

2B04: MEASUREMENTS OF THE RATE OF $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ ($\text{M} = \text{N}_2, \text{AR}, \text{H}_2\text{O}$) FROM IGNITION OF SYNGAS AT PRACTICAL CONDITIONS.

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Comment by Matthew Oehlschlaeger, Rensselaer Polytechnic Institute, USA

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You show a change in measured ignition time for mixtures with like H_2 and O_2 concentrations but different bath gases. How much does the reactant gas heat capacity influence this observation?

Reply by John Mertens

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The differences in ignition delay time between the mixtures having a nitrogen bath gas and those having an argon bath gas are due more to chemical kinetic effects than to thermal, i.e. specific heat, effects. When running CHEMKIN using the CO/hydrogen mechanism, the differences in specific heats for different bath gases are taken into account through the conservation of energy relation. Therefore, any differences in ignition delay time between the two mixtures with different bath gases as determined using CHEMKIN would then be due to the chemical kinetics, which in the present case can be attributed primarily to the collision efficiency of the inert species. Specific heat differences in the context of vibrational relaxation are also not the cause of the differences seen in the experiments herein. We have shown in a previous publication that vibrational relaxation times for such mixtures are a small fraction of the ignition delay time [1]. Even if the relaxation time were a significant percentage of the ignition delay time, the gas temperature for nitrogen would then be higher than the post-shock equilibrium temperature during the relaxation time, leading to a faster ignition. In contrast, we saw faster ignition in the mixture with argon as the inert species. Finally, specific heat effects in terms of heat loss to the facility walls is not a factor for the shock-tube experiments herein because the time scales needed for there to be any significant heat loss would be about a factor of ten longer than any of the ignition times in our paper.

Reference:

[1] D.M. Kalitan, J.D. Mertens, M.W. Crofton, E.L. Petersen, *Journal of Propulsion and Power* 23 (6) (2007) 1291–1303.

Comment by Hai Wang, University of Southern California, USA

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In a recent theoretical study [1], we concluded that the rate coefficient of $\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$ should be revised downward from what was used in the model of Davis et al. [2]. The new rate expression is $k \text{ (cm}^3/\text{mol}\cdot\text{s)} = 10^5 T^2 .18 \exp(-9030/T)$ for $300 < T < 2500$

K. For $1000 < T < 1500$ K, the new rate constant is a factor of ~ 4 smaller than what was used earlier. Could you comment on the impact of this downward revision on your data interpretation?

References:

[1]. X. You, H. Wang, E. Goos, C.J. Sung, S.J. Klippenstein, *J. Phys. Chem. A* 111, (2007) 4031–4042).

[2]. S.G. Davis, A.V. Joshi, H. Wang, F. Egolfopoulos, *Proc. Combust. Inst.* 30, (2005) 1283–1292.

Reply by John Mertens

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Using this new rate for $\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$ in the Davis mechanism has no effect on our determination of the rate of the title reaction for our low pressure (1 atm) experiments. It reduces our determination of the title reaction by about 15% for our intermediate pressures (2.5 atm), and by about 30% at our higher pressures (14 atm). This actually improves the agreement between our data and the rate expressions of Bates et al. (2000) for the falloff regime. All of our experiments for $M = \text{Ar}$ and $M = \text{H}_2\text{O}$ were at 1 atm, and are not affected.