Appendix E—The "Global Kinetics Model": OH+(NO_2,CO,O_2) and HO_2+(HCHO,NO)

This appendix contains the kinetics model used for simulating a wide range of small molecule HO_x and NO_x chemistry: OH + (NO_2,CO,O_2) and HO_2 + (HCHO,NO). We use the Kintecus 3.95 program for all of our modeling (available free of charge to academic users at http://www.kintecus.com).[191] This program allows for easy input of bimolecular reactions. We have made modifications to the standard input files to easily input special reactions from the NASA/JPL database:[27] termolecular reactions, reactions based on equilibrium constants, chemical activation reactions, and miscellaneous reactions with other dependences.

Items described in this chapter:

1) Setting up Kintecus 3.95
2) Calculation of Termolecular Rate Constants
3) Calculation of Other Reaction Rate Constants
4) Reactions Included in the "Global Kinetics Model"

1) Setting up Kintecus 3.95

At its core, Kintecus 3.95 is a numerical integrator that runs at the Windows NT command line. To permit ease of use, the author of the program has also written Microsoft Excel spreadsheets that contain all of the relevant simulation input (model, parameters) and compiled output. Figures E.1–E.3 show excerpts of the spreadsheets used to enter the model and specify simulation parameters.

	A	B	C	D	E
1	#	Model Description SpreadSheet			
2	# Reactions can be entered in as				
3	# k	Reaction	Comments		
4	# 1.2345	A+B==>C	A sample reaction with rate constant		
5	#				
6	# OR				
7	#				
8	# A	T^m	Ea	Reaction	Comments
9	# 50600	2.67	6290	O+H2=OH+H	KLEMM,ET AL
151	# Section I - HO2+HCHO Reactions				
152	7.70E-15	0	-625	HO2+CH2O==>HOCH2O2	Veyret, 1989
153	2.00E+12	0	7000	HOCH2O2==>HO2+CH2O	Veyret, 1989
154	7.20E-12	0	0	HO2+HOCH2O2==>O2+HOCH2O2H	Burrows 1989, 298K
155	4.80E-12	0	0	HO2+HOCH2O2==>HCO2H+H2O+O2	Burrows 1989, 298K
156	5.20E-12	0	0	HOCH2O2+HOCH2O2==>HOCH2O+HOCH2O+O2	Burrows 1989, 298K

Figure E.1. Portion of a kinetics model ("Model" tab) entered into a Kintecus Excel spreadsheet.

	A	B	C	D	E	F	G
1	#	Species Description Spreadsheet					
2	# Species	Residence	Initial	Display Output	External	SSA ?	Constant
3	#	Time in CSTR(s)	Conc.	(Y/N) ?	Conc.	(Y/N)	(Filename
4	CH2O	0	0.00E+00	yes	0	No	No
5	Cl	0	7.50E+12	yes	0	no	no
6	Cl2	0	3.00E+15	yes	0	No	No
7	CH3OH	0	1.00E+15	yes	0	No	No
8	NO	0	4.00E+15	yes	0	No	No

Figure E.2. Portion of the initial chemical concentrations ("Species tab) entered into a Kintecus Excel spreadsheet.

	A	B	C	D	E
1	#	Parameter Description SpreadSheet			
2	# See .pdf file for an explanation of each field				
3	#				
4	# Starting Integration Time	Maximum Integration Time	Ea UNITS (Kcal, KJ,J,CAL,K)	Conc. Units(moles/L, moles/cc, molecules/cc)	X0
5	1.00E-10	1.00E-06	Kelvin	Molecules/cm^3	0
6	#			External Heat Source/Sink # OR Profile (Filename)	
7	#Temperature (K) or Filename	Pressure (Constant ? (Yes/N	Volume Profile (Filename/No	OR Condutance:Extern. Temp OR Conductance:Ex	X0
8	300	NOPE	NO	No	0
9	# Simulation Length:				
10	# DAYS	Hours	Minutes	Seconds	PicoSeconds
11	0	0	0	3.00E-03	0
12	#				
13	#hv(filename)	Sampling Interval (s)	Percent(%)	Accuracy	X0
14	None1	1	0	1.00E-08	0
15	# THESE FIELDS BELOW (X0) ARE CURRENTLY NOT USED, LEAVE THEM AT 0				
16	# CSTR/PFR inlet Flow Temperature	X0	X0	X0	X0
17	0	0	0	0	0
18	#				
19	END				
20					

Figure E.3. Kinetics simulation parameters ("Parm" tab) entered into a Kintecus Excel spreadsheet.

Figure E.1 shows that reaction temperature dependencies can be expressed in two ways: T^n or Exp[$-E_a/RT$], where n or E_a are entered respectively (units of E_a specified on the "Parm" tab). The T^n column cannot be left blank: if there is no T^n dependence, 0

should be entered. Reactions based on equilibrium constants can be entered here (using <==> rather than ==> and entering K_{eq} in the *A* column); however, I have had terrible luck getting these reactions to work properly, especially in the case where the individual reactions are termolecular. Instead, I choose to use a rate constant calculator (described in Section 3 of this appendix).

Figure E.2 contains a list of all of the chemical species included in the kinetics model. This worksheet can be automatically generated by Kintecus on the "Control" tab (Make Species Spreadsheet from Model). The user needs to enter the initial concentrations (units specified on the "Parm" tab) and whether the concentration of that species should be written to the output file. All other options can be left as their defaults.

Figure E.3 contains all of the setting needed for the kinetics simulation, including the units of activation energy ("Ea units") and concentration ("Conc Units"), temperature, simulation time ("Seconds"), and step size ("Maximum Integration Time"). The user should not change any of the other parameters. Typically, Ea units should be set to Kelvin (same units as in the NASA/JPL Data Evaluation) and Conc Units should be set to Molecules/cm^3 (common units in atmospheric and gas phase chemistry). The maximum integration time should be set in relation to the simulation time; in general, no more than 30000 data points should be generated (plots in Excel 2003 or earlier cannot handle more than 32768 points).

2) Calculation of Termolecular Rate Constants

Termolecular reactions are typically modeled by "falloff" curves: i.e., linearly dependent on pressure at low pressures, and bimolecular at high pressure. This is represented in the NASA/JPL Data Evaluation by Equation E.1:

$$k = \left(\frac{k_0 [M]}{1 + \frac{k_0 [M]}{k_\infty}} \right) \times 0.6^{\left\{ 1 + \left[\log_{10} \left(\frac{k_0 [M]}{k_\infty} \right) \right]^2 \right\}^{-1}}, \tag{E.1}$$

where k_0 and k_{infinity} are the termolecular and bimolecular rate constants in the limits of zero and infinite pressure respectively, and [M] is the concentration of bath gas particles (pressure).

The problem is that Kintecus does not have the NASA/JPL form for termolecular falloff curves built in. Instead, Kintecus uses the IUPAC recommended form[118]

$$k = \left(\frac{k_0 [M]}{1 + \frac{k_0 [M]}{k_\infty}} \right) \times F, \tag{E.2}$$

where

$$\log F = \left[1 + \left[\frac{\log \left(\frac{k_o [M]}{k_\infty} \right)}{n - 0.14 \left(\log \frac{k_0 [M]}{k_\infty} + c \right)} \right]^2 \right]^{-1} \log F_{cent}, \tag{E.3}$$

$$c = -0.4 - 0.67 \log F_{cent}, \tag{E.4}$$

$$n = 0.75 - 1.27 \log F_{cent}. \tag{E.5}$$

Unfortunately, I cannot find a way to reconcile the NASA/JPL and Kintecus falloff curve formulations, especially because the k_0 and k_{infinity} derived from each formulation are not equal.[118]

To get around this problem, I wrote an Excel worksheet to calculate the effective bimolecular rate constant k from Equation E.1 and the NASA/JPL parameters. This worksheet is shown in Figure E.4. The user enters k_0, n, k_{inf}, and m (from the NASA/JPL database). Based on the total pressure (calculated from the sum of concentrations in the "Species" spreadsheet) and the temperature (from the "Parm" spreadsheet), the effective bimolecular rate constant is reported in the "A" column. The reactions are automatically copied into the main "Model" spreadsheet: therefore, any changes to pressure, temperature, or falloff parameters will be immediately updated in the kinetics model. For reactions with no high pressure limit listed, k_{inf} should be set to 1.

1	The user should enter k0(300), n, kinf(300), and m for each reaction								
2	For "chemical activation" reactions, the A column must be altered								
3	Temp (K)	300	DO NOT EDIT T or P, THEY ARE CALCULATED BASED ON THE SPECIES AND PARM WORKSHEETS						
4	p (torr)	524.9385							
5	# A	T^m	Ea	Reaction	Comments	k0(300)	n	kinf(300)	m
6	1.26288E-12	0	0	OH+NO2==>HOONO	Sample Reaction	9.10E-32	3.9	4.20E-11	0.5
7	1.02E-14	0	0	O+O2==>O3	Termolecular, JPL15 2-4, no high pressure limit	6.00E-34	2.4	1.00E+00	
8	4.75315E-17	0	0	O1D+N2==>N2O	Termolecular, JPL15 2-4, no high pressure limit	2.80E-36	0.9	1	
9	6.5288E-13	0	0	H+O2==>HO2	Termolecular, JPL15 2-4	4.40E-32	1.3	4.70E-11	0.2
10	5.12308E-12	0	0	OH+OH==>H2O2	Termolecular, JPL15 2-4	6.90E-31	1	2.60E-11	0
11	1.20279E-12	0	0	O+NO==>NO2	Termolecular, JPL15 2-4	9.00E-32	1.5	3.00E-11	0
12	2.54033E-12	0	0	O+NO2==>NO3	Termolecular, JPL15 2-4	2.50E-31	1.8	2.20E-11	0.7
13	5.90798E-12	0	0	OH+NO==>HONO	Termolecular, JPL15 2-4	7.00E-31	2.6	3.60E-11	0.1
14	8.7814E-12	0	0	OH+NO2==>HONO2	Termolecular, JPL15 2-4	1.80E-30	3	2.80E-11	0
15	7.36425E-13	0	0	CH3+O2==>CH3O2	Termolecular, JPL15 2-4	4.00E-31	3.6	1.20E-12	-1.1
16	2.69144E-11	0	0	CH3O+NO==>CH3ONO	Termolecular, JPL15 2-4	2.30E-29	2.8	3.80E-11	0.6
17	1.62727E-11	0	0	CH3O+NO2==>CH3ONO2	Termolecular, JPL15 2-5	5.30E-29	4.4	1.90E-11	1.8
18	2.13624E-13	0	0	Cl+Cl==>Cl2	Termolecular, NIST (no "falloff" listed, valid at 300	1.26E-32	1	1.00E+00	0
19	#DIV/0!	0	0		Termolecular				

Figure E.4. Termolecular falloff kinetics calculator worksheet. The effective bimolecular rate constants and reactions are automatically copied into the main kinetics model.

3) Calculation of other reaction rate constants

We can construct other worksheets to calculate rate constants similar to calculation of the termolecular falloff rate constants. We discuss two special reaction

types in this section: rate constants based on equilibrium constants, and treatment of $OH + O_2$.

Equilibrium constants are defined in the NASA/JPL database in terms of two parameters, A and B:

$$K_{eq} = A \exp\left[\frac{B}{T}\right],\ 200\ \text{K} < T < 300\ \text{K}. \tag{E.6}$$

Typically, either the forward or backward reaction is defined in terms of a bimolecular or termolecular rate constant. Using K_{eq} and one rate constant, we can define both the forward and backward rates. Figure E.5 shows the worksheet developed for these calculations. The user can input either bimolecular or termolecular rate constants for the forward rate, and the program will calculate effective bimolecular rate constants for both the forward and backward reactions. Note that if the user types in both bimolecular and termolecular rates, the bimolecular rate will take precedence. Similar to the termolecular falloff kinetics calculator, the rate constants are automatically copied to the main "Model spreadsheet," any updates to the equilibrium constant page will be immediately reflected in the main model.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	From JPL15 (p.3-1), K(T) = A*Exp[B/T], for 200K < T < 300K															
2	This table assumes the units for Ea are in Kelvin (that is, the Ea column has Ea/R)															
3	If the bimolecular parameters are left blank, then the table will automatically use the termolecular parameters to obtain rate constants															
4	T	300	K	DO NOT EDIT T or P, THEY ARE CALCULATED BASED ON THE SPECIES AND PARM WORKSHEETS												
5	p	300	torr				Equilibrium Values			Bimolecular			Termolecular			
6							cm3 molec-1	K		Forward Reaction Parameters						
7	# A	T^m	Ea	Reaction	Comments		Keq A	Keq B		A	Ea/R		k0(300)	n	kinf(300)	m
8	7.58E-13	0	0	OH+NO2==>HOONO	Sample Reaction		3.90E-27	10125					9.10E-32	3.9	4.20E-11	0.5
9	4.28E-01	0	0	HOONO==>OH+NO2	Sample Reaction											
10																
11	7.58E-13	0	0	OH+NO2==>HOONO	JPL15, 2-4, 3-2		3.90E-27	10125					9.10E-32	3.9	4.20E-11	0.5
12	4.28E-01	0	0	HOONO==>OH+NO2												
13	7.09E-13	0	0	HO2+NO2==>HO2NO2	JPL15, 2-4, 3-2		2.10E-27	10900					2.00E-31	3.4	2.90E-12	1.1
14	5.61E-02	0	0	HO2NO2==>HO2+NO2												
15	2.89E-15	0	0	NO+NO2==>N2O3	JPL15, 3-2, and NIST Kine		3.30E-27	4667					3.10E-34	7.7	7.80E-12	-1.4
16	1.54E+05	0	0	N2O3==>NO+NO2												
17	1.20E-14	0	0	NO2+NO2==>N2O4	JPL15, 3-2, and NIST Kine		5.90E-29	6643					1.40E-33	3.8	1.00E-12	0
18	4.91E+04	0	0	N2O4==>NO2+NO2												
19	1.05E-12	0	0	NO2+NO3==>N2O5	JPL15, 2-4, 3-2		2.70E-27	11000					2.00E-30	4.4	1.40E-12	0.7
20	4.62E-02	0	0	N2O5==>NO2+NO3												
21	2.50E-12	0	0	CH3O2+NO2==>CH3O2NO2	JPL15, 2-5, 3-2		9.50E-29	11234					1.00E-30	4.8	7.20E-12	2.1
22	1.44E+00	0	0	CH3O2NO2==>CH3O2+NO2												
23	5.70E-11	0	0	OH+O2==>HO3	Sridharan, and Stat Mech		3.95E-22	0		5.70E-11						
24	1.44E+11	0	0	HO3==>OH+O2												
25	2.07E-14	0	0	Cl+O2==>ClOO	JPL 15, 2-5, 3-2		6.60E-23	2502					2.20E-33	3.1	1.80E-10	0
26	7.50E+04	0	0	ClOO==>Cl+O2	JPL 15, 2-5, 3-2											
27	1.26E-14	0	0	Cl+CO==>ClCO	JPL 15, 1-8, 3-2		3.50E-25	3730					1.30E-33	3.8	1.00E+00	0
28	1.43E+05	0	0	ClCO==>Cl+CO	JPL 15, 1-8, 3-2											
29	1.15E-13	0	0	ClO+ClO==>Cl2O2	JPL 15, 1-8, 3-2		9.30E-28	8835					1.60E-32	4.5	2.00E-12	2.4
30	2.00E+01	0	0	Cl2O2==>ClO+ClO	JPL 15, 1-8, 3-2											

Figure E.5. Equilibrium reaction rate kinetics calculator worksheet. The effective bimolecular rate constants and reactions are automatically copied into the main kinetics model.

It has been suggested that OH + O_2 will combine to form the HO_3 radical, with binding energy on the order of 3-5 kcal mol^{-1}.[212-232] In our kinetics treatment, we estimate the rate constants for HO_3 using a theoretical equilibrium constant (calculated partition functions combined with an experimental binding energy[219, 224]) and a calculated forward rate constant.[233]

Further reactions of HO_3 are treated using OH + O_2 as the analogous reactant. For example, since OH + OH → H_2O_2 is present in our kinetics model, we also include the reaction HO_3 + OH → H_2O_2 + O_2. Bimolecular rate constants for HO_3 are taken to be equal to the OH reaction. Termolecular rate constants are taken to be equal to the high pressure limit (i.e., O_2 acts as the third body, and is always present for reaction).

4) Reactions included in the "Global Kinetics Model"

Our kinetics model includes over 150 reactions spanning small molecule HO_x and NO_x chemistry. We do not consider any organic species with more than one carbon. The model contains the chemistry necessary to model radical generation through O_3 photolysis in the presence of H_2 or CH_4 (OH) or Cl_2 photolysis in the presence of HCHO or CH_3OH (HO_2). The entire model is shown below in Table E.1. Rate constants are presented assuming 300 K, 760 torr (termolecular and specially calculated rate constants are updated when the pressure is varied).

Table E.1. Reactions included in the "Global Kinetics Model" used in this thesis. Termolecular and special rate constants calculated at 300 K, 760 torr for this table. All rate constants taken from NASA/JPL[27] or NIST Kinetics[117] unless otherwise specified.

A (cm^3 $molec^{-1}$ s^{-1})	Ea (K)	Reaction	Reference
Section A—Reactions defined by Equilibrium Constants			
7.58E−13		OH+NO2==>HOONO	
4.28E−01		HOONO==>OH+NO2	
7.09E−13		HO2+NO2==>HO2NO2	
5.61E−02		HO2NO2==>HO2+NO2	
2.89E−15		NO+NO2==>N2O3	
1.54E+05		N2O3==>NO+NO2	
1.20E−14		NO2+NO2==>N2O4	
4.91E+04		N2O4==>NO2+NO2	
1.05E−12		NO2+NO3==>N2O5	
4.62E−02		N2O5==>NO2+NO3	
2.50E−12		CH3O2+NO2==>CH3O2NO2	
1.44E+00		CH3O2NO2==>CH3O2+NO2	
5.70E−11		OH+O2==>HO3	Sridharan[233]
1.44E+11		HO3==>OH+O2	D_0=−4.5 kcal mol^{-1} [220, 224]
2.07E−14		Cl+O2==>ClOO	
7.50E+04		ClOO==>Cl+O2	
1.26E−14		Cl+CO==>ClCO	
1.43E+05		ClCO==>Cl+CO	
1.15E−13		ClO+ClO==>Cl2O2	
2.00E+01		Cl2O2==>ClO+ClO	
Section B—Termolecular Reactions following the Troe Falloff Curve			
5.82E−15		O+O2==>O3	
2.72E−17		O1D+N2==>N2O	
3.84E−13		H+O2==>HO2	
3.65E−12		OH+OH==>H2O2	
7.30E−13		O+NO==>NO2	
1.68E−12		O+NO2==>NO3	
4.09E−12		OH+NO==>HONO	

6.59E−12		OH+NO2==>HONO2	
6.11E−13		CH3+O2==>CH3O2	
2.36E−11		CH3O+NO==>CH3ONO	
1.55E−11		CH3O+NO2==>CH3ONO2	
1.22E−13		Cl+Cl==>Cl2	
Section C—Special Reactions			
1.49E−13		OH+HONO2==>H2O+NO3	
1.00E−13		OH+CO==>HOCO	
1.50E−13		OH+CO==>H+CO2	
2.40E−11		HOCO==>OH+CO	
9.30E−12		HOCO==>H+CO2	
Section D—O1D/H2 Chemistry			
8.00E−12	2060	O+O3==>O2+O2	
3.30E−11	−55	O1D+O2==>O+O2	
1.20E−10	0	O1D+O3==>O2+O2	
1.20E−10	0	O1D+O3==>O2+O+O	
1.10E−10	0	O1D+H2==>OH+H	
1.63E−10	−60	O1D+H2O==>OH+OH	
2.15E−11	−110	O1D+N2==>O+N2	
2.20E−11	−120	O+OH==>O2+H	
3.00E−11	−200	O+HO2==>OH+O2	
1.40E−12	2000	O+H2O2==>OH+HO2	
1.40E−10	470	H+O3==>OH+O2	
7.20E−11	0	H+HO2==>OH+OH	
1.60E−12	0	H+HO2==>O+H2O	
6.90E−12	0	H+HO2==>H2+O2	
1.70E−12	940	OH+O3==>HO2+O2	
2.80E−12	1800	OH+H2==>H2O+H	
1.80E−12	0	OH+OH==>H2O+O	
4.80E−11	−250	OH+HO2==>H2O+O2	
1.80E−12	0	OH+H2O2==>H2O+HO2	
1.00E−14	490	HO2+O3==>OH+O2+O2	
3.50E−13	−430	HO2+HO2==>H2O2+O2	
1.70E−33	−1000	HO2+HO2+M==>H2O2+O2+M	
Section E—O1D/CH4 Chemistry (O1D from N2O or O3)			
1.12E−10	0	O1D+CH4==>CH3+OH	
3.00E−11	0	O1D+CH4==>CH3O+H	
7.50E−12	0	O1D+CH4==>CH2O+H2	
4.70E−11	−20	O1D+N2O==>N2+O2	
6.70E−11	−20	O1D+N2O==>NO+NO	
5.10E−12	−210	O+NO2==>NO+O2	
1.00E−11	0	O+NO3==>O2+NO2	
4.00E−10	340	H+NO2==>OH+NO	
1.80E−11	390	OH+HONO==>H2O+NO2	
3.50E−12	−250	HO2+NO==>OH+NO2	
1.40E−14	−250	HO2+NO==>HONO2	Butkovskaya[234]
3.00E−12	1500	NO+O3==>NO2+O2	
1.10E−10	0	O+CH3==>CH3O	
2.45E−12	1775	OH+CH4==>CH3+H2O	
5.50E−12	−125	OH+CH2O==>H2O+HCO	
2.90E−12	345	OH+CH3OH==>CH2OH+H2O	
5.20E−12	0	HCO+O2==>HO2+CO	
9.10E−12	0	CH2OH+O2==>CH2O+HO2	
3.90E−14	900	CH3O+O2==>CH2O+HO2	
4.00E−12	0	CH3O+NO==>CH2O+HNO	IUPAC[118]

1.10E−11	1200	CH3O+NO2==>CH2O+HONO	
2.80E−12	−300	CH3O2+NO==>CH3O+NO2	
Section F—HOONO Chemistry			
3.00E−17	0	O+HONO2==>OH+NO3	
7.80E−11	3400	O+HO2NO2==>HO2+NO3	
2.20E−11	0	OH+NO3==>HO2+NO2	
1.30E−12	−380	OH+HO2NO2==>H2O+NO2+O2	
3.50E−12	0	HO2+NO3==>OH+NO2+O2	
1.50E−11	−170	NO+NO3==>NO2+NO2	
1.20E−13	2450	NO2+O3==>NO3+O2	
8.50E−13	2450	NO3+NO3==>NO2+NO2+O2	
5.00E−19	0	O3+HONO==>O2+HONO2	
2.00E−21	0	N2O5+H2O==>2HONO2	
5.00E−16	0	HO2+NO2==>HONO+O2	
Section G—HOCO Chemistry			
7.50E−11	−115	O1D+CO2==>O+CO2	
3.40E−11	1600	O+CH2O==>OH+HCO	
2.00E−12	0	O2+HOCO==>HO2+CO2	
2.70E−12	0	HOCO+NO==>HONO+CO	
1.03E−11	0	HOCO+OH==>CO2+H2O	
4.00E−19	0	NO3+CO==>NO2+CO2	
5.80E−16	0	NO3+CH2O==>HONO2+HCO	
Section H—Chlorine Chemistry (for Cl+MeOH)			
5.50E−11	0	Cl+CH3OH==>CH2OH+HCl	
9.10E−12	0	CH2OH+O2==>CH2O+HO2	
1.60E−13	6300	HOCH2O2+CH3OH==>HOCH2O2H+CH2OH	
2.00E−11	0	HOCH2O2+CH2OH==>HOCH2O2H+CH2O	
4.35E−13	345	CH3OH+OH==>CH3O+H2O	
8.10E−11	30	Cl+CH2O==>HCl+HCO	
1.80E−11	−170	HO2+Cl==>HCl+O2	
4.10E−11	450	HO2+Cl==>OH+ClO	
2.70E−12	−220	HO2+ClO==>HOCl+O2	
1.10E−11	980	Cl+H2O2==>HCl+HO2	
1.40E−12	900	OH+Cl2==>HOCl+Cl	
7.40E−12	−270	OH+ClO==>Cl+HO2	
6.00E−13	−230	OH+ClO==>HCl+O2	
2.60E−12	350	OH+HCl==>H2O+Cl	
3.00E−12	500	OH+HOCl==>H2O+ClO	
1.25E−12	130	Cl+HOCl==>Cl2+OH	
1.25E−12	130	Cl+HOCl==>HCl+ClO	
Section I—HO2+HCHO Reactions			
7.70E−15	−625	HO2+CH2O==>HOCH2O2	Veyret[26]
2.00E+12	7000	HOCH2O2==>HO2+CH2O	Veyret[26]
7.20E−12	0	HO2+HOCH2O2==>O2+HOCH2O2H	Burrows[25]
4.80E−12	0	HO2+HOCH2O2==>HCO2H+H2O+O2	Burrows[25]
5.20E−12	0	HOCH2O2+HOCH2O2==>HOCH2O+HOCH2O+O2	Burrows[25]
5.65E−14	−750	HOCH2O2+HOCH2O2==>HCO2H+CH2OHOH+O2	Veyret[26]
3.50E−14	0	HOCH2O+O2==>HCO2H+HO2	Burrows[25]
Section J—CH3ONO Reactions			
2.32E−11	2620	CH3ONO+O==>OH+CH2O+NO	
3.00E−20	0	CH3ONO+HONO2==>CH3OH+NO2+NO2	
4.45E−13	0	CH3ONO+CH3O==>CH3OH+CH2O+NO	
2.09E−12	0	CH3ONO+Cl==>CH3O+ClNO	

Section K—HO3 Reaction Analogs − O1D/CH4 Chemistry			
Part 1—Equilibrium Reaction Analogs			
4.20E−11		HO3+NO2==>HOONO+O2	OH+NO2 → HOONO, high pressure limit
Part 2—Termolecular Reaction Analogs			
2.60E−11		HO3+OH==>H2O2+O2	OH+OH high pressure limit
2.60E−11		HO3+HO3==>H2O2+O2+O2	OH+OH high pressure limit
3.60E−11		HO3+NO==>HONO+O2	OH+NO high pressure limit
2.80E−11		HO3+NO2==>HONO2+O2	OH+NO2 → Nitric Acid, high pressure limit
Part 3—Special Reaction Analogs			
1.52E−13		HO3+HONO2==>H2O+NO3+O2	OH+HONO2 high pressure limit
Part 4—O1D/H2 Chemistry Analogs			
2.20E−11	−120	O+HO3==>O2+H+O2	O+OH analog
1.70E−12	940	HO3+O3==>HO2+O2+O2	OH+O3 analog
2.80E−12	1800	HO3+H2==>H2O+H+O2	OH+H2 analog
1.80E−12	0	HO3+OH==>H2O+O+O2	OH+OH analog
1.80E−12	0	HO3+HO3==>H2O+O+O2+O2	OH+OH analog
4.80E−11	−250	HO3+HO2==>H2O+O2+O2	OH+HO2 analog
1.80E−12	0	HO3+H2O2==>H2O+HO2+O2	OH+H2O2 analog
Part 5—O1D/CH4 Chemistry Analogs			
1.80E−11	390	HO3+HONO==>H2O+NO2+O2	OH+HONO analog
2.45E−12	1775	HO3+CH4==>CH3+H2O+O2	OH+CH4 analog
5.50E−12	−125	HO3+CH2O==>H2O+HCO+O2	OH+CH2O analog
2.90E−12	345	HO3+CH3OH==>CH2OH+H2O+O2	OH+CH3OH analog
Part 6—HOONO Chemistry Analogs			
2.20E−11	0	HO3+NO3==>HO2+NO2+O2	OH+NO3 analog
1.30E−12	−380	HO3+HO2NO2==>OHHO2NO2+O2	OH+HO2NO2 analog
Part 7—Chlorine Chemistry Analogs			
4.35E−13	345	HO3+CH3OH==>CH3O+O2+H2O	OH+CH3OH analog
1.40E−12	900	HO3+Cl2==>HOCl+Cl+O2	OH+Cl2 analog
7.40E−12	−270	HO3+ClO==>Cl+HO2+O2	OH+ClO analog
6.00E−13	−230	HO3+ClO==>HCl+O2+O2	OH+ClO analog
2.60E−12	350	HO3+HCl==>H2O+Cl+O2	OH+HCl analog