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

<https://doi.org/10.1063/1.4950906>

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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.

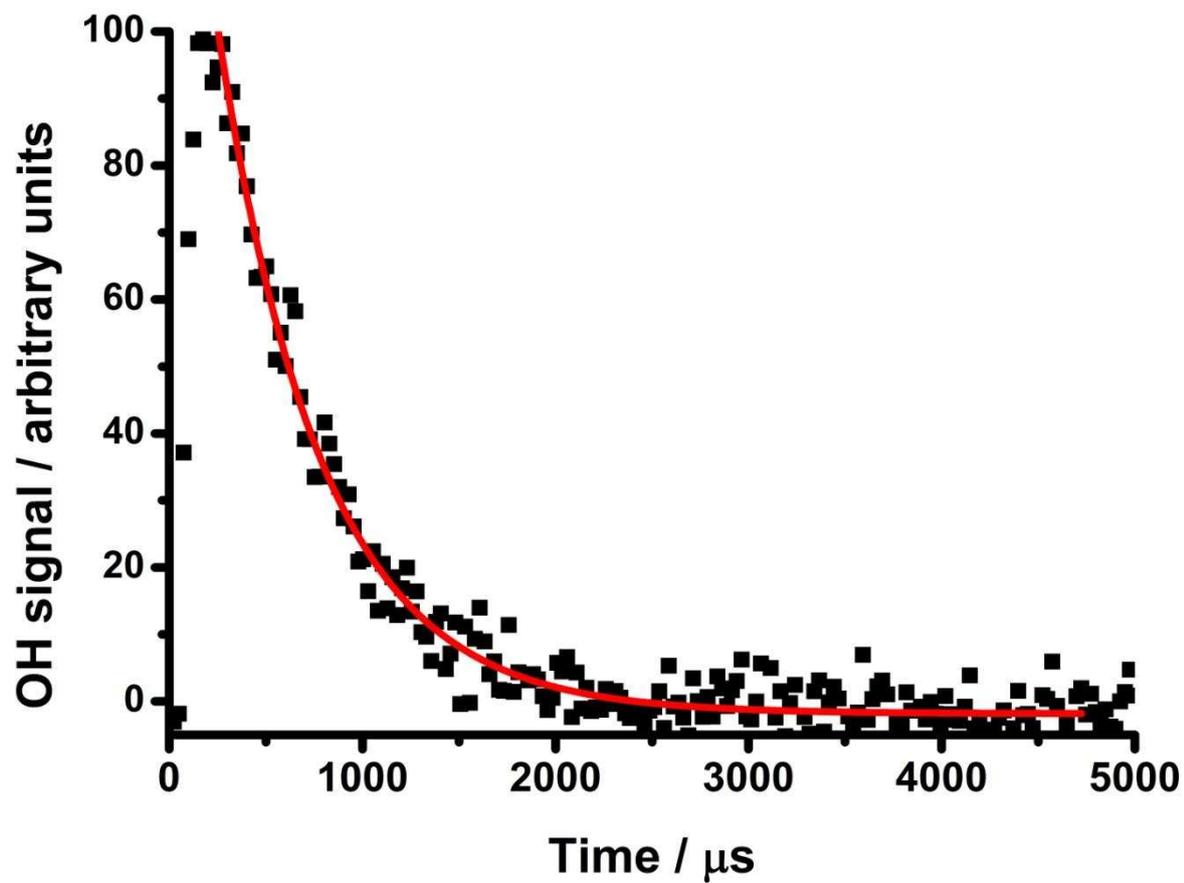


Figure S1: Temporal behaviour of OH signals for reaction of OH + CH<sub>4</sub> at a probe distance < 5 mm. The data shown were obtained with the reaction cell at 298 K, 760 Torr, detection cell at 0.8 Torr and [CH<sub>4</sub>] = 2.3 × 10<sup>17</sup> cm<sup>-3</sup>. The fit to the data is shown in red and gives  $k' = (1890 \pm 50) \text{ s}^{-1}$ .

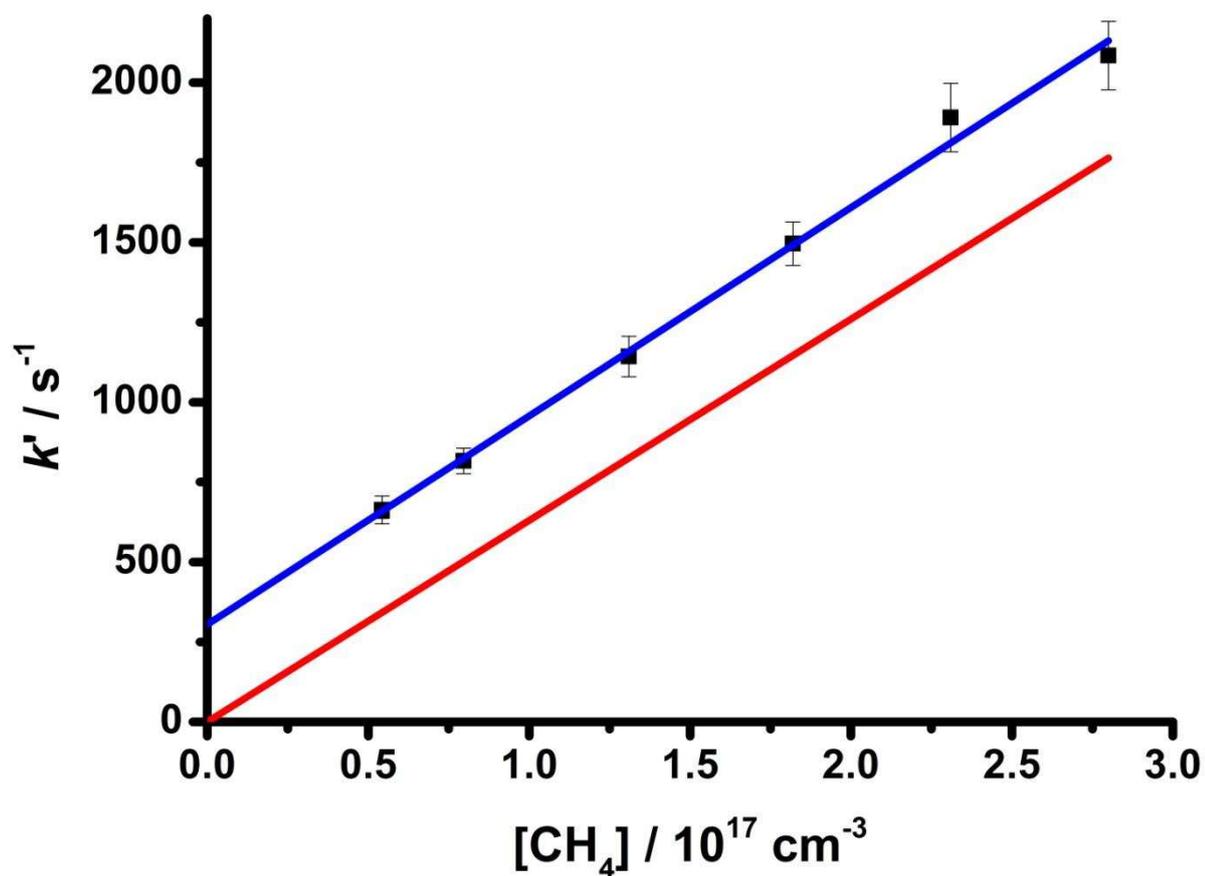


Figure S2: Bimolecular plots of observed OH decay kinetics at 298 K and 760 Torr, with the detection cell at a pressure of 0.8 Torr, for a sampling distances  $< 5$  mm, for the reaction of OH with  $\text{CH}_4$ . The best fit line is shown in blue; ( $k = (6.5 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ ). The literature recommendation is shown in red ( $k = 6.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ ) (1). Errors are  $2\sigma$ .

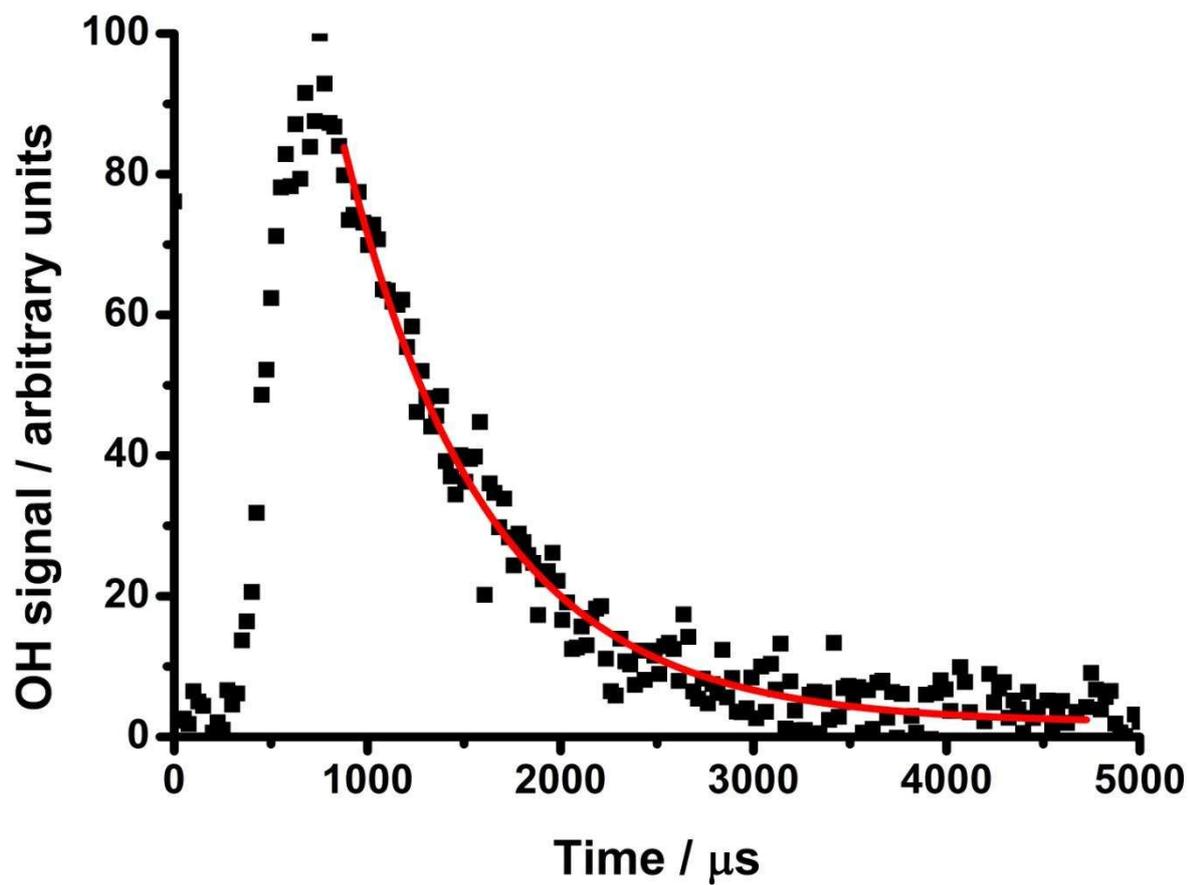


Figure S3: Temporal behaviour of OH signals for reaction of OH + CH<sub>4</sub> at a probe distance of 50 mm. The data shown were obtained with the reaction cell at 298 K, 760 Torr, detection cell at 0.8 Torr and [CH<sub>4</sub>] = 3.2 × 10<sup>17</sup> cm<sup>-3</sup>. The fit to the data is shown in red and gives  $k' = (1350 \pm 50) \text{ s}^{-1}$ .

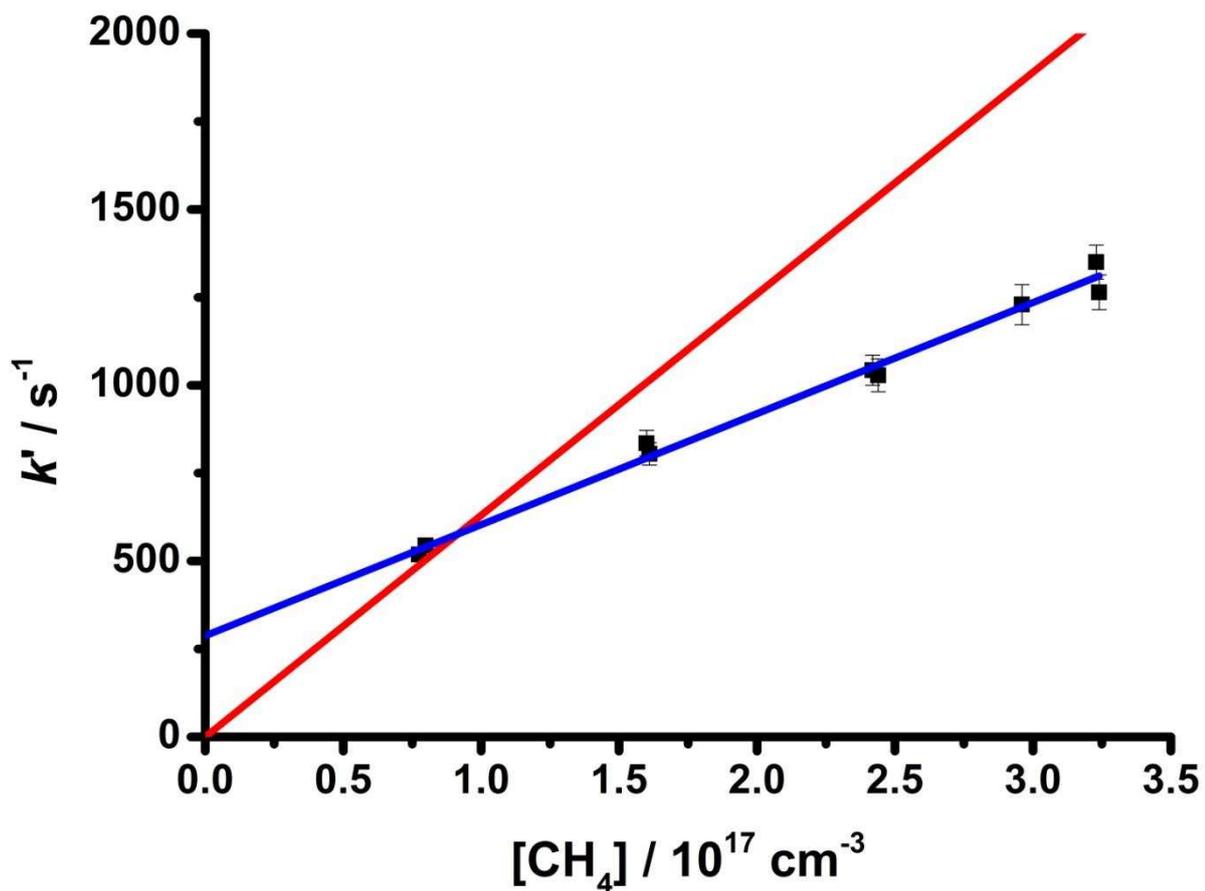


Figure S4: Bimolecular plots of observed OH decay kinetics at 298 K and 760 Torr, with the detection cell at a pressure of 0.8 Torr, for a sampling distance of 50 mm, for the reaction of OH with CH<sub>4</sub>. The best fit line is shown in blue; ( $k = (3.2 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ ). The literature recommendation is shown in red ( $k = 6.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ ) (1). Errors are  $2\sigma$ .

The reaction of OH with isoprene (2-methyl-1,3-butadiene, C<sub>5</sub>H<sub>8</sub>) 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<sub>2</sub>O<sub>2</sub>, 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).

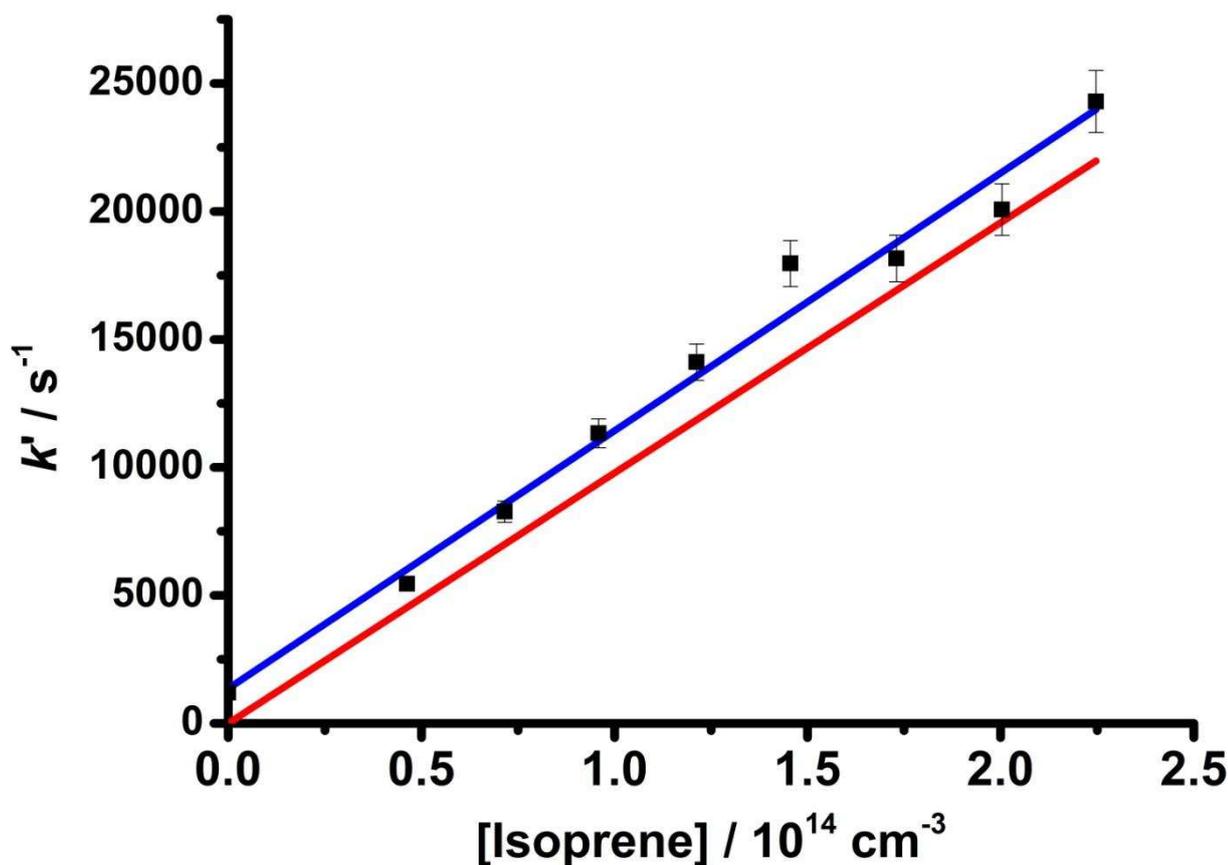


Figure S5: Bimolecular plot of observed decay kinetics at 303 K and 1400 Torr, with the detection cell at a pressure of 1 Torr and a sampling distance of < 5 mm, for the reaction of OH with isoprene (C<sub>5</sub>H<sub>8</sub>). The best fit line is shown in blue, giving  $k_{\text{OH}+\text{C}_5\text{H}_8} = (1.01 \pm 0.10) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . 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  $2\sigma$ .

## 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