Article:
Stone, D, Blitz, M orcid.org/0000-0001-6710-4021, Ingham, T et al. (3 more authors) (2016) An instrument to measure fast gas phase radical kinetics at hight temperatures and pressures. Review of Scientific Instruments, 87. 054102. ISSN 0034-6748

https://doi.org/10.1063/1.4950906

An instrument to measure fast gas phase radical kinetics at high temperatures and pressures

Daniel Stone,[1] Mark Blitz,[1,2] Trevor Ingham,[1,2] Lavinia Onel,[1] Diogo J. Medeiros[1]

and Paul W. Seakins[1,2]

[1] School of Chemistry, University of Leeds, Leeds, UK

[2] National Centre for Atmospheric Science, University of Leeds, Leeds, UK

Supplementary Information

The reaction of OH with methane was investigated at probe distances of < 5 mm and 50 mm at room temperature and a total pressure of 760 Torr. Kinetic results obtained at a probe distance of < 5 mm (Figures S1 and S2) gave $k_{OH+CH4} = (6.5 \pm 0.2) \times 10^{-15}$ cm^3 s^{-1}, in agreement with literature recommendations of $k_{OH+CH4} = 6.3 \times 10^{-15}$ cm^3 s^{-1} (1), while those at a probe distance of 50 mm (Figures S3 and S4) gave $k_{OH+CH4} = (3.2 \pm 0.2) \times 10^{-15}$ cm^3 s^{-1} owing to the effects of sampling outside the supersonic jet as discussed in the main text.

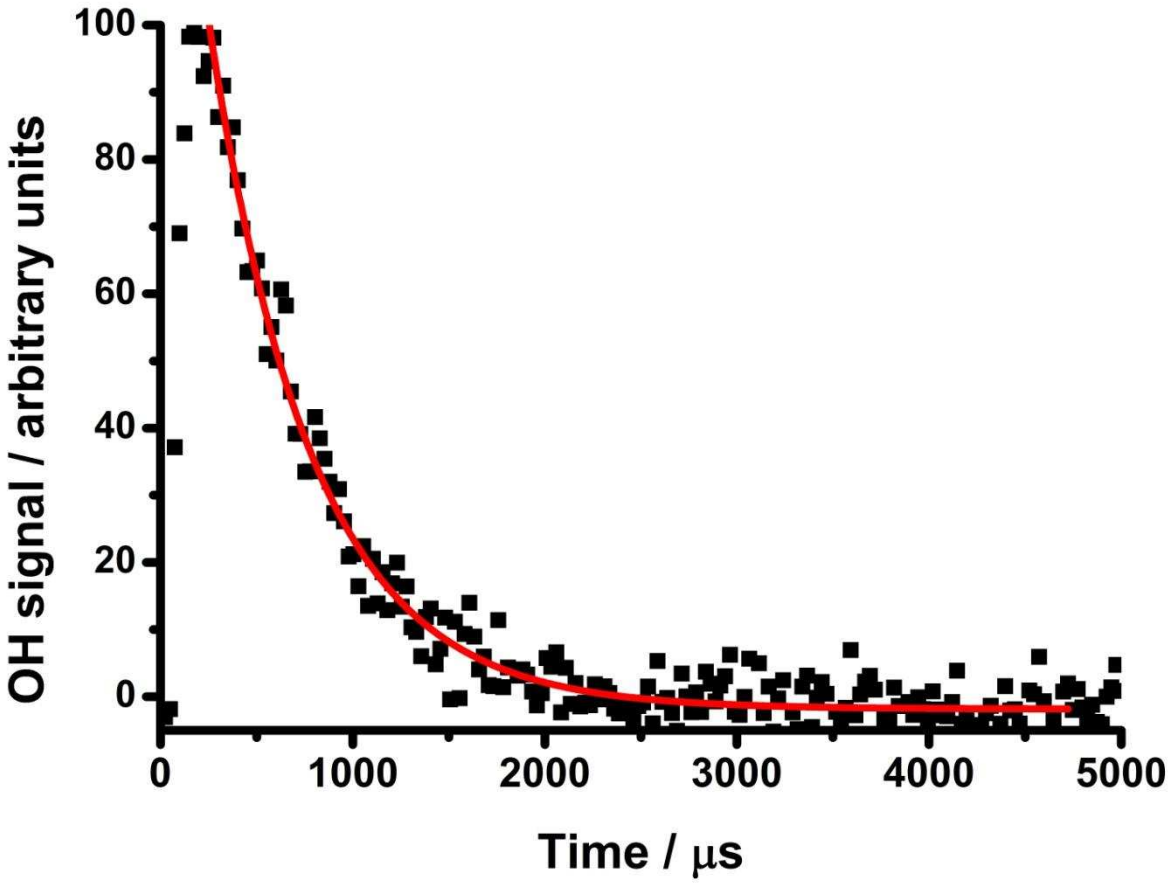

Figure S1: Temporal behaviour of OH signals for reaction of OH + CH_4 at a probe distance < 5 mm. The data shown were obtained with the reaction cell at 298 K, 760 Torr, detection cell at 0.8 Torr and [CH_4] = 2.3 × 10^{17} cm^{-3}. The fit to the data is shown in red and gives k' = (1890 ± 50) s^{-1}.

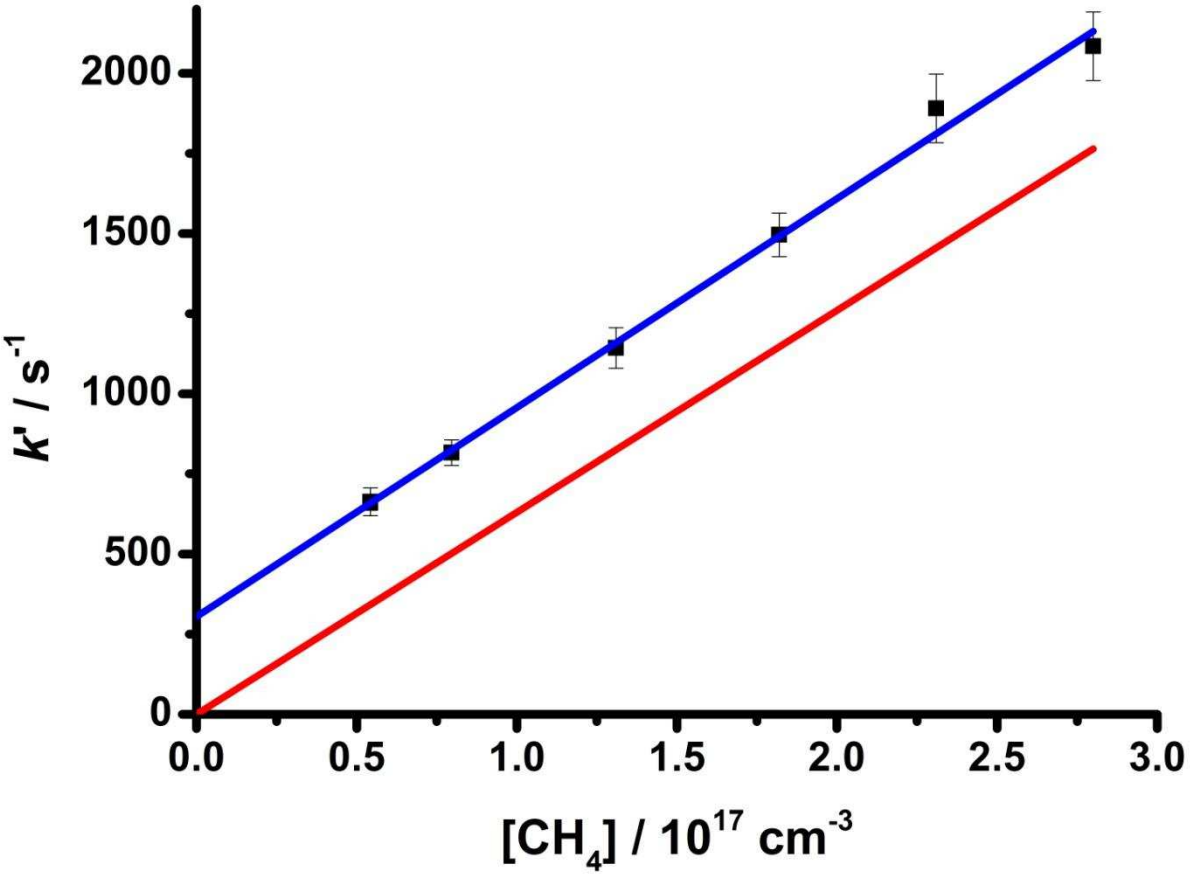

Figure S2: Bimolecular plots of observed OH decay kinetics at 298 K and 760 Torr, with the detection cell at a pressure of 0.8 Torr, for a sampling distances < 5 mm, for the reaction of OH with CH_4. The best fit line is shown in blue; ($k = (6.5 \pm 0.2) \times 10^{-15}$ cm^3 s^{-1}. The literature recommendation is shown in red ($k = 6.3 \times 10^{-15}$ cm^3 s^{-1}) (1). Errors are 2σ.

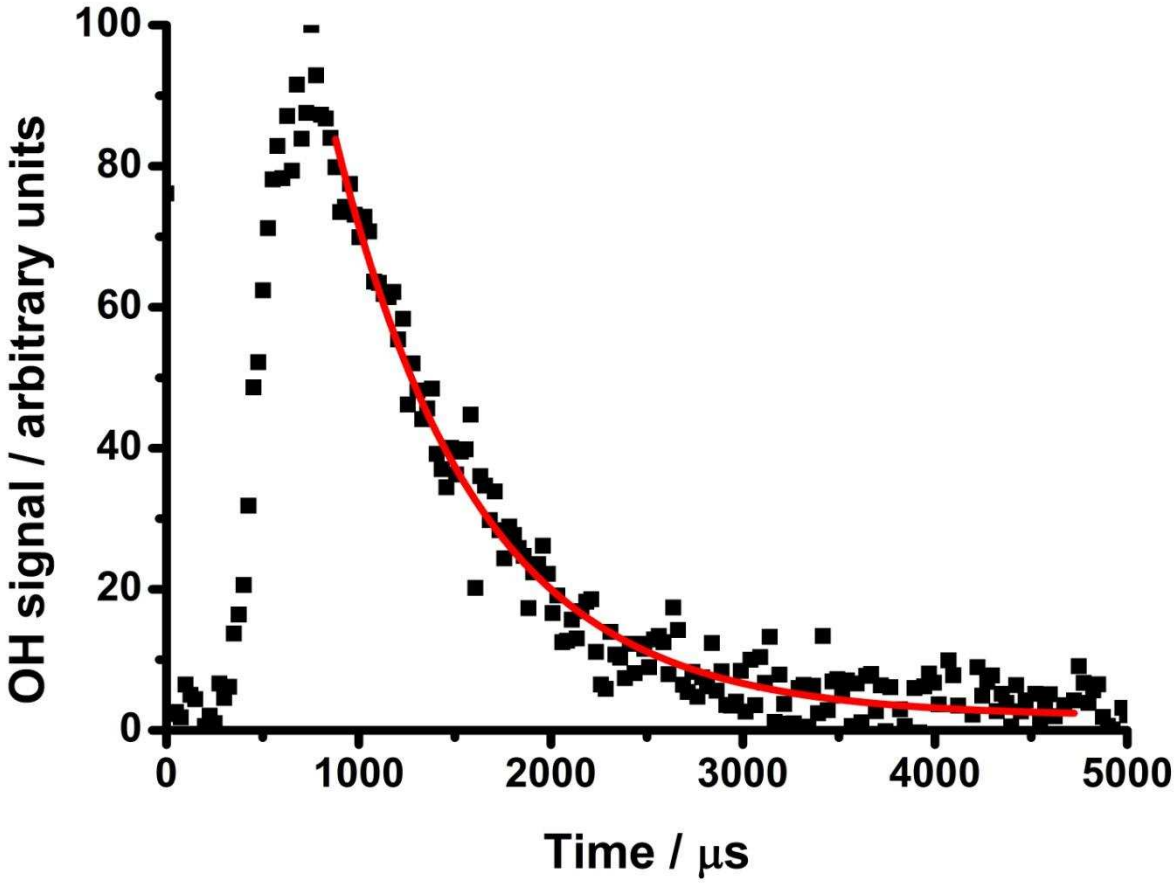

Figure S3: Temporal behaviour of OH signals for reaction of OH + CH_4 at a probe distance of 50 mm. The data shown were obtained with the reaction cell at 298 K, 760 Torr, detection cell at 0.8 Torr and [CH_4] = 3.2 × 10^{17} cm^{-3}. The fit to the data is shown in red and gives k' = (1350 ± 50) s^{-1}.

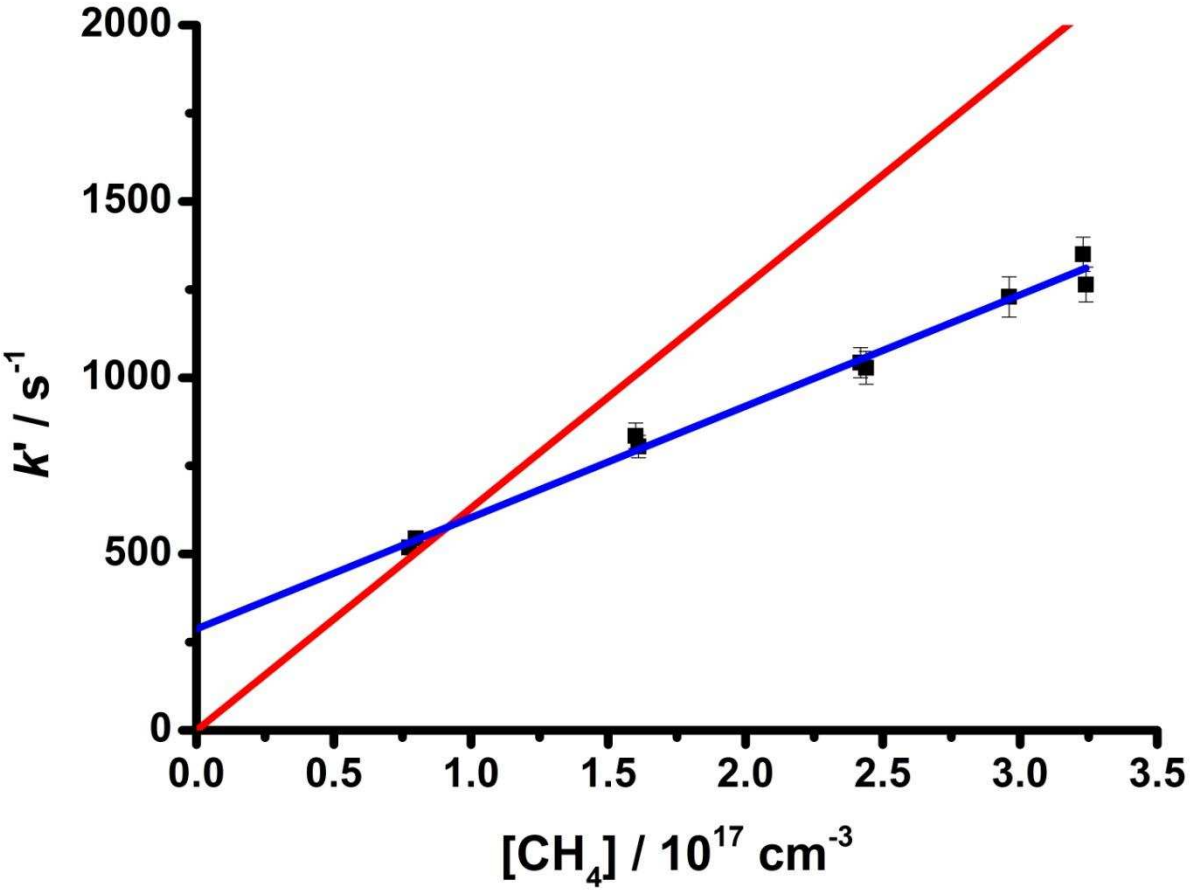

Figure S4: Bimolecular plots of observed OH decay kinetics at 298 K and 760 Torr, with the detection cell at a pressure of 0.8 Torr, for a sampling distance of 50 mm, for the reaction of OH with CH_4. The best fit line is shown in blue; ($k = (3.2 \pm 0.2) \times 10^{-15}$ cm^3 s^{-1}. The literature recommendation is shown in red ($k = 6.3 \times 10^{-15}$ cm^3 s^{-1}) (1). Errors are 2σ.

The reaction of OH with isoprene (2-methyl-1,3-butadiene, C_5H_8) was also investigated at room temperature (303 K) at a total pressure of 1400 Torr in order to demonstrate the capability of the instrument to measure the kinetics of a fast radical reaction. OH radicals were produced by the photolysis of hydrogen peroxide (H_2O_2, 50 % VWR Chemicals) at a wavelength of 248 nm, and probed at a distance of < 5 mm from the sampling point. Figure S5 shows the bimolecular plot obtained for these experiments, giving a bimolecular rate coefficient $k_{OH+C5H8}$ of (1.01 ± 0.10) × 10^{-10} cm^3 s^{-1}, in agreement with the literature recommendation of $k_{OH+C5H8}$ = 9.8 × 10^{-10} cm^3 s^{-1} at 303 K (1).

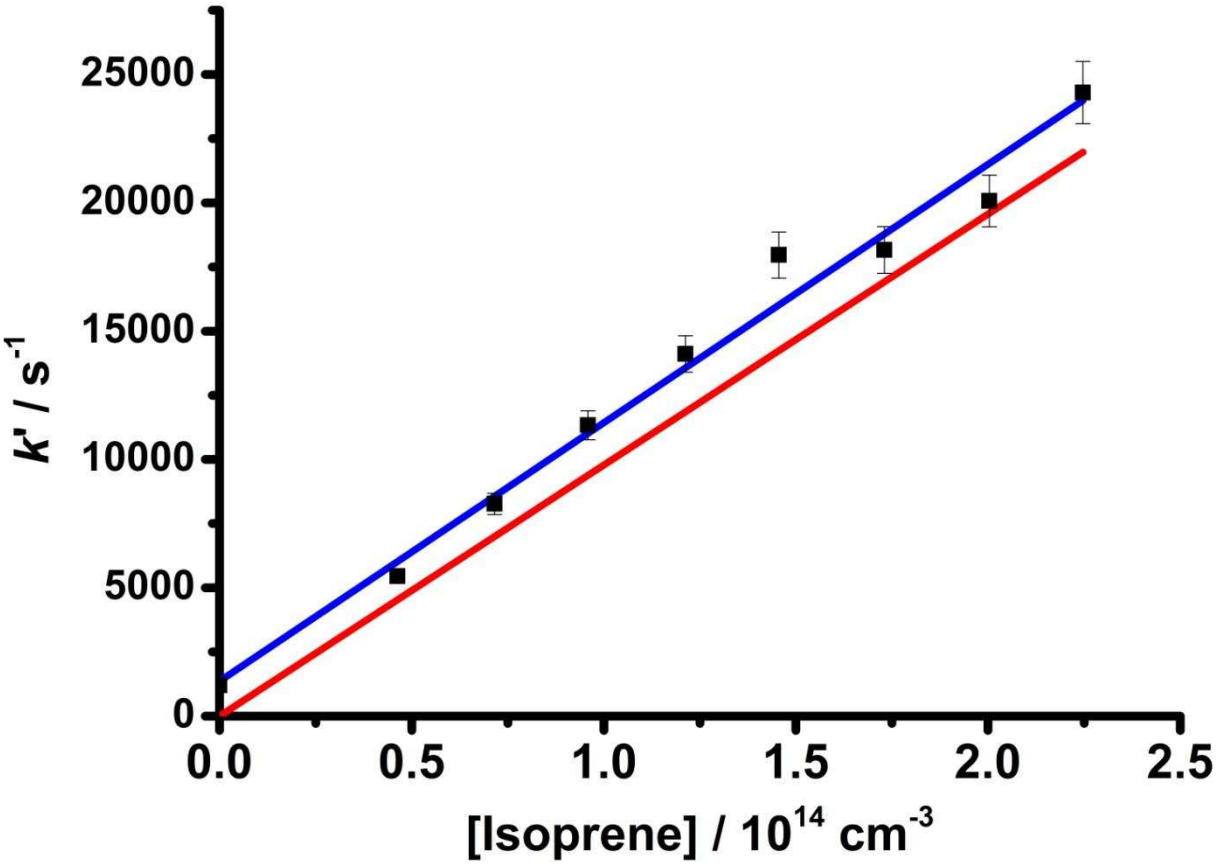

Figure S5: Bimolecular plot of observed decay kinetics at 303 K and 1400 Torr, with the detection cell at a pressure of 1 Torr and a sampling distance of < 5 mm, for the reaction of OH with isoprene (C_5H_8). The best fit line is shown in blue, giving $k_{OH+C5H8}$ = (1.01 ± 0.10) × 10^{-10} cm^3 s^{-1}. Literature recommendations are shown in red ($k_{OH+C5H8}$ = 9.8 × 10^{-10} cm^3 s^{-1} at 303 K) (1). Errors are 2σ.

References

(1) R. Atkinson, D.L. Baulch, R.A. Cox, J.N. Crowley, R.F. Hampson, R.G. Hynes, M.E. Jenkin, M.J. Rossi, J. Troe, Atmos. Chem. Phys. 6 (2006) 3625-4055