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EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE PRODUCT CHANNELS OF THE O + CH_3 REACTION

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DISCLAIMER

Abstract

The product channels of the $O(^3P) + CH_3$ reaction have been investigated in a combined experimental and theoretical study. In the experimental part the branching fraction for formaldehyde production ($O + CH_3 \longrightarrow H_2CO + H$) was measured at room temperature in a tubular flow reactor coupled to a photoionization mass spectrometer. The reactants (CH_3 and O) were generated homogeneously in the reactor by the simultaneous *in situ* 193-nm photolysis of acetone and SO_2. The yield of formaldehyde produced relative to the methyl radicals consumed by the reaction, i.e., the branching fraction, was determined to be 1.0±0.15. In the theoretical part calculations of the energetics of possible decomposition pathways of the energy-rich methoxy radical initially formed in the $O + CH_3$ reaction indicate that the dominant channel for decomposition is C-H bond cleavage leading to atomic hydrogen and formaldehyde. A possible, minor, secondary channel is hydrogen migration, followed by O-H bond cleavage, leading to the same final products. No energetically competitive pathways leading to H_2, HCO, HOC or CO could be found.

Introduction

The kinetics of the reaction of oxygen atoms with methyl radicals (reaction 1) has been the subject of numerous investigations[1] because of the importance of this radical-radical reaction in combustion processes.[2-4] Reaction 1 is one of the dominant steps removing CH_3 from the radical pool in flames, particularly under fuel-lean conditions. The rate constant for the $O(^3P) + CH_3$ reaction is considered to be well established with a recommended value of 1.4×10^{-10} cm^3 molecule^{-1} s^{-1} from 300 to 2500K.[5]

Although there are four possible energetically accessible product channels for the $O + CH_3$ reaction,

$$O + CH_3 \longrightarrow H_2CO + H \qquad \Delta H = -68 \text{ kcal mol}^{-1} \qquad (1a)$$

$$\longrightarrow CO + H + H_2 \qquad \Delta H = -69 \text{ kcal mol}^{-1} \qquad (1b)$$

$$\longrightarrow HCO + H_2 \qquad \Delta H = -84 \text{ kcal mol}^{-1} \qquad (1c)$$

$$\longrightarrow OH + CH_2 \qquad \Delta H = +8.2 \text{ kcal mol}^{-1} \qquad (1d)$$

reaction 1a has long been regarded as the dominant reaction route.[6] A number of experimental studies[7-9] has supported the existence of this mechanism by direct observation of the formaldehyde produced. Hoyermann and Sievert[7] detected product peaks from the $O + CH_3$ reaction corresponding to HCO and H_2CO using mass-spectrometric analysis. A majority of the peak at mass 29 (HCO) was ascribed to electron-impact fragmentation of the formaldehyde with an upper limit for reaction 1c estimated to be 20%. No products of reaction 1d were detected by Hoyermann and Sievert. Slagle et al.[8] monitored both the disappearance of CH_3 and the concurrent appearance of H_2CO in time-resolved experiments using a laser photolysis-photoionization mass spectrometric technique. These results confirmed that formaldehyde was a primary product of the O + CH_3 reaction. Neither HCO nor CH_2, products of reactions 1c and 1d respectively, were detected, suggesting that routes 1c and 1d were not significant compared to the importance of the formaldehyde channel, 1a. In the experiments of Slagle et al. CO, H_2, and H could not be detected because of their high ionization potentials and low detection sensitivity, making an assessment of the presence or importance of route 1b impossible. Zellner et al.[9] monitored the production of formaldehyde by reaction 1a using laser-induced fluorescence. Zellner et al. state that H_2CO was determined to be the "dominant product" on the basis of mass-balance considerations.

Recently, Seakins and Leone[10] found evidence of significant CO production from the O + CH_3 reaction. They investigated the O + CH_3 reaction using laser flash photolysis to produce the radical reactants and time-resolved Fourier transform infrared emission spectroscopy to detect the products. They observed not only emission corresponding to the formaldehyde C-H stretch but also strong molecular CO vibrational emission produced on the same time scale.

Earlier investigations[7-9] have clearly detected the products of route 1a in the O + CH_3 reaction and have also shown the absence of the products of routes 1c and 1d. The study of Seakins and Leone[10] provides the first measure of the importance of CO (route 1b) as a reaction product. The estimated significance of this route ($\leq 40 \pm 10$ %) is in contradiction with the belief that route 1a is the dominant reaction channel. To clarify this somewhat contradictory picture of the chemical branching in this important combustion reaction, we have conducted a combined experimental and theoretical investigation of product formation in the O + CH_3 reaction. The goal of this investigation is twofold: (1) to finally establish the branching ratio of reaction 1a by quantitatively measuring the yield of H_2CO from the O + CH_3 reaction and

(2) to provide a sound theoretical understanding of the observed chemical branching from knowledge of the energetics of the O + CH_3 reaction. The results of this investigation are presented here.

Experimental Section

Overview of Experimental Method. Oxygen atoms and methyl radicals were produced simultaneously by pulsed laser photolysis in a tubular flow reactor at room temperature. Initial conditions were chosen to assure that all CH_3 radicals were consumed by excess O-atoms in less than 5 ms. This rapid conversion provides ample observation time to measure the final H_2CO concentration. In our prior study of reaction 1[8] conditions were used which permitted characterization of the decaying CH_3 signal and the growth of the H_2CO signal which provided the information needed to establish that H_2CO was a primary product of the O + CH_3 reaction. The formaldehyde produced by reaction 1a was detected using photoionization mass spectrometry. The branching fraction of reaction 1a is the measured concentration of formaldehyde after all methyl radicals have been consumed by O-atoms ($[H_2CO]_f$) divided by the measured initial methyl-radical concentration ($[CH_3]_0$).

The experimental apparatus used and many of the procedures employed in this study have been described previously.[8,11] Pulsed, unfocused 193-nm radiation (3-4 Hz) from a Lambda Physik 201MSC laser was directed along the axis of a 1.05 cm i.d., boric-acid coated quartz reactor. Gas flowed through the tube at ≈ 4 m s^{-1} and was completely replaced between laser pulses. The flowing gas contained the reactants [acetone (the CH_3 source), SO_2 (the O-atom source) or Cl_2 (for titrating CH_3)] and the carrier gas (He) which was always in large excess

($X_{He} > 0.99$). Gas was continuously sampled through a 0.043-cm diameter hole (located at the end of a nozzle in the wall of the reactor) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized (using resonance lamps) and then mass selected. Temporal ion signals were recorded from a short time before each laser pulse to 20 ms following the pulse by using a multichannel scalar. Data from 600 to 5000 repetitions of the experiment were accumulated before the data were analyzed.

The two reactants (CH_3 and $O(^3P)$) were produced simultaneously by pulsed laser photolysis:

$$SO_2 \xrightarrow{193\ \text{nm}} SO + O(^3P) \qquad (2)$$

$$CH_3COCH_3 \xrightarrow{193\ \text{nm}} 2CH_3 + CO \qquad (3)$$

The initial concentration of O was determined from the measured extent of photodecomposition of the SO_2 (typically 8-10%).[8] In order to accurately measure the low initial concentrations of methyl radicals used in these experiments, a titration procedure was used. The initial concentrations of CH_3 used were determined in separate experiments in which the acetone used to produce the radicals was present but the SO_2 was removed. A large excess of Cl_2 was introduced to stoichiometrically convert the methyl radicals produced by photolysis into CH_3Cl by reaction 4 ($k_4 = 2.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298K[12]):

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl \qquad (4)$$

The mass spectrometric sensitivity to CH_3Cl was determined by calibration with known flows of pure CH_3Cl and used to obtain $[CH_3]_0$ from the CH_3Cl^+ ion signal after the stoichiometric conversion.

Initial conditions were chosen to provide an O-atom concentration which was at least a factor of 18 greater than the initial CH_3 concentration. Under these conditions oxygen atoms were not significantly depleted by reaction 1. Initial methyl concentrations were kept low to ensure that CH_3 recombination and secondary reactions had negligible rates compared to that of the O + CH_3 reaction. Experiments using totally deuterated acetone as the methyl precursor confirmed that no measurable ethane (from the $CH_3 + CH_3$ reaction), which has the same mass number as H_2CO, was produced under the conditions of these experiments, i.e., $[O]/[CH_3]_0 > 18$. Furthermore, there was no measurable signal at m/z=30 (the mass number of H_2CO) when either acetone or SO_2 was photolyzed separately.

The photodecomposition of acetone at 193 nm produces CH_3 which is vibrationally excited.[13] However, since the vibrational relaxation time of CH_3 under our experimental conditions[13] is short (<.1 ms) compared to the reaction time, it is the product of the thermal reaction between O and CH_3 that is observed in this study.

Determination of the Branching Fraction. The branching fraction for reaction 1a (F_{H_2CO}) is the concentration of formaldehyde after all methyl radicals have been consumed by O-atoms ($[H_2CO]_f$) divided by the initial methyl-radical concentration ($[CH_3]_0$). Since, in these experiments, $[CH_3]_0$ is determined by converting CH_3 to CH_3Cl with molecular chlorine, the branching fraction can be rewritten as $[H_2CO]_f$ / $[CH_3Cl]$.

$$F_{H_2CO} = \frac{[H_2CO]_f}{[CH_3]_0} = \frac{[H_2CO]_f}{[CH_3Cl]} \qquad \text{(I)}$$

The ion signals monitored in this study must be converted into concentrations in order to determine F_{H_2CO}. The ion signal of a stable (or labile) species R (S_R+) is directly proportional to the concentration of R in the flow reactor with a sensitivity constant (α_R) which depends, among other things, on the ionizing lamp intensity used and the conditions in the flow reactor.

$$S_{R^{\cdot}} = \alpha_R[R] \qquad \text{(II)}$$

The sensitivity constant can be determined by flowing a known concentration of R in the reactor and monitoring its ion signal. Such a calibration was easily accomplished for CH_3Cl. Production of an accurately known concentration of formaldehyde in the flow reactor is much more difficult. To minimize possible errors in the H_2CO sensitivity constant and, subsequently, in the branching fraction determination, sensitivity determinations for H_2CO were based on a relative sensitivity measurement of H_2CO to C_3H_6. Formaldehyde and C_3H_6 were produced simultaneously by the thermal decomposition of 3-buten-1-ol.

$$H_2C{=}CHCH_2CH_2OH \xrightarrow{\Delta} H_2CO + C_3H_6 \qquad (5)$$

Butenol in helium was decomposed in a separate flow tube heated to approximately 1073 K attached to a side-arm of the reactor. This source of formaldehyde was chosen for calibration purposes because the decomposition of 3-buten-1-ol is known to proceed predominantly by this molecular elimination mechanism.[14] Although the decomposition may produce minor amounts of other molecular elimination products,[14] e.g., $H_2O + C_4H_6$, equal concentrations of H_2CO and C_3H_6 are formed under all reaction conditions.

In order to establish the relative mass-spectral sensitivity to H_2CO and C_3H_6 the ion signals at m/z=30 (H_2CO^+) and 42 ($C_3H_6^+$) were recorded using an argon resonance lamp as the source of ionizing light. The butenol was then removed from the system and known flows of C_3H_6 and CH_3Cl were added to the main flow. Again using an argon lamp, the ion signals at m/z=42 ($C_3H_6^+$) and 50 (CH_3Cl^+) were recorded to obtain the relative sensitivity to C_3H_6 and CH_3Cl. These two carefully measured sensitivity ratios were then combined to obtain the conversion factor relating the relative ion signals of H_2CO and CH_3Cl to the ratio of their concentrations.

$$F_{H_2CO} = \frac{[H_2CO]_f}{[CH_3Cl]} = \left(\frac{S_{H_2CO^+}}{S_{CH_3Cl^+}}\right)\left(\frac{S_{C_3H_6^+}}{S_{H_2CO^+}}\right)_c\left(\frac{S_{CH_3Cl^+}}{S_{C_3H_6^+}}\right)_c\left(\frac{[C_3H_6]}{[CH_3Cl]}\right)_c \qquad \text{(III)}$$

Subscript c designates those quantities measured in the calibration experiments.

With the procedures used in this study the branching fraction depends only on the ratios of ion signals or concentrations of easily handled stable molecules. Such ratios can be measured very accurately. The absolute concentrations of CH_2O and CH_3 are *not* required in these calculations.

A potential source of error associated with the use of butenol as the formaldehyde source is the production of an ion signal at mass 42 due to photoionization fragmentation of butenol. At the temperatures used in the calibration experiments (1073 K), 99% of the butenol decomposes in less than 10 ms[14] and thus should not contribute to the mass 42 ion signal. Investigation of propylene production using less energetic ionizing light (10.2 eV) which reduces the fragmentation by a factor of 25 confirmed that there was no contribution to the mass 42 ion signal from residual butenol.

The following sequence of measurements was performed to determine the branching fraction of reaction 1a.

1. The relative mass-spectral sensitivities were determined as described above for each [He] used.

2. For each set of initial conditions ($[CH_3]_0$, [O] and [He]) the following series of measurements were made.

a. With acetone and Cl_2 in the flow reactor, the CH_3Cl^+ ion signal was monitored (CH_3 titration).

b. With acetone and SO_2 in the flow reactor, the H_2CO^+ ion signal was monitored (H_2CO yield).

c. Step a. was repeated.

3. The mass-spectral sensitivities were again determined.

An example of the ion signals monitored in steps a. and b. is shown in Figure 1. From the results of these measurements the branching fraction was calculated using Equation III.

Experiments were conducted using different initial conditions to confirm that the branching fraction is independent of [O], $[CH_3]_0$, [He], and laser intensity. The conditions and results of all experiments to measure the branching fraction are presented in Table 1. The average of six measurements covering over a three-fold range of initial methyl and oxygen concentrations and a two-fold range of densities results in $F_{H_2CO} = 1.0$. The statistical uncertainty (1σ) in these measurements is only $\pm 5\%$. The total uncertainty in the branching fraction is estimated to be $\pm 15\%$ when possible errors in ion signal ratios and concentration ratios are taken into account.

The branching fraction could be measured only at room temperature. At higher temperatures the presence of secondary reactions prevents an accurate determination of the branching fraction. For example, the Cl-atom produced in reaction 4 can attack the acetone.

$$Cl + CH_3COCH_3 \longrightarrow HCl + CH_3COCH_2 \qquad (6)$$

At high temperatures the acetonyl radical can then thermally decompose, producing ketene and additional methyl radicals.

$$CH_3COCH_2 \longrightarrow H_2CCO + CH_3 \qquad (7)$$

Use of CH_3I as a CH_3 Source. Attempts to use methyl radicals from a different precursor, CH_3I, were unsuccessful. Although the absorption coefficients at 193nm reported in the literature for acetone[15] and methyl iodide[16] are not very different ($\epsilon \approx 1000$ l mol^{-1} cm^{-1} for acetone and 400 l mol^{-1} cm^{-1} for CH_3I), decomposition yields are quite different. There was a negligible depletion of CH_3I upon photolysis ($< 1\%$ as compared to $> 5\%$ for acetone photolysis at room temperature using the same laser fluence). Reaction of CH_3 from the two sources with Cl_2 indicates that photolysis of acetone produces 12 times the concentration of methyl radicals as is produced by an equivalent concentration of CH_3I exposed to the same laser fluence.

When SO_2 was photolyzed in the presence of CH_3I, a fast reaction between O-atoms and CH_3I was observed. This reaction is known to be very rapid.[17] A lower limit for the rate constant of 1.7×10^{-14} cm^3 molecule^{-1} s^{-1} has been reported.[18] A set of ancillary experiments was performed at room temperature to determine the rate constant and possible products of the O + CH_3I reaction. The rate constant for the O + CH_3I reaction was measured under pseudo-first-order conditions ($[O]/[CH_3I]_0 = 30 - 290$). The rate constant was determined from the exponential decay of the CH_3I ion signal with time. An average of six such measurements at a density of 1.2×10^{17} molecule cm^{-3} yielded the rate constant $k_{O + CH3I} = 1.7(\pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}! The only observed products of the photolysis of CH_3I and subsequent reactions which occurred were I, HI and H_2CO (most probably from the O + CH_3 reaction). A small signal corresponding to HIO was observed but, because of its low intensity, could not be identified as either a primary or secondary product of the O + CH_3I reaction.

Gas Sources and Purification Procedures. The gases used were obtained from Matheson (He, 99.995%; SO_2, 99.98%; Cl_2, 99.99%; CH_3Cl, 99.5%; C_3H_6, 99.0%). Acetone (>99%), acetone-d_6 (99.8 atom-%), CH_3I (99%), and 3-buten-1-ol (99%) were obtained from Aldrich. Helium was used as provided while all other materials were degassed by freeze-pump-thaw cycles and used without further purification.

Photoionization Energies Used to Detect Reactants and Products. Three photoionization energies were used in the mass spectrometer during this investigation. A neon resonance lamp (16.67, 16.85 eV) was used to photoionize oxygen atoms and SO_2, an argon lamp (11.62, 11.83 eV) to detect H_2CO, C_3H_6, CH_3Cl, I and HI, and a hydrogen lamp (10.2 eV) to photoionize SO, CH_3, acetone, butenol, and CH_3I.

Electronic Structure Calculations

The theoretical study described here involves searching for and characterizing the transition states for rearrangements of the highly excited (94 kcal mol^{-1}) methoxy radical initially formed in the O + CH_3 reaction, focusing on decomposition pathways which can potentially yield CO (or HCO, a CO precursor) as a final product. Seakins and Leone[10] have discussed some of these isomerizations and possible decomposition paths qualitatively. Here these processes are dealt with quantitatively in order to assess their feasibility.

There have been a number of theoretical studies on the decomposition pathways of the methoxy radical[19-22]. Most have focused on the barriers to loss of atomic hydrogen and (1,2) hydrogen migration. The most recent of these[22] employed large basis sets, combined with multireference configuration interaction methods and was said to be accurate to ±1 kcal mol^{-1}. The focus of the present study will be to examine possible alternative pathways for the decomposition of methoxy radical, in particular pathways that might lead to formation of CO.

The calculations employ the double zeta (3s,2p,1d/2s,1p) and triple zeta (4s,3p,2d,1f/3s,2p,1d) correlation consistent basis sets of Dunning[23], denoted here DZ and TZ, respectively. The calculational method used is quite standard, consisting of a restricted Hartree-Fock (RHF) calculation followed by a singles and doubles configuration interaction (RHF+1+2) calculation. An estimate of the importance of higher order excitations (triples and quadruples) is made using the normalized Davidson correction[24], (RHF+1+2+QC). Geometry optimizations were all carried out using RHF+1+2+QC calculations with the DZ basis set. Single point calculations were then done with the TZ basis set at the optimum, DZ geometries. All calculations were carried out using the COLUMBUS electronic structure codes[25].

The calculated energies are summarized in Table 2 and illustrated schematically in Figure 2. The one reaction on this potential surface for which there is the most detailed experimental information available for comparison is the abstraction reaction, (8).

$$H + H_2CO \longrightarrow H_2 + HCO \qquad (8)$$

At the highest level of theory used here the calculated barrier for this reaction is 6.9 kcal mol^{-1} (including zero point corrections), and the calculated exothermicity is -16.2 kcal mol^{-1}. The measured exothermicity for this reaction is -16.7 ± 0.25 kcal mol^{-1} [26] and it has been shown[27] that the measured rate[28] is consistent with a barrier of 4.9 kcal mol^{-1}. Thus the calculated exothermicity is in error by 0.5 kcal mol^{-1} and the calculated barrier height is high by 2 kcal mol^{-1}. Another point of comparison to experiment are the exothermicities of reactions (9) and

(10).

$$H + H_2CO \longrightarrow H_3CO \qquad (9)$$

$$H + H_2CO \longrightarrow H_2COH \qquad (10)$$

The experimentally derived exothermicities (0 K) are -21.0 and -28.7 kcal mol^{-1}, respectively. The corresponding numbers from the highest level of theory are -21.6 and -28.2 kcal mol^{-1}. In this case the calculations are well within the experimental error bars for both reactions (± 0.9 kcal mol^{-1}). These errors are typical for this level of calculation and should be indicative of the overall accuracy of the calculations.

The calculations clearly predict that the lowest pathway to decomposition of methoxy radical is through loss of atomic hydrogen. The next lowest pathway is (1,2) hydrogen migration, forming hydroxymethyl radical. In the present calculations migration is predicted to lie 6.2 kcal mol^{-1} above the C-H bond cleavage route. This is in good agreement with the calculations of Walch[22] who found these two transition states to be separated by 6.7 kcal mol^{-1}. The following discussion focuses primarily on possible alternative pathways to decomposition of both CH_3O and H_2COH. In particular, we will consider the possibility of direct elimination of molecular hydrogen from both radicals, a necessary first decomposition step to ultimately lead to the production of CO.

For methoxy radical, only a (1,1) elimination is possible leading to H_2+HCO. For hydroxymethyl, either a (1,2) elimination, leading again to H_2+HCO, or a (1,1) elimination, leading to H_2+HOC are possible. Extensive geometry searches were made for all three pathways. In only one case was a transition state located; this being the (1,1) elimination from hydroxymethyl forming H_2+HOC. The calculated barrier for this process is quite high, 81.6

kcal mol^{-1}, or 54 kcal mol^{-1} above the lowest competing pathway, CH bond cleavage from methoxy radical to form H_2CO + H. Thus, although this barrier is energetically accessible in the $O+CH_3$ reaction, the existence of much lower energy pathways makes it unlikely that this route will be observable. Note that these results imply a fairly large barrier of 35.8 kcal mol^{-1} to the reverse reaction, insertion of HOC into H_2.

No transition states leading directly to H_2+HCO were located. For the case of (1,1) elimination from methoxy radical, the geometry search was initially constrained to force the simultaneous loss of two hydrogens. This was done by keeping two of the CH distances equal. With this constraint, a pathway from H_3CO to H_2+HCO was located, having a barrier of 50.6 kcal mol^{-1} (DZ). However, at this point there is a non-zero gradient for the anti-symmetric CH stretch (CH_a - CH_b). Optimization of this coordinate is found to lead down to the transition state for CH bond cleavage, i.e., loss of atomic hydrogen rather than molecular hydrogen. The search for a transition state for (1,2) elimination of hydrogen from hydroxymethyl radical was initially constrained to have an H_aCOH_b dihedral angle of zero degrees. With this constraint the calculations predict a barrier to loss of molecular hydrogen of 85.9 kcal mol^{-1}. However, the calculations also show a non-zero gradient at this point for the constrained torsional coordinate. When this constraint is relaxed the geometry collapses down to that of the transition state for (1,2) hydrogen migration.

The calculations predict the existence of a third H_3CO isomer, $HCOH_2$, a weak complex between CH and H_2O, having a binding energy of 7.8 kcal mol^{-1}, relative to $CH+H_2O$. There appears to be no barrier to the formation of this complex from the addition of CH and H_2O and only very small barriers to collapse of this complex to H_2COH. Thus relative to $CH+H_2O$, it is predicted that there is no net barrier to insertion of the CH into an OH bond forming H_2COH. This implies that the reverse of this insertion is a route for production of $CH+H_2O$ that is also energetically accessible in the $O+CH_3$ reaction. However, again because of the high energetic requirements, this route is not expected to compete effectively with loss of atomic hydrogen.

Discussion

The results of both the experimental and theoretical study of the product channels of the $O + CH_3$ reaction indicate that the $O(^3P) + CH_3$ reaction produces $H_2CO + H$ dominantly, if not exclusively. The primary mechanism is the formation of an energy-rich CH_3O radical which decomposes by simple C-H bond cleavage. A possible, minor, secondary channel involves 1,2 hydrogen migration, followed by O-H bond cleavage, leading to the same final products. A similar kinetic picture was found in the theoretical study of the reaction routes of the $O + C_2H_5$ reaction.[29] No energetically competitive pathways leading to H_2, HCO, HOC or CO could be found.

This conclusion that route 1a is the dominant product channel in the $O + CH_3$ reaction appears to contradict the results of Seakins and Leone.[10] Seakins and Leone monitored the time-resolved infrared emission from both formaldehyde and CO following 193-nm photolysis of SO_2 / CH_3I (or acetone) mixtures. The temporal behavior and concentration dependencies of these signals as well as the absence of emission when either SO_2 or CH_3I alone was photolyzed demonstrated that these emissions arise from reactions occurring after photolysis, not from direct photodissociation, and indicated that these emissions originated from initial products of the O

+ CH_3 reaction.

In order to avoid the complications arising from interfering CO^* from acetone photodissociation,[30] the majority of the experiments conducted by Seakins and Leone to confirm the identity of the reaction responsible for the observed CO emission were carried out with CH_3I as the methyl radical precursor. The fact that O reacts very rapidly with CH_3I was not considered in the FTIR emission study. (There have been no prior direct studies of this reaction rate constant reported in the literature.) However, using the rate constant for O + CH_3I determined in this study along with our relative photolysis yields, we calculate that the radical pool in Seakins and Leone's study is dominated by products from the O + CH_3I reaction to the extent that, even at short reaction times (10 μs), methyl radicals from direct photolysis constitute less than one-tenth of the carbon-centered radical pool. The primary products of the O + CH_3I reaction are not known but are most likely CH_3O + I. The route to produce CH_3 + IO is thermoneutral and probably not important. Kwong and Tse[18] report observing chemiluminescence from a variety of sources (I_2, CO_2, CO and OH) in the O + CH_3I system while Herron and Huie reported deposits from this system on the walls of their reactor which included polymeric formaldehyde and oxides of iodine. It is possible that primary or secondary products from the O + CH_3I reaction could interfere with the determination of the branching fraction to CO in Seakins and Leone's measurements.

A feasible origin of the discrepancy between the results of Seakins and Leone[10] and those reported in this study is more difficult to suggest when the same methyl radical precursor (acetone) is used in both studies. We speculate that CO, if present, is a minor product with a branching <0.15, within the error limits of our experimental study. Further experiments, perhaps those that directly probe the ground state of CO, are necessary to resolve the differences in the measured branching fractions.

Summary

The branching fraction to formaldehyde production in the $O(^3P) + CH_3$ reaction has been experimentally determined to be 1.0 ± 0.15. The conclusion that formaldehyde and hydrogen atom are the only products of the O + methyl reaction is supported by the results of theoretical calculations on the pathways to decomposition of the methoxy radical initially formed in the reaction. The dominant channel for decomposition of methoxy radicals is C-H bond cleavage leading to atomic hydrogen and formaldehyde. A possible, minor, secondary channel is hydrogen migration, followed by O-H bond cleavage, leading to the same final products. No energetically competitive pathways leading to H_2, HCO, HOC or CO could be found.

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References

1. Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F.; Frizzell, D. H. *NIST Chemical Kinetics Database -- Ver. 5.0*, NIST Standard Reference Data: Gaithersburg, MD, 1993.
2. Warnatz, J. In *Combustion Chemistry*; Gardiner. J. C., Ed.; Springer-Verlag: New York, 1984; Chapter 5.
3. Miller, J. A.; Kee, R. J.; Westbrook, C. K. *Annu. Rev. Phys. Chem.* **1990**, *41*, 345.
4. Warnatz, J. *Combust. Sci. Tech.* **1982**, *26*, 203.
5. Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. A.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411.
6. Tsang, W.; Hampson, R. F. *J. Chem. Phys. Ref. Data* **1986**, *15*, 1087.
7. Hoyermann, K.; Sievert, R. *Symp. (Int.) Combust. [Proc.]* **1979**, *17*, 517.
8. Slagle, I. R.; Sarzyński, D,; Gutman, D. *J. Phys. Chem.* **1987**, *91*, 4375.
9. Zellner, R.; Hartmann, D.; Karthäuser, J.; Rhäsa, D.; Weibring, G. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 549.
10. Seakins, P. W.; Leone, S. R. *J. Phys. Chem.* **1992**, *96*, 4478.
11. Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1982**, *104*, 4741.
12. Timonen, R. S.; Gutman, D. *J. Phys. Chem.* **1986**, *90*, 2987.
13. Donaldson, D. J.; Leone, S. R. *J. Chem. Phys.* **1986**, *85*, 817.
14. August, R.; McEwen, I.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, 1683.
15. Baba, M.; Shinohara, H.; Nishi, N.; Hirota, N. *Chem. Phys.* **1984**, *83*, 221.

16. Pence, W. H.; Baughcaum, S. L.; Leone, S. R. *J. Phys. Chem.* **1981**, *85*, 3844.

17. Herron, J. T.; Huie, R. E. *J. Phys. Chem.* **1969**, *73*, 1326.

18. Kwong, B. C. L.; Tse, R. S. *J. Phys. Chem.* **1994**, *98*, 823.

19. Saebo, S.; Radom, L,; Schaefer, H. F. III *J. Chem. Phys.* **1983**, *78*, 845.

20. Page, M.; Lin, M. C.; He, Y.; Choudhury, T. K. *J. Phys. Chem.* **1989**, *93*, 4404.

21. Curtiss, L. A.; Kock, L. D.; Pople, J. A. *J. Chem. Phys.* **1991**, *95*, 4040.

22. Walch, S. P. *J. Chem. Phys.* **1993**, *98*, 3076.

23. Dunning, T. H. Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

24. (a)Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61. (b)Silver, D. W.; Davidson, E. R. *Chem. Phys. Lett.* **1978**, *52*, 403.

25. Shepard, R.; Shavitt, I.; Pitzer, R. C.; Pepper, M.; Lischka, H.; Szalay, P. G.; Ahlrichs, R.; Brown, F. B.; Zhao, J.-G. *Int. J. Quantum Chem.* **1988**, *S22*, 149.

26. The experimental heats of formation (298 K) are as follows: H_2CO, -108.6±0.5 kJ/mole [Baulch, D. L.; Cox, R. A.; Crutzen, P. J.; Hampson, R. F. Jr.; Troe, J.; Watson, R. T. *J. Phys. Chem. Ref. Data* **1982**, *11*, 493.]; HCO, 41.8±0.8 kJ/mole [Chuang, M.-C.; Foltz, M. F.; Moore, C. B. *J. Chem. Phys.* **1987**, *87*, 3855.]; H, 217.999±0.006 kJ/mole [JANAF, 1985]. In all cases JANAF data was used to correct these to 0 K.

27. Harding, L. B.; Schatz, G. C. *J. Chem. Phys.* **1982**, *76*, 4296.

28. (a) Klemm, R. B. *J. Chem. Phys.* **1979**, *71*, 1987. (b) Baldwin, R. R.; Cowe, D. W. *Trans. Faraday Soc.* **1962**, *58*, 1768. (c) Dean, A. H.; Johnson, R. L.; Steiner, D. C. *Combust. Flame* **1980**, *37*, 41.

29. Slagle, I. R.; Sarzyński, D.; Gutman, D.; Miller, J. A.; Melius, C. F. *J. Chem. Soc., Faraday Trans. II* **1988**, *84*, 491.

30. Seakins, P. Private communication.

31. Lightfoot, P. D.; Kirwan, S. P.; Pilling, M. J. *J. Phys. Chem.* **1988**, *92*, 4938.

32. Shaub, W. M.; Hsu, D. S. Y.; Burks, T. L.; Lin, M. C. *Symp. (Int.) Combust., [Proc.]* **1981**, *18*, 811.

33. Alvarez, R. A.; Moore, C. B. *J. Phys. Chem.* **1994**, *98*, 174.

Table 1. Conditions and Results of Experiments to Measure the Yield of Formaldehyde from the O + CH_3 Reaction.

T (K)	10^{-17}[He] (atoms cm^{-3})	$10^{-11}[CH_3]_0$ (molec. cm^{-3})	10^{-12}[O] (atoms cm^{-3})	F_{H_2CO}
299	1.20	1.7	5.8	1.04
295	1.20	2.8	5.3	0.92
295	1.20	2.8	18.	0.97
295	1.20	5.6	18.	0.99
297	2.40	2.0	5.7	1.06
297	2.40	6.6	16.	0.99
			average =	1.0±0.05[a]

[a] Error limits are one standard deviation and indicate statistical uncertainties only.

Table 2. Summary of Calculated Relative Energies for the Minima and Transition States on the H_3CO Potential Surface.[a]

	RHF+1+2+QC DZ	RHF TZ	RHF+1+2 TZ	RHF+1+2+QC TZ	
Minima:					
H_3CO ($^2A'$)[b]	0.0	0.0	0.0	0.0	(0.0)
H_3CO ($^2A''$)	0.2				
H_2COH	-5.3	1.6	-6.5	-7.3	(-6.6)
$HCOH_2$	70.4	76.3	73.0	71.1	(69.1)
$H+H_2CO$	24.6	31.0	28.2	27.5	(21.6)
H_2+HCO	11.2	26.1	17.3	13.7	(5.4)
H_2+HOC	51.6	57.1	55.4	53.5	(45.8)
H_2O+CH	84.1	79.8	83.7	83.2	(76.9)
Transition States:					
$H_3CO \longrightarrow H+H_2CO$	31.2	44.9	36.1	32.7	(27.7)
$H_3CO \longrightarrow H_2COH$	36.8	55.9	38.9	35.2	(33.9)
$H_3CO \longrightarrow H_2+HCO$[c]	50.6				

Table 2 (continued). Summary of Calculated Relative Energies for the Minima and Transition States on the H_3CO Potential Surface.[a]

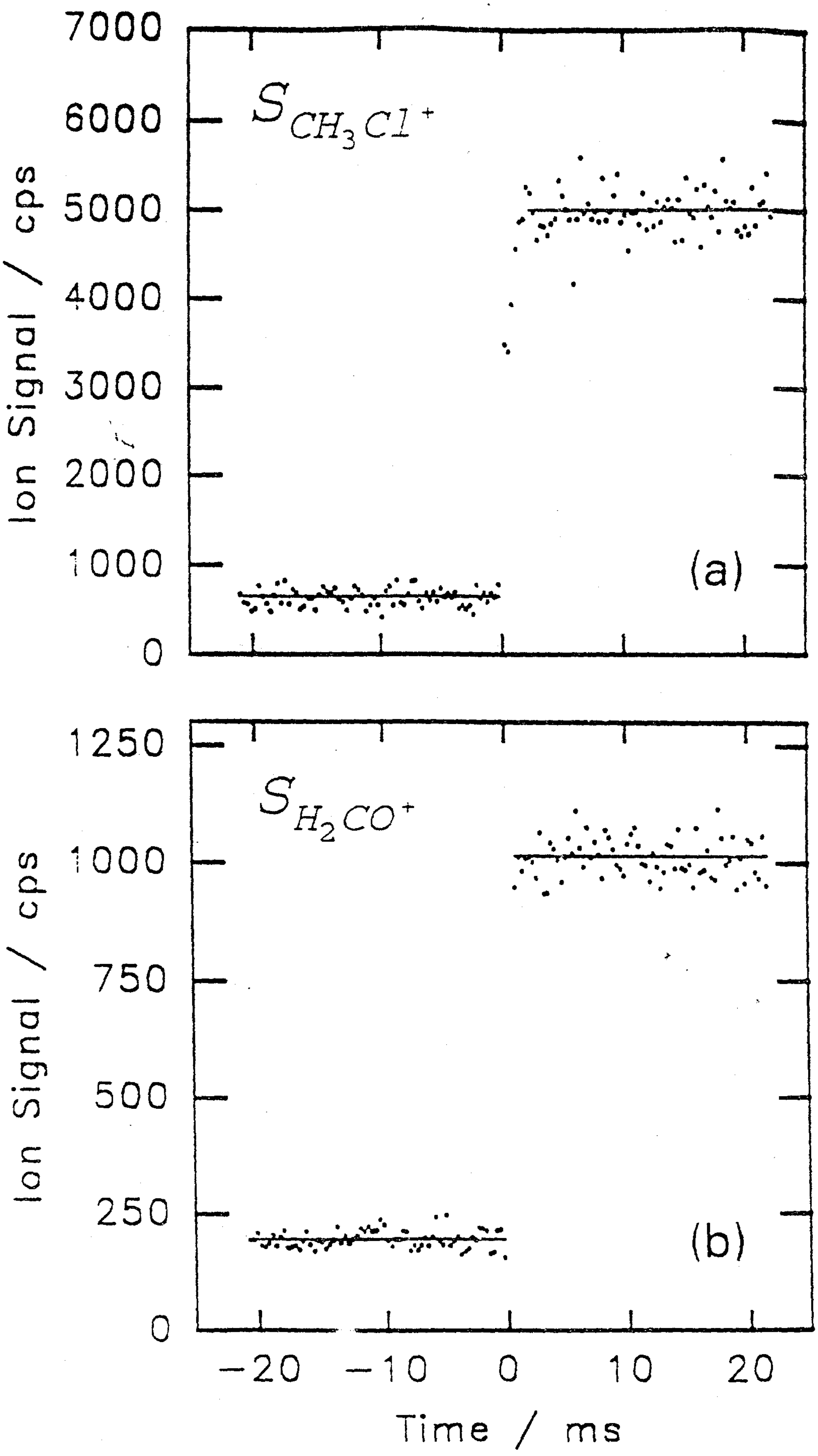
	RHF+1+2+QC	RHF	RHF+1+2	RHF+1+2+QC
	DZ	TZ	TZ	TZ
$H_2COH \longrightarrow H+H_2CO$	38.0	56.4	44.3	39.7 (34.7)
$H_2COH \longrightarrow H_2+HOC$	87.0	104.0	91.5	86.9 (81.6)
$H_2COH \longrightarrow H_2+HCO$[d]	80.6			
$H_2CO+H \longrightarrow H_2+HCO$	32.7	53.3	40.8	35.9 (28.5)

[a] All energies (kcal mol^{-1}) are relative to $H_3CO(^2A')$. Those in parenthesis include zero point corrections.

[b] The total electronic energies for columns 1-4 are -114.671019, -114.459430, -114.830635 and -114.867668 hartrees, respectively. The calculated zero point energy is 22.75 kcal mol^{-1}.

[c] Geometry optimized under the constraint $R(CH_a) = R(CH_b)$. See text.

[d] Geometry optimized under the constraint H_aCOH_b dihedral angle = 0. See text.



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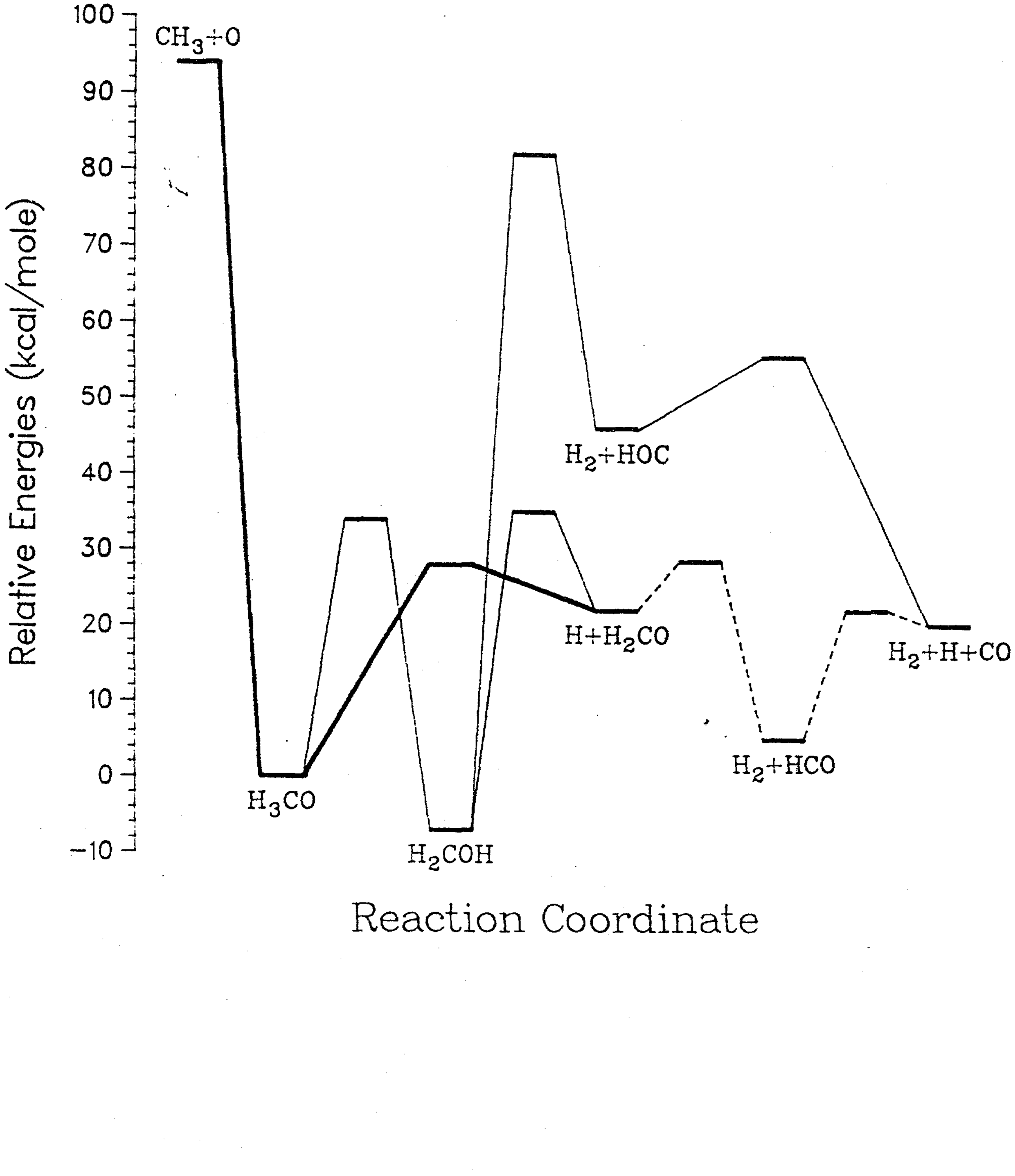

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Figure 2