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A Computational Study of the Reaction of Methyl Formate with ·H and ·CH_3 Radicals

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Ab initio molecular orbital theory has been used to examine the kinetics and mechanism for the reaction of hydrogen and methyl radicals with methyl formate. From the ab initio results the rate of reaction of hydrogen atoms with methyl formate is found to be significantly faster than the analogous reactions initiated by methyl radicals. Under oxygen rich combustion conditions reactions with H and OH are likely to dominate. Abstraction of the carbonyl hydrogen of methyl formate by H atom is significantly (85%) favored at 298 K. As the temperature increases, however, methyl and carbonyl hydrogen abstraction pathways become more equally probable.

I. Introduction

Concerns about mobile source emissions and their impact on urban tropospheric ozone formation have spurred research into alternative fuels. Engine makers and automotive companies are looking for ways to decrease emissions of CO and NO_x. Fuel composition affects the tendency of a fuel to form soot particulates and NO_x. Oxygenated hydrocarbons such as ethers can be added to fuels to maintain performance while lowering tailpipe emissions of CO.[1] Dimethyl ether, DME, is a fuel anti-knock agent and proposed diesel fuel substitute. DME has also been used as a methanol ignition improver in diesel engines where it has been reported to reduce hydrocarbon emissions. Japar et al.[2] used ·Cl and ·OH radical initiated hydrogen abstraction to simulate the reaction of DME with tropospheric OH radical in the presence of NO. Reaction products were determined using FTIR spectroscopy. The production of methyl formate accompanied the loss of dimethyl ether quantitatively. The yield of methyl formate relative to DME loss was found to be 0.90.

Generally, four main pathways lead to the destruction of organic molecules in the atmosphere: reaction with OH radicals, UV photolysis, reaction with $O(^1D)$, and reaction with chlorine atoms. Three investigators have measured the rate constant of OH radicals with methyl formate. Wallington et al.,[3] using a flash photolysis−resonance fluorescence technique, measured a 296 K rate constant to be $2.27 \pm 0.34 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Le Calvé et al.,[4] using a laser photolysis−laser induced fluorescence technique, measured the 298 K rate constant to be $1.723 \pm 0.21 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Good et al.[5] used ab initio molecular orbital theory to examine the kinetics and mechanism for the reaction of hydroxyl radical with methyl formate. A rate constant of 1.85×10^{-13} cm^3 molecule^{-1} s^{-1} was determined. It was found that approximately 86% of the reaction proceeds via abstraction of the carbonyl hydrogen from methyl formate, resulting in the formation of the CH_3OCO radical. The methyl formate/OH rate constant was experimentally determined to be $1.77 \pm 0.28 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. All four values are in good agreement.

Using a simple relation that the lifetime is equal to the concentration of methyl formate divided by its loss rate, the following expression can be derived:

$$\tau = 1/k_{OH}[OH]$$

where $k_{OH}[OH]$ represents the rate of removal by OH in the troposphere. In the troposphere the concentration of OH is on the order of 10^6 molecules cm^{-3}. Using these data an estimate for the atmospheric lifetime of methyl formate with respect to loss from OH radical is 51 to 67 days.

Chlorine atom reactions can be important in the marine troposphere where significant concentrations of chlorine exist. The same simple lifetime expression can be used to determine the atmospheric lifetime of methyl formate with respect to loss from chlorine radicals. Typical tropospheric concentrations of chlorine atoms are approximately 3 orders of magnitude smaller (10^3 molecules cm^{-3}) than tropospheric concentrations of OH radicals. The reaction rate of methyl formate with chlorine radicals has been measured by Wallington et al.,[6] Notario et al.,[7] and Good et al.,[8] who find 298 K rate constants of 1.4 ± 0.1, 1.8 ± 0.2, and $1.4 \pm 0.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively. The lifetime of methyl formate ranges from 17.6 years to 22.6 years. Thus, reactions with tropospheric hydroxyl radical dominate over reactions with Cl atoms.

Reactions with oxygen atoms in their excited states (O^1D) are typically very fast and proceed without barrier; concentrations of O^1D are typically very small. In the stratosphere between 20 and 30 km, the number density of O^1D is only on the order of 10 molecules cm^{-3}.[9] Thus, even if the reaction rate were gas kinetic, the atmospheric lifetime would be on the order of six years. This does not include the time it takes to reach that height nor the fact that the methyl formate concentration in the stratosphere would be at least an order of magnitude smaller than in the troposphere. Thus, reactions of methyl formate with $O(^1D)$ are not expected to be significant.

The final possible atmospheric removal mechanism is photolysis. Vesine et al.[10] measured absorption cross sections for methyl formate and found negligible absorption at wavelengths longer than 260 nm. From this, Vesine concludes that photolysis is unimportant in the troposphere since solar radiation at wavelengths lower than 300 nm does not exist to any appreciable extent.

While the possible atmospheric pathways have been thoroughly investigated, the plausible combustion pathways have, to the best of our knowledge, not. Under combustion conditions where temperatures can reach on the order of 10^3 K, significant concentrations of CH_3 radicals and H atoms may contribute to the loss of methyl formate. This work investigates hydrogen

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TABLE 1: Optimized Geometries of Reactants, Radical Products, and Transition Structures[a]

coordinate	CH_3OCOH	CH_3-CH_3OCOH	$CH_3OCOH-CH_3$	$H-CH_3OCOH$	$CH_3OCOH-H$	CH_3OCO	CH_2OCOH
C_1O_1	1.441	1.415	1.448	1.401	1.451	1.456	1.373
C_2O_1	1.341	1.347	1.337	1.355	1.327	1.322	1.361
C_2O_2	1.207	1.206	1.199	1.203	1.195	1.192	1.202
H_1C_2	1.091	1.090	1.315	1.089	1.359	-	1.089
H_2C_1	1.080	1.079	1.080	1.078	1.079	1.079	1.070
H_3C_1	1.083	1.082	1.083	1.080	1.083	1.083	1.071
H_4C_1	1.083	1.315	1.083	1.366	1.083	1.083	-
$C_1O_1C_2$	114.0	115.0	114.0	115.3	114.0	114.1	116.8
$O_1C_2O_2$	125.5	125.5	127.1	125.4	128.8	130.5	125.5
$H_1C_2O_1$	109.4	109.1	107.4	108.9	106.5	-	108.6
$H_2C_1O_1$	105.4	107.9	105.4	109.0	105.3	105.4	113.2
$H_3C_1O_1$	110.2	112.9	109.9	114.0	109.8	109.5	118.2
$H_4C_1O_1$	110.2	107.1	109.9	107.0	109.8	109.5	-
$H_1C_2O_1C_1$	180.0	−179.6	180.0	−179.7	180.0	-	179.2
$O_2C_2O_1C_1$	0.0	0.6	0.0	0.6	0.0	0.0	−0.8
$H_2C_1O_1C_2$	180.0	−173.2	180.0	−170.3	180.0	180.0	172.7
$H_3C_1O_1C_2$	−60.3	−44.8	−60.4	−37.8	−60.4	−60.4	11.1
$H_4C_1O_1C_2$	60.3	71.2	60.4	76.4	60.4	60.4	-
$*XH_1$	-	-	1.354	-	0.918	-	-
XH_1C_2	-	-	178.6	-	176.9	-	-
$XH_1C_2O_1$	-	-	0.0	-	0.0	-	-
XH_4	-	1.336	-	0.898	-	-	-
XH_4C_1	-	174.7	-	175.7	-	-	-
$XH_4C_1O_1$	-	−6.6	-	7.2	-	-	-
H_5C_3	-	1.081	1.080	-	-	-	-
H_6C_3	-	1.081	1.080	-	-	-	-
H_7C_3	-	1.080	1.080	-	-	-	-
$*H_5C_3HY$	-	104.2	103.5	-	-	-	-
H_6C_3HY	-	104.6	104.6	-	-	-	-
H_7C_3HY	-	105.1	104.6	-	-	-	-
$H_5C_3H_4CZ$	-	50.0	0.0	-	-	-	-
$H_6C_3H_4CZ$	-	170.0	−59.8	-	-	-	-
$H_7C_3H_4CZ$	-	−69.8	60.0	-	-	-	-

[a] *X represents H_5 (attacking atom) or C_3: Y and Z represent H_1 and C_2 or H_4 and C_1 respectively. All angles in degrees, distances in angstroms. The structures of the stationary states are plotted in Figure 1.

and methyl radical initiated abstraction reactions from methyl formate to determine their significance over a range of temperatures.

II. Methods

All calculations were perfomed with the GAUSSIAN 94 package of programs.[11] Geometry optimizations for all species were carried out for all structures to better than 0.001 Å for bond lengths and 0.1° for angles (Table 1). The geometries were fully optimized, and with these geometries, frequency calculations (Table 2) were performed using the second-order Møeller−Plesset perturbation method (MP2) with the 6-311++G(2d,2p) basis set. In addition, single point energies were calculated using the quadratic configuration interaction method, which includes the effect of single, double, and triple substitutions, QCISD(T). The large 6-311++G(2d,2p) basis set was used with this method. Restricted wave functions are used for closed-shell and unrestricted wave functions for open-shell systems with all orbitals active. For each species the degree of spin contamination was monitored. For doublet systems, the $\langle S^2 \rangle$ value did not exceed 0.78, thus indicating that the wave functions were not significantly contaminated by higher order spin states. To obtain the energy at 298 K, the thermal energy of each species was added to its total energy instead of the zero-point energy.

III. Results and Discussion

1. Structure. The structure of methyl formate, the two possible transition states of the two reactions, and the two alkyl radical products are illustrated in Figure 1. The two C−O single bonds of methyl formate are predicted to be 1.441 and 1.341 Å while the carbonyl bond is predicted to be 1.207 Å in length. The experimentally determined values reported by Curl[12] are 1.437, 1.334, and 1.200 Å, respectively. Thus, the error associated with the present methodology is less than one percent.

Abstraction of the carbonyl hydrogen by methyl radical is illustrated in Figure 1b. In the transition structure, the rupturing CH bond lengthens to 1.315 Å while the forming CH bond decreases to 1.354 Å. Both the carbonyl C═O bond and the adjacent methyl CO bond decrease slightly as the transition state forms. The CO bond adjacent to the methyl group lengthens only slightly to 1.448 Å.

The removal of a methyl hydrogen by methyl radical to form the CH_2OCOH radical is illustrated in Figure 1c. As has been shown for Cl and OH radical initiated hydrogen abstraction from methyl formate, abstraction is found to occur at one of the out-of-plane hydrogen atoms.[5,8] The cleaving CH bond lengthens to 1.315 Å as the methyl radical approaches to within 1.336 Å of the departing H atom. The methyl CO bond decreases in length significantly to 1.415 Å while the opposing CO bond lengthens only slightly and the C═O bond is left unchanged.

Abstraction of the carbonyl hydrogen atom by hydrogen is illustrated in Figure 1d. The incoming hydrogen radical approaches to within 0.918 Å of the departing hydrogen atom. This carbonyl CH bond lengthens to 1.359 Å. The remaining bonds in methyl formate change in accord with those previously described for reactions initiated by methyl radical.

TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) for Reactants and Transition States

CH_3OCOH	CH_3	CH_3-CH_3OCOH	$CH_3OCOH-CH_3$	$H-CH_3OCOH$	$CH_3OCOH-H$
163	485	40	13	120	146
310	1453	73	92	241	184
348	1454	106	97	329	271
777	3182	311	154	386	321
945	3372	337	300	551	452
1054	3373	346	368	772	754
1195		517	403	981	929
1196		608	563	1044	1124
1245		699	600	1097	1140
1419		791	795	1166	1185
1494		974	950	1199	1220
1518		1045	1148	1240	1248
1528		1171	1185	1273	1482
1762		1183	1193	1420	1517
3117		1212	1219	1485	1525
3121		1257	1337	1755	1588
		1416	1433	1771	1854
		1420	1469	3135	3120
		1439	1486	3167	3217
		1479	1490	3293	3250
		1483	1516		
		1506	1526	−1852i	−1992i
		1761	1794		
		3120	3118		
		3125	3123		
		3152	3212		
		3264	3245		
		3270	3272		
		3273	3274		
		−2043i	−2143i		

The removal of a methyl hydrogen atom from methyl formate by the attacking hydrogen atom also proceeds at one of the two out-of-plane hydrogen atoms (Figure 1e). The approaching hydrogen radical is 0.898 Å from the departing hydrogen atom in the transition structure. The rupturing CH bond lengthens to 1.366 Å in the transition structure.

The CH_3OCO and CH_2OCOH radicals are illustrated in Figures 1f and 1g respectively. In CH_3OCO the methyl CO bond is slightly longer than the analogous bond in methyl formate. Alternatively the CO bond on the carbonyl carbon atom decreases its length relative to methyl formate. This structural progression suggests that further bond cleavage reactions CH_3-OCO may prefer formation of CH_3 and CO_2 rather than CH_3O and CO. For CH_2OCOH the opposite trends are found. The methyl CO bond decreases while the carbonyl CO bond increases relative to the parent molecule. This pattern suggests that the formation of CH_2O and HCO may be preferred over CH_2 and HCO_2 formation.

2. Energetics. The relevant kinetic parameters for each reactant, product, and transition state are reported in Tables 3, 4, and 5. For the following reactions removal of the carbonyl hydrogen is predicted to be thermodynamically and kinetically favored.

$$CH_3OCOH + CH_3 \rightarrow CH_3OCO + CH_4 \tag{1a}$$

$$CH_3OCOH + CH_3 \rightarrow CH_2OCOH + CH_4 \tag{1b}$$

At the QCISD(T)/6-311++G(2d,2p)//UMP2/6-311++G(2d,2p) level of theory the reaction enthalpy for removal of the carbonyl hydrogen is slightly more favorable, having a reaction enthalpy of −5.1 kcal mol^{-1}, while the removal of a methyl hydrogen (reaction 1b) is calculated to be exothermic by −4.1 kcal mol^{-1}. Using G2 (Gaussian-2 is a general procedure for computing the energies of molecules at their equilibrium geometries by an algorithm consisting of several component calculations whose results are then combined to achieve a result of comparable accuracy to a QCISD(T)/6-311+G(3df,2p) computation) and G2(MP2) methodology along with isodesmic reactions, Good et al.[13] determined the 298 K heat of formation of CH_3OCO and CH_2OCOH to be −37.5 and −36.5 kcal mol^{-1}, respectively. These values along with literature values for the 298 K heats of formation of methyl formate (−85.0 kcal mol^{-1}),[14] CH_4 (−17.88 kcal mol^{-1}),[9] and CH_3 (35.0 kcal mol^{-1})[9] yield reaction enthalpies for reactions 1a and 1b of −5.5 and −4.4 kcal mol^{-1}, respectively. These values are in good agreement with the values determined in this work.

For the hydrogen radical initiated reactions (reactions 2a and 2b), analogous trends exist:

$$CH_3OCOH + H \rightarrow CH_3OCO + H_2 \tag{2a}$$

$$CH_3OCOH + H \rightarrow CH_2OCOH + H_2 \tag{2b}$$

Removal of the carbonyl hydrogen atom is predicted to be thermodynamically favored by about 1 kcal mol^{-1}. Using published values for the heats of formation of H (52.1 kcal mol^{-1}) and H_2, the reaction enthalpies for reactions 2a and 2b are predicted to be −4.6 and −3.6 kcal mol^{-1}, respectively. These values are in reasonable agreement with our values in Table 5. The reaction enthalpies for reactions 1a and 1b are shown to be more accurate than 2a and 2b due to the fact that reactions 1a and 1b are isodesmic and isogiric reactions.

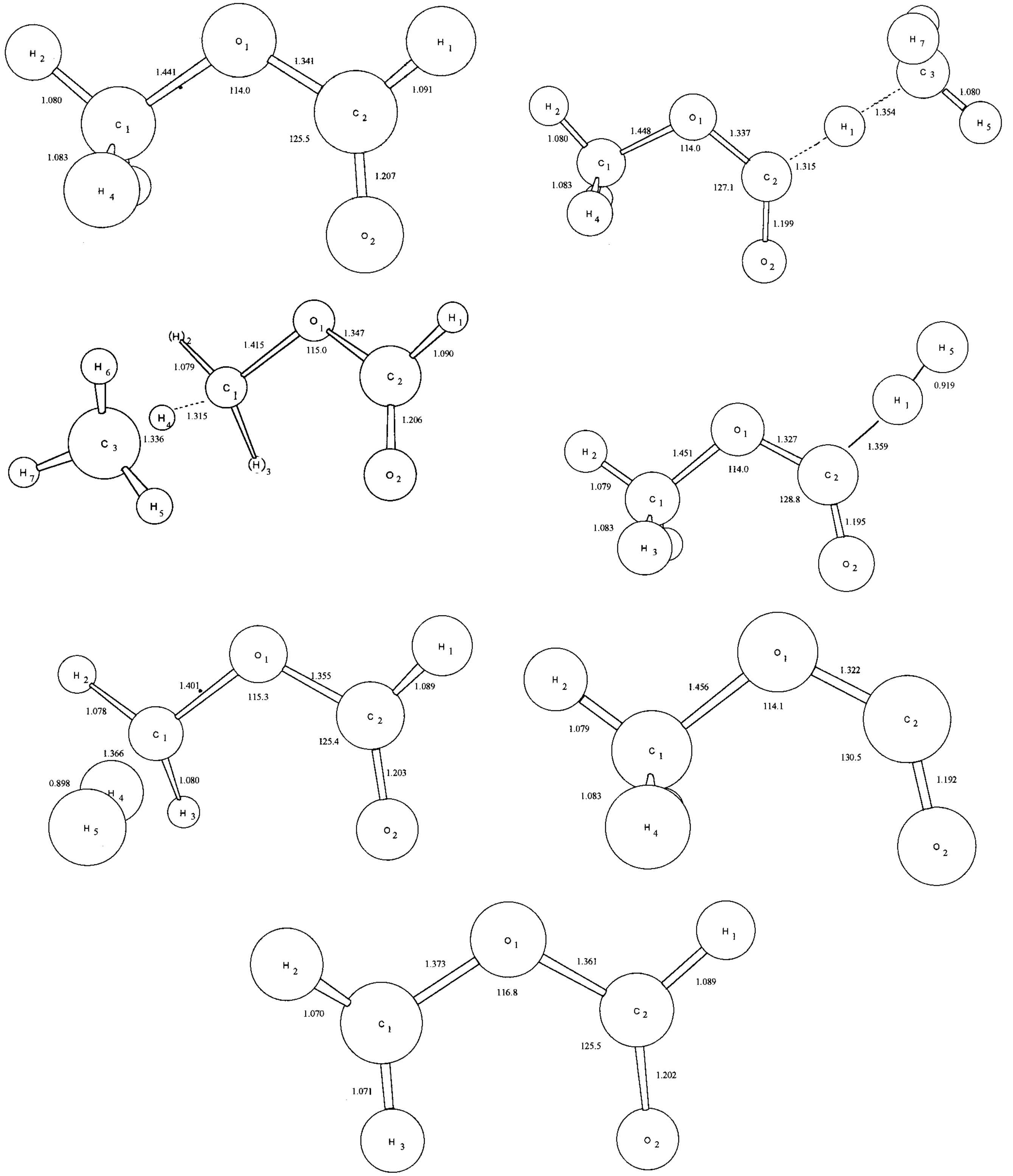

Figure 1. Equilibrium geometries for H/methyl formate and CH_3/methyl formate systems as calculated using the Møeller−Plesset perturbation method (MP2) with the 6-311++G(2d,2p) basis set. All distances expressed in angstroms; all angles expressed in degrees. (1a) Structure of methyl formate; the COCO dihedral is 0.0°. (1b) Transition structure of CH_3/methyl formate reaction in which the carbonyl hydrogen is removed. (1c) Transition structure of CH_3/methyl formate in which an out-of-plane methyl hydrogen is removed. (1d) Transition structure of H/methyl formate reaction in which the carbonyl hydrogen is abstracted. (1e) Transition structure of H/methyl formate reaction in which an out-of-plane methyl hydrogen is abstracted. (1f) CH_3OCO radical. (1g) CH_2OCOH radical.

Isodesmic reactions are those in which reactants and products contain the same type and same number of bonds. Isogiric reactions have equal numbers of unpaired electrons on both reactant and product sides of the reaction.[15] Because of the electronic similarity between reactants and products, errors in the calculated energy may cancel between them.

3. Kinetics. While the thermodynamics of both CH_3 and H radical systems are similar, the kinetics are not. From

TABLE 3: Energetic Parameters for Methyl Formate, Transition States, and Products at 298 K

species	^{a,d}energy	^{a,e}zero point energy	^{b,e}rotational constants	^{c,e}imaginary frequency
CH_3OCOH	−228.642	0.0630	19.8, 6.98, 5.33	-
$CH_3{-}CH_3OCOH$	−268.363	0.092	6.46, 3.28, 2.56	−2043i
$CH_3OCOH{-}CH_3$	−268.366	0.092	8.54, 2.63, 2.06	−2143i
$H{-}CH_3OCOH$	−229.121	0.060	16.16, 6.37, 5.11	−1852i
$CH_3OCOH{-}H$	−229.123	0.060	15.95, 6.54, 4.78	−1992i
H	−0.4998	0.0	-	-
CH_3	−39.745	0.030	290.8, 290.8, 145.4	-
CH_3OCO	−227.978	0.050	-	-
CH_2OCOH	−227.974	0.048	-	-
CH_4	−40.420	0.046	-	-
H_2	−1.171	0.010	-	-

[a] Energies and zero point energies in hartrees. [b] Rotational constants in GHz. [c] Imaginary frequencies in units of cm^{-1}. [d] Calculated at the QCISD(T)/6-311++G(2d,2p). [e] Calculated at the MP2/6-311+G(2d,2p).

transition state theory each rate constant is given by the following expression:

$$k = \frac{LTk_b}{h}\frac{Q_{TS}}{Q_{methylformate}}\,e^{-E_0/RT} \tag{3}$$

where X = CH_3 or H, E_0 is the energy difference between the transition state and reactants, including the zero point energy, T is the temperature, h is Plank's constant, R is the gas constant, Q is the total partition function incorporating translational, rotational, vibrational, and electronic partition functions ($Q_T = Q_eQ_vQ_rQ_t$), L is the number of equivalent carbon−hydrogen bonds, and k_b is Boltzmann's constant. For all systems, the effects of tunneling have been taken into consideration using the imaginary frequencies in Table 3 and the well-known Wigner expression.[16]

$$Q_{tunnel} = 1 - \frac{1}{24}\left(\frac{h\nu}{k_bT}\right)^2\left(1 + \frac{k_bT}{E_0}\right) \tag{4}$$

As shown in Table 5, the H radical initiated abstraction reactions are kinetically favored by roughly 3 kcal mol^{-1} over the analogous reactions in the CH_3 radical initiated system. Additionally, examination of the Arrhenius parameters in Table 5 suggests that steric factors play a more important role in reactions mediated by CH_3 as compared to H atom initiated reactions. The resulting rate constants for the methyl radical reactions are thus significantly slower than the H radical system. This finding is reasonable considering similar systems. Abstraction of a primary hydrogen from ethanol by H radical has an activation energy of 4.6 kcal mol^{-1}, while the same reaction initiated by methyl radical has an activation energy of 7.2 kcal mol^{-1}. For the ethanol system, removal of the carbonyl hydrogen has an activation energy of 4.2 kcal mol^{-1} and 8.4 kcal mol^{-1} as initiated by H and CH_3, respectively.[17]

Common to both systems is the finding that abstraction of the carbonyl hydrogen is kinetically favored over abstraction of a methyl hydrogen at 298 K. Examination of the structure of methyl formate (Figure 1) shows the carbonyl CH bond to be approximately 0.01 C longer than the methyl CH bonds. The longer CH bond on the carbonyl carbon atom may thus be weaker and easier to abstract. In the case of H radical initiation, 84.6% of the reaction occurs at the carbonyl hydrogen at 298 K; for the reaction mediated by CH_3, the preference for the carbonyl hydrogen is greater, 98%. As the temperature increases, preference for the carbonyl hydrogen decreases. For the CH_3 radical system, the preference for the carbonyl hydrogen is down to 83.3% at 2500 K. In the H atom system, both pathways contribute equally at this temperature (Figure 2).

Also listed in Table 5 are kinetic data for the methyl formate/OH radical system as studied by Good et al.[8] At 298 K, reactions initiated by OH radical are orders of magnitude faster than the other systems due to the much lower reaction barrier. At this temperature removal of the carbonyl hydrogen is again favored. At higher temperatures, however, the Arrhenius term begins to dominate and removal of the methyl hydrogen is predicted to dominate (Figure 2).

IV. Conclusions

Ab initio molecular orbital theory has been used to investigate hydrogen abstraction reactions from methyl formate by H and

TABLE 4: Partition Functions (cm^{-3} molecule s) as at Several Temperatures

temp (K)	CH_3OCOH	H	CH_3	$CH_3{-}CH_3OCOH$	$CH_3OCOH{-}CH_3$	$H{-}CH_3OCOH$	$CH_3OCOH{-}H$
298	4.41×10^{31}	1.96×10^{24}	3.09×10^{28}	1.76×10^{34}	7.96×10^{34}	1.96×10^{32}	2.51×10^{32}
600	2.37×10^{33}	5.59×10^{24}	3.52×10^{29}	1.10×10^{37}	6.46×10^{37}	2.26×10^{34}	3.34×10^{34}
1000	1.56×10^{35}	1.20×10^{25}	2.80×10^{30}	9.28×10^{39}	6.06×10^{40}	3.49×10^{36}	5.37×10^{36}
1500	1.20×10^{37}	2.21×10^{25}	1.92×10^{31}	8.97×10^{42}	6.10×10^{43}	5.96×10^{38}	9.26×10^{38}
2000	4.60×10^{38}	3.40×10^{25}	9.10×10^{31}	2.71×10^{45}	1.87×10^{46}	4.19×10^{40}	6.50×10^{40}
2500	1.06×10^{40}	4.75×10^{25}	3.41×10^{31}	3.57×10^{47}	2.48×10^{48}	1.55×10^{42}	2.41×10^{42}

TABLE 5: Energetics and Kinetics of Methyl Formate Hydrogen Abstraction Reactions[a]

	$H{-}CH_3OCOH$	$CH_3OCOH{-}H$	$CH_3{-}CH_3OCOH$	$CH_3OCOH{-}CH_3$	$OH{-}CH_3OCOH$	$CH_3OCOH{-}OH$
ΔH (kcal mol^{-1})	−4.2	−5.1	−4.1	−5.1	−17.5	−18.6
E_0 (kcal mol^{-1})	11.6	10.2	14.9	12.8	4.0	2.4
A_{298}	2.8×10^{-11}	1.8×10^{-11}	1.6×10^{-13}	3.62×10^{-13}	1.27×10^{-12}	8.74×10^{-13}
A_{600}	4.28×10^{-11}	3.16×10^{-11}	3.29×10^{-13}	9.70×10^{-13}	1.65×10^{-12}	1.26×10^{-12}
A_{1000}	7.76×10^{-11}	5.97×10^{-11}	8.87×10^{-13}	2.90×10^{-12}	2.88×10^{-12}	2.26×10^{-12}
A_{1500}	1.41×10^{-10}	1.09×10^{-10}	2.44×10^{-12}	8.30×10^{-12}	5.22×10^{-12}	4.10×10^{-12}
A_{2000}	2.23×10^{-10}	1.73×10^{-10}	5.41×10^{-12}	1.87×10^{-11}	8.30×10^{-12}	6.52×10^{-12}
A_{2500}	3.22×10^{-10}	2.49×10^{-10}	1.03×10^{-11}	3.58×10^{-11}	1.20×10^{-11}	9.40×10^{-12}
k_{298}	8.4×10^{-19}	4.6×10^{-18}	1.6×10^{-23}	8.2×10^{-22}	2.7×10^{-14}	1.1×10^{-13}
k_{600}	6.9×10^{-15}	1.5×10^{-14}	3.2×10^{-18}	4.4×10^{-17}	3.9×10^{-13}	4.3×10^{-13}
k_{1000}	3.7×10^{-13}	5.4×10^{-13}	7.8×10^{-16}	6.4×10^{-15}	1.7×10^{-12}	1.1×10^{-12}
k_{1500}	3.8×10^{-12}	4.5×10^{-12}	2.1×10^{-14}	1.3×10^{-13}	4.9×10^{-12}	2.3×10^{-12}
k_{2000}	1.5×10^{-11}	1.5×10^{-11}	1.5×10^{-13}	8.2×10^{-13}	1.0×10^{-11}	4.1×10^{-12}
k_{2500}	3.6×10^{-11}	3.6×10^{-11}	5.8×10^{-13}	2.9×10^{-12}	1.7×10^{-11}	6.3×10^{-12}

[a] Rate constants include tunneling corrections. Arrhenius parameters and rate constants in units of cm^3 $molecule^{-1}$ s^{-1}

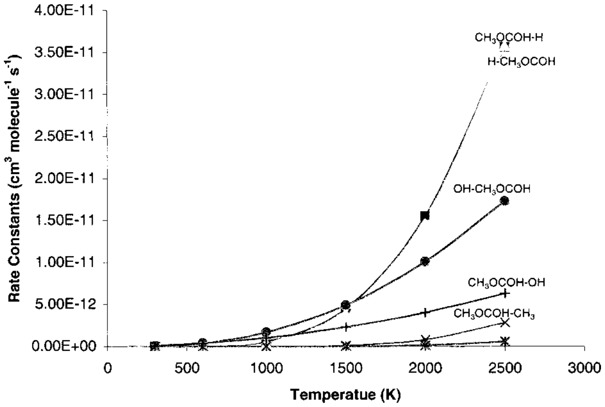

Figure 2. Temperature dependent rate constants (cm^3 molecule^{-1} s^{-1}) for reaction of methyl formate with H, CH_3, and OH.

CH_3 radicals. In all systems (H, CH_3, and OH) the channel with the lowest reaction barrier dictates the favored reaction path at lower temperatures. At 298 K, the dominant reaction channel in all three systems is removal of the carbonyl hydrogen. As the energy of the system increases, however, the preexponential factor begins to influence the overall reaction rate more significantly. For the CH_3 radical initiated system, removal of the carbonyl hydrogen is favored at all temperatures due to both a lower reaction barrier and higher preexponential factor. For the OH radical initiated system, the preference is for removal of the carbonyl hydrogen until a temperature of 600−1000 K is reached, at which point the system favors removal of the methyl hydrogen. Similarly, in the H atom system the methyl hydrogen abstraction channel increases in significance with increasing temperature.

The H radical system reacts significantly faster than the CH_3 system, which is sufficiently slow, that under combustion conditions reactions with H and OH are likely to dominate. At temperatures more consistent with combustion conditions, H atoms effectively compete with OH radicals for reaction with methyl formate.

Regardless of the initiating agent (H, CH_3, OH), dominant reaction products include CH_3OCO and CH_2OCOH. For CH_3-OCO, Good et al.,[13] using ab initio methodology, estimated a barrier height of roughly 14.7 kcal mol^{-1} for dissociation of CH_3OCO to CH_3 and CO_2. This is a modest barrier for a unimolecular reaction and under combustion conditions it is probable that methyl formate combustion would result in the formation of CH_3 and CO_2 through this pathway. For CH_2-OCOH, dissociation to CH_2O and HCO is predicted to have a barrier of 31 kcal mol^{-1}. For this system, molecular oxygen addition reactions may compete.

References and Notes

(1) Rouhi, A. M. *Chem. Eng. News* **1985**, *44*, 37.

(2) Japar, S. M.; Wallington, T. J.; Richert, J. F. O.; Ball, J. C. *Int. J. Chem. Kinet*. **1990**, *22*, 1257.

(3) Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Int. J. Chem. Kinet*. **1988**, *20*, 17.

(4) Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem*. **1997**, *101*, 5489.

(5) Good, D. A.; Francisco, J. S. *J. Phys. Chem*. A **1999**, *103*, 10893.

(6) Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Jenkin, M. E. *Chem. Phys. Lett*. **1993**, *211*, 41.

(7) Notario, A.; Le Bras, G.; Mellouki, A. *J. Phys. Chem*. **1998**, *102*, 3112.

(8) Good, D. A.; Francisco, J. S. *J. Phys. Chem. A* **2000**, *104*, 1505.

(9) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J.; *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling Evaluation #12*, January 1997, Jet Propulsion Laboratory, Pasadena, Ca.

(10) Vesine, E.; Mellouki, A. *J. Chem. Phys*. **1997**, *94*, 1634.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision D.2; Gaussian, Inc: Pittsburgh, PA, 1995.

(12) Curl, R. F. *J. Chem. Phys*. **1959**, *30*, 1529.

(13) Good, D. A.; Francisco, J. S. *J. Phys. Chem. A* **2000**, *104*, 1171.

(14) Curtiss, L. A.; Ragavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys*. **1997**, *106*, 1063.

(15) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(16) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. In *Chemical Kinetics and Dynamics*; Prentice Hall: New York, 1998.

(17) Norton, T. A.; Dryer, F. L. *Int. J. Chem. Kinet*. **1992**, *24*, 319.