# A new product channel in the reaction OH + CH$_3$CHO

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Acyl radicals play an important role in atmospheric and combustion chemistry.[1] In the atmosphere they react (O_2/NO_2) to form peroxy acyl nitrate, which is an important component of polluted environments.[2]
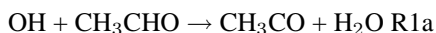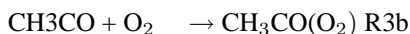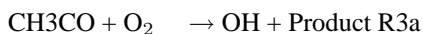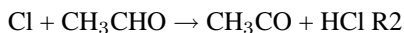
A major source of acetyl studies in the atmosphere is from the reaction between OH and acetaldehyde. Previous studies [3] indicate that the reaction occurs almost exclusively via the abstraction of the aldehydic H to produce acetyl and water:

$$OH + CH_3CHO \rightarrow CH_3CO + H_2O \quad R1a$$
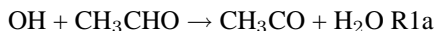
In the present study we have investigated this reaction, R1a, using laser flash photolysis to initiate the reaction and a time-of-flight mass spectrometer to monitor the time evolution of the reaction products. In the system acetyl was observed to be the major product but there was also a significant amount of methyl:

$$OH + CH_3CHO \rightarrow CH_3 + CO + H_2O \quad R1b$$

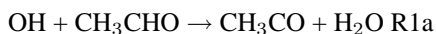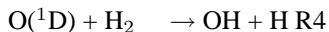We have conducted a series of experiments in order to quantify the CH3 yield, R1b / R1a+R1b. The first type of experiment used a recycling scheme:

$$Cl + CH_3CHO \rightarrow CH_3CO + HCl \quad R2$$

$$CH3CO + O_2 \rightarrow OH + Product \quad R3a$$

$$CH3CO + O_2 \rightarrow CH_3CO(O_2) \quad R3b$$

$$OH + CH_3CHO \rightarrow CH_3CO + H_2O \quad R1a$$

$$OH + CH_3CHO \rightarrow CH_3 + CO + H_2O \quad R1b$$

These experiments determined that CH$_3$ was formed with a significant yield (~ 0.3) but with large uncertainty due to the inherent problems associated with recycling.

Generating OH in the absence of oxygen avoids the problems associated with recycling:

O(^{1}D) + H$_2$ $\quad \rightarrow$ OH + H R4

OH + CH$_3$CHO $\rightarrow$ CH$_3$CO + H$_2$O R1a

OH + CH$_3$CHO $\rightarrow$ CH$_3$ + CO + H$_2$O R1b

We have generated O(^{1}D) by photolysing ozone, with added H$_2$O to relax the excited OH. However, the ozone was produced in the presence of oxygen but under conditions where R1 and recycling (R3) were significantly decoupled, i.e. smaller inherent errors. These experiments determined the CH$_3$ yield from R1 to be > 0.25; this lower limit is due to OH wall losses.

Further experiments are being conducted using a coated, wall reactor in order to reduce wall losses and also using N$_2$O (193 nm photolysis) as the O^{1}D source in order to produce OH in the absence of oxygen. These further experiments should better quantify the CH$_3$ yield from R1.

In addition, the OH + CH$_3$CHO reaction has also been studied theoretically by assigning the statistical energy distribution of the CH$_3$CO and then performing a Master Equation on the resultant CH$_3$CO dissociation. This calculation predicts a CH$_3$ yield for R1 of $\sim$0.5.

This new CH$_3$ channel has very important implications because it significantly reduces the amount of acetyl radicals available for PAN formation. In addition, the ozone potential of acetyl, R1a, is greater than CH$_3$, R1b. These effects on PAN and ozone formation require further quantifying by modelling.

[1] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi and J. Troe, 6, 3625, (2006).

[2] Finlayson-Pitts; and J. N. B. J.; Pitts *Chemistry of the Upper and Lower Atmosphere : Theory, Experiments, and Applications*; Academic Press, 1999.

[3] M. Cameron, V. Sivakumaran, T. J. Dillon and J. N. Crowley, *Phys. Chem. Chem. Phys.* 4, 3628, (2002).