A Shock Tube Laser Schlieren Study of Methyl Acetate Dissociation

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The pyrolysis of methyl acetate, 2% dilute in krypton, was investigated in a diaphragmless shock tube (DFST) using laser schlieren densitometry (LS). Experiments were performed at 121±4, and 61±3 Torr over the temperature range of 1548-2334 K. Density gradient profiles obtained from the LS experiments are sensitive to all dissociation channels, primarily resulting in CH$_3$ + CH$_3$ + CO$_2$ through a short lived CH$_3$CO$_2$ intermediate, as well as producing CH$_3$OCO + CH$_3$, and CH$_2$CO + CH$_3$OH. Fitting the density gradients shows close agreement to the calculations based on master equation models. Rate coefficients for dissociation of methyl acetate were satisfactorily simulated with a master equation model with k$_{120\text{Torr}}$ = 1.41x10$^{82}$ ×T$^{-19.08}$ × exp[- 62410/T] s$^{-1}$, and k$_{60\text{Torr}}$ = 2.54×10$^{85}$ ×T$^{-20.25}$ × exp[- 62250/T] for the major channel.

1. Introduction

Biofuels that are being considered as potential replacements for more conventional fuel sources generally contain large fractions of oxygenates, for instance C$_{16}$-C$_{18}$ methyl esters (Kohse-Höinghaus et al. 2010). Typically, precise kinetic and mechanistic studies of the pyrolysis and oxidation of these fuels have not been performed rendering development of accurate combustion models difficult. Obtaining sufficiently accurate kinetic data for the large molecules found in real fuels is challenging; however, general rules can be obtained by analogy with decomposition of smaller species, e.g. methyl formate and methyl acetate, where it is possible to study the fundamental kinetics with sufficient accuracy.

![Figure 1: Reaction scheme of first steps of dissociation. Shown here are the three different reactions possible for the initial breakdown of methyl acetate. The branching between these channels is the target of this study.](image-url)
The current work focuses on the pyrolysis of methyl acetate which initially decomposes by three competing pathways, shown in Fig. 1, leading to either radical products or molecular products. Clearly, the branching ratios between these paths will have a very large effect on the radical pool available to a combustion process, and by determining accurate kinetics, it becomes possible to model the effect this would have on a practical combustor.

Michael and coworkers recently performed some of the first detailed kinetic studies of the decomposition of methyl acetate at high temperature. They used H-ARAS to look at hydrogen atom production as well as detailed electronic structure and master equation methods from the decomposition (Peukert et al. 2012) and bimolecular reactions (Peukert et al. 2013) of methyl acetate. The goal of the studies presented here is to extend the data set available to a larger pressure and temperature range. Furthermore, the technique employed, laser schlieren densitometry (LS), is sensitive to reactions based on their enthalpy and reaction rate instead of hydrogen atom production and loss rates, thus complementary information to the H-ARAS studies about the decomposition process can be obtained. By combining these two data sets with theory this and related decompositions can be thoroughly understood aiding the development of predictive models.

2. Methods

The diaphragmless shock tube has been fully described previously, and as such, only the critical details will be presented here (Tranter and Giri 2008). The driver and driven sections are separated by a bellows actuated fast acting valve, allowing each to be to be loaded to the desired pressures. Both the driver pressure (P4) and the driven pressure (P1) can be independently set allowing for tight control over the post shock pressure after the incident shock (P2) while varying the temperature (T2) over a broad range. A set of five pressure transducers evenly spaced along the side of the driven section are centered around the laser schlieren windows, and incident shock wave velocities were obtained by interpolation of time intervals taken for the shock wave to pass between successive transducers. From these velocities and the loading conditions, the temperature and pressure behind the incident shock wave are calculated assuming frozen conditions. The uncertainty in velocity is estimated as 0.2%, corresponding to a temperature error of less than 0.5%, here amounting to the order of 10-15 K.

The LS technique has also been described previously (Kiefer et al. 1981; Kiefer 1981). The laser schlieren technique utilizes deflection of a narrow beam from a He/Ne laser to measure density gradients behind the incident shock wave. The driven section of the shock tube has quartz windows, through which the laser beam passes, that are located sufficiently far downstream to allow the shock wave to be fully developed after firing. The molar refractivity of Kr is 6.367 (Gardiner et al. 1981) while that of methyl acetate, 17.54, was calculated from its refractive index and molar density. The normal assumption was made that the mixture molar refractivity does not vary with extent of reaction. The normal assumption was made that the mixture molar refractivity does not vary with extent of reaction.

Mixtures containing 2% methyl acetate dilute in krypton were prepared manometrically in a 50 L glass vessel that had been evacuated to <10-3 Torr. Krypton (AirGas 99.999%), was used as supplied. Methyl Acetate (Aldrich Chemical Co., 99.5%) was degassed by repeated freeze–pump–thaw cycles with liquid nitrogen prior to preparing the mixture. Reagent mixtures were stirred for 1 hour using a Teflon-coated magnetic stirrer before use.
3. Results and Discussion
Experiments were performed at $P_2 = 34 \pm 2$, $61 \pm 3$ and $121 \pm 4$ Torr over the range 1548-2334 K. Examples of the raw experimental data are shown in Fig. 2. The valley and large peak evident in each figure are due to interaction of the shock front with the laser beam. The tailing signal to the right of the large peak is due to chemical reaction and is the region of interest. The location of $t_0$, the start of reaction, is obscured by the large spike and located by a well-established procedure to within 0.1-0.2 µs. The raw data are converted to density gradients and displayed on semi-log plots such as those shown in Fig. 3. In these plots the first few steeply falling points are the tail of the large schlieren spike from Fig. 2 and the ‘chemical’ signal is located by the sharp excursion in the signal. At $t_0$ the sole reaction occurring is dissociation of methyl acetate and the density gradient at $t_0$ is directly proportional to the rate of dissociation. Thus, by extrapolating the data back to $t_0$ the rate can be obtained. Initially, these extrapolations are done by eye and latter refined through simulation of the complete density gradient with a chemical mechanism.

Methyl acetate decomposes by three channels, R1-R3, and initial rates of decomposition were taken from Peukert et al. (2012) but recalculated for the pressures of the current experiment. As mentioned earlier the initial dissociation is the only contributor to the signal at time zero, and as there are three potential paths that methyl acetate can dissociate by it is potentially difficult to obtain anything but a total rate of dissociation. However, LS experiments are sensitive to both the rate of reaction and the enthalpy of reaction and as shown in the simplified mechanism in Table 1 R1-R3 have very different heats of reaction. Reactions 1 and 2 are strongly endothermic bond breaking reactions generating radicals and differ only by which side of the C-O-C(=O)-C moiety breaks, as shown in Fig. 1. In the first channel, R1, the bond between the methyl group and the acetate group breaks creating a methyl radical and an acetate radical, $\text{CH}_3\text{C}(O)\text{O}$, which immediately dissociates by ejecting a second $\text{CH}_3$ radical and forming a stable $\text{CO}_2$ molecule. $R_2$ proceeds by breaking the C-C bond in the acetate moiety forming $\text{CH}_3$ and $\text{CH}_3\text{OCO}$ radicals. The $\text{CH}_3\text{OCO}$ rapidly decomposes along two channels creating $\text{CH}_3^+ + \text{CO}_2$, $R_4$, and $\text{CH}_3\text{O} + \text{CO}$, $R_5$. The methoxy radical further decomposes at the temperature
of the current work to formaldehyde and a hydrogen atom (McCunn et al. 2008; Farooq et al. 2009). The third channel for pyrolysis of methyl acetate, R₃, generates only molecular products methanol (CH₃OH), and ketene (CH₂CO).

Table 1: Reaction rates and enthalpies for the most important reactions in the decomposition of methyl acetate (MA). \( k = A T^n \exp(-E_a/RT) \). Units: mol, cm, s, kcal.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log A</th>
<th>N</th>
<th>Ea</th>
<th>( \Delta H_{\text{rxn}}(298 \text{ K}) )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MA = (CH₃CO₂ + CH₃) = CH₃ + CH₃ + CO₂ (120 Torr)</td>
<td>82.15</td>
<td>-19.07</td>
<td>124</td>
<td>64.5</td>
<td>This work</td>
</tr>
<tr>
<td>2 MA = CH₂OCO + CH₃ (120 Torr)</td>
<td>85.45</td>
<td>-20.24</td>
<td>129</td>
<td>93.2</td>
<td>This work</td>
</tr>
<tr>
<td>3 MA = CH₂CO + CH₃OH</td>
<td>69.73</td>
<td>-16.10</td>
<td>110.2</td>
<td>26.5</td>
<td>This work</td>
</tr>
<tr>
<td>4 CH₂OCO = CH₃ + CO₂</td>
<td>10.90</td>
<td>1.11</td>
<td>15.9</td>
<td>-28.7</td>
<td></td>
</tr>
<tr>
<td>5 CH₂OCO = CH₂O + H + CO</td>
<td>12.48</td>
<td>0</td>
<td>21.1</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>6 MA + CH₃ = CH₂OC(O)CH₂</td>
<td>-0.69</td>
<td>3.88</td>
<td>8.2</td>
<td>-4.9</td>
<td>Peukert et al. 2012</td>
</tr>
<tr>
<td>7 MA + CH₃ = CH₂OC(O)CH₃</td>
<td>-0.89</td>
<td>3.93</td>
<td>8.8</td>
<td>1.3</td>
<td>Peukert et al. 2012</td>
</tr>
<tr>
<td>8 MA + H = CH₂OC(O)CH₂</td>
<td>5.02</td>
<td>2.40</td>
<td>5.1</td>
<td>21.8</td>
<td>Peukert et al. 2012</td>
</tr>
<tr>
<td>9 MA + H = CH₂OC(O)CH₃</td>
<td>5.85</td>
<td>2.58</td>
<td>7.4</td>
<td>15.8</td>
<td>Peukert et al. 2012</td>
</tr>
<tr>
<td>10 CH₂OC(O)CH₂ = CH₂CO + CH₂O + H</td>
<td>13.51</td>
<td>0</td>
<td>41.7</td>
<td>64.4</td>
<td>Westbrook et al. 2009</td>
</tr>
<tr>
<td>11 CH₂OC(O)CH₃ = CH₂O + CH₃ + CO</td>
<td>13.92</td>
<td>0</td>
<td>13.0</td>
<td>38.1</td>
<td>Westbrook et al. 2009</td>
</tr>
<tr>
<td>12 C₂H₆ + M = CH₃ + CH₃ + M</td>
<td>18.50</td>
<td>0</td>
<td>69.99</td>
<td>90.2</td>
<td>Yang et al. 2009</td>
</tr>
<tr>
<td>13 CH₃ + CH₃ = C₂H₆ + H</td>
<td>13.68</td>
<td>0</td>
<td>16.05</td>
<td>10.6</td>
<td>Yang et al. 2009</td>
</tr>
</tbody>
</table>

From consideration of the enthalpies of reaction in Table 1 it might be expected the LS experiments would be most sensitive to R₂ and show little sensitivity to R₃ unless R₃ was by far the dominant reaction path. Furthermore, if R₃ was dominant then only weak initial density gradients would be observed rather than the strong ones seen in Fig.3. Consequently, simple examination of the experimental data indicates that R₃ must be a minor channel and this is compatible with the rates of reaction obtained from Peukert et al. (2012).

Simulation of the density gradient profiles show that R₁ is by far the dominant channel accounting for around 80% of the observed density gradient at t₀ with R₂ and R₃ each contributing around 10% of the signal. Thus the rates coefficients for reactions R₂ and R₃ were fixed at the values obtained from Peukert et al. (2012), with R₂ recalculated for these pressures from the master equation calculations based on Peukert et al. (2012) and \( k_{R₁} \) was varied to obtain the best fit to the experimental data. The sensitivity to the rate of reaction 1 is shown in Fig. 3 through increasing and decreasing the rate by 30%. The \( k_{R₁} \) obtained from each experiment are shown on an Arrhenius plot in Fig. 4 where the pressure dependence is clearly resolved.
Figure 3: Shown are two representative density gradients from 2% methyl acetate dilute in krypton. These correspond to the raw signals in Fig. 1. The open circles indicate a positive value for the density gradient, while the closed circles represent a negative density gradient. (a) A low temperature experiment where the majority of the signal is from the decomposition of methyl acetate. (b) An intermediate temperature experiment that shows the classical switch from positive to negative density gradients as a strong exothermic process begins to dominate the observed signal. Also shown with the different broken lines is the sensitivity to the rate of reaction 1, where it is clear that a 30% change in rate no longer fits the data.

The decomposition of methyl acetate produces two reactive radicals, H and CH₃, and thus secondary, bimolecular reactions involving these species are significant. In Fig. 3b the experimental density gradients go negative prior to returning to the baseline at long times. This behavior is actually seen at all temperatures in methyl acetate decomposition and as the temperature increases the crossing point from positive to negative simply occurs at shorter reaction times. In a system containing a large number of methyl radicals this behavior is symptomatic of the strongly exothermic recombination of methyl radicals, R₁₂. Methyl recombination has been previously studied under similar conditions by Yang et al. (2009) and the complete mechanism, not shown in Table 1, is incorporated in the simulations.

At low to intermediate temperatures, most of the reactive species, primarily hydrogen atoms and methyl radicals, are most likely to encounter a parent molecule before any other organic species. The reaction of methyl acetate with hydrogen atoms has been studied previously by Peukert et al (2013) and their rate is used without adjustment. Similarly, the rate of reaction of methyl radicals with methyl acetate was also taken from Peukert et al. (2012). Both H-atom and methyl radical can abstract H-atoms from either the esteric methyl or the alkyl backbone (reactions R₈, R₉, R₆ and R₇). Abstraction from the esteric methyl ultimately leads to formation of formaldehyde, carbon monoxide and a methyl radical. Whereas, abstraction from the alkyl side generates formaldehyde, ketene and an H-atom. Dissociation of the radicals produced by reaction of H-atoms and methyl radicals with methyl acetate are quite strongly endothermic and contribute significantly to the observed density gradient before the very exothermic methyl recombination reaction dominates the signal. Finally, at the higher temperatures of this work reactions of H-atoms and methyl radicals with methanol produced from the molecular channel (R₃) also influence the observed density gradient by effectively generating large positive gradients. Again this is due to strongly endothermic decompositions of
radical products formed by the abstraction reactions rather than the abstraction reactions themselves. Correctly estimating the effect of H/CH$_3$ +CH$_3$OH is problematic because the LS technique is nearly blind to R3 and it is necessary to rely on branching ratios for methyl acetate decomposition from other studies to estimate the production of methanol and the effect is further exacerbated by uncertainty in the rate of CH$_3$ +CH$_3$OH (Alecu and Truhlar 2011a; Alecu and Truhlar 2011b). Further experiments at higher and lower concentrations are in progress in an attempt to refine the secondary chemistry.

**Pressure Dependence**

The potential energy surface and associated master equation calculations are based on the work of Peukert et al. (2012). Briefly, the minima and transition states were found with B3LYP/6-311++G(d,p), with the energies estimated with CCSD(T)/cc-pV$\infty$Z. Master equation calculations were performed with the VariFlex code. Rate constants were calculated for all pressures used in this study, as well as the previous study by Peukert et al. The rates were then scaled by 1.4. this scaling results in good fits to the 120 and 30 Torr data but under predicts the 60 Torr data by a factor of 1.6. The source of this disagreement is not yet clear nor is the reason for the need to scale the master equation results. However, the scaling factor can result from many different factors such as error in barrier heights to requiring a different $\Delta E$. Further refinement of rate constants and more data points are necessary for a through fitting of this and finding where this factor comes from within the model.

**4. Conclusions**

The pyrolysis of methyl acetate has been studied over a broad range of temperatures and pressures expanding the range of experimental data available and resolving the high temperature pressure dependence for the initial dissociation. The LS experiments were particularly sensitive to R1 and rate coefficients were obtained for this channel. These are in good agreement with master equation calculations based on work by Peukert et al. (2012) apart from at 60 Torr.
Currently, the scope of the LS experiments is being expanded to refine the estimates of $k_{R1}$ and examine the effects of secondary chemistry on simulation of the density gradient profiles.

**Acknowledgements**

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy, under contract number DE-AC02-06CH11357.

**References**


