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

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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 $k_{\text{OH}+\text{CH}_4} = (6.5 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$, in agreement with literature recommendations of $k_{\text{OH}+\text{CH}_4} = 6.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (1), while those at a probe distance of 50 mm (Figures S3 and S4) gave $k_{\text{OH}+\text{CH}_4} = (3.2 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ owing to the effects of sampling outside the supersonic jet as discussed in the main text.

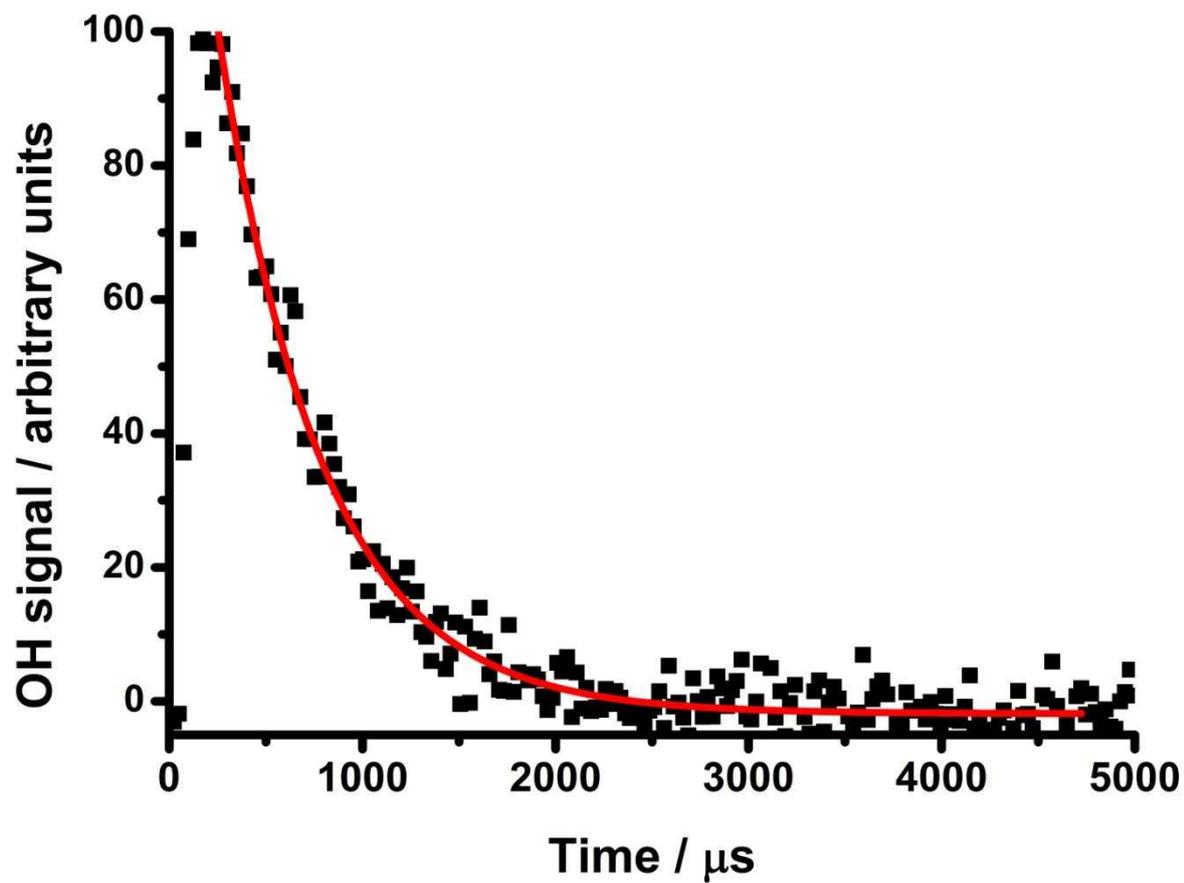


Figure S1: Temporal behaviour of OH signals for reaction of OH + CH₄ at a probe distance < 5 mm. The data shown were obtained with the reaction cell at 298 K, 760 Torr, detection cell at 0.8 Torr and [CH₄] = 2.3 × 10¹⁷ cm⁻³. The fit to the data is shown in red and gives $k' = (1890 \pm 50) \text{ s}^{-1}$.

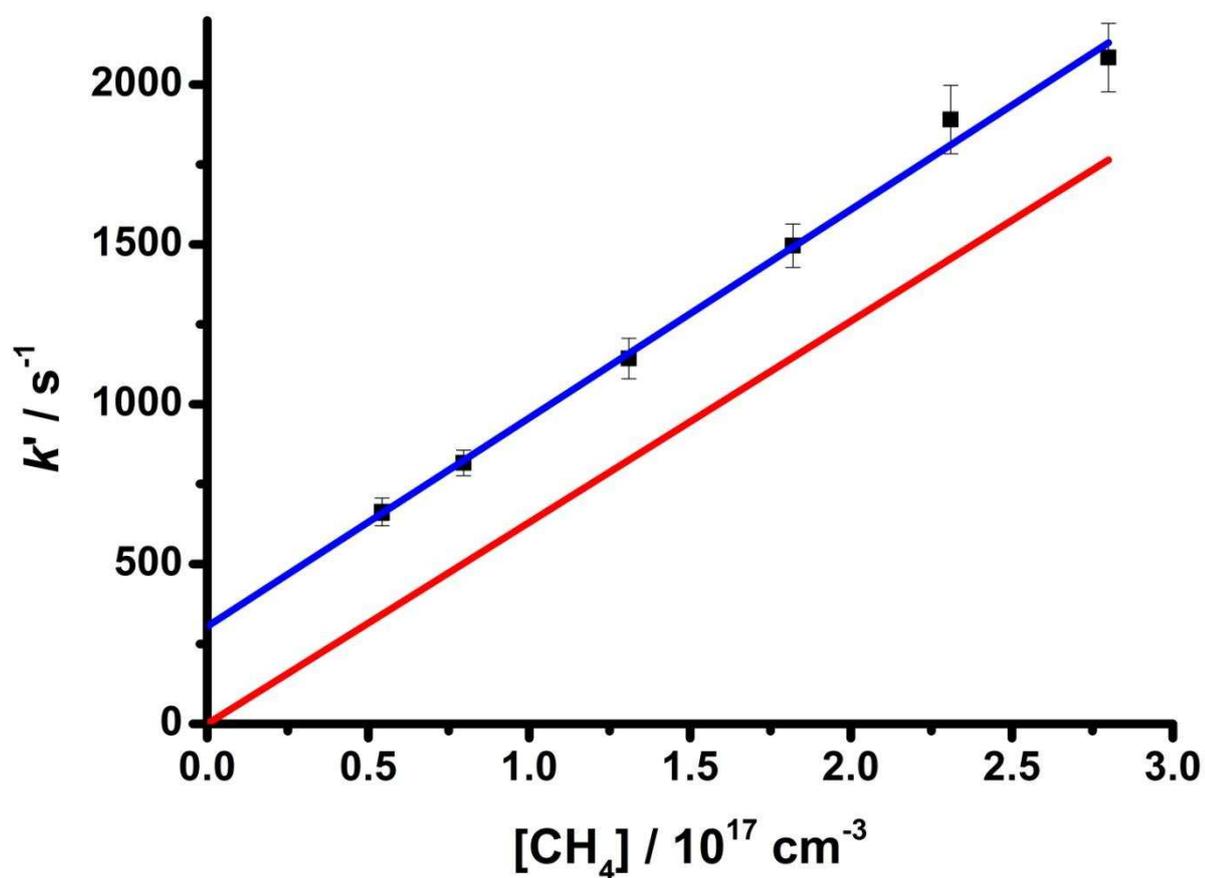


Figure S2: Bimolecular plots of observed OH decay kinetics at 298 K and 760 Torr, with the detection cell at a pressure of 0.8 Torr, for a sampling distances < 5 mm, for the reaction of OH with CH_4 . The best fit line is shown in blue; ($k = (6.5 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$).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

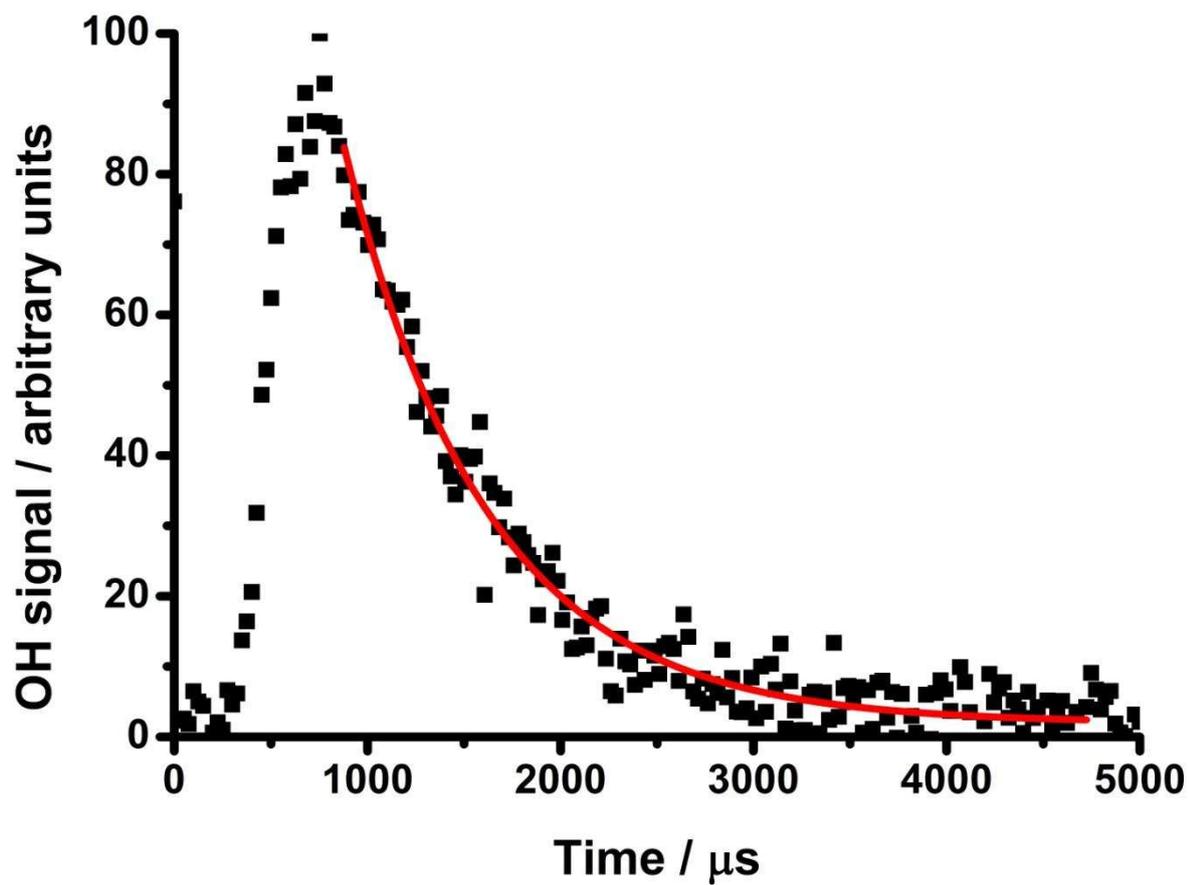


Figure S3: Temporal behaviour of OH signals for reaction of OH + CH₄ at a probe distance of 50 mm. The data shown were obtained with the reaction cell at 298 K, 760 Torr, detection cell at 0.8 Torr and [CH₄] = 3.2 × 10¹⁷ cm⁻³. The fit to the data is shown in red and gives $k' = (1350 \pm 50) \text{ s}^{-1}$.

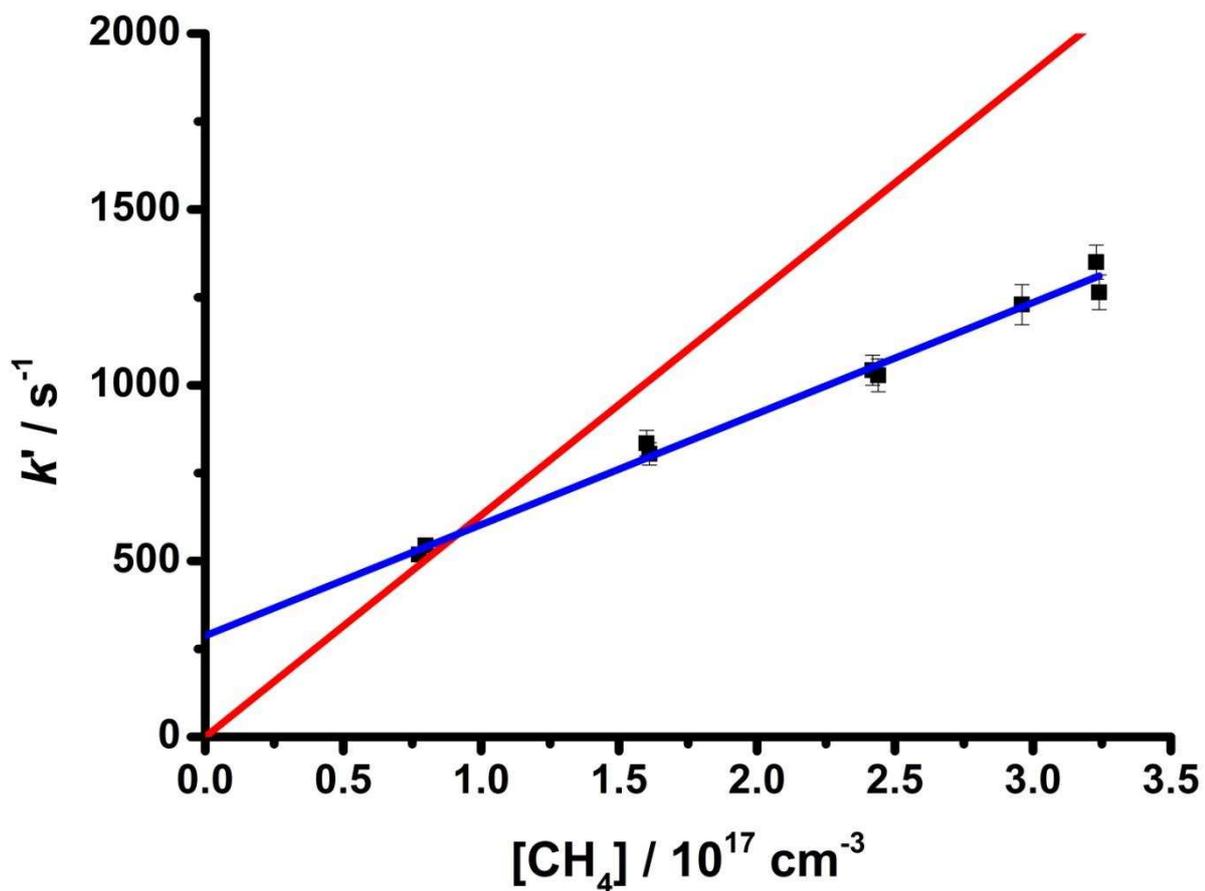


Figure S4: Bimolecular plots of observed OH decay kinetics at 298 K and 760 Torr, with the detection cell at a pressure of 0.8 Torr, for a sampling distance of 50 mm, for the reaction of OH with CH₄. The best fit line is shown in blue; ($k = (3.2 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$). The literature recommendation is shown in red ($k = 6.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$) (1). Errors are 2σ .

The reaction of OH with isoprene (2-methyl-1,3-butadiene, C₅H₈) 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 (H₂O₂, 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 $k_{\text{OH}+\text{C}_5\text{H}_8}$ of $(1.01 \pm 0.10) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, in agreement with the literature recommendation of $k_{\text{OH}+\text{C}_5\text{H}_8} = 9.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 303 K (1).

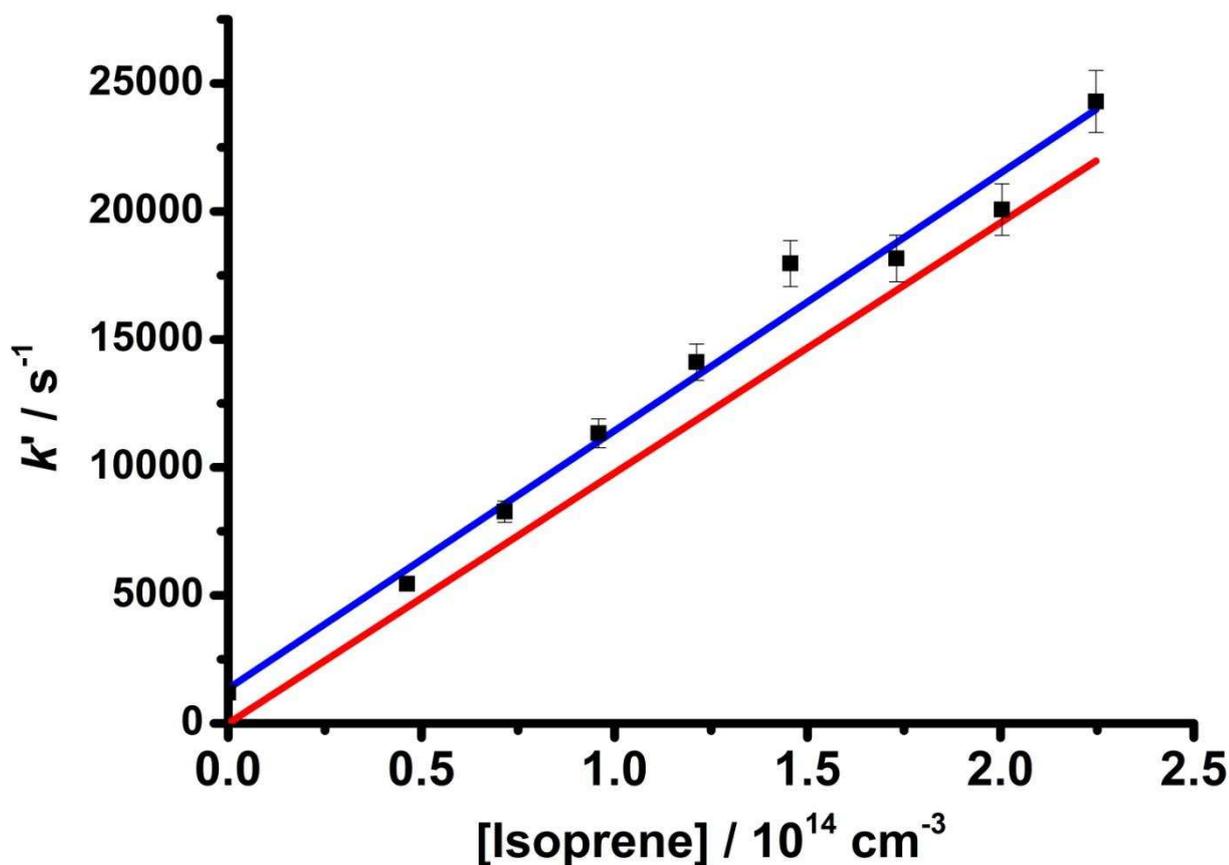


Figure S5: Bimolecular plot of observed decay kinetics at 303 K and 1400 Torr, with the detection cell at a pressure of 1 Torr and a sampling distance of < 5 mm, for the reaction of OH with isoprene (C₅H₈). The best fit line is shown in blue, giving $k_{\text{OH}+\text{C}_5\text{H}_8} = (1.01 \pm 0.10) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Literature recommendations are shown in red ($k_{\text{OH}+\text{C}_5\text{H}_8} = 9.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ 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