Kinetics Study of the Reaction of OH Radicals with C_5–C_8 Cycloalkanes at 240–340K using the Relative Rate/Discharge Flow/Mass Spectrometry Technique

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Supporting Information

Table 1S. Reaction scheme for chemical model simulation to assess the effect of atomic oxygen and atomic hydrogen on the decay of target and reference compounds in RR/DF/MS kinetic data analysis**.**

Reaction[a]	*k (cm^3 molecule^{-1} s^{-1})*	*Reference*
F + H_2O → HF +OH	1.4 x 10^{-11}	[1]
OH +OH → H_2O + O	1.9 x 10^{-12}	[1]
OH + wall → product	10[b]	Estimated[c]
O + F_2 → FO + F	1.0 x 10^{-16}	[2]
FO + OH → O_2 + HF	1.3 x 10^{-12}	Estimated[d]
H + F_2 → HF + F	1.38 x 10^{-12}	[3]
O + OH → O_2 +H	3.3 x 10^{-11}	[1]
H + wall→ product	10[b]	Estimated[c]
H + OH + M → H_2O + M	2.3 x 10^{-31}[e]	[4]
c-alkane + OH → Products	4.89 x 10^{-12}[f]	This work
ref + OH → Products	6.52 x 10^{-12}[g]	[5],[6]
O + c-alkane →OH + other products	1.22x 10^{-13}[h]	[7]
O + ref → OH + other products	8.86 x 10^{-14}[i]	[8]
H + c-alkane →H_2 + other products	5.80 x 10^{-15}	Estimated[j]
H + ref →H_2 + other products	5.80 x 10^{-15}	Estimated[j]

[a]Initial concentrations are $[F_2]_0$=2.4 x 10^{12}, $[H_2O]_0$= 7.0x10^{14}, $[OH]_0$ =9.0 x10^{13}, [c-alkane]$_0$=1.5 x 10^{14}, and [reference]$_0$=6x10^{13} molecules cm^{-3}, respectively. The initial concentrations of all other species are set to zero.
[b]The unit is s^{-1} for the wall loss process
[c]Estimate is based on OH wall loss.
[d]Estimate based on *k*(ClO + OH)
[e]The unit is cm^6 molecule^{-2}s^{-1}
[f]A rate constant of 4.88 x 10^{-12}, 6.36 x 10^{-12}, 9.69 x 10^{-12}, and 1.37 x 10^{-11} cm^3 molecule^{-1} s^{-1} was used for the reaction of OH with cyclopentane, cyclohexane, cycloheptane and cyclooctane, respectively.
[g]A rate constant of 4.95 x 10^{-12}, 6.66 x 10^{-12}, 8.48 x 10^{-12}, and 1.13 x 10^{-11} cm^3 molecule^{-1} s^{-1} was used for the reaction of OH with n-hexane, n-heptane, n-octane, and n-nonane, respectively.
[h]A rate constant of 1.22 x 10^{-13}, 1.82 x 10^{-13}, 2.48 x 10^{-13}, and 3.0 x 10^{-13} cm^3 molecule^{-1} s^{-1} was used for the reaction of O with cyclopentane, cyclohexane, cycloheptane and cyclooctane, respectively.
[i]A rate constant of 8.86 x 10^{-14}, 1.24 x 10^{-13}, 1.57 x 10^{-13}, and 1.8 x 10^{-13} cm^3 molecule^{-1} s^{-1} was used for the reaction of O with n-hexane, n-heptane, n-octane, and n-nonane, respectively.
[j]Estimate based on H+ n-C_4H_{10}.

Table 2S. Literature rate constant for OH + cyclopentane.

T (K)	Reference Compound[a]	$k_1 \times 10^{12}$ (cm^3 $molecule^{-1}$ s^{-1})	P_{total} (torr)	Technique[a]	Reference
300		5.89±0.26	30	HPFS-LIF	9
325		6.35±0.59	30	HPFS-LIF	9
340		6.18±0.19	30	HPFS-LIF	9
360		7.64±0.23	30	HPFS-LIF	9
375		7.25±0.38	30	HPFS-LIF	9
390		7.53±0.45	30	HPFS-LIF	9
240	cyclohexane/n-butane	3.20	760	GC/MS	10
260	cyclohexane/n-butane	3.77	760	GC/MS	10
277	cyclohexane/n-butane	4.25	760	GC/MS	10
298	cyclohexane/n-butane	4.84	760	GC/MS	10
320	cyclohexane/n-butane	5.44	760	GC/MS	10
340	cyclohexane/n-butane	5.97	760	GC/MS	10
298		5.18±0.38		FP-LIF	11
296	n-nonane propene trans-2-butene butadiene	5.1±0.1 4.8±0.08 4.8±0.2 4.3±0.04	760± 10	GC/FID	12
295		5.02±0.22	0.53bar	FP-LIF	13
344		6.12±0.27		FP-LIF	13
402		7.23±0.32		FP-LIF	13
491		9.46±0.41		FP-LIF	13
250		4.78	0.23-0.67bar	GC/MS	14
300		5.33		GC/MS	14
273	n-butane/n-hexane	4.15	1.01 bar	GC-FID	15
275	n-butane/n-hexane	4.21		GC-FID	15
300	n-butane/n-hexane	4.89		GC-FID	15
325	n-butane/n-hexane	5.56		GC-FID	15
350	n-butane/n-hexane	6.2		GC-FID	15
375	n-butane/n-hexane	6.82		GC-FID	15
400	n-butane/n-hexane	7.41		GC-FID	15
423	n-butane/n-hexane	7.93		GC-FID	15

[a.] MS: Mass Spectrometry, FP: Flash photolysis, GC: Gas Chromatography, FID: Flame Ionization Detection; HPFS-LIF: High pressure flow system- laser induced fluorescence; FP-LIF: Flash Photolysis-laser induced fluorescence.

Table 3S. Literature rate constant for OH + cyclohexane.

T (K)	Reference Compound	$k_2 \times 10^{12}$ (cm^3 $molecule^{-1}$ s^{-1})	P_{total} (torr)	Technique[a]	Reference
298	ethane	6.69	760	RR/GC/FID	15
326	ethane	7.72		RR/GC/FID	15
350	ethane	8.58		RR/GC/FID	15
363	ethane	9.03		RR/GC/FID	15
298	*n*-butane	6.38	760	RR/GC/MS	10
225	*n*-butane	4.02		RR/GC/MS	10
253	*n*-butane	5.17		RR/GC/MS	10
267	*n*-butane	5.67		RR/GC/MS	10
304	*n*-butane	6.68		RR/GC/MS	10
344	*n*-butane	8.27		RR/GC/MS	10
386	*n*-butane	9.12		RR/GC/MS	10
288	*n*-butane	5.84		RR/GC/MS	10
323	*n*-butane	7.12		RR/GC/MS	10
369	*n*-butane	8.26		RR/GC/MS	10
408	*n*-butane	9.31		RR/GC/MS	10
300		7.66±0.23	30	HPFS	9
292		7.14±0.31		LP-LIF	13
342		8.49±0.37		LP-LIF	13
401		10.1±0.44		LP-LIF	13
491		12.9±0.56		LP-LIF	13
295		5.24±0.36		P/Abs	16
296		8.6±0.8		DF-RF	17
298		6.7±0.9		DF-LIF	18
299	*n*-hexane	7.52±0.26		FP-GC	19
298	*n*-butane	6.7			20
299	propene	6.80±0.41		FP-GC	21
300	*n*-butane	7.44		GC	22
295		5.38±0.26		FP	23

[a.] RR: Relative rate; DF: Discharge Flow; MS: Mass Spectrometry; RF: Resonance Fluorescence; FP: Flash photolysis; GC: Gas Chromatography; LP: laser Photolysis; LIF: Laser Induced Fluorescence; GC: Gas Chromatography; FID: Flame Ionization Detection; P: Photolysis.

Table 4S. Literature rate constant for OH + cycloheptane.

T (K)	Reference Compound	$k_3 \times 10^{12}$ (cm^3 $molecule^{-1}$ s^{-1})	P_{total} (torr)	Technique[a]	Reference
300		12.0±0.3	30	HPFS-LIF	9
325		13.4±0.4	30	HPFS-LIF	9
340		13.3±0.4	30	HPFS-LIF	9
375		13.9±0.4	30	HPFS-LIF	9
390		16.4±1.4	30	HPFS-LIF	9
274	n-hexane/ cyclohexane	9.07	760	GC/MS	10
300	n-hexane/ cyclohexane	10.5	760	GC/MS	10
326	n-hexane/ cyclohexane	11.8	760	GC/MS	10
351	n-hexane/ cyclohexane	13.1	760	GC/MS	10
373	n-hexane/ cyclohexane	14.1	760	GC/MS	10
404	n-hexane/ cyclohexane	15.5	760	GC/MS	10
298		13.1±2.3	20-30	FP-Vis/UV	11
298		12.4		Review	24

[a.] RR: Relative rate; MS: Mass Spectrometry; FP: Flash photolysis; GC: Gas Chromatography; HPFS-LIF: High pressure flow system- laser induced fluorescence.

Table 5S. Literature rate constant for OH + cyclooctane.

T (K)	$k_2 \times 10^{11}$ (cm^3 $molecule^{-1}$ s^{-1})	P_{total} (torr)	Technique[a]	Reference
298	1.41		HPFS-LIF	25
300	1.34	30	HPFS-LIF	9
325	1.50	30	HPFS-LIF	9
340	1.49	30	HPFS-LIF	9
375	1.66	30	HPFS-LIF	9
390	1.91	30	HPFS-LIF	9

[a.] HPFS-LIF: High pressure flow system- laser induced fluorescence.

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