Supporting Information

Chemically Activated Formation of Organic Acids in Reactions of the Criegee Biradical with Aldehydes and Ketones

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1 Additional Plots

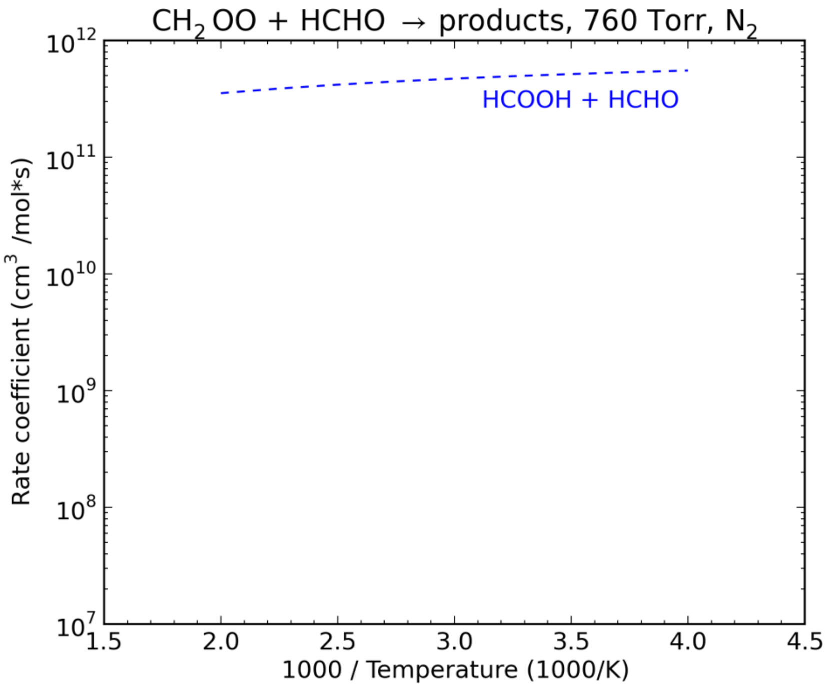

Figure 1: Predicted rate coefficients $k(T, P)$ versus temperature for $\bullet CH_2OO\bullet + HCHO \rightarrow$ products at 760 Torr N_2.

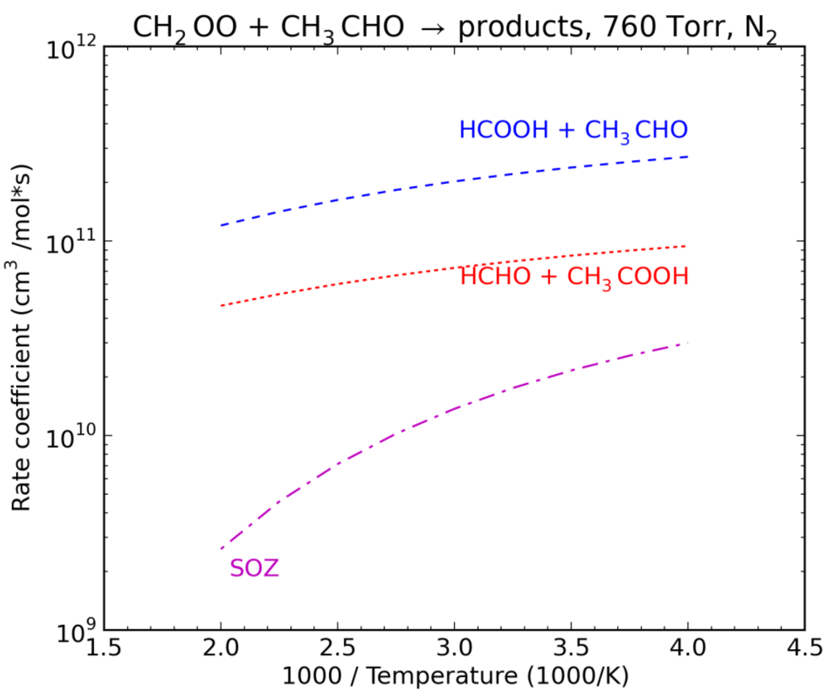

Figure 2: Predicted rate coefficients $k(T, P)$ versus temperature for $\bullet CH_2OO\bullet + CH_3CHO \rightarrow$ products at 760 Torr N_2.

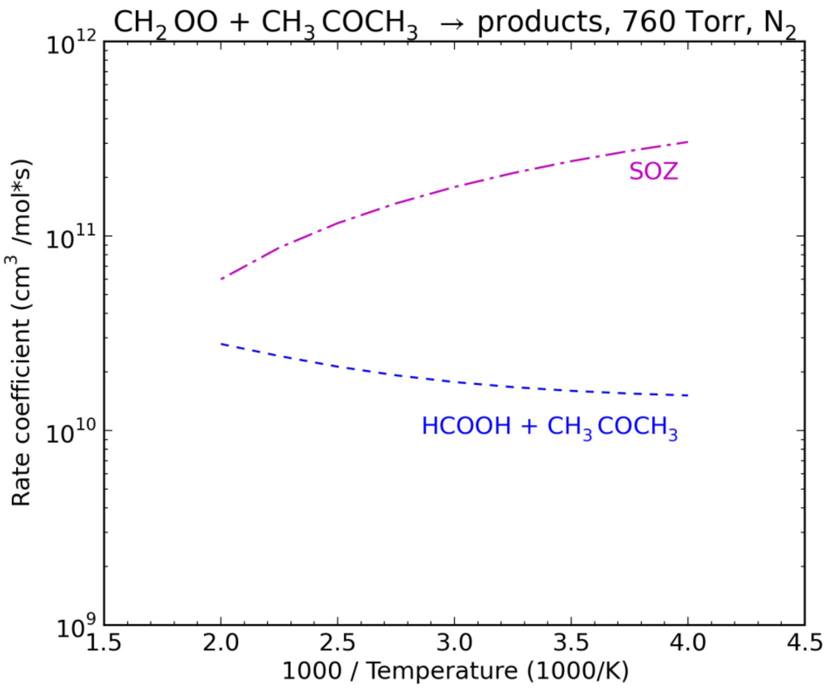

Figure 3: Predicted rate coefficients $k(T, P)$ versus temperature for $\bullet CH_2OO\bullet + CH_3COCH_3 \rightarrow$ products at 760 Torr N_2.

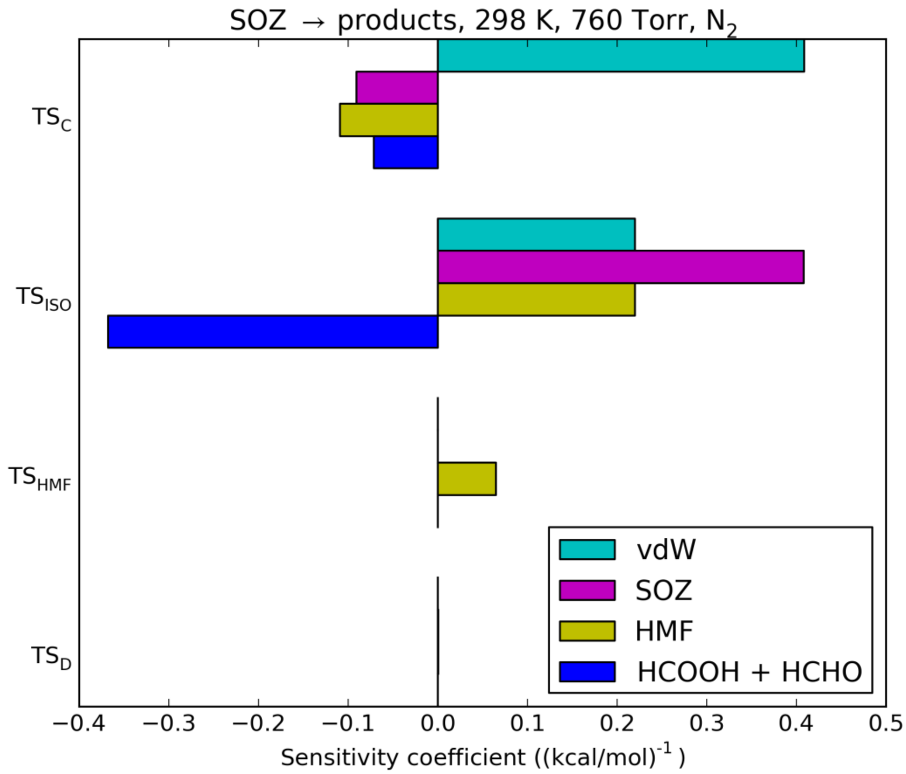

Figure 4: Normalized sensitivities coefficients, $\frac{\partial \ln Y_i}{\partial E_j}$ of the product yields (Y_i) to the transition state barrier heights (E_j) for the •CH_2OO• + HCHO network at 298 K and 760 Torr, with nitrogen as the bath gas. Each cluster of bars corresponds to the transition state barrier height of one reaction, indicated at left. The bars indicate how each product's yield is affected by adjusting the associated barrier height, and are ordered and colored by product as shown in the legend.

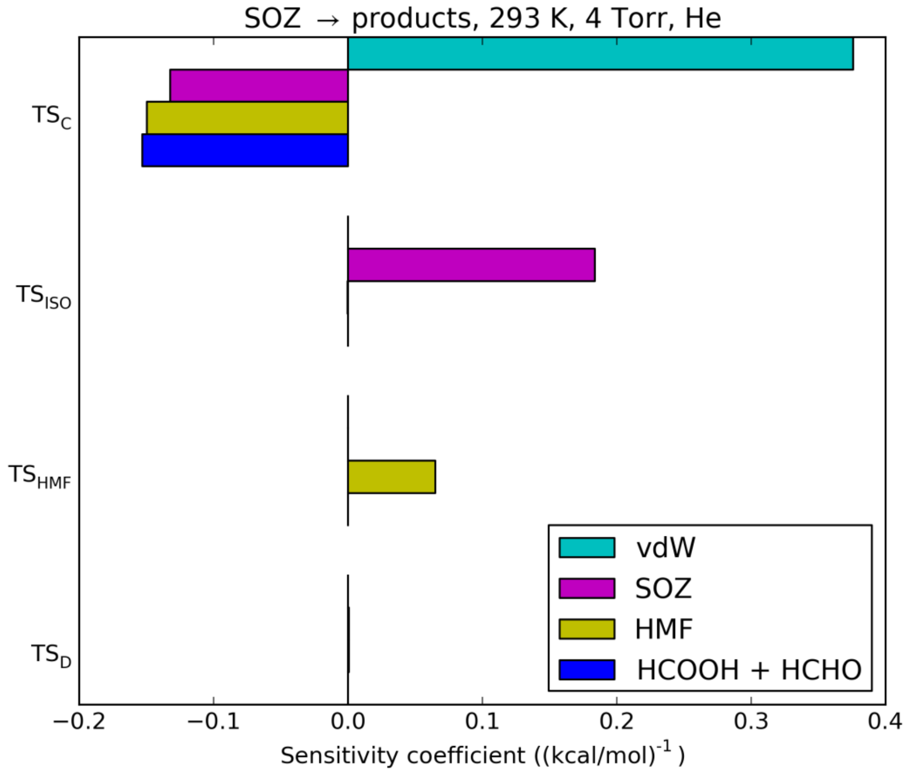

Figure 5: Normalized sensitivities coefficients, $\frac{\partial \ln Y_i}{\partial E_j}$ of the product yields (Y_i) to the transition state barrier heights (E_j) for the •CH_2OO• + HCHO network at 293 K and 4 Torr, with helium as the bath gas. Each cluster of bars corresponds to the transition state barrier height of one reaction, indicated at left. The bars indicate how each product's yield is affected by adjusting the associated barrier height, and are ordered and colored by product as shown in the legend.

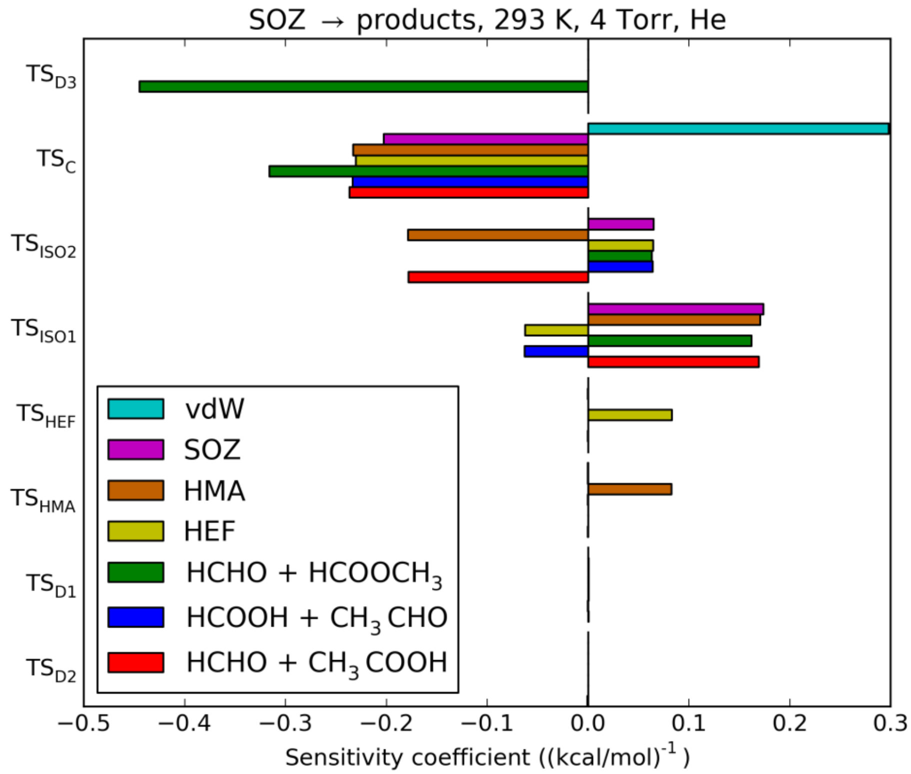

Figure 6: Normalized sensitivities coefficients, $\frac{\partial \ln Y_i}{\partial E_j}$ of the product yields (Y_i) to the transition state barrier heights (E_j) for the •CH_2OO• + CH_3CHO network at 293 K and 4 Torr, with helium as the bath gas. Each cluster of bars corresponds to the transition state barrier height of one reaction, indicated at left. The bars indicate how each product's yield is affected by adjusting the associated barrier height, and are ordered and colored by product as shown in the legend.

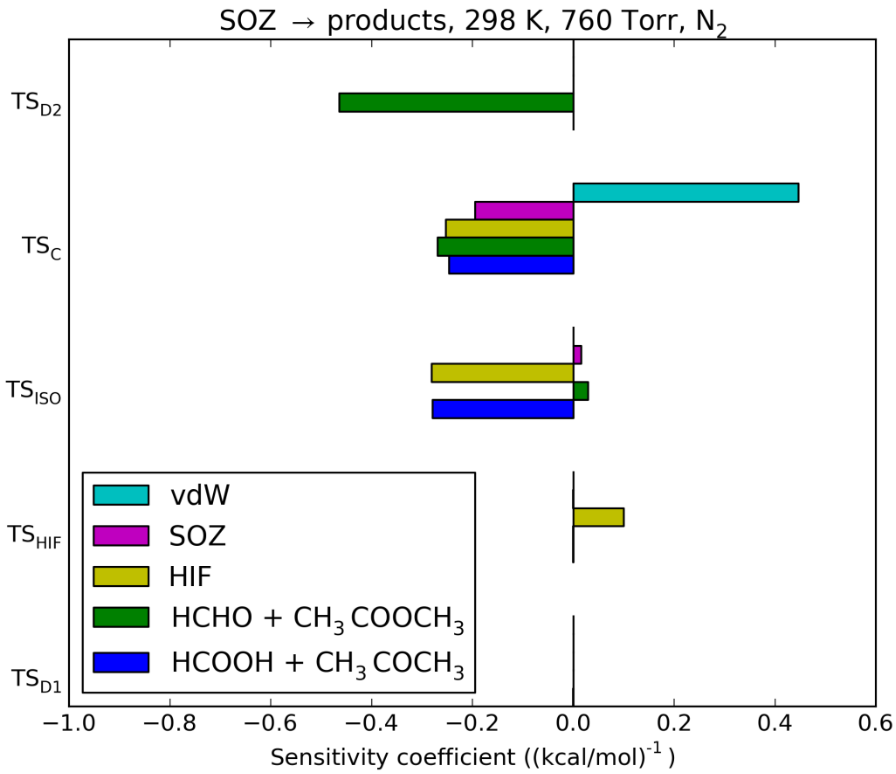

Figure 7: Normalized sensitivities coefficients, $\frac{\partial \ln Y_i}{\partial E_j}$ of the product yields (Y_i) to the transition state barrier heights (E_j) for the •CH_2OO• + CH_3COCH_3 network at 298 K and 760 Torr, with nitrogen as the bath gas. Each cluster of bars corresponds to the transition state barrier height of one reaction, indicated at left. The bars indicate how each product's yield is affected by adjusting the associated barrier height, and are ordered and colored by product as shown in the legend.

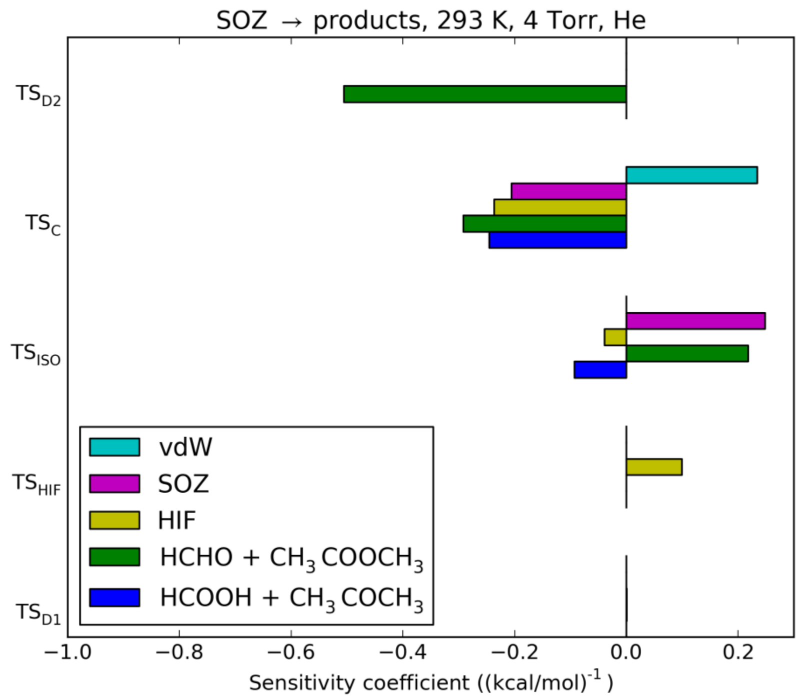

Figure 8: Normalized sensitivities coefficients, $\frac{\partial \ln Y_i}{\partial E_j}$ of the product yields (Y_i) to the transition state barrier heights (E_j) for the •CH_2OO• + CH_3COCH_3 network at 293 K and 4 Torr, with helium as the bath gas. Each cluster of bars corresponds to the transition state barrier height of one reaction, indicated at left. The bars indicate how each product's yield is affected by adjusting the associated barrier height, and are ordered and colored by product as shown in the legend.

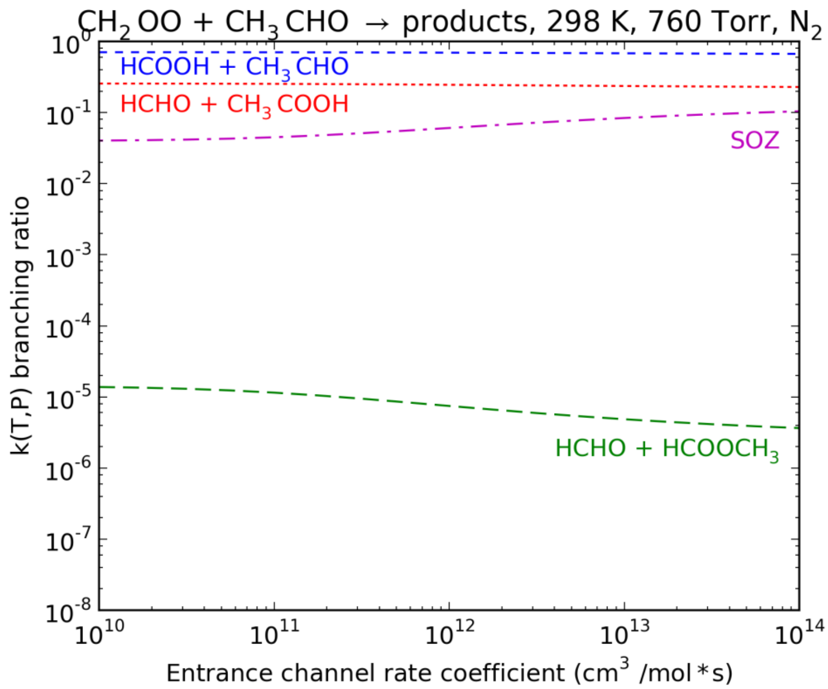

Figure 9: Effect of changing the rate of the adduct-forming entrance channel on the product branching ratios for •CH_2OO• + CH_3CHO → products at 298 K and 760 Torr N_2.

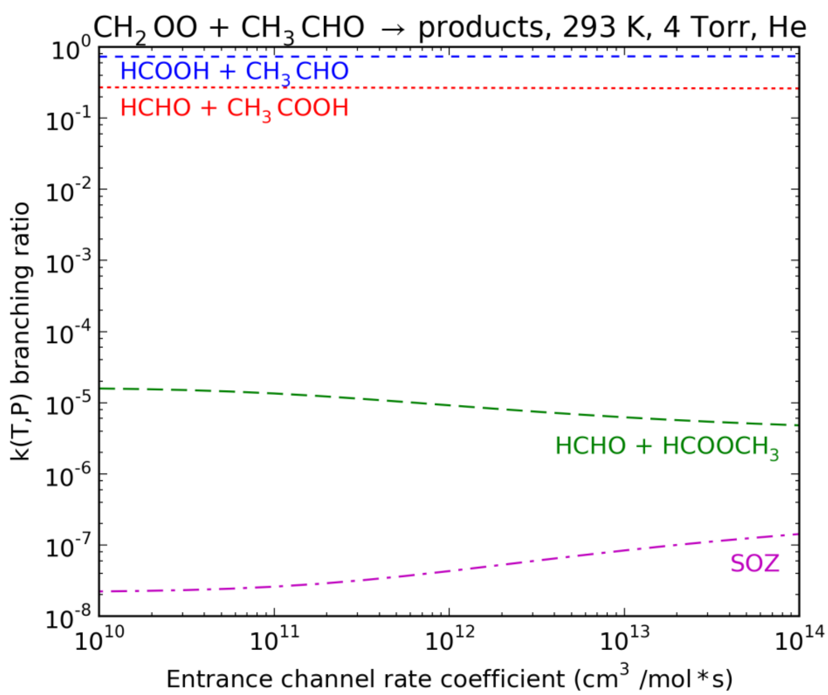

Figure 10: Effect of changing the rate of the adduct-forming entrance channel on the product branching ratios for •CH_2OO• + CH_3CHO → products at 293 K and 4 Torr He.

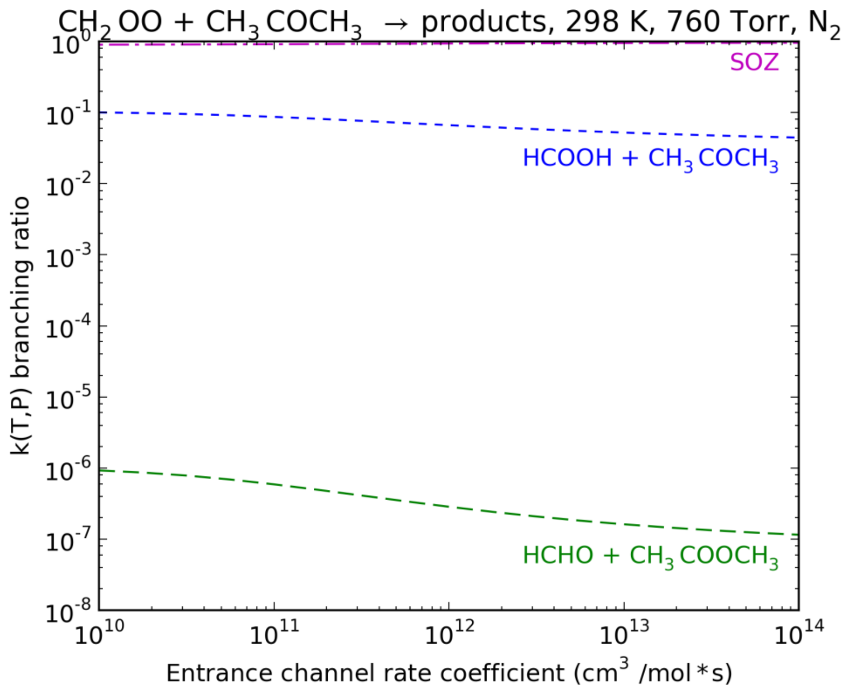

Figure 11: Effect of changing the rate of the adduct-forming entrance channel on the product branching ratios for •CH_2OO• + CH_3COCH_3 → products at 298 K and 760 Torr N_2.

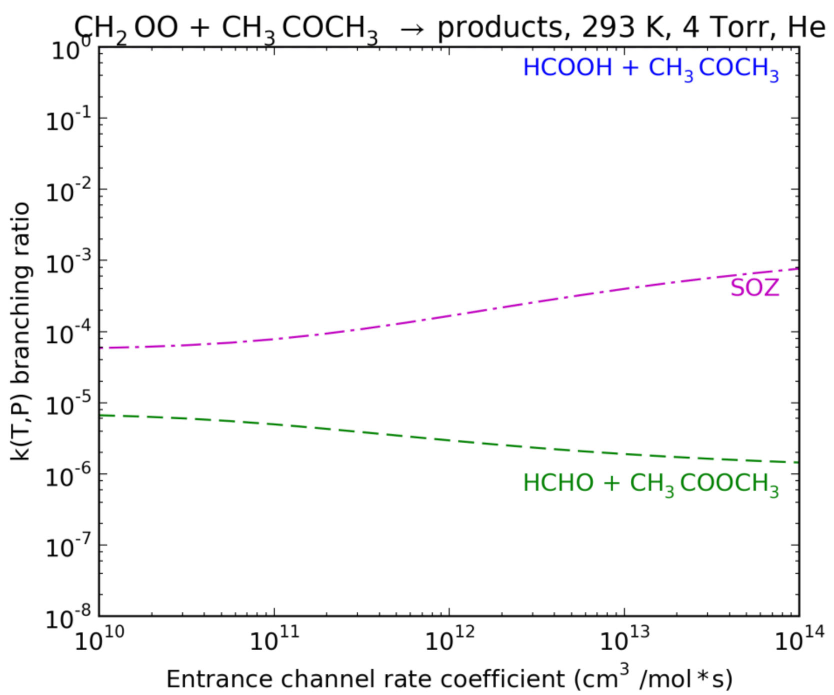

Figure 12: Effect of changing the rate of the adduct-forming entrance channel on the product branching ratios for •CH_2OO• + CH_3COCH_3 → products at 293 K and 4 Torr He.

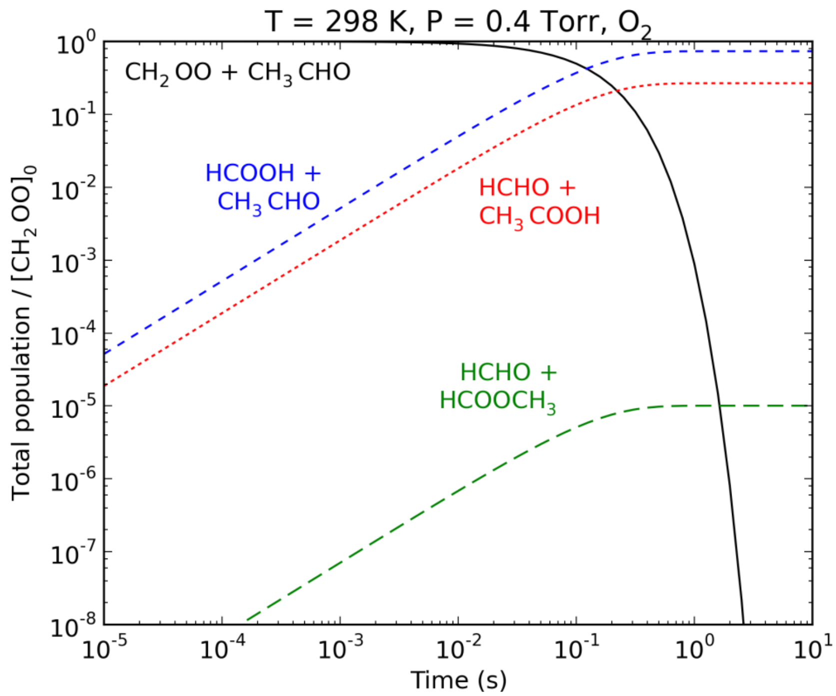

Figure 13: Predicted concentration profiles for the •CH_2OO• + CH_3CHO network at 293 K and 0.4 Torr O_2, using a CH_3COCH_3 mole fraction of 0.01. The yield of SOZ due to collisional stabilization by O_2 is so low that the SOZ profile never appears on this plot, justifying the neglecting of O_2 collisions.

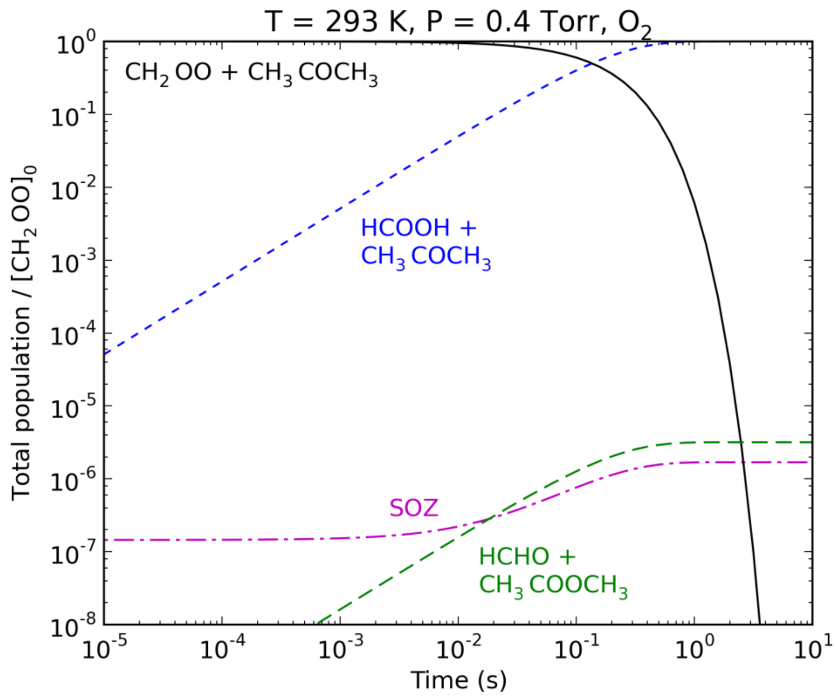

Figure 14: Predicted concentration profiles for the •CH_2OO• + CH_3COCH_3 network at 293 K and 0.4 Torr O_2, using a CH_3COCH_3 mole fraction of 0.01. The yield of SOZ due to collisional stabilization by O_2 is much lower than that due to the He in Taatjes' experiment, justifying the neglecting of O_2 collisions.

2 High-Pressure Limit Rate Coefficients

Table 1: Arrhenius parameters corresponding to high-pressure limit rate coefficients for elementary reactions on the •CH_2OO• + HCHO PES[a]

Reaction			A (s^{-1})	n	E_a (kcal/mol)
SOZ	⇌	[•CH_2OO• + HCHO]	2.4×10^{12}	0.85	46.1
SOZ	⇌	[HCOOH + HCHO]	1.1×10^{9}	1.70	40.7
SOZ	⇌	HMF	6.7×10^{7}	1.97	26.9
HMF	⇌	[HCOOH + HCHO]	1.7×10^{12}	-0.03	19.1

[a]The rate coefficient is $k(T) = A(T/1\ [K])^n \exp(-E_a/RT)$.

Table 2: Arrhenius parameters corresponding to high-pressure limit rate coefficients for elementary reactions on the •CH_2OO• + CH_3CHO PES[a]

Reaction			A (s^{-1})	n	E_a (kcal/mol)
SOZ	⇌	[•CH_2OO• + CH_3CHO]	4.8×10^{12}	0.73	45.3
SOZ	⇌	HEF	1.1×10^{9}	1.64	28.0
SOZ	⇌	HMA	4.0×10^{8}	1.75	29.4
HEF	⇌	[HCOOH + CH_3CHO]	1.9×10^{14}	-0.52	17.6
HMA	⇌	[CH_3COOH + HCHO]	1.7×10^{13}	-0.24	18.9
SOZ	⇌	[HCOOH + CH_3CHO]	2.7×10^{10}	1.33	39.5
SOZ	⇌	[CH_3COOH + HCHO]	1.3×10^{8}	1.90	38.6
SOZ	⇌	[$HCOOCH_3$ + HCHO]	8.8×10^{11}	0.99	47.0

[a]The rate coefficient is $k(T) = A(T/1\ [K])^n \exp(-E_a/RT)$.

Table 3: Arrhenius parameters corresponding to high-pressure limit rate coefficients for elementary reactions on the •CH_2OO• + CH_3COCH_3 PES[a]

Reaction			A (s^{-1})	n	E_a (kcal/mol)
SOZ	⇌	[•CH_2OO• + CH_3COCH_3]	9.1×10^{12}	0.62	45.0
SOZ	⇌	HIF	3.2×10^{8}	1.81	30.2
HIF	⇌	[HCOOH + CH_3COCH_3]	9.1×10^{14}	-0.73	15.6
SOZ	⇌	[HCOOH + CH_3COCH_3]	9.4×10^{10}	1.18	40.9
SOZ	⇌	[CH_3COOCH_3 + HCHO]	6.2×10^{11}	0.62	45.0

[a]The rate coefficient is $k(T) = A(T/1\ [K])^n \exp(-E_a/RT)$.