Supporting Information *for* Temperature Dependent Branching Ratios of Deuterated Methoxy Radicals ($CH_2DO\cdot$) Reacting with O_2

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Table S1: CH_2O formation from cyclohexane subsequent to CD_3ONO photolysis at 295K

At 295K, CH_3ONO impurity in CD_3ONO (%)				5.2
Δ [CD_2O] (10^{14} molecule/cm^3)	Δ [CH_2O] (10^{13} molecule/cm^3)	Δ [cyclohexane] (10^{14} molecule/cm^3)	Δ[CH_2O] from cyclohexane (10^{12} molecule/cm^3)	Yield(CH_2O) from cyclohexane (%)
2.44	1.43	1.40	1.62	1.2
2.73	1.61	1.68	1.89	1.1
2.90	1.85	1.96	3.44	1.8
1.75	1.01	1.04	1.00	1.0
1.94	1.19	1.54	1.81	1.2
2.12	1.37	1.71	2.68	1.6
2.23	1.58	2.16	4.20	1.9
Average (±1σ)				1.4±0.4

Table S2: CH_2O formation from cyclohexane subsequent to CD_3ONO photolysis at 320 K

At 320K, CH_3ONO impurity in CD_3ONO (%)				3.6
Δ [CD_2O](10^{14} molecule/cm^3)	Δ [CH_2O] (10^{13} molecule/cm^3)	Δ [cyclohexane] (10^{14} molecule/cm^3)	Δ [CH_2O] from cyclohexane (10^{12} molecule/cm^3)	Yield(CH_2O) from cyclohexane (%)
1.59	1.10	1.46	5.32	3.6
1.88	1.25	1.71	5.69	3.3
2.26	1.83	1.96	10.18	5.2
2.51	2.14	2.49	12.33	4.9
1.34	1.01	0.84	5.33	6.3
1.59	1.37	1.15	7.99	6.9
1.89	1.60	1.32	9.22	7.0
2.10	1.94	1.71	11.84	6.9
Average (±1σ)				5.5±1.5

Figure S1: Full Scheme of the mechanism of cyclohexane oxidation (to produce CH_2O).

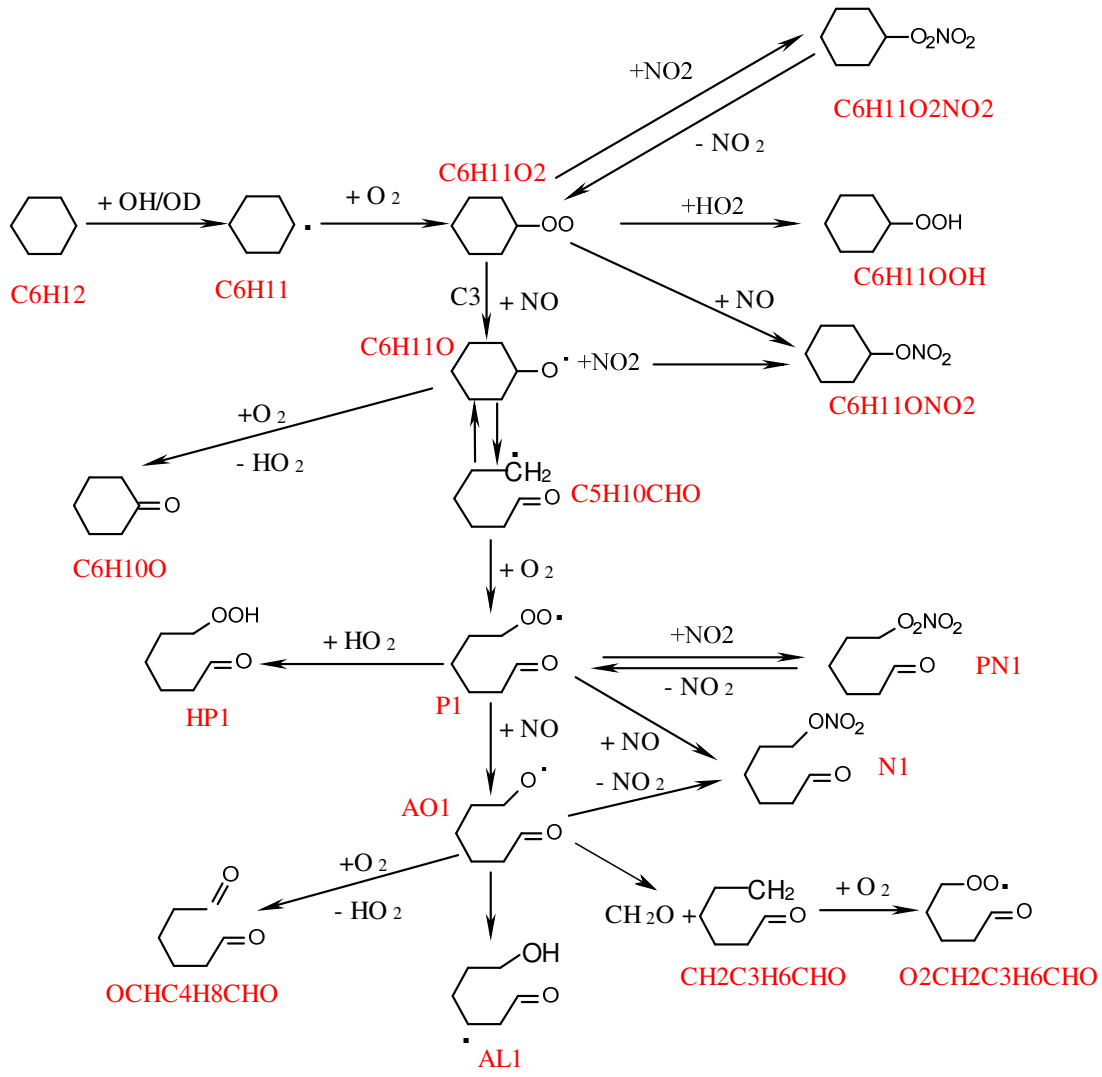

Figure S1-cont.: Full Scheme of the mechanism of cyclohexane oxidation (to produce CH_2O)

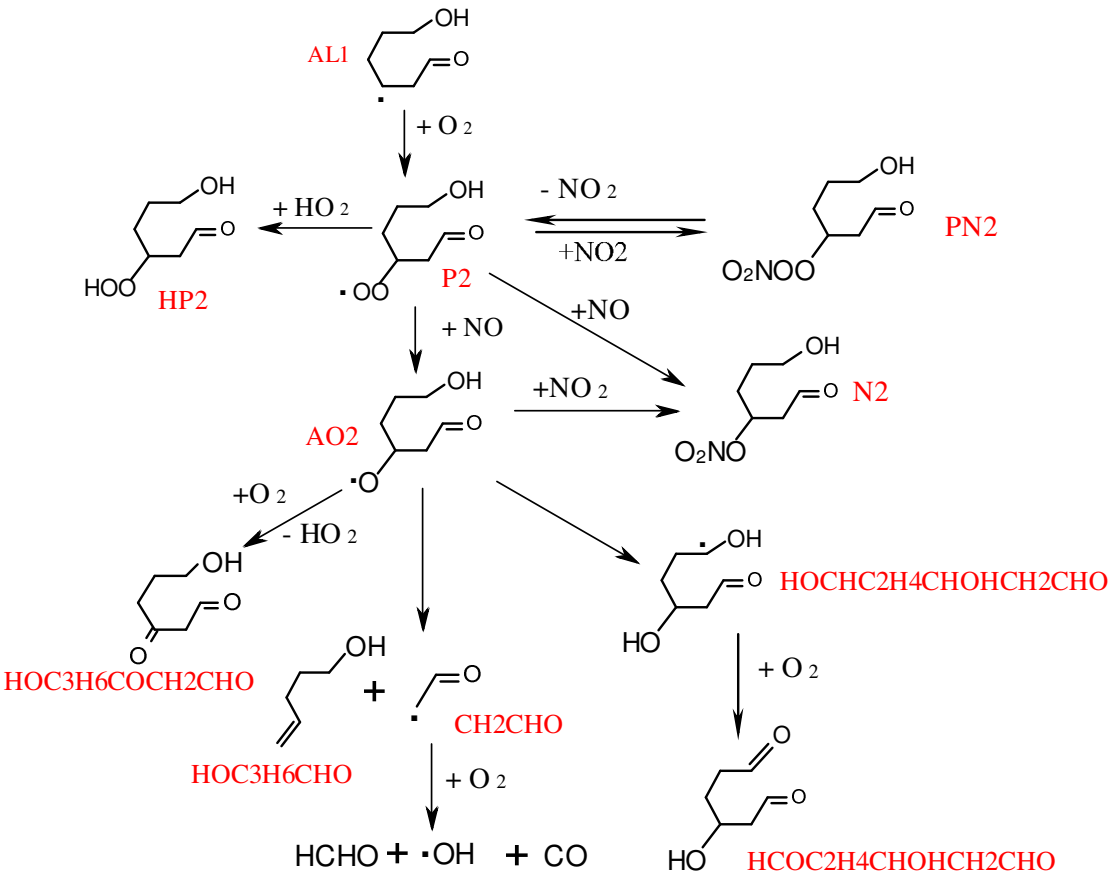

Table S3: Reactions and the rate constants used in the model

Reaction	A	Ea (kJ/mol)	Ref.
CH2DONO ==> CH2DO + NO	1.00E-04	0.00	1
CH2DO+O2==>CH2O + DO2	6.67E-15	8.98	2, 3
CH2DO+O2==>CHDO + HO2	4.80E-14	8.98	4
CH2DO+NO2 ==>CH2DONO2	1.76E-11	0.00	2,5
CH2DO + NO==>CH2DONO	2.77E-11	0.00	2, 5
HO2 + NO ==> OH + NO2	3.45E-12	-2.24	2
DO2 + NO ==> OD + NO2	3.45E-12	-2.24	2,3
OH + CH2O ==> H2O + HCO	5.40E-12	-1.12	2
OH + CHDO ==> H2O + DCO	2.70E-12	-1.12	3,6
OH + CHDO ==> HDO + HCO	2.70E-12	0.30	3,6
OD+ CH2O ==> HDO + HCO	5.40E-12	-1.12	2,3
OD + CHDO ==> HDO + DCO	2.70E-12	-1.12	3
OD + CHDO ==> D2O + HCO	2.70E-12	0.30	3
HCO + O2 ==> HO2 + CO	5.20E-12	0.00	7,i
DCO + O2 ==> DO2 + CO	4.00E-12	0.00	3
NO2 ==> NO + O	2.30E-04	0.00	1
O + O2 ==> O3	1.43E-14	0.00	2, 5
O + O3 ==> O2 + O2	8.00E-12	17.13	7
OH + NO2 ==> HNO3	1.16E-11	0.00	2, 5
OD + NO2 ==> DNO3	1.16E-11	0.00	3
OH + CH2DONO ==> CHDO + NO + H2O	1.74E-13	0.00	3,8
OH + CH2DONO ==> CH2O + NO + HDO	4.14E-14	0.00	4
OD + CH2DONO ==> CHDO + NO + HDO	1.74E-13	0.00	3
OD + CH2DONO ==> CH2O + NO + D2O	4.14E-14	0.00	3
HO2 + NO2 ==> HO2NO2	1.36E-12	0.00	2, 5
HO2NO2 ==> HO2 + NO2	4.61E-02	0.00	2, 5
DO2 + NO2 ==> DO2NO2	1.36E-12	0.00	3
DO2NO2 ==> DO2 + NO2	4.61E-02	0.00	3
O3 + NO ==> NO2 + O2	1.40E-12	10.89	2
O + NO2 ==> NO + O2	5.50E-12	-1.56	2
NO2 + O3 ==> NO3 + O2	1.40E-13	20.54	2
CH2O ==> CO + H2	5.50E-06	0.00	1
CH2O ==> CO + H + H	1.80E-06	0.00	1
CHDO ==> CO + HD	3.37E-06	0.00	3,6
CHDO ==> CO + H + D	1.10E-06	0.00	3,6
HO2 + CH2O ==> HOCH2O2	9.70E-15	-5.20	2
HOCH2O2 ==> CH2O + HO2	2.40E12	58.20	2
HO2 + CHDO ==> HOCHDO2	9.70E-15	-5.20	3
HOCHDO2 ==> CHDO + HO2	2.40E12	58.20	3
DO2 + CH2O ==> DOCH2O2	9.70E-15	-5.20	3
DOCH2O2 ==> CH2O + DO2	2.40E12	58.20	3

Reaction	A	Ea (kJ/mol)	Ref.
DO2 + CHDO ==> DOCHDO2	9.70E-15	-5.20	3
DOCHDO2 ==> CHDO + DO2	2.40E12	58.20	3
HO2 + HO2 ==> H2O2 + O2	2.89E-12	0.00	2,9
DO2 + DO2 ==> D2O2 + O2	9.47E-13	0.00	9,10
HO2 + DO2 ==> HDO2 + O2	1.59E-12	0.00	3,9
HNO3 ==> OH + NO2	9.33E+15	205.00	11
DNO3 ==> OD + NO2	9.33E+15	205.00	3
NO2 + CO ==> CO2 + NO	2.48E-35	0.00	1
O + NO ==> NO2	2.03E-12	0.00	2, 5
OH + CH2DONO2 ==> CH2O + HDO + NO2	1.51E-15	0.00	3,13
OH + CH2DONO2 ==> CHDO + H2O + NO2	1.72E-14	0.00	3,13
OD + CH2DONO2 ==> CH2O + D2O + NO2	1.51E-15	0.00	3
OD + CH2DONO2 ==> CHDO + HDO + NO2	1.72E-14	0.00	3
OH + CO ==>H + CO2	2.33E-13	0.00	2, 5
H + O2 ==> HO2	1.00E-12	0.00	2
OD + CO ==>D + CO2	1.10E-13	0.00	14
D + O2 ==> DO2	1.00E-12	0.00	3
OH + HNO3 ==> H2O + NO3	1.59E-13	0.00	2
OD + HNO3 ==> HDO + NO3	1.91E-13	0.00	15, 5
OH + DNO3 ==> HDO + NO3	9.21E-15	0.00	15, 5
OD + DNO3 ==> D2O + NO3	1.32E-14	0.00	15, 5
H2O2 ==> OH + OH	5.47E-07	0.00	1
HDO2 ==> OH + OD	5.47E-07	0.00	3
D2O2 ==> OD + OD	5.47E-07	0.00	3
HO2 + HOCH2O2 ==> O2 + HOCH2OOH	2.80E-15	-19.12	2
DO2 + HOCH2O2 ==> O2 + HOCH2OOD	2.80E-15	-19.12	3
HO2 + HOCHDO2 ==> O2 + HOCHDOOH	2.80E-15	-19.12	3
DO2 + HOCHDO2 ==> O2 + HOCHDOOD	2.80E-15	-19.12	3
HO2 + DOCH2O2 ==> O2 + DOCH2OOH	2.80E-15	-19.12	3
DO2 + DOCH2O2 ==> O2 + DOCH2OOD	2.80E-15	-19.12	3
HO2 + DOCHDO2 ==> O2 + DOCHDOOH	2.80E-15	-19.12	3
DO2 + DOCHDO2 ==> O2 + DOCHDOOD	2.80E-15	-19.12	3
HO2 + HOCH2O2 ==> O2 + HCOOH + H2O	1.68E-15	-19.12	3
DO2 + HOCH2O2 ==> O2 + HCOOH + HDO	1.68E-15	-19.12	3
HO2 + DOCH2O2 ==> O2 + HCOOD + H2O	1.68E-15	-19.12	3
DO2 + DOCH2O2 ==> O2 + HCOOD + HDO	1.68E-15	-19.12	3
HO2 + HOCHDO2 ==> O2 + HCOOH + HDO	8.40E-16	-19.12	2
HO2 + HOCHDO2 ==> O2 + DCOOH + H2O	8.40E-16	-19.12	3
HO2 + DOCHDO2 ==> O2 + HCOOD + HDO	8.40E-16	-19.12	3
HO2 + DOCHDO2 ==> O2 + DCOOD + H2O	8.40E-16	-19.12	3
DO2 + HOCHDO2 ==> O2 + HCOOH + D2O	8.40E-16	-19.12	3
DO2 + HOCHDO2 ==> O2 + DCOOH + HDO	8.40E-16	-19.12	3

Reaction	A	Ea (kJ/mol)	Ref.
DO2 + DOCHDO2 ==> O2 + HCOOD + D2O	8.40E-16	-19.12	3
DO2 + DOCHDO2 ==> O2 + DCOOD + HDO	8.40E-16	-19.12	3
HO2 + HOCH2O2 ==> O2 + OH + HOCH2O	1.12E-15	-19.12	2
DO2 + HOCH2O2 ==> O2 + OD + HOCH2O	1.12E-15	-19.12	3
HO2 + DOCH2O2 ==> O2 + OH + DOCH2O	1.12E-15	-19.12	3
DO2 + DOCH2O2 ==> O2 + OD + DOCH2O	1.12E-15	-19.12	3
HO2 + HOCHDO2 ==> O2 + OH + HOCHDO	1.12E-15	-19.12	3
DO2 + HOCHDO2 ==> O2 + OD + HOCHDO	1.12E-15	-19.12	3
HO2 + DOCHDO2 ==> O2 + OH + DOCHDO	1.12E-15	-19.12	3
DO2 + DOCHDO2 ==> O2 + OD + DOCHDO	1.12E-15	-19.12	3
HOCH2O2 + NO ==> HOCH2O + NO2	5.60E-12	0.00	2
DOCH2O2 + NO ==> DOCH2O + NO2	5.60E-12	0.00	3
HOCHDO2 + NO ==> HOCHDO + NO2	5.60E-12	0.00	3
DOCHDO2 + NO ==> DOCHDO + NO2	5.60E-12	0.00	3
HOCH2O + O2 ==> HO2 + HCOOH	3.50E-14	0.00	16
DOCH2O + O2 ==> HO2 + HCOOD	3.50E-14	0.00	3
HOCHDO + O2 ==> HO2 + DCOOH	1.75E-14	0.00	3
HOCHDO + O2 ==> DO2 + HCOOH	1.75E-14	0.00	3
DOCHDO + O2 ==> HO2 + DCOOD	1.75E-14	0.00	3
DOCHDO + O2 ==> DO2 + HCOOD	1.75E-14	0.00	3
OH + C6H12 ==> H2O + C6H11	3.58E-11	4.16	17
OD + C6H12 ==> HDO + C6H11	3.58E-11	4.16	3
C6H11 + O2 ==> C6H11O2	1.10E-11	0.00	2,18
C6H11O2 + NO ==> C6H11O + NO2	5.70E-12	0.00	19
C6H11O2 + NO ==> C6H11ONO2	1.07E-12	0.00	19
C6H11O2 + NO2 ==> C6H11O2NO2	9.51E-12	0.00	19
C6H11O2NO2 ==> C6H11O2 + NO2	4.09E+00	0.00	20,27
C6H11O2 + HO2 ==> C6H11OOH + O2	2.60E-13	-10.39	21
C6H11O + NO2 ==> C6H11ONO2	1.50E-11	-2.08	2,28
C6H11O + O2 ==> C6H10O + HO2	4.94E-14	3.96	22
C6H11O ==> C5H10CHO	3.80E+13	50.10	23
C5H10CHO ==> C6H11O	3.02E+08	23.80	23
C5H10CHO + O2 ==> O2C5H10CHO (P1)	7.50E-12	0.00	2,29
O2C5H10CHO (P1) + HO2 ==> HO2C5H10CHO (HP1)+ O2	2.08E-13	-10.39	30,24
O2C5H10CHO (P1) + NO ==> OC5H10CHO (AO1)+ NO2	7.92E-12	0.00	2,31
O2C5H10CHO (P1) + NO ==> O2NOC5H10CHO (N1)	8.80E-13	0.00	2,31
OC5H10CHO (AO1) + NO2 ==> O2NOC5H10CHO (N1)	1.50E-11	-2.08	2,32
O2C5H10CHO (P1) + NO2 ==> O2NO2C5H10CHO (PN1)	7.50E-12	0.00	20
O2NO2C5H10CHO (PN1) ==> O2C5H10CHO (P1) + NO2	4.09E+00	0.00	20

Reaction	A	Ea (kJ/mol)	Ref.
OC5H10CHO (AO1) + O2 ==> OCHC4H8CHO + HO2	8.90E-14	4.57	2,33
OC5H10CHO (AO1) ==> HOC3H6CHCH2CHO (AL1)	3.04E+06	0.00	25,34
OC5H10CHO (AO1) ==> CH2O + CH2C3H6CHO	3.98E+13	79.90	35,26
CH2C3H6CHO + O2 ==> O2CH2C3H6CHO	7.50E-12	0.00	2,36
HOC3H6CHCH2CHO (AL1) + O2 ==> HOC3H6CHO2CH2CHO (P2)	1.66E-11	0.00	37
HOC3H6CHO2CH2CHO (P2)+ HO2 ==> HOC3H6CHO2HCH2CHO (HP2) + O2	1.81E-13	-10.39	24
HOC3H6CHO2CH2CHO (P2) + NO ==> HOC3H6CHONO2CH2CHO (N2)	8.80E-13	0.00	20
HOC3H6CHO2CH2CHO (P2) + NO ==> HOC3H6CHOCH2CHO (AO2) + NO2	3.12E-12	0.00	20
HOC3H6CHO2CH2CHO (P2)+ NO2 ==> HOC3H6CHO2NO2CH2CHO (PN2)	7.50E-12	0.00	20
HOC3H6CHO2NO2CH2CHO (PN2)==> HOC3H6CHO2CH2CHO (P2) + NO2	4.09E+00	0.00	20
HOC3H6CHOCH2CHO (AO2)+ NO2 ==> HOC3H6CHONO2CH2CHO (N2)	3.50E-11	0.00	2, 38
HOC3H6CHOCH2CHO (AO2) + O2 ==> HOC3H6COCH2CHO + HO2	1.40E-14	1.75	2,39
HOC3H6CHOCH2CHO ==> HOCHC2H4CHOHCH2CHO	9.20E+10	30.50	25,40
HOCHC2H4CHOHCH2CHO + O2 ==> HO2 + HCOC2H4CHOHCH2CHO	1.90E-11	0.00	2,41
HOC3H6CHOCH2CHO ==> HOC3H6CHO + CH2CHO	1.08E+13	47.89	42
CH2CHO + O2 ==> CH2O + OH + CO	3.00E-14	0.00	43

Notes:

1. Derived from experiments
2. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. and IUPAC Subcommittee *Atmos. Chem. Phys.* **2006**, *6*, 3625-4055
3. Derived from the rate constant of the isotopologue
4. Calculated with the branching ratio
5. The rate constant is pressure dependent. The rate constant showing here is at 295 K.
6. See text
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27. Use the rate constant of the $C_6H_{13}O_2NO_2$->$C_6H_{13}O_2$+NO_2 reaction
28. Use the rate constant of the i-C_3H_7O + NO_2 reaction
29. Use the rate constant of the n-C_4H_9 + O_2 reaction
30. Use the rate constant of the $C_5H_{11}O_2$ + HO_2 reaction
31. Use the rate constant of the $HOC_5H_8O_2$ + NO reaction
32. Use the rate constant of the i-C_3H_7O + NO_2 reaction
33. Use the rate constant of the n-C_4H_9O+O_2 reaction
34. Use the rate constant of the n-C_5H_9O isomerization
35. Use the rate constant of the n-C_4H_9O --> CH_2O + C_3H_7 reaction
36. Use the rate constant of the n-C_4H_9+O_2 reaction
37. Use the rate constant of the sec-C_4H_9+ O_2 reaction. Lenhardt, T.M.; McDade, C.E.; Bayes, K.D. *J. Chem. Phys.* **1980**, *72*, 304
38. Use the rate constant of the i-C_3H_7O + NO_2 reaction
39. Use the rate constant of the CH_3CHOCH_3 + O_2 reaction
40. Use the rate constant of the $CH_3CHOC_2H_4CH_3$ isomerization
41. Use the rate constant of the CH_3CHOH + O_2 reaction
42. Assume the branching ratio between O2 reaction and isoerization reaction is the same as $C_6H_{11}O$.
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Discussion of modeling results in the absence of cyclohexane.

In the absence of cyclohexane, the reactions of OH with methyl nitrite are expected to be very significant, and the value of the rate constant OH/OD + CH_2DONO → HDO + CH_2O + NO (reaction 4b) is needed for reliable modeling. The rate constant of OH + CH_2DONO →H_2O + CHDO + NO (reaction 4a) was assumed to be two-thirds of the rate constant of OH + CH_3ONO reaction at 298 K. In order to obtain a value of this rate constant, we estimate the branching ratio for the OH + CH_2DONO reaction (k_{4a}/k_{4b}) by fitting the modeling product branching ratio in the absence of the cyclohexane to the experimental results. This approach is not expected to obtain reliable values of k_{4b}, especially given the assumption necessary to estimate k_{4a} and the absence of data on the temperature dependence of OH + CH_3ONO. Nevertheless, this approach to estimating k_{4b} can be seen as reasonable for the present work, especially when reaction 4 is of negligible importance in the experiments carried out in the presence of cyclohexane. A stringent test of our model is that the modeling results for both the time history of formaldehyde and the product branching ratio ([CHDO]:[CH_2O]) is consistent with the experimental result. As an example, the comparisons are shown in

Figure S2, for 278 K in the absence of cyclohexane.

Figure S3 illustrates the relative importance of various sources and sinks of formaldehyde in the absence of cyclohexane as a function of time at 278 K. In the absence of cyclohexane, the OH/OD + CH_2DONO reaction and the OH/OD + CH_2O (CHDO) reaction are significant formaldehyde sources and sinks, respectively. The OH/OD + CH_2DONO reactions, due to the smaller branching ratio than the title reaction, cause the observed product ratio ([CHDO]:[CH_2O]) to be smaller than the branching ratio of the CH_2DO• + O_2 reaction. On the other hand, the OH/OD + CH_2O reactions have larger rate

constants than the OH/OD + CHDO reactions, which causes the observed concentration ratio {[CHDO]: [CH_2O]} to be larger than the branching ratio of the CH_2DO• + O_2 reaction. Thus, these two reactions tend to counteract each other, and the overall effect was found to depend on the extent of reaction. The model shows that in the initial stages, the OH/OD + CH_2DONO reactions dominate due to the lack of formaldehyde, while OH/OD + CH_2O (CHDO) become more important at later times.

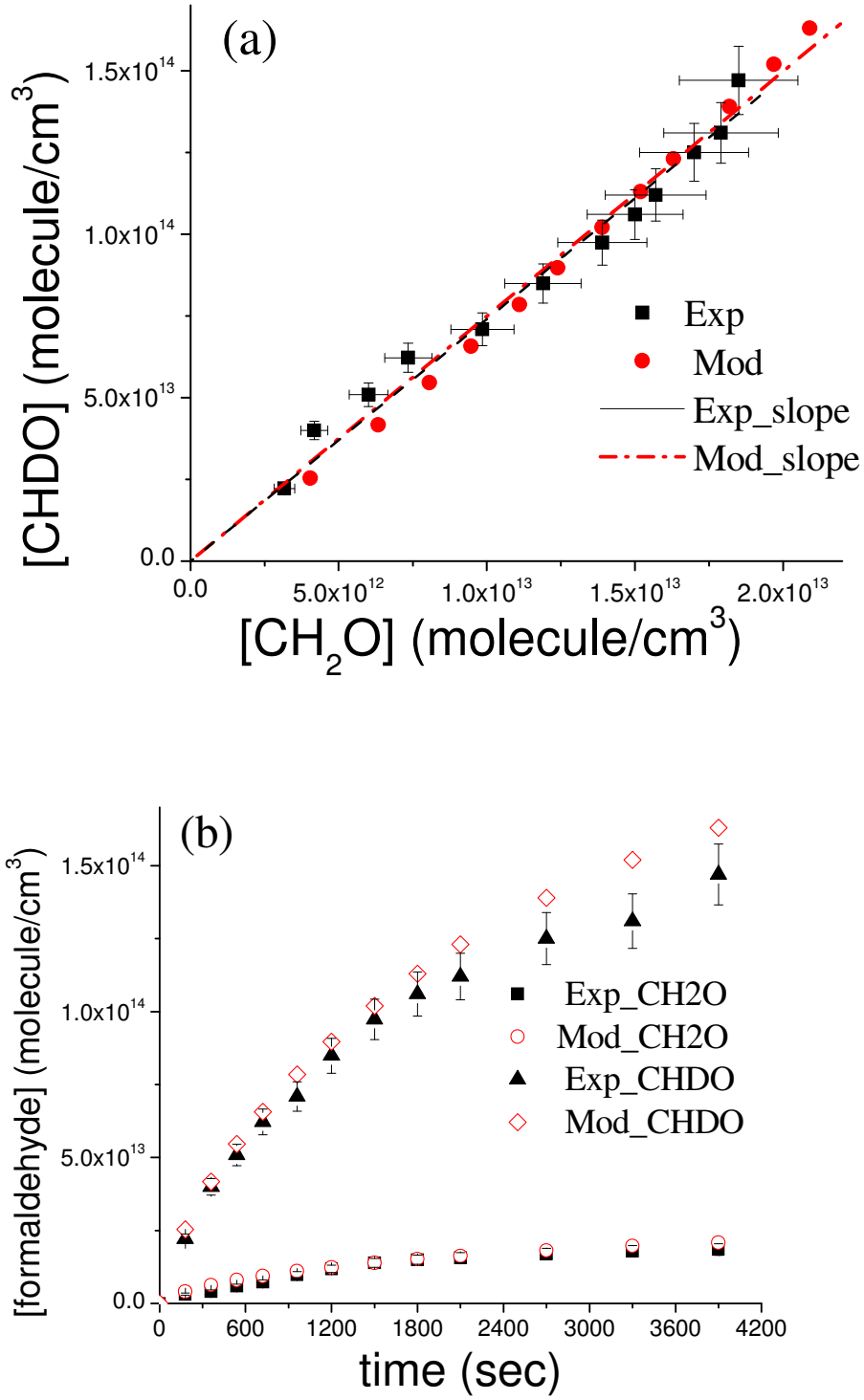

Figure S2: In the absence of cyclohexane, the comparison of the experimental and modeling formaldehyde branching ratio ([CHDO]:[CH_2O]) (a) and the comparison of the experimental and modeling time history of formaldehyde formation (b) at 278 K. The unit of the concentration is molecule/cm^3. In this case, the initial CH_2DONO concentration and O_2 concentration was 1.28 $\times 10^{15}$ and 5.42$\times 10^{18}$ molecule/cm^3, respectively. (a) The fitting slope for experimental result (in black) is 7.40±0.13, while the fitting slope for modeling result (in red) is 7.49±0.09.

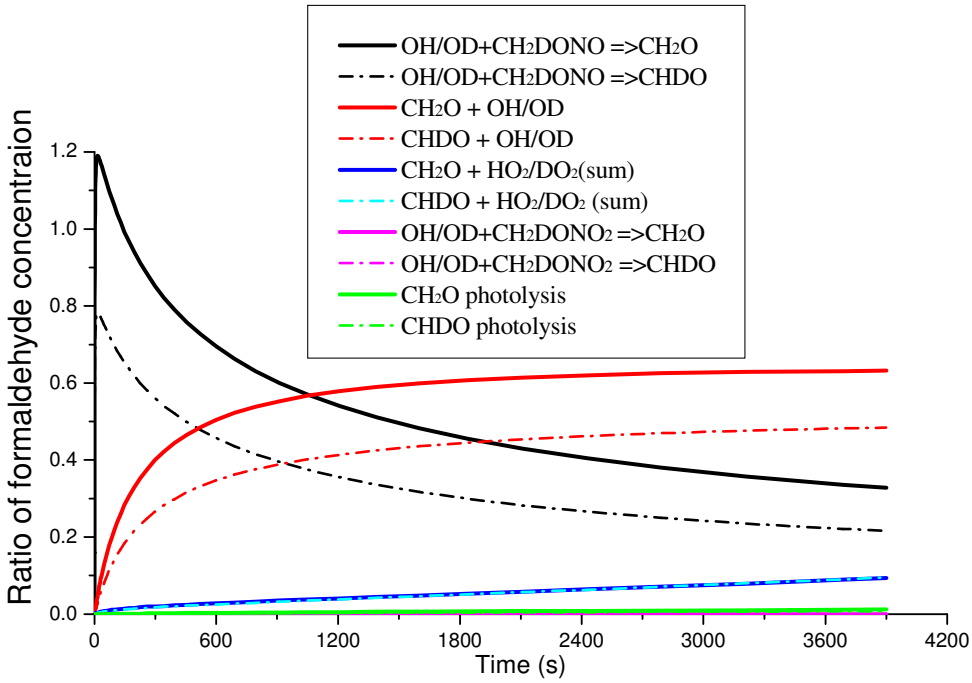

Figure S3: The ratio of CH_2O (CHDO) concentration produced or consumed by individual side reactions to CH_2O (CHDO) produced by $CH_2DO\bullet + O_2$ reaction in the absence of cyclohexane at 278 K. The branching ratio of $CH_2DO\bullet + O_2$ was set to 7.3 and the branching ratio of CH_2DONO + OH was set to 4.6. Reactions that have major effect are OH/OD + CH_2DONO, OH/OD + CH_2O (or CHDO).

Table S4: The changed inputs for calculating $\delta D(H_2)$ during the methane oxidation. The calculation used equation 36 of the reference 12 in the text (Feilberg, K. L.; Johnson, M. S.; Bacak, A.; Röckmann, T.; Nielsen, C. J. *J. Phys. Chem. A* **2007**, *111*, 9034). The number sequences of all reactions remain the same as in reference 12, as well as the input values that are not listed in the table. The OH concentration is fixed at 1×10^{6} molecule/cm^{3} regardless of the temperature, and the photolysis rate constants of CH_2O/CHDO are assumed to be the same as the temperature-dependent pseudo first-order rate constant of CH_2O/CHDO reacting with OH.

Item	Note
k1(T)	IUPAC recommendation: $1.88\times10^{-12} \times \exp(-1695/T)$
k10b(T)/k10a(T)	Use this experimental results
k11(T), k12(T)	Assume the decomposition rate is 0
k13(T)	Same as in Table : $5.4\times10^{-12} \times \exp(135/T)$
k14(T)	Same as in Table : $2.7\times10^{-12} \times \exp(135/T)+ 2.7\times10^{-12} \times \exp(-36/T)$
k15a/k15b	Reference 14 in the text: 1.63
k17(T)	Reference 9 in the text: $7.21\times10^{-20}\times (T)^{2.69} \times \exp(-1150/T)$
k18(T)	Reference 9 in the text: $5.57\times10^{-20}\times (T)^{2.7} \times \exp(-1258/T)$