

ADDITIONS AND CORRECTIONS

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John D. DeSain, Stephen J. Klippenstein, James A. Miller, and Craig A. Taatjes*: Measurements, Theory, and Modeling of OH Formation in Ethyl + O₂ and Propyl + O₂ Reactions

Page 4415. Several concentrations are reported incorrectly in the text of this paper. The methanol concentration employed in the reference experiments is $8.4 \times 10^{14} \text{ cm}^{-3}$ (reference for ethane measurements below 700 K) or $1.27 \times 10^{15} \text{ cm}^{-3}$ (ethane at 700 K and all propane reference measurements). The O₂ concentration used is $6.5 \times 10^{16} \text{ cm}^{-3}$. Additionally, because of programming errors, the kinetic simulations used to extract relative OH concentrations were incorrect. This error leads to slightly altered peak OH concentrations for both propane and ethane oxidation. The correct values for peak OH concentrations

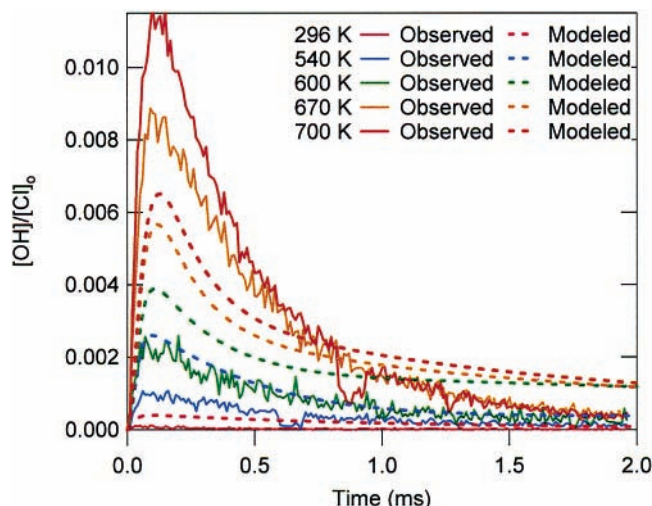


Figure 7. Observed OH time traces for the reaction of C₂H₅ + O₂ at the five temperatures measured: 296 K (magenta); 530 K (cyan); 600 K (green); 670 K (orange); 700 K (red). The signal amplitudes have been scaled to [Cl]₀ as described in the original text. Also shown, as dashed lines, are the OH time traces predicted by the corrected integrated rate equation model at the same 5 temperatures.

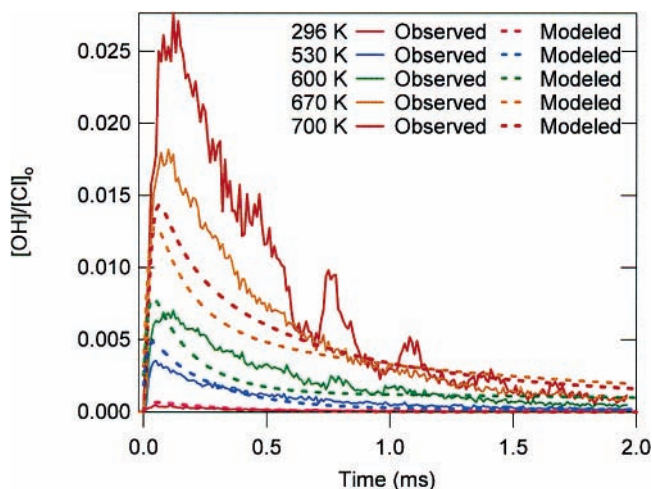


Figure 8. Observed OH time traces for the reaction of C₃H₇ + O₂ at the five temperatures measured: 296 K (magenta); 530 K (cyan); 600 K (green); 670 K (orange); 700 K (red). The signal amplitudes have been scaled to [Cl]₀ as described in the original text. Also shown, as dashed lines, are the OH time traces predicted by the corrected integrated rate equation model at the same 5 temperatures.

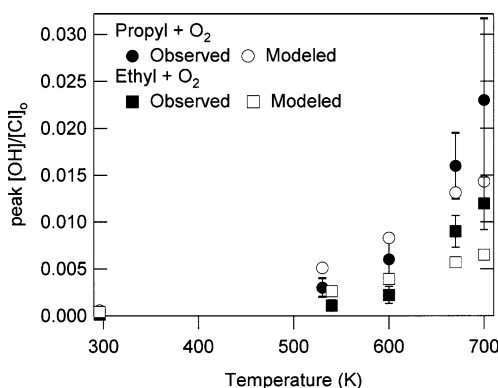


Figure 9. Corrected peak [OH]/[Cl]₀ from the OH time traces for the reaction of C₃H₇ + O₂ (solid circles) and C₂H₅ + O₂ (solid squares) at several temperatures. The peak [OH]/[Cl]₀ predicted by the corrected integrated rate equation model for the reaction of C₃H₇ + O₂ (open circles) and C₂H₅ + O₂ (open squares) is also shown.

TABLE 2: Peak Intensity of the Observed OH Signal and Peak Intensity of the Modeled Reference OH Signal and the Observed OH Signal Scaled by Eq 6 for Both C₂H₅ + O₂ and C₃H₇ + O₂ at Several Different Temperatures^a

<i>T</i> (K)	<i>I</i> _{pk,R+O₂} / <i>I</i> _{pk,ref}	([OH] _{pk,ref} /[Cl] ₀) _{model} ^b	[OH] _{pk,R+O₂} /[Cl] ₀	([OH] _{pk} /[Cl] ₀) _{model}
C ₂ H ₅ + O ₂				
296	0.00023(8)	0.58	0.00013(6)	0.00041
540	0.0022(6)	0.48	0.0011(4)	0.0026
600	0.005(1)	0.46	0.0023(9)	0.0039
670	0.023(3)	0.39	0.009(2)	0.0057
700	0.035(4)	0.35	0.012(3)	0.0065
C ₃ H ₇ + O ₂				
296	.00061(8)	0.49	0.00032(8)	0.00056
30	.007(2)	0.44	0.003(1)	0.0051
600	.014(4)	0.41	0.007(2)	0.0083
670	0.041(5)	0.40	0.018(4)	0.013
700	0.071(9)	0.35	0.024(9)	0.014

^a The number in parentheses represents the estimated experimental uncertainty in the final digit. The predicted peak OH concentration from the full kinetic model, employing the time-dependent master equation solution for the R + O₂ system, is given in the final column. ^b Estimated uncertainty ±15%.

TABLE 6: Reactions and Rate Coefficients Used To Model the OH Signal from the Cl/C₂H₆/O₂ System^a

reaction	A^b	n	E_a/R (K)	ref
OH + OH → O + H ₂ O	6.2×10^{-14}	2.60	-945	1
HOOC ₂ H ₄ O ₂ → C ₂ H ₄ OOH + O ₂	7.11×10^{16}	-2.45	17700	2
HOOC ₂ H ₄ O ₂ → OH + HOOC ₂ CHO	1.98×10^{10}	3.27	14000	2
HOOC ₂ H ₄ O ₂ → OH + HOOC ₂ CHO	1.37×10^{11}	3.19	20300	2
HOOC ₂ H ₄ O ₂ → OH + OCH ₂ CH ₂ OO	3.0×10^{15}		21900	2
HOOC ₂ H ₄ O ₂ → HO ₂ + HOOC ₂ CHO	4.17×10^{10}	3.51	14300	2
C ₂ H ₅ O + C ₂ H ₅ O → C ₂ H ₅ OH + CH ₃ CHO	3.0×10^{-11}			3 ^c

^a Rate coefficients are written in the form $A(T/298)^n e^{-E_a/RT}$. ^b Units of s⁻¹ for first-order reactions, cm³ molecule⁻¹ s⁻¹ for second-order reactions, and cm⁶ molecule⁻² s⁻¹ for third-order reactions. ^c Estimated based on CH₃/O₂ system.

TABLE 7: Reactions and Rate Constants Used To Model the OH Signal Generated from the Cl/C₃H₈/O₂ System^a

reaction	A^b	n	E_a/R (K)	ref
C ₃ H ₈ + OH → <i>n</i> -C ₃ H ₇ + H ₂ O	$\phi \times 1.87 \times 10^{-12}$	1.72	145	4 ^c
C ₃ H ₈ + OH → <i>i</i> -C ₃ H ₇ + H ₂ O	$(1-\phi) \times 1.87 \times 10^{-12}$	1.72	145	4 ^c
OH + OH → O + H ₂ O	6.2×10^{-14}	2.60	-945	1
HOOC ₃ H ₆ O ₂ → C ₃ H ₆ OOH + O ₂	7.11×10^{16}	-2.45	17700	<i>d</i>
HOOC ₃ H ₆ O ₂ → OH + HOOC ₃ H ₅ O	1.98×10^{10}	3.27	14000	<i>d</i>
HOOC ₃ H ₆ O ₂ → OH + HOOC ₃ H ₅ O	1.37×10^{11}	3.19	20300	<i>d</i>
HOOC ₃ H ₆ O ₂ → OH + OOC ₃ H ₆ O	3.0×10^{15}		21900	<i>d</i>
HOOC ₃ H ₆ O ₂ → HO ₂ + C ₃ H ₆ O ₂	4.17×10^{10}	3.51	14300	<i>d</i>

^a The rate constants are written in the form $A(T/298)^n e^{-E_a/RT}$. ^b Units of s⁻¹ for first-order reactions, cm³ molecule⁻¹ s⁻¹ for second-order reactions, and cm⁶ molecule⁻² s⁻¹ for third-order reactions. ^c The branching fraction of ref 4 has been fit to the function $\phi = -0.293 + 0.00286T - 3.47 \times 10^{-6}T^2 + 1.51 \times 10^{-9}T^3$. ^d Estimated on the basis of C₂H₅OOH + O₂.²

are given below; these changed values will also change the scaling, and to some degree the shape, of the observed and modeled signals in Figures 7 and 8. The OH profiles from the corrected model display a longer decay than shown in the original manuscript. The overall conclusions of the paper are not substantially altered; the qualitative agreement between the model and the experiment remains, and the kinetic model still predicts a shallower temperature dependence of the peak OH yield than that observed experimentally. Typographical errors in Tables 6 and 7 are also corrected here. Finally, in the computation of the rate coefficients for the *i*-propyl + O₂ reaction, incorrect rotational constants were inadvertently used for some of the master equation calculations. As a result, the adjustments to the stationary point energies, used to produce agreement with the available body of experimental work, may be in error. A detailed reinvestigation of the *i*-propyl + O₂ reaction will be published in conjunction with new experimental measurements of product formation in single-isomer propyl + O₂ reactions.

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References and Notes

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