{CH}_3$  and  $\text{CO}_2$  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–Cl bond fission channel produces  $\text{CH}_3\text{OCO}$  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–Cl bond fission channel produces  $\text{CH}_3\text{OCO}$  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  $60 \mu\text{s}$  arrival time shows a contribution of Cl from dissociation of  $\text{OCOCl}$  radicals (reaction 7), as explained later in this section.

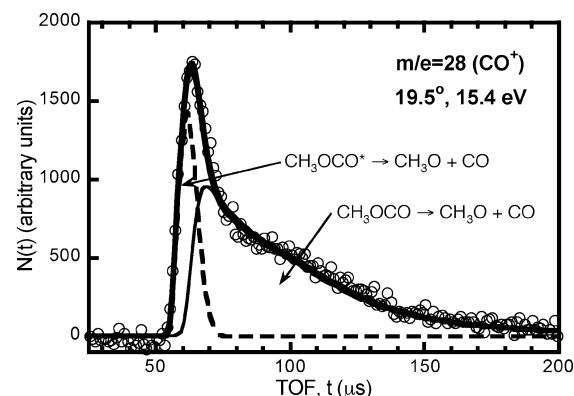
The internal energy range of the nascent  $\text{CH}_3\text{OCO}$  radicals, although they all dissociate, is easily deduced from the momentum-matched Cl atom velocities using conservation of energy:

$$E_{\text{parent}} + h\nu = D_0(\text{C–Cl}) + E_{\text{int}} + E_{\text{Cl}} + E_T$$

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.  $D_0(\text{C–Cl})$  was calculated by G3//B3LYP and CCSD(T) methods, with the results shown in Table 1. We used the G3//B3LYP value for C–Cl bond fission leading to the most stable (trans) conformer of the radical,  $D_0 = 85.2$  kcal/mol.  $E_{\text{parent}}$  is the internal energy of the methyl chloroformate



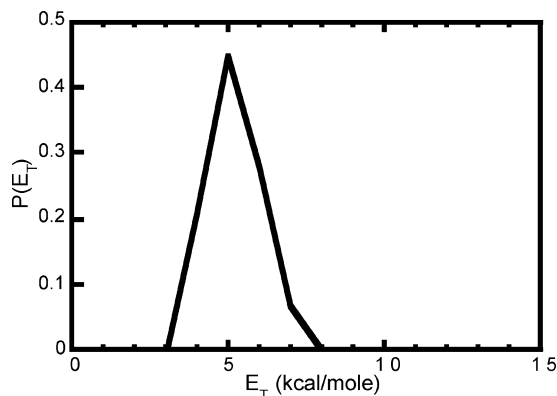
**Figure 4.** Recoil kinetic energy distribution,  $P(E_T)$ , in C–Cl bond fission derived from forward convolution fitting of the data in Figure 3. The solid gray line shows the total  $P(E_T)$ . The total  $P(E_T)$  is divided into two subdistributions used in fitting of subsequent spectra. The black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



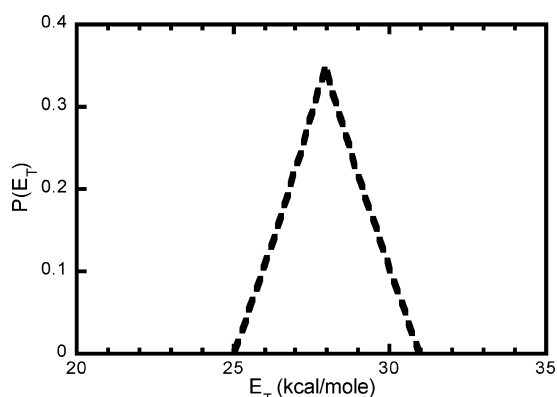
**Figure 5.** TOF spectrum of  $m/e = 28$  ( $\text{CO}^+$ ),  $19.5^\circ$  source angle, obtained from 100000 laser shots at an ionization energy of  $15.4$  eV. Open circles are experimental data, while the bold solid line is the overall fit to the data. The thin solid line shows CO produced by unimolecular dissociation of ground-state  $\text{CH}_3\text{OCO}$  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  $\text{CH}_3\text{OCO}$  radicals, fit by the dashed line  $P(E_T)$ s in Figures 4 and 7.

mate 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,<sup>34</sup> we determined the average vibrational energy of the methyl chloroformate molecule to be 2.8 kcal/mol at the  $107^\circ\text{C}$  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  $^2\text{P}_{3/2}$  state and 2.5 kcal/mol in the  $^2\text{P}_{1/2}$  state.<sup>35</sup> 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  $\text{Cl}(^2\text{P}_{3/2})$  and  $\text{Cl}(^2\text{P}_{1/2})$  are produced. The internal energy distribution of the radicals produced in our experiment is shown overlaid with the energetics of the  $\text{CH}_3\text{OCO}$  reaction in Figure 1.

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



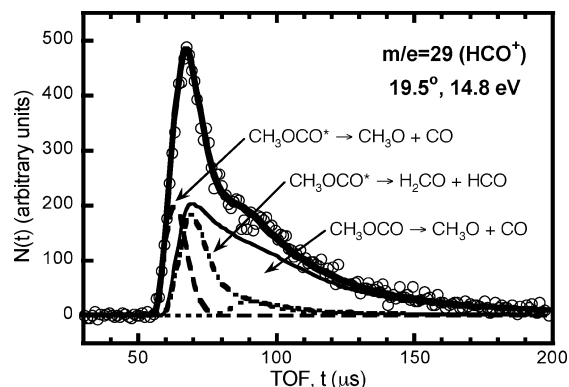
**Figure 6.** Recoil translational energy distribution of CH<sub>3</sub>O + CO in the dissociation of ground-state CH<sub>3</sub>OCO radicals. The solid line shows the  $P(E_T)$  used for the dissociation dynamics of the radicals, produced in the C–Cl fission of the precursor that produces ground-state radicals via the  $P(E_T)$  in the solid black line of Figure 4, to fit the CO<sup>+</sup> and HCO<sup>+</sup> data in Figures 5 and 8, respectively.



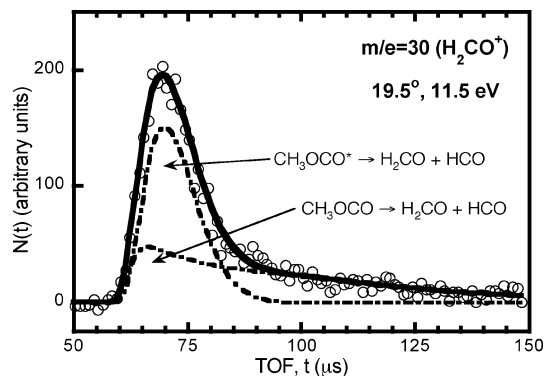
**Figure 7.** Recoil translational energy distribution of CH<sub>3</sub>O + CO in the dissociation of excited-state CH<sub>3</sub>OCO radicals. The dashed line shows the  $P(E_T)$ , which gave a good fit to the CO<sup>+</sup> and HCO<sup>+</sup> data in Figures 5 and 8, respectively. The fitting also uses the velocity of the excited-state CH<sub>3</sub>OCO as produced by the  $P(E_T)$  in the dashed line of Figure 4.

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<sub>3</sub>OCO radicals shown by the gray line in Figure 4. This led us to believe that the low  $E_T$  CH<sub>3</sub>OCO radicals, ~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<sub>3</sub>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<sub>3</sub>OCO radicals fit by the dashed lines of Figures 4 and 7. The dissociation of the excited-state CH<sub>3</sub>OCO radicals to CH<sub>3</sub>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<sup>+</sup>) TOF spectrum. The majority of the signal is due to dissociative ionization of CH<sub>3</sub>O fragments produced as partners to CO in reaction 2. The CH<sub>3</sub>O<sup>+</sup> ion is known to predissociate to CHO<sup>+</sup> + H<sub>2</sub> even at the zero point level, so  $m/e = 29$  is the value at which we detect CH<sub>3</sub>O products.<sup>36</sup> The data are momentum-matched to the CO<sup>+</sup> data



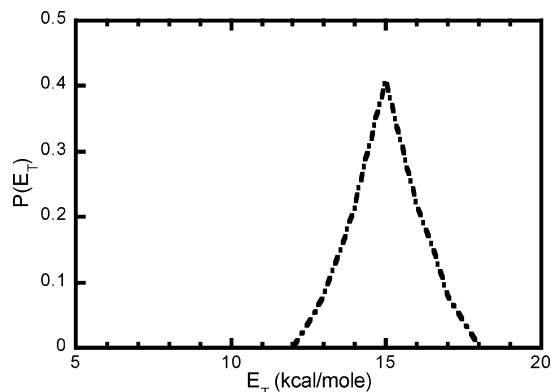
**Figure 8.** TOF spectrum of  $m/e = 29$  (HCO<sup>+</sup>) taken at a 19.5° source angle and 14.8 eV ionization energy for 100000 laser shots. Open circles are experimental data points, and the bold solid line is the overall fit to the data. CH<sub>3</sub>O products, which dissociatively ionize to HCO<sup>+</sup>, appear in this spectrum and are momentum-matched to CO fragments. The data are fit in an identical manner to the CO<sup>+</sup> data in Figure 5, with the solid and dashed lines showing products of reaction 2 for ground-state and excited-state CH<sub>3</sub>OCO radicals, respectively. The dot–dashed line shows signal from HCO and dissociative ionization of H<sub>2</sub>CO, assigned to reaction 4 for CH<sub>3</sub>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<sub>3</sub>OCO radicals that may not dissociate before reaching the ionizer.



**Figure 9.** TOF spectrum of  $m/e = 30$  (H<sub>2</sub>CO<sup>+</sup>) obtained from 200000 laser shots at a 19.5° source angle and 11.5 eV ionization energy. Open circles are experimental data and the solid line is the overall fit. The dot–dashed line in the TOF range of 60–90 μs is well-fit by excited-state CH<sub>3</sub>OCO radicals dissociating with the  $P(E_T)$  shown in Figure 10. The slower signal, shown by the dot–dashed line extending to 150 μs, could be due to high internal energy ground-state radicals dissociating with less than 10 kcal/mol partitioned into product recoil. Both of these contributions also appear in Figure 8.

in Figure 5 and are fit in an identical manner, with the thin solid line in Figure 8 showing CH<sub>3</sub>O from dissociation of ground-state CH<sub>3</sub>OCO and the dashed line showing CH<sub>3</sub>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<sup>+</sup> signal from HCO and from dissociative ionization of H<sub>2</sub>CO. The source of neutral HCO and H<sub>2</sub>CO is explained directly below.

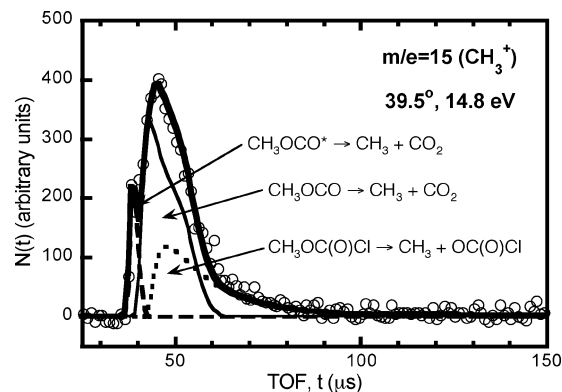
The presence of H<sub>2</sub>CO was confirmed in a  $m/e = 30$  (H<sub>2</sub>CO<sup>+</sup>) TOF spectrum (Figure 9); and is assigned to the minor dissociation of CH<sub>3</sub>OCO radicals to H<sub>2</sub>CO + HCO (reaction 4). Note that the HCO and H<sub>2</sub>CO products of reaction 4 would have 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



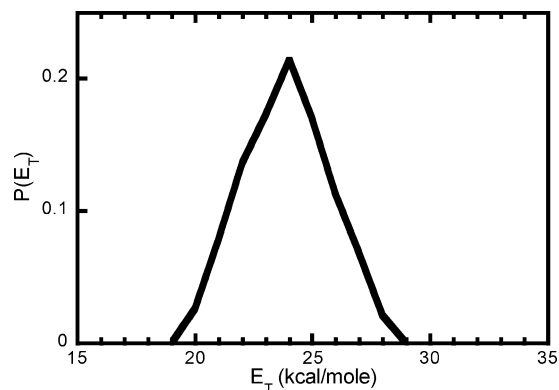
**Figure 10.** Recoil translational energy distribution for  $\text{CH}_3\text{OCO}^* \rightarrow \text{H}_2\text{CO} + \text{HCO}$ . The dot-dashed line shows the  $P(E_T)$  determined from forward convolution fitting of the data in Figure 9, also used to fit the corresponding contribution in Figure 8.

10. The tail in the  $m/e = 30$  TOF spectrum could be accounted for by dissociation of ground-state radicals, using those radicals with  $E_{\text{int}}$  above Wang's G2/B3LYP barrier of 40 kcal/mol,<sup>16</sup> coming from C-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  $\mu\text{s}$  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  $\text{H}_2\text{CO}$ , but the signal for its cofragment at  $m/e = 64$  is comparatively low. For a  $m/e = 64$  ( $\text{HCOCl}^+$ ) 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  $\text{HCOCl}$  or  $\text{HOCl}$  fragments would have sufficient internal energy to dissociate by reactions 9 or 12,<sup>21</sup> but we observed virtually no  $\text{HCl}^+$  signal and no obvious contribution to the  $\text{CO}^+$  TOF spectrum. Therefore, we conclude that reactions 8 and 11 are negligible channels in the precursor photodissociation.

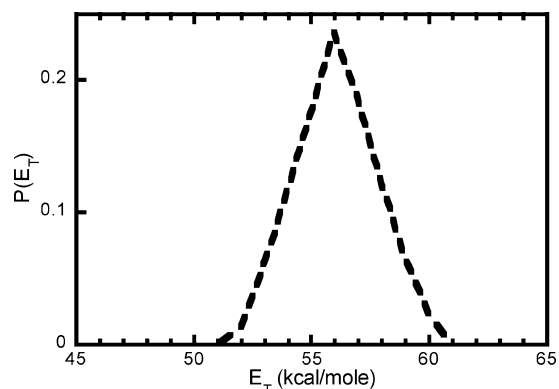
Unimolecular dissociation of  $\text{CH}_3\text{OCO}$  radicals also produced significant amounts of  $\text{CH}_3$  and  $\text{CO}_2$  via reaction 3. Figure 11 shows the  $m/e = 15$  ( $\text{CH}_3^+$ ) TOF spectrum taken at a  $39.5^\circ$  source angle and an ionization energy of 14.8 eV. The thin solid line shows  $\text{CH}_3$  produced by the dissociation of ground-state radicals. We first fit these data using the distribution of  $\text{CH}_3\text{-OCO}$  radicals with internal energy above the G2(B3LYP/MP2/CC) predicted dissociation barrier of 32.3 kcal/mol calculated by Wang et al.<sup>16</sup> (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  $\text{CH}_3\text{OCO}$  radical in the initial C-Cl bond fission (reaction 1) as well as the velocity imparted during the recoil of  $\text{CH}_3$  from  $\text{CO}_2$  in reaction 3. Figure 12 shows the distribution of recoil kinetic energies imparted to the  $\text{CH}_3$  and  $\text{CO}_2$  fragments. Excited-state  $\text{CH}_3\text{OCO}$  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  $\text{CH}_3$  TOF distribution to that of  $\text{CO}_2$  (Figure 15) revealed that the two signals are not completely momentum-matched, as would be expected if reaction 3 were the only source of  $\text{CH}_3$  and  $\text{CO}_2$ . We concluded that there must be another source of  $\text{CH}_3^+$  signal. The dotted line in Figure 11 shows signal from the initial photolysis of methyl chloroformate, reaction 6:



**Figure 11.** Preliminary fit of a  $m/e = 15$  ( $\text{CH}_3^+$ ) 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  $\text{CH}_3$  produced by unimolecular dissociation of ground-state  $\text{CH}_3\text{OCO}$  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  $\text{CH}_3$  from excited-state  $\text{CH}_3\text{OCO}$  radicals, fit by the dashed lines in Figures 4 and 13. The dotted line is assigned to  $\text{CH}_3$  produced by reaction 6 and fit by the  $P(E_T)$  in Figure 14.



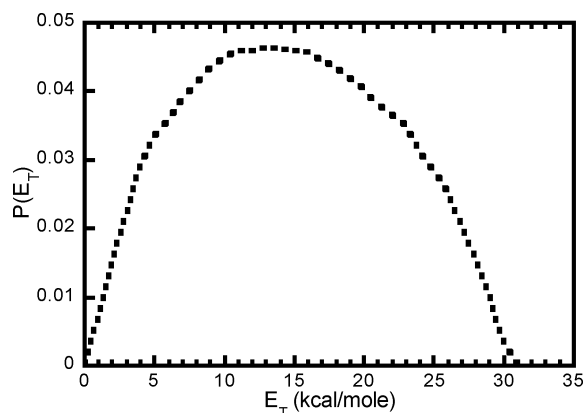
**Figure 12.**  $P(E_T)$  describing the distribution of translational energies imparted during the recoil of  $\text{CH}_3$  and  $\text{CO}_2$  in the dissociation of ground-state  $\text{CH}_3\text{OCO}$  radicals.



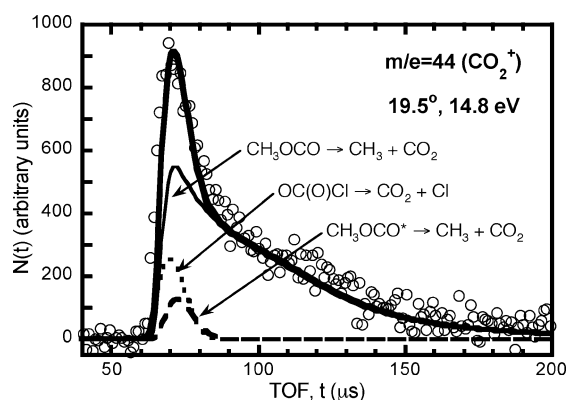
**Figure 13.**  $P(E_T)$  describing the distribution of translational energies imparted during the recoil of  $\text{CH}_3$  and  $\text{CO}_2$  in the dissociation of excited-state  $\text{CH}_3\text{OCO}$  radicals.

$\text{CH}_3\text{OC(O)Cl} \rightarrow \text{CH}_3 + \text{OC(O)Cl}$ . The  $P(E_T)$  for this minor photolysis pathway is shown in Figure 14.

Figure 15 shows the  $m/e = 44$  ( $\text{CO}_2^+$ ) TOF spectrum obtained at a  $19.5^\circ$  source angle and 14.8 eV ionization energy. The thin solid and dashed lines show  $\text{CO}_2$  produced in the unimolecular dissociation of ground- and excited-state  $\text{CH}_3\text{OCO}$  radicals, respectively. These distributions are momentum-matched to



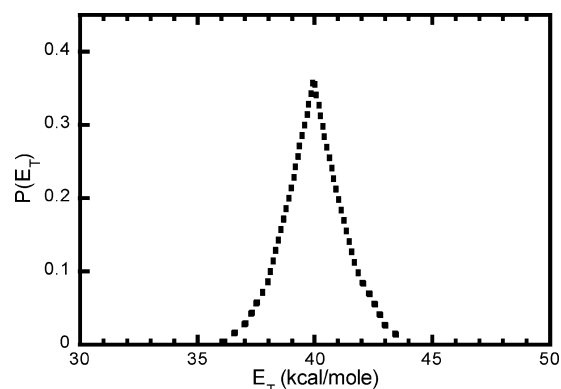
**Figure 14.** Recoil kinetic energy distribution in the initial photolytic step  $\text{CH}_3\text{OCOCl} \rightarrow \text{CH}_3 + \text{OCOCl}$ . This distribution produced the dotted line fit in Figure 11.



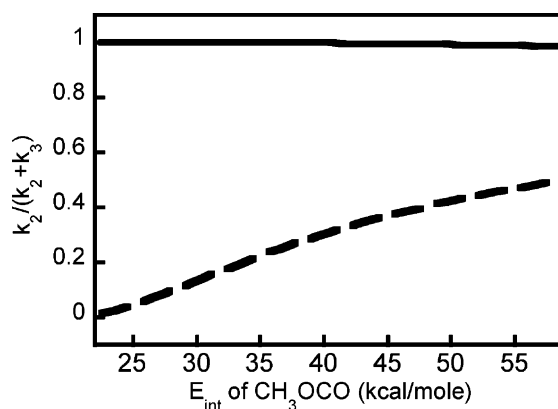
**Figure 15.** Preliminary fit of an experimental  $m/e = 44$  ( $\text{CO}_2^+$ ) TOF spectrum taken at a  $19.5^\circ$  source angle and 14.8 eV ionization energy for 150000 laser shots. Open circles are experimental data points and the bold solid line is the total fit to the data. The thin solid and dashed lines describe unimolecular dissociation of  $\text{CH}_3\text{OCO}$  radicals and are momentum-matched to those in the  $m/e = 15$  TOF spectrum in Figure 11. The dotted line is assigned to  $\text{CO}_2$  produced by dissociation of  $\text{OCOCl}$  radicals and fit by the  $P(E_T)$  in Figure 16 in conjunction with the velocities of the  $\text{OCOCl}$  radical products from C–C bond fission in the precursor.

those of the  $\text{CH}_3^+$  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  $\text{CH}_3^+$  TOF, we also include a contribution from the  $\text{CH}_3\text{-OC(O)Cl} \rightarrow \text{CH}_3 + \text{OC(O)Cl}$  photolysis channel. The  $\text{OC(O)Cl}$  radical has a predicted dissociation barrier of 2 kcal/mol.<sup>20</sup> Thus, we can reasonably expect the full distribution of  $\text{OC(O)Cl}$  to be unstable and produce  $\text{CO}_2 + \text{Cl}$ . We show this contribution to the  $\text{CO}_2^+$  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  $\text{CH}_3$  and  $\text{CO}_2$  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<sup>37</sup> to predict rate constants for the two dissociation channels of  $\text{CH}_3\text{OCO}$  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.<sup>16</sup> Figure 17 reports energy-specific branching fractions derived from the RRKM calculations when the external moments of inertia are treated as adiabatic and the torsional mode associated with rotation of the methyl group is treated as a free



**Figure 16.**  $P(E_T)$  describing the distribution of translational energies imparted during the recoil of  $\text{CO}_2$  and  $\text{Cl}$  in the dissociation of  $\text{OCOCl}$  radicals.



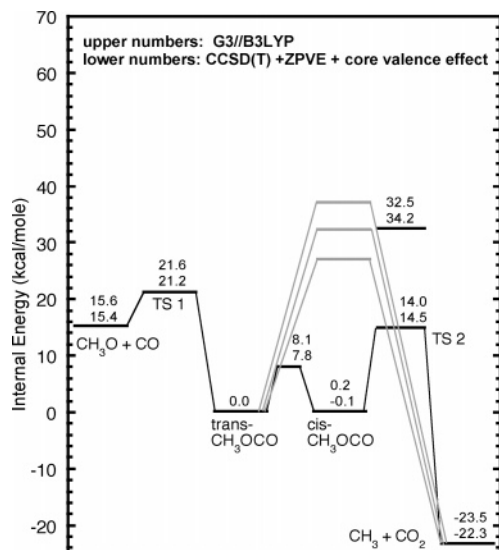
**Figure 17.** RRKM predictions for the unimolecular dissociation of ground-state  $\text{CH}_3\text{OCO}$  radicals. The label  $k_2$  refers to the rate constant for reaction 2 ( $\text{CH}_3\text{O} + \text{CO}$  products) and  $k_3$  refers to reaction 3 ( $\text{CH}_3 + \text{CO}_2$  products). 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  $k_2/(k_2 + k_3)$  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.

internal rotor. The solid line in Figure 17 shows that branching to the  $\text{CH}_3\text{O} + \text{CO}$  products is heavily favored, based on RRKM calculations using the transition states of Wang et al. The dashed line in Figure 17 will be discussed below. The RRKM results are presented with the caveat that some of the higher internal energy radicals are in a low-lying excited state of  $\text{CH}_3\text{OCO}$ ; the RRKM calculations are not relevant to the dissociation of the excited-state radicals.

The RRKM calculations, using the transition states of Wang et al., predicted a  $\text{CO}/\text{CO}_2$  branching ratio of 280:1 for the dissociation of ground-state radicals in our experiment. Because the  $E_{\text{int}}$  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  $E_{\text{int}}$  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  $\text{CO}/\text{CO}_2$  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  $\text{CO}$  and  $\text{CO}_2$  TOF spectra. The spectra were taken under identical beam conditions, with the same source





**Figure 18.** Energetics of the  $\text{CH}_3\text{O} + \text{CO} \rightarrow \text{CH}_3 + \text{CO}_2$  reaction calculated by G3//B3LYP and CCSD(T) methods in this work. Included is the isomerization barrier for the  $\text{CH}_3\text{OCO}$  radical and the energies for both the cis and trans conformers of the transition state for the  $\text{CH}_3 + \text{CO}_2$  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.

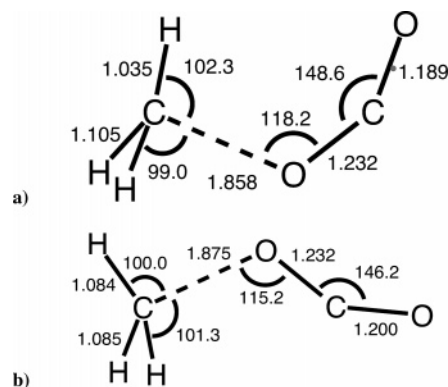
angle, ionization energy and number of laser shots. The experimental branching ratio  $R$  was found as follows:

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

$$R = \frac{\sigma_{\text{CH}_3\text{O} + \text{CO}}}{\sigma_{\text{CH}_3 + \text{CO}_2}} = \frac{6441 \text{ counts}}{4576 \text{ counts}} \frac{11258 \text{ counts}}{21098 \text{ counts}} \frac{12 \text{ Mb}}{22.7 \text{ Mb}} \frac{1}{1} = \frac{1}{2.5}$$

Here we integrate the spectra in the range 61.4–89.4  $\mu\text{s}$  for the  $\text{CO}^+$  data and 77.4–96.4  $\mu\text{s}$  for the  $\text{CO}_2^+$  data. The expected signals are the predicted integrated signals in the same TOF ranges when it is assumed that the  $\text{CO}/\text{CO}_2$  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  $\text{CO}$  and  $\text{CO}_2$  molecules<sup>38,39</sup> 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  $\text{CO}$  and  $\text{CO}_2$ .<sup>40</sup>

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  $\text{CH}_3 + \text{CO}_2$  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.<sup>13–18</sup> Our predicted transition state with lower energy has a cis geometry. Figure 18 shows our calculated transition state energy, along with energetics and isomerization



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

**TABLE 2: Vibrational Frequencies and Moments of Inertia for Transition States Calculated at the B3LYP/6-311G(2df,p) Level of Theory**

	moments of inertia ( $\text{amu}\cdot\text{\AA}^2$ )	frequencies ( $\text{cm}^{-1}$ )
<i>trans</i> - $\text{CH}_3\text{OCO}$	8.492, 107.443, 112.718	17, 219, 319, 621, 995, 1122, 1174, 1221, 1477, 1493, 1500, 1882, 3051, 3126, 3156
TS1 ( $\text{CH}_3\text{O} + \text{CO}$ channel)	11.822, 138.223, 146.729	300i, 94, 154, 201, 323, 1000, 1125, 1151, 1413, 1415, 1515, 2151, 2959, 3016, 3048
TS2 ( $\text{CH}_3 + \text{CO}_2$ channel)	22.703, 94.575, 113.890	740i, 49, 190, 507, 671, 778, 788, 1064, 1180, 1436, 1440, 2034, 3106, 3258, 3265

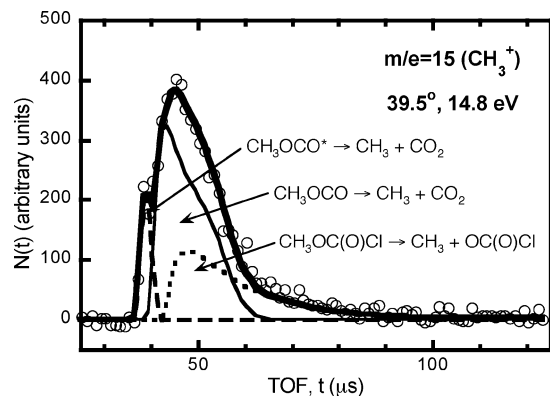
**TABLE 3: Product Branching Ratios,  $R$ , Obtained from RRKM Predictions and Experimental Data**

method	$R = \sigma_{\text{CH}_3\text{O} + \text{CO}}/\sigma_{\text{CH}_3 + \text{CO}_2}$
RRKM using transition states from ref 16	280/1
RRKM using transition states from this work	1/2
Experimental	1/(2.5 $\pm$ 0.5)

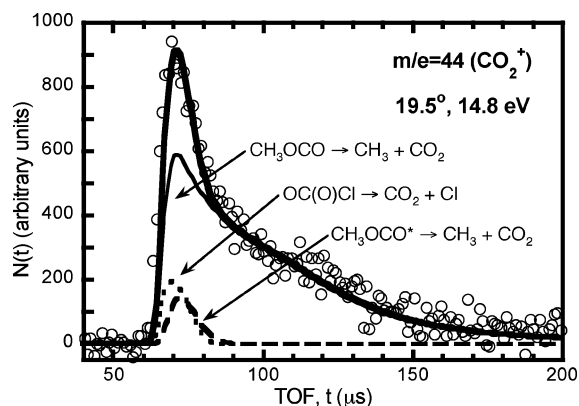
barriers for the  $\text{CH}_3\text{O} + \text{CO}$  reaction, on the same scale as previous theoretical predictions. Figure 19 shows the G3//B3LYP geometries of both the cis and trans transition state conformers. The critical implication of our results is that the lowest-energy barrier to dissociation of the  $\text{CH}_3\text{OCO}$  radical actually leads to  $\text{CH}_3 + \text{CO}_2$ , not  $\text{CH}_3\text{O} + \text{CO}$ . We executed RRKM calculations using the vibrational frequencies and moments of inertia in Table 2. The dashed line in Figure 17 shows that the  $\text{CH}_3\text{O} + \text{CO}$  channel is not dominant; rather, the  $\text{CH}_3 + \text{CO}_2$  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  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3 + \text{CO}_2$ , which proceeds through the trans conformation of the transition state found by Wang et al., as it would make a negligible addition to the total  $\text{CH}_3 + \text{CO}_2$  product branching. Table 3 summarizes the branching ratios determined by RRKM calculations using the two different transition states, as well as our experimentally measured branching ratio.

Assuming our transition states are indeed correct, it is necessary to revise the fitting of our  $\text{CH}_3$  and  $\text{CO}_2$  TOF data. With the lower barrier to the  $\text{CH}_3 + \text{CO}_2$  channel, the entire internal energy range of the nascent  $\text{CH}_3\text{OCO}$  radicals lies above the energy barriers to both reactions 2 and 3. Therefore, we ought to fit the  $\text{CH}_3$  and  $\text{CO}_2$  data using the full distribution of





**Figure 20.** Refit  $m/e = 15$  ( $\text{CH}_3^+$ ) TOF spectrum. The data and fit are identical to that of Figure 11, except that the full distribution of ground-state radicals from Figure 4 is considered, as we now know that the energy barrier to reaction 3 is lower than previously thought.



**Figure 21.** Refit  $m/e = 44$  ( $\text{CO}_2^+$ ) TOF spectrum. The data and fit are identical to that of Figure 15, except that the full distribution of ground-state radicals from Figure 4 is considered, as we now know that the energy barrier to reaction 3 is lower than previously thought.

radicals represented in Figure 4, appropriately weighted across the distribution so that it accounts for the fact that the  $\text{CH}_3 + \text{CO}_2$  products dominate from the high  $E_T$ , low  $E_{\text{int}}$ , portions of the  $P(E_T)$  in Figure 4. Figures 20 and 21 show the refit  $\text{CH}_3^+$  and  $\text{CO}_2^+$  TOF spectra, respectively.

## Discussion

Photolysis of methyl chloroformate at 193 nm resulted in C–Cl bond fission, along with C–C bond fission and a minor  $\text{H}_2\text{CO}$  elimination channel. C–Cl bond fission produced  $\text{CH}_3\text{-OCO}$  radicals with sufficient energy to overcome dissociation barriers to both the  $\text{CH}_3\text{O} + \text{CO}$  and the  $\text{CH}_3 + \text{CO}_2$  product channels. The branching to the  $\text{CH}_3 + \text{CO}_2$  channel is much larger than the predicted branching based on previous transition state calculations. Our own calculations found another transition state for the  $\text{CH}_3 + \text{CO}_2$  channel, which is consistent with our experimentally observed branching ratio. This transition state has a *cis* conformation with significantly lower energy than the *trans* conformer. The situation is very similar to that of the  $\text{HOCO}$  radical, which has two transition states leading to  $\text{H} + \text{CO}_2$  products. The *cis*- $\text{HOCO}$  transition state is predicted to be 6.4 kcal/mol lower than the *trans*- $\text{HOCO}$  transition state.<sup>3</sup> The same ordering of *cis* and *trans* dissociation barriers is seen in the  $\text{CO} + \text{SO}_2 \rightarrow \text{CO}_2 + \text{SO}$  reaction.<sup>41</sup> A more general description of this trend is that the breaking bond of the radical is *trans* relative to the radical electron. This is the case when the vinyl radical dissociates to  $\text{H} + \text{acetylene}$ <sup>42</sup> and also when the 2-buten-2-yl radical accesses its C–C and C–H bond fission channels.<sup>43</sup>

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  $\text{CH}_3\text{OCO}$  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  $\text{CH}_3\text{OCO}$  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  $\text{CH}_3\text{-OCO}$  radicals with an internal energy range that spans both barriers to dissociation. If this photolysis wavelength is coupled with detection of stable  $\text{CH}_3\text{OCO}$  radicals, it would be possible to determine the lowest barrier to dissociation. This could be done by measuring the translational energy distribution of the stable radicals and comparing it to the full C–Cl bond fission  $P(E_T)$ .

Both the  $\text{CH}_3 + \text{CO}_2$  and  $\text{CH}_3\text{O} + \text{CO}$  channels are peculiar in that they could not be fit simply by the  $P(E_T)$  for initial C–Cl bond fission coupled with a single secondary  $P(E_T)$  for the kinetic recoil of the final product fragments. The data required two drastically different  $P(E_T)$ s to describe the recoil products from the high- and low- internal energy  $\text{CH}_3\text{OCO}$  radicals, respectively. This suggests that there are two different mechanisms at work, leading us to assign low  $E_T$ , high  $E_{\text{int}}$   $\text{CH}_3\text{-OCO}$  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  $\text{CH}_3\text{O} + \text{CO}$  bimolecular addition reaction. Although a handful of kinetics studies have been published for the  $\text{CH}_3\text{O} + \text{CO}$  reaction, the recommended study<sup>10</sup> 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  $\text{CH}_3\text{O} + \text{CO}$  kinetics experiments. One caution in applying the results of this paper to the  $\text{CH}_3\text{O} + \text{CO}$  bimolecular reaction is that our experiments can only reveal the portion of the dynamics that would proceed via the radical intermediate. Though the  $\text{CH}_3\text{-OCO}$  intermediate has been consistently predicted by theory, a direct pathway to  $\text{H}_2\text{CO} + \text{HCO}$  has also been identified.<sup>15,16</sup> The technique used in this paper cannot probe such direct reactions, nor would it easily lend itself to determination of the  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3\text{O} + \text{CO}$  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  $\text{CH}_3\text{OCO} \rightarrow \text{CH}_3 + \text{CO}_2$  barrier.

After we submitted this paper and presented the work at national conferences, another recent paper concerning  $\text{CH}_3\text{OCO}$  was brought to our attention. Glaude et al.<sup>44</sup> have studied the chemical kinetics of dimethyl carbonate (DMC), a compound of interest as an oxygenate additive for diesel fuel. The  $\text{CH}_3\text{-OCO}$  radical is a key intermediate in the decomposition of DMC, so the ultimate fate of  $\text{CH}_3\text{OCO}$  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<sub>2</sub> 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<sub>3</sub>OCO decomposition to be 78% to CH<sub>3</sub> + CO<sub>2</sub> (14.7 kcal/mol barrier), and 22% to CH<sub>3</sub>O + CO (22.7 kcal/mol barrier) at 1100 K. The Glaude paper also references previous work by Good and Francisco<sup>45</sup> that includes a recalculation of the transition state for CH<sub>3</sub>OCO → CH<sub>3</sub> + CO<sub>2</sub> 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<sup>14,15,17</sup> cited in the present work.

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