

Kinetics of Reactions of Combustion Importance at Elevated Temperatures and Pressures

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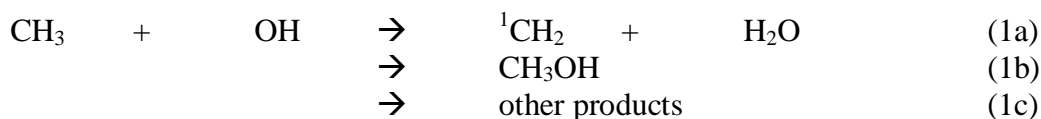
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An experimental study of several elementary reactions of methyl and hydroxyl radicals over extended (0.01 - 100 bar, 298 – 834 K for OH+OH, 1-100 bar, 298 – 715 K for CH₃+OH and CH₃+CH₃) pressure and temperature ranges by pulsed excimer laser photolysis coupled with transient absorption spectroscopy was completed. Acetone was used as a photochemical precursor of CH₃ radicals at 193 nm, photolysis of N₂O/H₂O was used to produce OH radicals at 193 nm (via the fast reaction O(¹D) + H₂O). Methyl and hydroxyl radicals were monitored by transient absorption at 215 nm and 308 nm, respectively.

In the reaction of methyl radicals with hydroxyl radicals



no pressure dependence was found over the pressure range 1 – 100 bar at all temperatures, indicating negligible contribution of the pressure dependent stabilization channel 1b. These measurements fill the gap between the near ambient temperature and high temperature shock tube studies of reaction 1.^{1,2}

In the self-reaction of hydroxyl radical

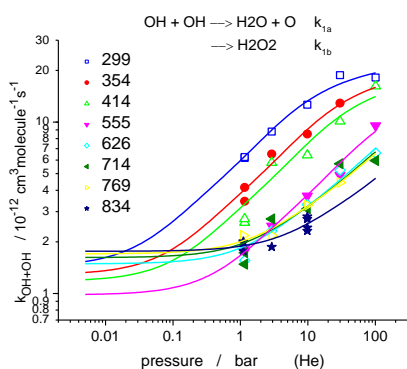
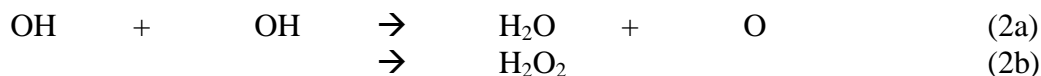


Figure 1.

new parameterization of the pressure dependent channel 2b was obtained (Fig. 1). The low pressure extrapolation of the high temperature data combined with the literature data and our recent measurements at low temperatures unambiguously indicate a turning point in the temperature dependence of the rate constant of reaction 2a at about 500 K.

The rate constant of recombination of methyl radicals 3 was characterized over the extended temperature and pressure ranges.



References

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- (2) Vasudevan, V.; Cook, R. D.; Hanson, R. K.; Bowman, C. T.; Golden D. M. *Int. J. Chem. Kin.* **2008**, 40, 488-495.