

Experimental and Theoretical study of the reaction of OH with the aromatic molecule p-cymene, proceeding via two adducts

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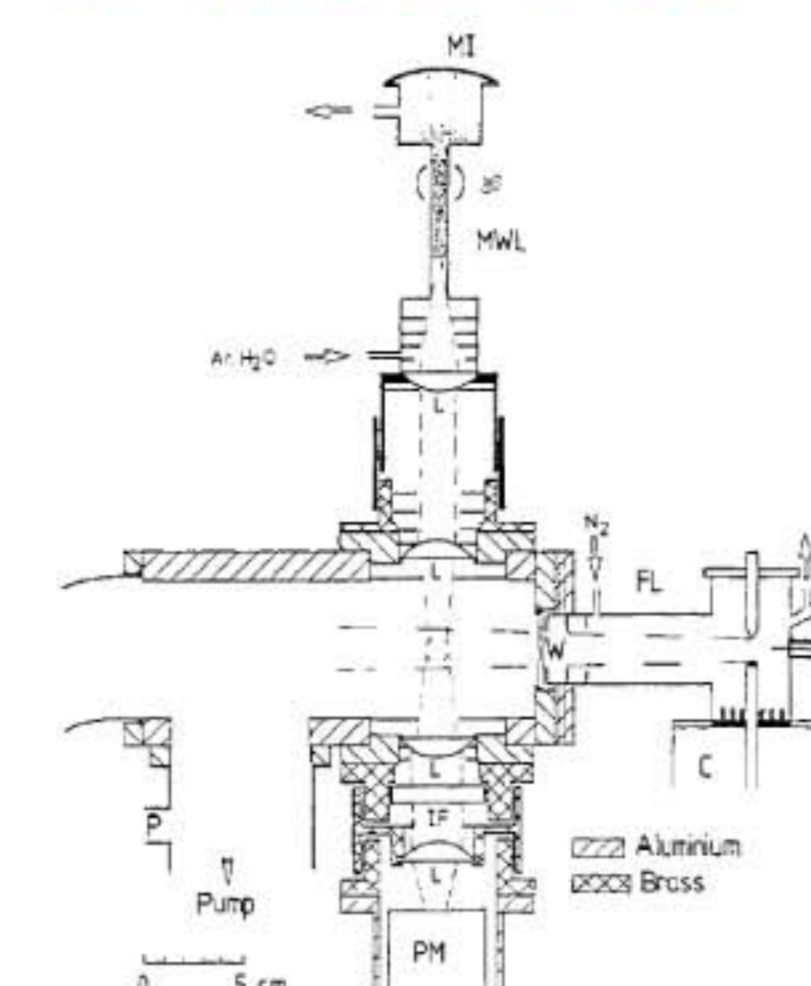
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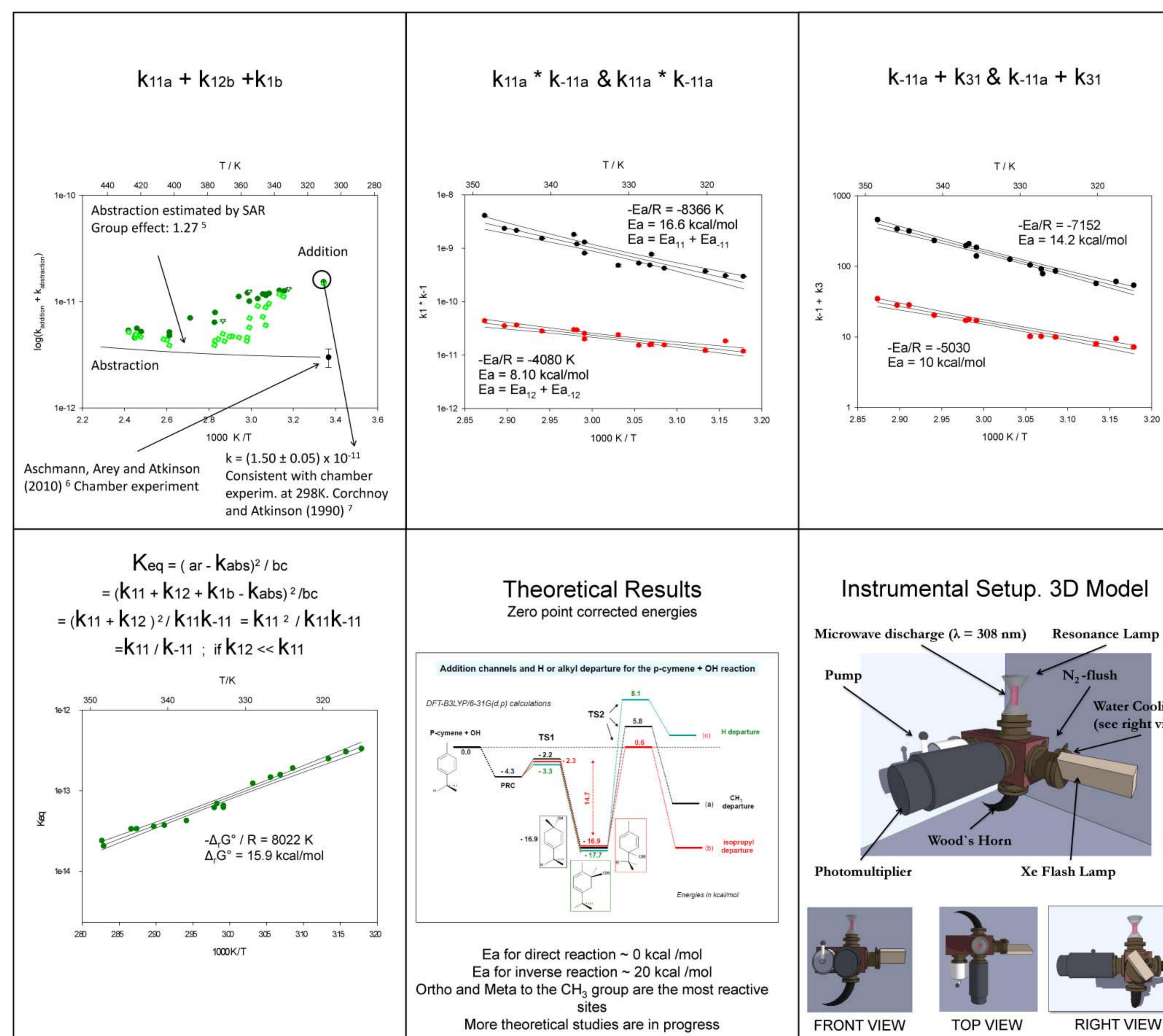
INTRODUCTION

Nonmethane volatile organic compounds (NMVOCs) play a major role in the photochemical formation of ozone and secondary aerosols, and both processes are initiated by OH radicals^{1,2}, which are important in combustion as well. The biogenic NMVOC p-cymene has four available positions where the OH radical may add to the aromatic ring: two equivalent ones ortho to the isopropyl group and two equivalent ortho to the methyl group. Ipso addition, i.e., addition to an already substituted position, is generally considered as unimportant^{3,4}, but cannot be excluded.

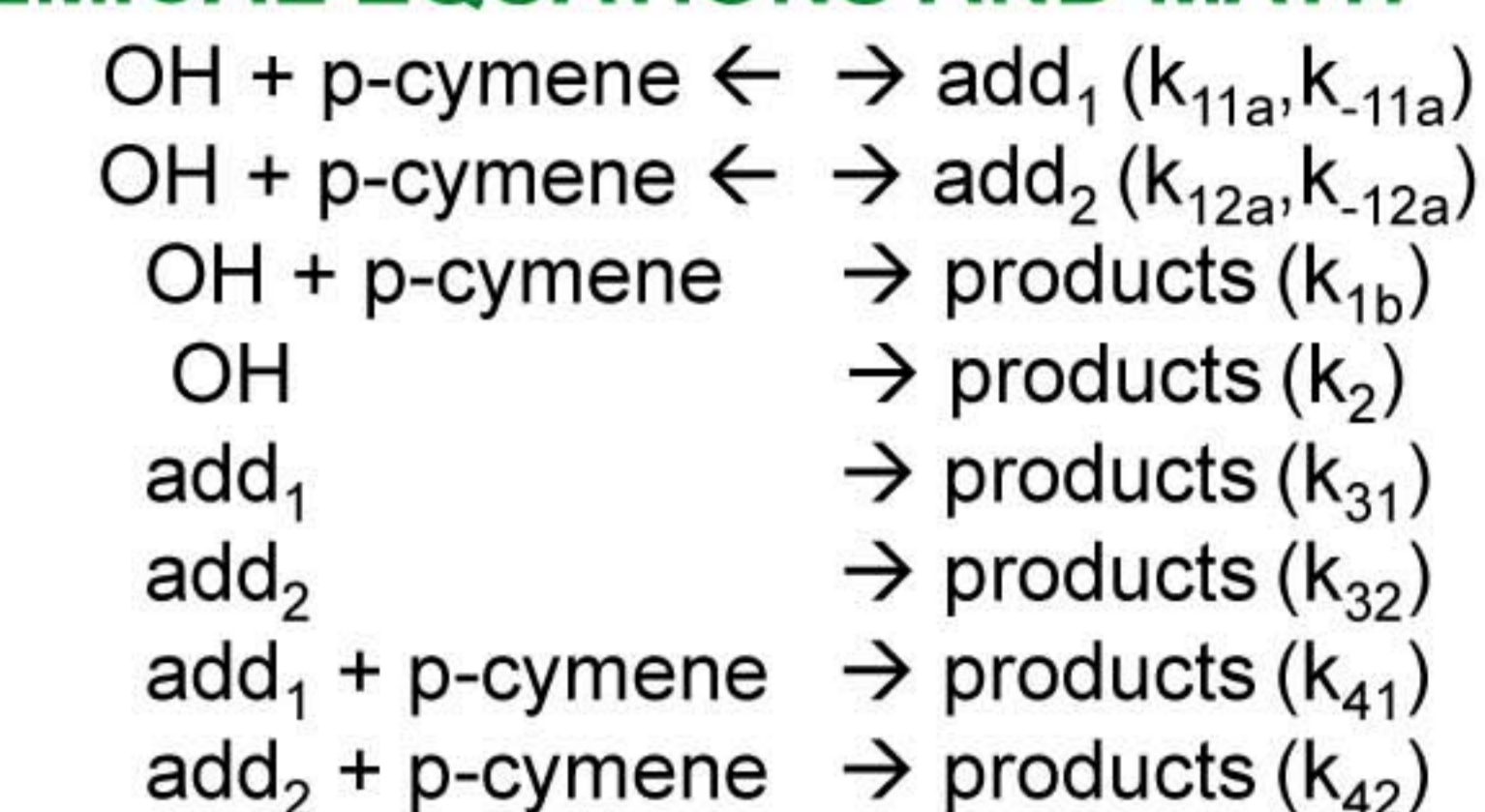
METHODS

Reactions of OH radicals with aromatics is studied by pulsed vacuum UV flash photolysis of water and time resolved resonance fluorescence. Initial concentrations of OH are around 10^{10} cm^{-3} and are small against those of the aromatics, providing pseudo-first-order decays of the resonance fluorescence intensity (known to be strictly proportional to OH concentration).

Temperature of the system was varied between 298 and 403 K at a total pressure of He of 195 mbar. Concentration of p-cymene was varied between 0 and $40 \times 10^{12} \text{ cm}^{-3}$.



CHEMICAL EQUATIONS AND MATH



$$\begin{aligned} \frac{d[\text{OH}]}{dt} &= -a[\text{OH}] + b[\text{add}_1] + e[\text{add}_2] \\ \frac{d[\text{add}_1]}{dt} &= c[\text{OH}] - d[\text{add}_1] \\ \frac{d[\text{add}_2]}{dt} &= f[\text{OH}] - g[\text{add}_2] \end{aligned}$$

$$\begin{aligned} a &= (k_{11a} + k_{12a} + k_{1b}) [\text{aromat}] + k_2 \\ b &= k_{-11a} \\ c &= k_{11a} [\text{aromat}] \\ d &= (k_{-11a} + k_{31}) + k_{41} [\text{aromat}] \\ e &= k_{-12a} \\ f &= k_{12a} [\text{aromat}] \\ g &= (k_{-12} + k_{32}) + k_{42} [\text{aromat}] \end{aligned}$$

CONCLUSIONS

- Obtained total rate constant, $(1.50 \pm 0.05) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, is consistent with the published value by Corchnoy and Atkinson in a chamber study at 298K ($1.51 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$)
- The Arrhenius plot shows a linear dependence up to 350 K. Above that temperature, the formation of the second adduct is not negligible against the formation the first adduct.

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