

Supplementary material (ESI) for PCCP

Table S1 Experimental conditions and data for the OH quantum yield determination from H₂O₂ photolysis at 308 and 320 nm. All experiments were performed at 296 K.

λ (nm)	P (Torr)	v (cm s ⁻¹)	[H ₂ O ₂] ^a	[O ₃] ^a	S _{H₂O₂} ⁰ /S _{O₃} ⁰ ^b
308	100.4	31.1	6.3	0.83	0.322 ± 0.043
	100.4	30.6	6.4	0.83	0.297 ± 0.050
	100.2	31.1	6.9	0.66	0.404 ± 0.072
	100.5	31.1	7.3	0.66	0.379 ± 0.070
	100.5	30.9	7.4	1.14	0.240 ± 0.042
	100.5	30.9	7.4	1.14	0.211 ± 0.048
	100.2	31.1	8.3	0.51	0.697 ± 0.050
	100.4	31.4	9.2	0.51	0.776 ± 0.044
	100.5	31.4	9.8	0.67	0.557 ± 0.082
	100.6	31.4	9.9	0.67	0.638 ± 0.086
320	99.9	35.1	31.3	4.12	0.298 ± 0.054
	100.4	36.1	44.7	3.44	0.416 ± 0.108
	100.3	36.1	44.7	3.51	0.450 ± 0.112
	100.5	36.1	44.7	6.79	0.252 ± 0.068
	100.6	36.1	47.1	7.52	0.199 ± 0.100
	100.6	21.7	14.5	3.45	1.446 ± 0.050
	100.5	21.7	14.5	5.40	1.208 ± 0.104
	100.6	21.7	14.9	5.40	1.239 ± 0.082
	100.3	21.0	16.7	4.92	1.617 ± 0.092
	100.2	21.0	17.1	4.92	1.453 ± 0.070
320	100.6	21.7	18.0	3.45	1.827 ± 0.066
	100.4	22.0	19.5	5.24	1.402 ± 0.120
	101.8	21.7	19.7	0.98	8.905 ± 0.124
	100.6	21.5	20.0	1.25	6.951 ± 0.130
	100.2	22.0	20.4	4.41	1.877 ± 0.070
	100.6	21.5	20.5	1.25	5.687 ± 0.106
	101.8	21.7	20.8	0.98	9.103 ± 0.144
	100.4	22.0	20.9	4.41	1.701 ± 0.078
	100.7	21.2	21.2	5.16	1.910 ± 0.090
	100.5	22.0	21.5	5.24	1.723 ± 0.088
320	100.8	21.2	23.2	5.16	2.487 ± 0.088
	100.3	21.2	28.5	5.45	2.047 ± 0.098
	100.4	21.2	33.4	5.45	2.504 ± 0.096
	100.0	21.2	37.2	4.46	3.627 ± 0.092

	100.0	21.2	38.2	4.46	2.920 ± 0.160
	99.3	21.2	44.3	3.83	4.377 ± 0.106
	99.3	21.2	50.7	3.83	4.753 ± 0.110
	101.0	21.7	52.4	3.98	5.293 ± 0.172
	101.1	21.7	56.4	3.98	5.612 ± 0.148

^a Concentrations are in units of 10^{14} molecule cm⁻³; ^b uncertainties are 2σ precision of the initial signals added in quadrature.

Table S2 Experimental conditions and data for the OH quantum yield determination from HNO₃ photolysis at 248 and 308 nm. All experiments were performed at 296 K.

λ (nm)	P (Torr)	v (cm s ⁻¹)	[HNO ₃] ^a	[Ref] ^a	Reference compound	S _{HNO₃} ⁰ /S _{ref} ⁰ ^b
248	100.0	34.6	21.0	17.6	H ₂ O ₂	0.125 ± 0.026
	100.4	34.6	21.2	14.8	H ₂ O ₂	0.151 ± 0.028
	100.4	34.6	21.2	15.0	H ₂ O ₂	0.155 ± 0.034
	100.0	31.6	26.5	13.1	H ₂ O ₂	0.195 ± 0.088
	99.7	34.8	33.2	14.8	H ₂ O ₂	0.219 ± 0.088
	99.7	34.8	33.2	15.5	H ₂ O ₂	0.209 ± 0.088
	101.0	33.6	42.3	21.3	H ₂ O ₂	0.252 ± 0.048
	101.0	33.6	42.3	25.5	H ₂ O ₂	0.162 ± 0.044
	101.0	32.1	42.4	21.3	H ₂ O ₂	0.196 ± 0.004
	100.3	33.6	42.8	16.1	H ₂ O ₂	0.274 ± 0.034
	100.3	33.6	42.8	17.0	H ₂ O ₂	0.245 ± 0.030
	100.5	33.3	43.9	14.1	H ₂ O ₂	0.346 ± 0.030
	100.5	33.3	43.9	16.3	H ₂ O ₂	0.271 ± 0.030
	100.0	33.6	46.9	19.5	H ₂ O ₂	0.206 ± 0.030
	100.0	33.6	46.9	19.5	H ₂ O ₂	0.299 ± 0.046
	101.0	31.6	55.2	8.5	H ₂ O ₂	0.646 ± 0.014
	100.8	35.1	55.9	14.8	H ₂ O ₂	0.403 ± 0.026
	100.8	35.1	55.9	15.3	H ₂ O ₂	0.371 ± 0.032
	101.0	34.8	58.6	7.92	H ₂ O ₂	0.732 ± 0.020
	101.0	34.8	58.6	8.08	H ₂ O ₂	0.673 ± 0.024
	100.9	33.8	62.5	13.6	H ₂ O ₂	0.457 ± 0.038
	100.9	33.8	62.5	14.5	H ₂ O ₂	0.411 ± 0.040
	101.4	34.3	70.4	9.34	H ₂ O ₂ ^c	0.715 ± 0.024
	100.9	34.8	71.0	9.16	H ₂ O ₂ ^c	0.664 ± 0.034
	100.9	34.6	71.0	9.86	H ₂ O ₂ ^c	0.801 ± 0.104
	100.6	34.6	77.4	14.2	H ₂ O ₂	0.571 ± 0.036
	100.6	34.6	77.4	15.4	H ₂ O ₂	0.523 ± 0.042
308	102.0	20.7	20.3	0.67	O ₃ ^c	0.196 ± 0.114
	102.1	20.7	21.6	0.67	O ₃ ^c	0.201 ± 0.132
	102.3	20.5	22.8	0.65	O ₃ ^c	0.196 ± 0.112
	102.5	20.5	24.2	0.31	O ₃ ^c	0.397 ± 0.126
	100.7	31.6	25.0	0.42	O ₃ ^c	0.301 ± 0.092
	102.3	20.7	25.2	0.65	O ₃ ^c	0.223 ± 0.102
	100.7	31.4	25.7	0.33	O ₃ ^c	0.364 ± 0.076
	100.7	31.6	26.5	0.42	O ₃ ^c	0.322 ± 0.096

	100.6	31.4	28.7	0.33	O ₃ ^c	0.417 ± 0.080
	100.5	31.6	29.5	0.60	O ₃ ^c	0.217 ± 0.060
	100.5	31.6	30.5	0.60	O ₃ ^c	0.265 ± 0.068
	101.2	31.4	30.6	0.80	O ₃ ^c	0.199 ± 0.072
	101.5	31.4	31.1	0.80	O ₃ ^c	0.196 ± 0.088
	100.2	31.4	41.4	0.43	O ₃ ^c	0.505 ± 0.106
	101.1	37.8	52.9	31.7	H ₂ O ₂	0.194 ± 0.060
	100.5	37.8	53.4	13.0	H ₂ O ₂	0.559 ± 0.032
	100.5	37.8	53.4	13.3	H ₂ O ₂	0.564 ± 0.034
	100.3	37.8	54.1	24.4	H ₂ O ₂	0.271 ± 0.054
	100.3	37.8	54.1	24.6	H ₂ O ₂	0.247 ± 0.048
	100.9	37.8	54.3	32.0	H ₂ O ₂	0.183 ± 0.060
	100.9	37.8	54.3	33.4	H ₂ O ₂	0.226 ± 0.066
	101.1	37.8	54.5	31.9	H ₂ O ₂	0.201 ± 0.044
	101.1	37.8	54.5	33.0	H ₂ O ₂	0.228 ± 0.050
	101.4	37.5	55.5	33.1	H ₂ O ₂	0.173 ± 0.080
	100.5	37.3	69.4	20.5	H ₂ O ₂	0.489 ± 0.044
	100.5	37.3	69.4	21.0	H ₂ O ₂	0.486 ± 0.042
	100.2	37.5	71.2	14.4	H ₂ O ₂	0.564 ± 0.074
	100.2	37.5	71.2	17.5	H ₂ O ₂	0.504 ± 0.072
	100.4	37.3	79.7	13.0	H ₂ O ₂	0.745 ± 0.052
	100.3	37.3	80.3	13.0	H ₂ O ₂	0.880 ± 0.064
	100.7	37.5	88.8	18.8	H ₂ O ₂	0.697 ± 0.062
	100.7	37.5	88.8	19.2	H ₂ O ₂	0.620 ± 0.066

^a Concentrations are in units of 10^{14} molecule cm⁻³; ^b uncertainties are 2σ precision of the initial signals added in quadrature; ^c Measurements made with $\sim 1 \times 10^{17}$ molecule cm⁻³ of H₂O added to the reaction mixture.