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# Pressure Dependent Quantum Yields of $CH_3$ Formation from Photolysis of Acetone, MethylEthylKetone and Acetyl Bromide

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The photochemistry and photophysics of acetone has received much attention over the last few years. Much of the recent research has been stimulated by the recognition that acetone can play an important role in the chemistry of the atmosphere, where it may provide a significant (or even dominant) fraction of the HO$x$ radical and PAN production rate in the cold upper troposphere. So, a correct description of the wavelength, temperature and pressure dependence ($\lambda$, P, T) of the primary quantum yield is essential for understanding the role of acetone in the chemistry of the free and upper troposphere.

Dissociation of acetone can occur with fission of the C-C bond to form acetyl (CH3CO) and methyl (CH3) radicals as a primary step (R1) and could be described by following scheme:

CH3C(O)CH3 + $h\nu \rightarrow$ CH3 + CH3CO$^{\#}$ (R1)

CH3CO$^{\#} \rightarrow$ CH3 + CH3CO$^{\#}$ (R2)

CH3CO$^{\#}$ + M $\rightarrow$ CH3CO + M (R3)

If the amount of available energy is enough, the excited co fragment CH3CO$^{\#}$ could be decomposed through channel (R2) or thermalized, channel (R3).

In the present study, the formation of CH3 in the 248 nm or 266 nm photolysis of acetone (CH3C(O)CH3), 2-butanone (methylethylketone, MEK, CH3C(O)C2H5) and acetyl bromide (CH3C(O)Br) was examined using the pulsed photolytic generation of the radical and its detection by transient absorption spectroscopy at 216.4 nm. Experi-

ments were carried out at room temperature (298±3 K) and at pressures between ≈ 5 and 1500 Torr N2. Quantum yields for CH3 formation were derived relative to CH3I photolysis at the same wavelength in back-to-back experiments.

We have determined that:

- the yield of CH3 radicals from the photolysis of both CH3C(O)CH3 and CH3C(O)C2H5 at 248 nm depends on the bath gas pressure indicating competition between the dissociation (to CH3 + CO) and quenching of vibrationally excited nascent CH3CO radicals.
- For acetone, at other wavelengths (193 and 266 nm) CH3 quantum yields are independent of pressure due to either complete dissociation (193 nm) or no dissociation of acetyl (266 nm).

Although our experiments were carried out at wavelengths which are not important for acetone photolysis in the atmosphere, they may have some implications for acetone photolysis rates which have been derived assuming that the CH3CO yield at 248 nm is independent of pressure.