Pressure-Dependent Kinetics of Methyl Formate Reaction with OH at Combustion, Atmospheric and Interstellar Temperatures

Junjun Wu [a], Hongbo Ning [a,b], Liuhao Ma [a], and Wei Ren [a,b,*]

[a] *Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, New Territories, Hong Kong*

[b] *Shenzhen Research Institute, The Chinese University of Hong Kong, New Territories, Hong Kong*

[*] Corresponding author. Fax: +852 2603 6002. Email: renwei@mae.cuhk.edu.hk (W. Ren)

I. Optimized Geometries at M06-2x/ma-TZVP

1. Reactant: MF

Conformer #1

	X	Y	Z
C 6	0.82527383	0.43152491	-0.00003200
O 8	1.28292474	-0.67192186	0.00001900
O 8	-0.47256690	0.72765185	0.00007300
C 6	-1.35372072	-0.39789892	-0.00004400
H 1	-1.18674476	-1.00537079	0.88834982
H 1	-1.18254776	-1.00855579	-0.88541182
H 1	-2.35896152	0.01115500	-0.00308400
H 1	1.41607071	1.35518172	-0.00013300

Conformer #2

	X	Y	Z
6	-0.68238686	0.31144894	-0.00616400
8	-1.80205663	-0.08490198	0.00843700
8	0.37682192	-0.50606190	-0.01017300

6	1.65613366	0.11724598	0.00724400
1	1.83544062	0.60449188	0.96668580
1	1.74951964	0.84440183	-0.80096684
1	2.38457251	-0.67459486	-0.13698897
1	-0.41013192	1.38124572	-0.02132900

2. Transition States-TS1

Conformer #1

	X	Y	Z
6	0.16162197	0.22472995	-0.00909400
8	-0.04360199	1.39676371	-0.00114500
8	-0.73255885	-0.74552885	-0.00674600
6	-2.10155157	-0.31416794	0.00782400
1	1.23407175	-0.24805595	-0.01941300
1	-2.31096353	0.28564794	-0.87623482
1	-2.29458953	0.27677094	0.90157282
1	-2.69499545	-1.22227675	0.00874700
8	2.62320046	-0.52090889	0.00221100
1	2.92973840	0.40193692	0.03838899

Conformer #2

	X	Y	Z
6	0.14400797	0.49403990	-0.00033400
8	-0.38311592	1.55743168	0.00022600
8	-0.44866491	-0.69211686	-0.00037700
6	-1.88370362	-0.65937787	0.00018300
1	1.30518173	0.32847193	-0.00065500
1	-2.24303054	-0.14358397	-0.88867082
1	-2.24233654	-0.14338297	0.88919882
1	-2.20254455	-1.69644665	0.00040900
8	2.53545248	-0.37396492	-0.00000200

1	2.19152955	-1.28382674	0.00185800

Conformer #3

	X	Y	Z
6	0.33315800	-0.68711118	0.04949004
8	0.67967375	-1.81879731	0.00234605
8	1.14032992	0.35849076	-0.06638794
6	0.53076339	1.65236813	0.01663805
1	-0.76512145	-0.36952910	0.19753801
1	0.06019463	1.78908360	0.98961685
1	-0.21089333	1.77574188	-0.77058479
1	1.33802497	2.36640915	-0.10947593
8	-2.19904563	0.13204629	0.00789205
1	-2.57339745	-0.72716515	-0.25466390

Conformer #4

	X	Y	Z
6	0.33789652	-0.68512197	0.04928777
8	0.69246452	-1.81432403	0.00238478
8	1.13775521	0.36611716	-0.06629721
6	0.51912340	1.65566941	0.01666678
1	-0.76259101	-0.37529313	0.19693074
1	-0.22276236	1.77429499	-0.77106706
1	1.32152782	2.37529660	-0.10860520
1	0.04688760	1.78884576	0.98933858
8	-2.19971131	0.11787195	0.00782978
1	-2.56924894	-0.74374957	-0.25366317

Conformer #5

	X	Y	Z
6	-0.32481521	-0.69044859	0.05008009
8	-0.65699971	-1.82639420	0.00231810
8	-1.14474652	0.34505960	-0.06695489
6	-0.55102198	1.64628704	0.01671309

1	0.76924374	-0.35914022	0.19957406
1	0.18883893	1.77904264	-0.77065775
1	-0.08178401	1.78810677	0.98960989
1	-1.36697046	2.35052931	-0.10864488
8	2.19748570	0.15688296	0.00797610
1	2.57977919	-0.69795606	-0.25735485

Conformer #6

	X	Y	Z
6	0.31611894	0.69386186	0.05025999
8	0.63346387	1.83402962	0.00225000
8	1.14928977	-0.33103393	-0.06688499
6	0.57214688	-1.63974867	0.01658100
1	-0.77355884	0.34852793	0.20016496
1	1.39701571	-2.33353652	-0.10879398
1	-0.16588697	-1.78164963	-0.77093384
1	0.10461998	-1.78762764	0.98939480
8	-2.19588555	-0.18275396	0.00813600
1	-2.58673247	0.66767287	-0.25888495

Conformer #7

	X	Y	Z
6	-0.01435500	0.73632185	0.05596499
8	0.16164197	1.90712961	0.01648600
8	-1.18873675	0.14140697	-0.10137698
6	-1.23228775	-1.28326074	0.03244399
1	0.84131583	-0.01996500	0.22362195
1	-2.09032457	-1.61464467	-0.54431789
1	-1.36581272	-1.54772668	1.08070078
1	-0.32067993	-1.73575564	-0.35537893
8	2.00003959	-0.98449880	0.00612500
1	2.63180246	-0.31257294	-0.30494894

Conformer #8

	X	Y	Z
6	-0.14179797	0.73697485	0.05812299
8	-0.17316596	1.92014760	0.01003900
8	-1.19372776	-0.05587899	-0.09242698
6	-0.96298680	-1.46467170	0.02730599
1	0.83076883	0.14118997	0.23300895
1	-0.14011797	-1.77424564	-0.61485987
1	-1.88639561	-1.94219060	-0.28421194
1	-0.74160185	-1.72234665	1.06257978
8	2.10662057	-0.66651386	0.00631700
1	2.64824346	0.08173398	-0.30051594

2. Transition States-TS2

Conformer #1

	X	Y	Z
6	1.24768574	-0.37487992	-0.24167395
8	0.74156285	-1.22476275	0.43038891
8	0.79943084	0.87562182	-0.36118193
6	-0.34526593	1.19658875	0.39139892
1	-0.21279196	0.97960080	1.44958170
1	-1.26107074	0.52409889	0.02426500
1	-0.60183588	2.22961854	0.18155896
1	-1.46556970	-1.21674275	0.06586699
8	-2.04364358	-0.51815289	-0.29038994
1	2.14794556	-0.50847090	-0.85015983

Conformer #2

	X	Y	Z
6	1.37236872	-0.15838097	-0.41156792
8	1.45922270	-0.94849881	0.47417390
8	0.46634690	0.83174083	-0.48219790

6	-0.45952591	0.90323081	0.57392488
1	-0.01027800	0.66806086	1.53716068
1	-1.29147074	0.09227098	0.40916592
1	-0.92915281	1.88070962	0.53789689
1	-2.37529751	-0.27924994	-0.99855480
8	-2.28709353	-0.72223785	-0.13779397
1	2.02133058	-0.11892398	-1.29326974

Conformer #3

	X	Y	Z
6	-1.49718758	-0.54767727	-0.00031807
8	-2.18506347	0.42533951	-0.00165307
8	-0.15667786	-0.54011923	0.00175193
6	0.44729199	0.73592052	0.00173593
1	0.22617402	1.29431640	-0.90559589
1	1.62920175	0.51401860	-0.00085907
1	0.22993102	1.29242440	0.91116974
1	2.46745062	-1.00630407	0.00290293
8	2.79243653	-0.09048925	-0.00204507
1	-1.85894548	-1.58176307	-0.00055507

Conformer #4

	X	Y	Z
6	1.09708877	-0.18701896	0.30331294
8	2.11094457	-0.65375487	-0.09519998
8	0.39051592	0.71155385	-0.41625091
6	-0.81574983	1.14811477	0.14617297
1	-0.71269886	1.45871870	1.18758976
1	-1.58358568	0.26654595	0.15446497
1	-1.21468875	1.93951160	-0.48017390
1	-1.85611362	-1.19279875	-0.90242182
8	-2.12062257	-1.03404279	0.02033500
1	0.63235487	-0.42860591	1.27256074

Conformer #5

	X	Y	Z
6	-1.05442579	-0.30291494	0.23092195
8	-2.14300956	-0.66504687	-0.06591699
8	-0.49190390	0.79627384	-0.31963493
6	0.77377384	1.15306576	0.15454097
1	1.10830177	2.02516059	-0.39887992
1	1.51199769	0.28024094	-0.07890698
1	0.79014584	1.31730373	1.23316975
1	2.88741841	-0.85842283	0.39350692
8	2.10796557	-1.01341679	-0.16677597
1	-0.39836692	-0.80766684	0.95695680

3. Product

P_1: $(CO)OCH_3$

	X	Y	Z
C	-0.81284400	0.50899500	-0.00000600
O	-1.41335600	-0.50629000	0.00000100
O	0.47587500	0.73398600	0.00002100
C	1.30786700	-0.45078200	-0.00002600
H	1.09625800	-1.04191500	-0.88897500
H	1.10231700	-1.03747900	0.89332100
H	2.33113500	-0.09145900	-0.00432200

P_2: $H(CO)OCH_2$

	X	Y	Z
C	0.76453500	0.44516200	-0.00492700
O	1.29579300	-0.62026900	0.00448200
O	-0.56990000	0.64669200	-0.00082800

C	-1.38286600	-0.44452900	0.02911700
H	-2.42784100	-0.21110900	-0.06229800
H	-0.94154200	-1.41865300	-0.09273100
H	1.27222900	1.41457300	-0.01934200

4. H-bonded Complexes

RC_1:

	X	Y	Z
C	-0.25077200	0.82031300	0.00055100
O	-1.31773600	1.35098800	-0.00054000
O	-0.05717400	-0.50594200	0.00068600
C	-1.25040500	-1.29688300	-0.00023000
H	0.71718000	1.33796900	0.00175700
H	-1.83957700	-1.08114100	-0.88981200
H	-1.84429600	-1.07623700	0.88494400
H	-0.92402300	-2.33196100	0.00341400
O	2.72544500	-0.00075400	-0.00040500
H	2.09349900	-0.74354300	-0.00016200

PC_1:

	X	Y	Z
C	-0.28866800	0.78514900	-0.00909600
O	-1.22402300	1.49941400	0.00872400
O	-0.21110700	-0.52346400	-0.01445100
C	-1.47988200	-1.22633200	0.00501300
H	2.59585800	0.78468200	-0.04875500
H	-2.05510500	-0.95349700	-0.87706700
H	-2.02546600	-0.95811800	0.90713100
H	-1.22954300	-2.28139700	-0.00192700
O	2.84881800	-0.14113900	0.00984100
H	2.01604500	-0.62305900	0.01219800

RC_2:

	X	Y	Z
C	1.13919300	-0.79211500	0.00021500
O	0.05211300	-1.30209100	-0.00053400
O	1.38239800	0.50570700	0.00049200
C	0.23404700	1.36393900	-0.00041700
H	-0.36910500	1.18578100	0.88943400
H	-0.36868800	1.18448900	-0.89029200
H	0.62268800	2.37668800	-0.00104200
H	-1.76219900	-0.63411300	-0.00022900
O	-2.48952600	0.02290800	0.00036800
H	2.07798800	-1.35598500	0.00073100

PC_2:

	X	Y	Z
C	0.70487900	-0.85240500	-0.37891100
O	0.25892500	-1.30558900	0.63143200
O	0.99645300	0.44737000	-0.57410800
C	0.75085700	1.31558200	0.44423700
H	0.62983200	0.91078300	1.43599900
H	-1.94291500	1.08608500	0.03308600
H	1.06896500	2.32135400	0.23230100
H	-1.78478900	-0.38022400	0.43108900
O	-2.21161000	0.19596500	-0.21260300
H	0.94434700	-1.41902900	-1.28220500

II. IRC Analysis at M06-2x/ma-TZVP

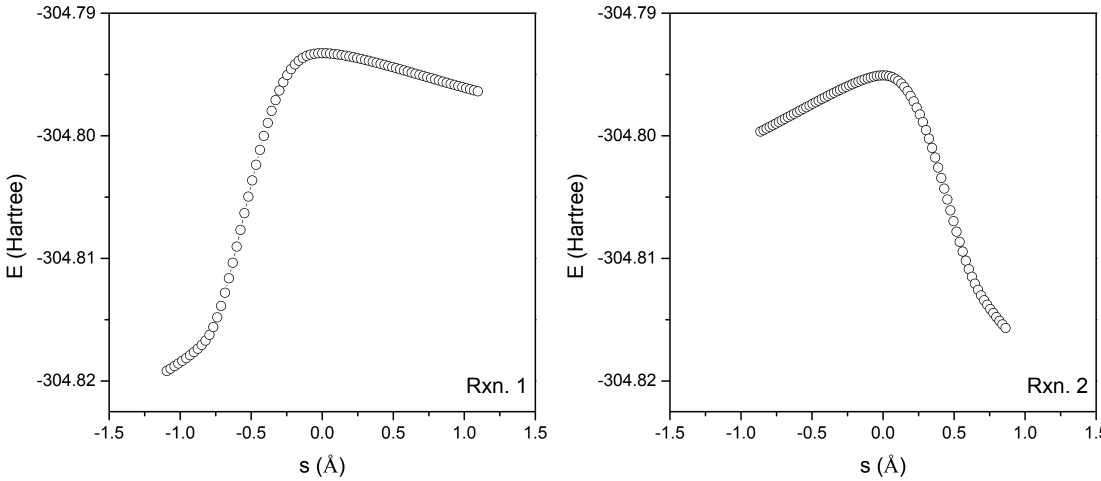
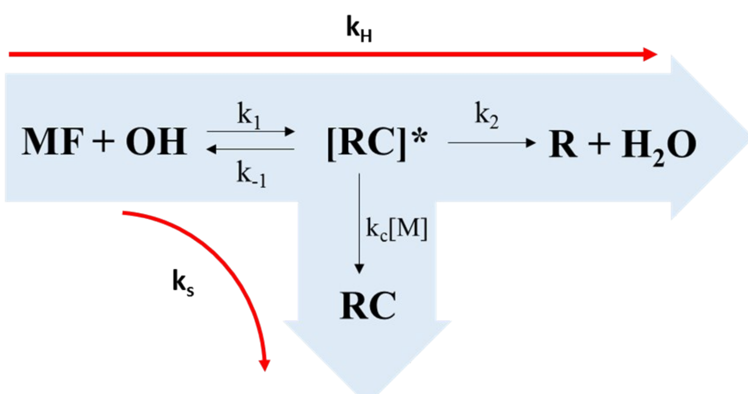


Figure S1. IRC analysis for Rxn. 1 and Rxn. 2 at M06-2x/ma-TZVP level of theory

III. Summary of Kinetic Data

The whole reaction involves two pathways: one is to form products by abstracting with rate coefficient k_H, the other is to form stabilized RC by collision with rate coefficient k_s. Note that the k_H and k_s are global rate coefficient (lumped rather than elementary) and therefore, k_H is not necessarily pressure-independent. A simple analysis is provided here to interpret the pressure-dependence of the two rate coefficient.



Scheme 1. Demonstration of the MF + OH reaction: H-abstraction (k_H) and collisional stabilization (k_s)

For the pure H-abstraction channel that forms final products, we have:

$$\frac{d[R]}{dt} = k_H[MF][OH] = k_2[RC^*], \tag{1}$$

For the stabilization channel that forms products, we have:

$$\frac{d[RC]}{dt} = k_s[MF][OH] = k_c[M][RC^*], \tag{2}$$

The fate of RC* can be determined as:

$$\frac{d[RC^*]}{dt} = k_1[MF][OH] - k_{-1}[RC^*] - k_2[RC^*] - k_c[M][RC^*], \tag{3}$$

By adopting the quasi-steady state approximation, we can obtain k_H and k_s as:

$$k_H = \frac{k_1 k_2}{k_{-1} + k_2 + k_c[M]}, \tag{4a}$$

$$k_s = \frac{k_1 k_c[M]}{k_{-1} + k_2 + k_c[M]}. \tag{4b}$$

It's seen that both k_H and k_s involve the [M] term and thus the pressure effect. It's also seen that k_H and k_s are internally correlated by k_c[M] term. At high-temperatures, k_c that represents the deactivation rate coefficient becomes extremely small, i.e. $k_c \rightarrow 0$. Therefore, the rate coefficient of pure H-abstraction k_H becomes pressure-independent (close to HPL) since:

$$k_H \approx \frac{k_1 k_2}{k_{-1} + k_2}, \tag{5}$$

At very low temperatures where k_c matters, the rate coefficient becomes pressure-dependent. Increased pressure leads to larger [M] and thus k_H will decreases. As the pressure decreases to extremely low, i.e. $[M] \rightarrow 0$, the rate coefficient will again approach to the HPL. On the contrary, k_s will increase due to increased pressures, as seen in Equation (4b).

Table S1 Rate coefficient of H-abstraction at 20 K from MF by OH radical with He and N2 as the bath gas (units in $cm^3 \cdot molec^{-1} \cdot s^{-1}$)

	0.001 bar	0.01 bar	0.1 bar	1.0 bar	10 bar	100 bar
in He	6.31E-11	8.09E-11	2.85E-12	3.67E-13	5.84E-15	6.34E-17
in N_2	6.97E-11	6.94E-11	3.73E-11	8.57E-12	1.14E-12	1.21E-13

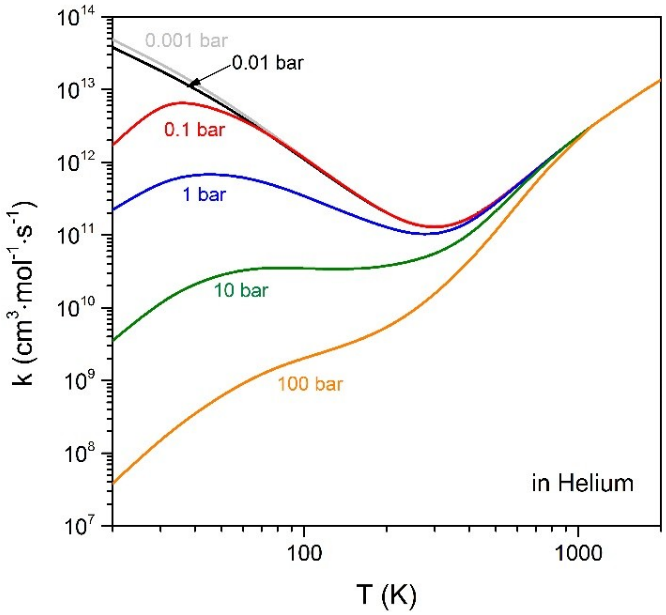


Figure S2. Rate coefficient of H-abstraction from MF by OH radical with He as bath gas

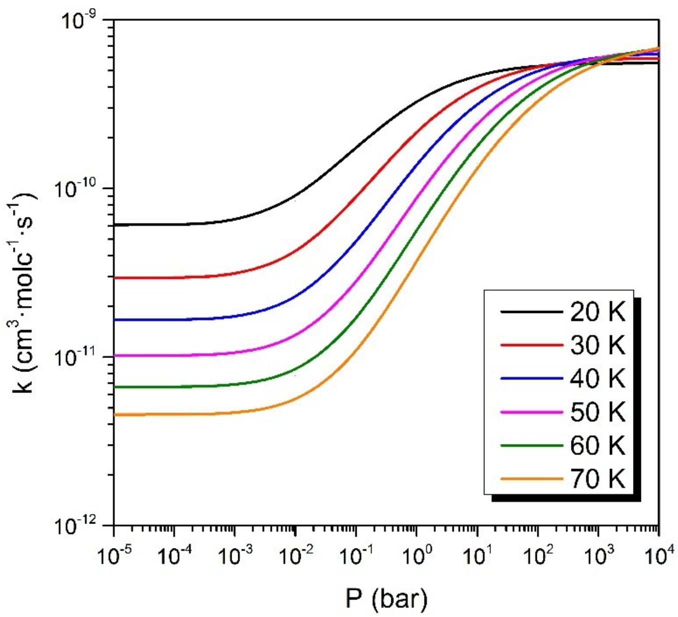


Figure S3. Plots of the pressure-and temperature-dependent rate coefficient of MF + OH with He as the bath gas.

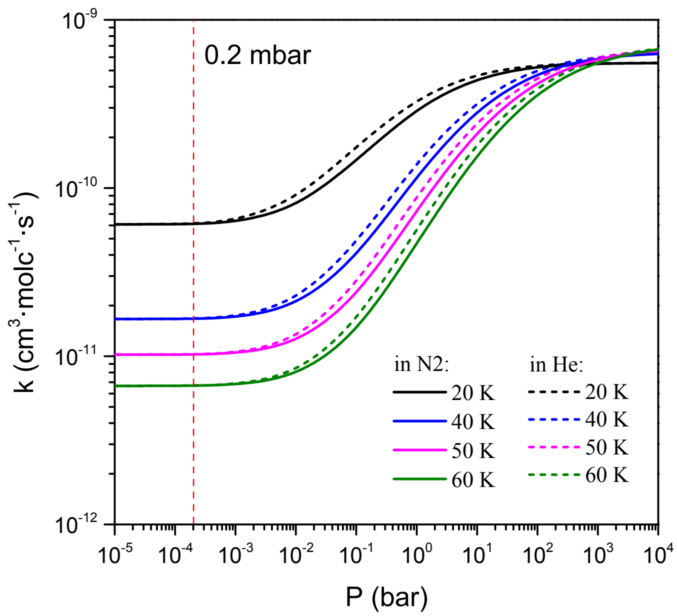


Figure S4. Rate coefficients of MF + OH as the function of pressures at 20,40,50, 60 K. Bath gas including nitrogen (N2) and helium (He) are considered. The experimental measurements at interstellar temperatures were benchmarked by Jiménez et al[11].

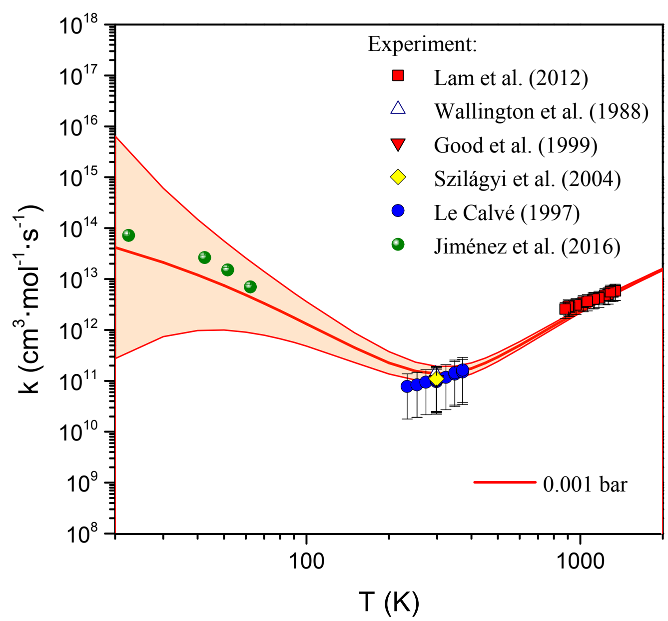


Figure S5. The rate coefficient of MF+OH reactions at 20-2000 K and at 0.001 bar in N_2. The shadow region indicate the uncertainty caused by an uncertainty of 0.2 kcal·mol-1 in energy barrier.

Table S2. Detailed H-abstraction rate coefficient k_H of MF + OH with He as the bath gas (units in $cm^3 \cdot molec^{-1} \cdot s^{-1}$)

T	0.001 Bar	0.01 Bar	0.1 Bar	1.0 Bar	10 Bar	100 bar
20	6.31E-11	8.09E-11	2.85E-12	3.67E-13	5.84E-15	6.34E-17
30	3.04E-11	3.77E-11	1.14E-11	9.17E-13	2.04E-14	2.60E-16
40	1.70E-11	2.03E-11	1.08E-11	1.14E-12	3.57E-14	5.87E-16
50	1.04E-11	1.21E-11	8.43E-12	1.13E-12	4.73E-14	1.02E-15
60	6.76E-12	7.64E-12	6.25E-12	1.03E-12	5.46E-14	1.53E-15
70	4.62E-12	5.12E-12	4.56E-12	9.00E-13	5.80E-14	2.04E-15
80	3.28E-12	3.58E-12	3.34E-12	7.71E-13	5.88E-14	2.51E-15
90	2.41E-12	2.59E-12	2.50E-12	6.62E-13	5.84E-14	2.95E-15
100	1.82E-12	1.94E-12	1.90E-12	5.70E-13	5.75E-14	3.36E-15
150	6.28E-13	6.46E-13	6.47E-13	3.09E-13	5.56E-14	5.39E-15
200	3.27E-13	3.30E-13	3.27E-13	2.08E-13	6.15E-14	8.71E-15
250	2.33E-13	2.33E-13	2.27E-13	1.70E-13	7.31E-14	1.49E-14
300	2.13E-13	2.12E-13	2.07E-13	1.70E-13	9.11E-14	2.57E-14
350	2.33E-13	2.33E-13	2.27E-13	1.95E-13	1.21E-13	4.40E-14
400	2.85E-13	2.84E-13	2.79E-13	2.49E-13	1.69E-13	7.28E-14
450	3.67E-13	3.66E-13	3.62E-13	3.34E-13	2.43E-13	1.18E-13
500	4.81E-13	4.81E-13	4.78E-13	4.53E-13	3.53E-13	1.88E-13
600	8.18E-13	8.18E-13	8.16E-13	7.98E-13	6.96E-13	4.36E-13
700	1.31E-12	1.31E-12	1.31E-12	1.30E-12	1.21E-12	8.78E-13
800	1.97E-12	1.97E-12	1.97E-12	1.97E-12	1.90E-12	1.53E-12
900	2.81E-12	2.81E-12	2.81E-12	2.81E-12	2.81E-12	2.41E-12
1000	3.80E-12	3.80E-12	3.80E-12	3.80E-12	3.80E-12	3.45E-12
1100	4.96E-12	4.96E-12	4.96E-12	4.96E-12	4.96E-12	4.96E-12
1200	6.28E-12	6.28E-12	6.28E-12	6.28E-12	6.28E-12	6.28E-12
1300	7.76E-12	7.76E-12	7.76E-12	7.76E-12	7.76E-12	7.76E-12
1400	9.40E-12	9.40E-12	9.40E-12	9.40E-12	9.40E-12	9.40E-12
1500	1.12E-11	1.12E-11	1.12E-11	1.12E-11	1.12E-11	1.12E-11
1600	1.31E-11	1.31E-11	1.31E-11	1.31E-11	1.31E-11	1.31E-11
1700	1.53E-11	1.53E-11	1.53E-11	1.53E-11	1.53E-11	1.53E-11
1800	1.76E-11	1.76E-11	1.76E-11	1.76E-11	1.76E-11	1.76E-11
1900	2.00E-11	2.00E-11	2.00E-11	2.00E-11	2.00E-11	2.00E-11
2000	2.26E-11	2.26E-11	2.26E-11	2.26E-11	2.26E-11	2.26E-11

Table S3. Detailed H-abstraction rate coefficient k_H of MF + OH with N_2 as the bath gas (units in $cm^3 \cdot molec^{-1} \cdot s^{-1}$)

T	0.001 Bar	0.01 Bar	0.1 Bar	1.0 Bar	10 Bar	100 bar
20	6.97E-11	6.94E-11	3.73E-11	8.57E-12	1.14E-12	1.21E-13
30	3.52E-11	3.52E-11	2.98E-11	1.09E-11	2.12E-12	2.66E-13
40	2.00E-11	2.00E-11	1.73E-11	1.05E-11	2.80E-12	4.41E-13
50	1.24E-11	1.24E-11	1.08E-11	8.87E-12	3.05E-12	6.05E-13
60	8.08E-12	8.08E-12	7.21E-12	7.18E-12	3.00E-12	7.38E-13
70	5.54E-12	5.54E-12	5.02E-12	5.02E-12	2.76E-12	8.19E-13
80	3.94E-12	3.94E-12	3.63E-12	3.63E-12	2.44E-12	8.51E-13
90	2.90E-12	2.90E-12	2.71E-12	2.71E-12	2.12E-12	8.51E-13
100	2.19E-12	2.19E-12	2.08E-12	2.08E-12	1.80E-12	8.14E-13
150	7.43E-13	7.43E-13	7.18E-13	7.18E-13	6.36E-13	5.42E-13
200	3.76E-13	3.76E-13	3.69E-13	3.69E-13	3.34E-13	3.02E-13
250	2.58E-13	2.58E-13	2.57E-13	2.57E-13	2.38E-13	2.20E-13
300	2.28E-13	2.28E-13	2.28E-13	2.28E-13	2.15E-13	2.04E-13
350	2.43E-13	2.44E-13	2.44E-13	2.44E-13	2.35E-13	2.27E-13
400	2.92E-13	2.92E-13	2.93E-13	2.93E-13	2.89E-13	2.85E-13
450	3.73E-13	3.73E-13	3.74E-13	3.75E-13	3.75E-13	3.75E-13
500	4.88E-13	4.88E-13	4.88E-13	4.89E-13	4.89E-13	4.89E-13
600	8.29E-13	8.29E-13	8.29E-13	8.29E-13	8.29E-13	8.29E-13
700	1.34E-12	1.34E-12	1.34E-12	1.34E-12	1.34E-12	1.34E-12
800	2.03E-12	2.03E-12	2.03E-12	2.03E-12	2.03E-12	2.03E-12
900	2.90E-12	2.90E-12	2.90E-12	2.90E-12	2.90E-12	2.90E-12
1000	3.97E-12	3.97E-12	3.97E-12	3.97E-12	3.97E-12	3.97E-12
1100	5.23E-12	5.23E-12	5.23E-12	5.23E-12	5.23E-12	5.23E-12
1200	6.69E-12	6.69E-12	6.69E-12	6.69E-12	6.69E-12	6.69E-12
1300	8.35E-12	8.35E-12	8.35E-12	8.35E-12	8.35E-12	8.35E-12
1400	1.02E-11	1.02E-11	1.02E-11	1.02E-11	1.02E-11	1.02E-11
1500	1.23E-11	1.23E-11	1.23E-11	1.23E-11	1.23E-11	1.23E-11
1600	1.45E-11	1.45E-11	1.45E-11	1.45E-11	1.45E-11	1.45E-11
1700	1.70E-11	1.70E-11	1.70E-11	1.70E-11	1.70E-11	1.70E-11
1800	1.97E-11	1.97E-11	1.97E-11	1.97E-11	1.97E-11	1.97E-11
1900	2.26E-11	2.26E-11	2.26E-11	2.26E-11	2.26E-11	2.26E-11
2000	2.57E-11	2.57E-11	2.57E-11	2.57E-11	2.57E-11	2.57E-11

Table S4. Collection of the pressure-dependent rate coefficient for Rxn. 1 (units in $cm^3 \cdot molec^{-1} \cdot s^{-1}$)

T	0.001 Bar	0.01 Bar	0.1 Bar	1.0 Bar	10 Bar	100 bar	LPL	HPL	PEM
20	5.48E-13	5.41E-13	3.57E-13	1.60E-13	4.38E-14	6.94E-15	1.14E-15	1.73E-10	2.06E-08
30	1.98E-13	2.29E-13	1.86E-13	1.13E-13	4.70E-14	1.14E-14	1.03E-15	1.93E-10	2.39E-11
40	9.58E-14	1.18E-13	1.07E-13	7.67E-14	4.12E-14	1.41E-14	1.04E-15	8.43E-11	8.85E-13
50	5.51E-14	6.84E-14	6.62E-14	5.26E-14	3.35E-14	1.47E-14	1.13E-15	3.90E-12	1.37E-13
60	3.54E-14	4.37E-14	4.40E-14	3.75E-14	2.69E-14	1.43E-14	1.23E-15	4.17E-13	4.28E-14
70	2.54E-14	3.04E-14	3.12E-14	2.79E-14	2.17E-14	1.35E-14	1.44E-15	9.51E-14	2.06E-14
80	1.94E-14	2.26E-14	2.32E-14	2.14E-14	1.79E-14	1.25E-14	1.73E-15	3.52E-14	1.31E-14
90	1.59E-14	1.78E-14	1.83E-14	1.73E-14	1.52E-14	1.16E-14	2.06E-15	1.81E-14	9.88E-15
100	1.35E-14	1.48E-14	1.52E-14	1.46E-14	1.33E-14	1.09E-14	2.49E-15	1.18E-14	8.50E-15
150	1.22E-14	1.26E-14	1.32E-14	1.34E-14	1.20E-14	1.16E-14	6.33E-15	8.17E-15	9.61E-15
200	1.81E-14	1.83E-14	1.83E-14	1.84E-14	1.84E-14	1.84E-14	1.39E-14	1.43E-14	1.68E-14
250	3.04E-14	3.04E-14	3.05E-14	3.05E-14	3.05E-14	3.05E-14	2.71E-14	2.66E-14	2.99E-14
300	5.05E-14	5.05E-14	5.05E-14	5.05E-14	5.05E-14	5.05E-14	4.77E-14	4.70E-14	5.06E-14
350	8.12E-14	8.12E-14	8.12E-14	8.12E-14	8.12E-14	8.12E-14	7.90E-14	7.82E-14	8.24E-14
400	1.26E-13	1.26E-13	1.26E-13	1.26E-13	1.26E-13	1.26E-13	1.24E-13	1.23E-13	1.28E-13
450	1.88E-13	1.88E-13	1.88E-13	1.88E-13	1.88E-13	1.88E-13	1.88E-13	1.86E-13	1.91E-13
500	2.71E-13	2.71E-13	2.71E-13	2.71E-13	2.71E-13	2.71E-13	2.72E-13	2.69E-13	2.76E-13
600	5.08E-13	5.08E-13	5.08E-13	5.08E-13	5.08E-13	5.08E-13	5.13E-13	5.05E-13	5.18E-13
700	8.55E-13	8.55E-13	8.55E-13	8.55E-13	8.55E-13	8.55E-13	8.67E-13	8.47E-13	8.72E-13
800	1.31E-12	1.31E-12	1.31E-12	1.31E-12	1.31E-12	1.31E-12	1.33E-12	1.29E-12	1.34E-12
900	1.89E-12	1.89E-12	1.89E-12	1.89E-12	1.89E-12	1.89E-12	1.91E-12	1.84E-12	1.93E-12
1000	2.57E-12	2.57E-12	2.57E-12	2.57E-12	2.57E-12	2.57E-12	2.61E-12	2.49E-12	2.62E-12
1100	3.35E-12	3.35E-12	3.35E-12	3.35E-12	3.35E-12	3.35E-12	3.42E-12	3.20E-12	3.42E-12
1200	4.23E-12	4.23E-12	4.23E-12	4.23E-12	4.23E-12	4.23E-12	4.32E-12	4.02E-12	4.32E-12
1300	5.20E-12	5.20E-12	5.20E-12	5.20E-12	5.20E-12	5.20E-12	5.33E-12	4.88E-12	5.33E-12
1400	6.26E-12	6.26E-12	6.26E-12	6.26E-12	6.26E-12	6.26E-12	6.43E-12	5.81E-12	6.43E-12
1500	7.40E-12	7.40E-12	7.40E-12	7.40E-12	7.40E-12	7.40E-12	7.62E-12	6.81E-12	7.60E-12
1600	8.62E-12	8.62E-12	8.62E-12	8.62E-12	8.62E-12	8.62E-12	8.90E-12	7.85E-12	8.88E-12
1700	9.91E-12	9.91E-12	9.91E-12	9.91E-12	9.91E-12	9.91E-12	1.03E-11	8.97E-12	1.03E-11
1800	1.13E-11	1.13E-11	1.13E-11	1.13E-11	1.13E-11	1.13E-11	1.17E-11	1.01E-11	1.17E-11
1900	1.27E-11	1.27E-11	1.27E-11	1.27E-11	1.27E-11	1.27E-11	1.32E-11	1.13E-11	1.32E-11
2000	1.42E-11	1.42E-11	1.42E-11	1.42E-11	1.42E-11	1.42E-11	1.49E-11	1.26E-11	1.49E-11

Table S5. Collection of the pressure-dependent rate coefficient for Rxn. 2 (units in $cm^3 \cdot molec^{-1} \cdot s^{-1}$)

T	0.001 Bar	0.01 Bar	0.1 Bar	1.0 Bar	10 Bar	100 bar	LPL	HPL	PEM
20	7.02E-11	7.01E-11	3.75E-11	8.55E-12	1.11E-12	1.17E-13	2.61E-13	3.67E-10	3.20E+35
30	3.50E-11	3.75E-11	2.96E-11	1.08E-11	2.08E-12	2.54E-13	1.91E-13	4.00E-10	3.82E+17
40	1.99E-11	2.16E-11	2.09E-11	1.04E-11	2.76E-12	4.27E-13	1.53E-13	4.25E-10	4.25E+08
50	1.23E-11	1.33E-11	1.44E-11	8.82E-12	3.02E-12	5.91E-13	1.46E-13	4.43E-10	1.86E+03
60	8.05E-12	8.63E-12	9.96E-12	7.14E-12	2.97E-12	7.24E-13	1.13E-13	4.57E-10	5.08E-01
70	5.51E-12	5.88E-12	6.99E-12	5.63E-12	2.74E-12	8.05E-13	9.51E-14	4.65E-10	1.53E-03
80	3.92E-12	4.15E-12	5.00E-12	4.40E-12	2.42E-12	8.38E-13	8.68E-14	4.72E-10	1.99E-05
90	2.87E-12	3.02E-12	3.67E-12	3.47E-12	2.11E-12	8.38E-13	8.47E-14	4.73E-10	7.12E-07
100	2.17E-12	2.27E-12	2.74E-12	2.71E-12	1.79E-12	8.04E-13	7.55E-14	4.60E-10	5.20E-08
150	7.31E-13	7.47E-13	8.50E-13	9.40E-13	7.95E-13	5.30E-13	6.23E-14	1.48E-11	3.14E-11
200	3.59E-13	3.62E-13	3.90E-13	4.23E-13	3.97E-13	3.24E-13	6.13E-14	9.98E-13	1.51E-12
250	2.27E-13	2.29E-13	2.37E-13	2.47E-13	2.41E-13	2.17E-13	7.45E-14	3.14E-13	4.00E-13
300	1.78E-13	1.78E-13	1.83E-13	1.99E-13	1.81E-13	1.73E-13	6.99E-14	1.94E-13	2.26E-13
350	1.62E-13	1.62E-13	1.64E-13	1.71E-13	1.74E-13	1.76E-13	8.47E-14	1.65E-13	1.81E-13
400	1.66E-13	1.66E-13	1.68E-13	1.69E-13	1.71E-13	1.71E-13	1.04E-13	1.66E-13	1.78E-13
450	1.86E-13	1.86E-13	1.86E-13	1.88E-13	1.88E-13	1.88E-13	1.30E-13	1.83E-13	1.94E-13
500	2.17E-13	2.17E-13	2.17E-13	2.17E-13	2.19E-13	2.19E-13	1.65E-13	2.14E-13	2.24E-13
600	3.20E-13	3.20E-13	3.20E-13	3.20E-13	3.20E-13	3.20E-13	2.72E-13	3.14E-13	3.29E-13
700	4.83E-13	4.83E-13	4.83E-13	4.83E-13	4.83E-13	4.83E-13	4.48E-13	4.68E-13	4.95E-13
800	7.11E-13	7.11E-13	7.11E-13	7.11E-13	7.12E-13	7.12E-13	6.86E-13	6.82E-13	7.26E-13
900	1.01E-12	1.01E-12	1.01E-12	1.01E-12	1.01E-12	1.01E-12	9.80E-13	9.65E-13	1.03E-12
1000	1.40E-12	1.40E-12	1.40E-12	1.40E-12	1.40E-12	1.40E-12	1.39E-12	1.32E-12	1.43E-12
1100	1.88E-12	1.88E-12	1.88E-12	1.88E-12	1.88E-12	1.88E-12	1.88E-12	1.76E-12	1.91E-12
1200	2.46E-12	2.46E-12	2.46E-12	2.46E-12	2.46E-12	2.46E-12	2.46E-12	2.29E-12	2.51E-12
1300	3.14E-12	3.14E-12	3.14E-12	3.14E-12	3.14E-12	3.14E-12	3.20E-12	2.91E-12	3.20E-12
1400	3.95E-12	3.95E-12	3.95E-12	3.95E-12	3.95E-12	3.95E-12	4.10E-12	3.62E-12	4.02E-12
1500	4.86E-12	4.86E-12	4.86E-12	4.86E-12	4.86E-12	4.86E-12	5.01E-12	4.45E-12	4.96E-12
1600	5.91E-12	5.91E-12	5.91E-12	5.91E-12	5.91E-12	5.91E-12	6.06E-12	5.40E-12	6.03E-12
1700	7.11E-12	7.11E-12	7.11E-12	7.11E-12	7.11E-12	7.11E-12	7.39E-12	6.44E-12	7.26E-12
1800	8.42E-12	8.42E-12	8.42E-12	8.42E-12	8.42E-12	8.42E-12	8.67E-12	7.62E-12	8.60E-12
1900	9.88E-12	9.88E-12	9.88E-12	9.88E-12	9.88E-12	9.88E-12	1.02E-11	8.92E-12	1.01E-11
2000	1.15E-11	1.15E-11	1.15E-11	1.15E-11	1.15E-11	1.15E-11	1.19E-11	1.03E-11	1.18E-11

Table S6. The MS-T scaling factors for Rxn. 1 and Rxn. 2 over 20-20000 K at the theory level of M06-2x/ma-TZVP

T	Rxn. 1	Rxn. 2
20	0.988922	1.853978
30	0.988922	1.853978
40	1.012871	1.880198
50	1.037938	1.892023
60	1.060172	1.888252
70	1.080827	1.87594
80	1.097222	1.855556
90	1.112431	1.832724
100	1.125792	1.80905
150	1.180531	1.704425
200	1.233304	1.634907
250	1.302452	1.603996
300	1.391993	1.620112
350	1.50622	1.694737
400	1.634936	1.828263
450	1.772864	2.020101
500	1.910678	2.262834
600	2.157672	2.853968
700	2.34338	3.523143
800	2.456216	4.195676
900	2.508073	4.835307
1000	2.514408	5.427962
1100	2.483667	5.955743
1200	2.436004	6.436004
1300	2.374101	6.86742
1400	2.304569	7.249746
1500	2.231928	7.593373
1600	2.158052	7.898608
1700	2.086785	8.178501
1800	2.01665	8.428012
1900	1.949367	8.648491
2000	1.885548	8.85354

Sample input file for MS-T calculation

```
### Template of input file for MSTor program ###
### User needs to input correct values for all the keywords ###

$GENERAL
  natoms    8
  nstr    2
  ntor 2

  elec
   1 0.0
  end
  freqscale  1.000
  deltat  0.5
END

$framechain
 1 2
 1 2 3
end

$framedef
 1 : 1 2 8
 2 : 3
 3 : 4 5 6 7
end

$INTDEF
2-1 8-1 1-3 3-4 4-5 4-6 4-7
2-1-8 2-1-3 8-1-3
3-4-6 3-4-7 5-4-6 5-4-7 6-4-7
1-3-4
4-3-1-8 5-4-3-1

END
```

```
$TEMP
 20 30 40 50 60 70 80 90 100 150 200 250 300 350 400 450 500 600. 700. 800. 900. 1000. 1100. 1200. 1300.
 1400. 1500. 1600. 1700. 1800. 1900. 2000.
END


 $structure           1
  geom
    6    0.82527383  0.43152491 -0.00003200
    8    1.28292474 -0.67192186  0.00001900
    8   -0.47256690  0.72765185  0.00007300
    6   -1.35372072 -0.39789892 -0.00004400
    1   -1.18674476 -1.00537079  0.88834982
    1   -1.18254776 -1.00855579 -0.88541182
    1   -2.35896152  0.01115500 -0.00308400
    1    1.41607071  1.35518172 -0.00013300
  end

 energy           0.00000
 weight      1
 rotsigma    1
# Symmetry point group:    Cs
 mtor
   2.0180 3.
 end

END

 $structure           2
  geom
    6   -0.68238686  0.31144894 -0.00616400
    8   -1.80205663 -0.08490198  0.00843700
    8    0.37682192 -0.50606190 -0.01017300
    6    1.65613366  0.11724598  0.00724400
    1    1.83544062  0.60449188  0.96668580
    1    1.74951964  0.84440183 -0.80096684
```

```
    1    2.38457251 -0.67459486 -0.13698897
    1   -0.41013192  1.38124572 -0.02132900
  end

 energy          5.44041
 weight      2
 rotsigma    1
# Symmetry point group:    C1
 mtor
   3.9646 3.
 end

END
```

Sample input file for MESS calculation (TST)

```
! Global Section
TemperatureList[K]          20. 30. 40. 50. 60. 70. 80. 90. 100. 150. 200. 250. 300. 350. 400. 450. 500.
600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000
PressureList[bar]          0.001 0.01 0.1 1. 10. 100
EnergyStepOverTemperature          .2
ExcessEnergyOverTemperature          30
ModelEnergyLimit[kcal/mol]          400
CalculationMethod          direct
RateOutput          Rxn1.out
LogOutput          Rxn1.log
!EigenvalueOutput          Rxn1ep.out
 WellCutoff          10
 ChemicalEigenvalueMax          .2
 ChemicalEigenvalueMin          1.e-6
! Model Section
Model
 EnergyRelaxation
  Exponential
   Factor[1/cm]          250 !200
   Power          0.8 !.85
   ExponentCutoff          15
  End
 CollisionFrequency
  LennardJones
   Epsilons[1/cm]          282.5 57.0 !227   67.8
   Sigmas[angstrom]          4.71 3.74 !5.85  3.621
   Masses[amu]          60 28
  End
!Species
 Well    W1   # MF~OH1
  Species
   RRHO
    Geometry[angstrom]          10
          C          -0.25077200    0.82031300    0.00055100
          O          -1.31773600    1.35098800   -0.00054000
```

O	-0.05717400	-0.50594200	0.00068600
C	-1.25040500	-1.29688300	-0.00023000
H	0.71718000	1.33796900	0.00175700
H	-1.83957700	-1.08114100	-0.88981200
H	-1.84429600	-1.07623700	0.88494400
H	-0.92402300	-2.33196100	0.00341400
O	2.72544500	-0.00075400	-0.00040500
H	2.09349900	-0.74354300	-0.00016200

Core RigidRotor

SymmetryFactor 1

End

Frequencies[1/cm] 24

44.2814

71.4963

128.3625

165.5097

296.2958

328.2133

338.7320

504.8841

790.3547

977.4539

1056.5992

1193.6528

1202.3594

1251.3466

1426.1566

1482.0710

1492.4851

1504.8799

1862.0931

3095.2097

3123.6237

3175.7209

3203.0190

3727.6231

ZeroEnergy[kcal/mol] 0 !-1.875

```
    End
  End
Bimolecular          R          # MF + OH
  Fragment    C2H4O2
    RRHO
      Geometry[angstrom]      8
            C     0.82527400    0.43152500   -0.00003200
            O     1.28292500   -0.67192200    0.00001900
            O    -0.47256700    0.72765200    0.00007300
            C    -1.35372100   -0.39789900   -0.00004400
            H    -1.18674500   -1.00537100    0.88835000
            H    -1.18254800   -1.00855600   -0.88541200
            H    -2.35896200    0.01115500   -0.00308400
            H     1.41607100    1.35518200   -0.00013300
          Core   RigidRotor
            SymmetryFactor           1
          End
        Frequencies[1/cm]       18
        91.3023
        318.5380
        350.6410
        792.5903
        985.1802
        1067.7163
        1184.5877
        1204.2954
        1272.8776
        1405.5534
        1475.2131
        1487.0945
        1500.4241
        1850.7900
        3077.6375
        3102.3855
        3157.1877
        3184.8780
      ZeroEnergy[1/cm]        0
```

```
    ElectronicLevels[1/cm]    1
      0       1
    End
  Fragment    OH
   RRHO
   Geometry[angstrom] 2
   O          0.00000000    0.00000000    0.10815400
   H          0.00000000    0.00000000   -0.86523400
   Core  RigidRotor
              SymmetryFactor                        1
            End
            Frequencies[1/cm]                       1
              3738.6669
    ZeroEnergy[1/cm]          0
    ElectronicLevels[1/cm]       1
      0       2
    End
  GroundEnergy[kcal/mol]                                   1.874495963
End
Bimolecular                    P1                      # (CO)OCH3 + H2O
  Fragment         C2H3O2
    RRHO
      Geometry[angstrom]             7
      C              -0.81284400    0.50899500   -0.00000600
      O              -1.41335600   -0.50629000    0.00000100
      O               0.47587500    0.73398600    0.00002100
      C               1.30786700   -0.45078200   -0.00002600
      H               1.09625800   -1.04191500   -0.88897500
      H               1.10231700   -1.03747900    0.89332100
            H               2.33113500   -0.09145900   -0.00432200
            Core RigidRotor
              SymmetryFactor                     1
            End
        Frequencies[1/cm]              15
        126.8874
        293.2097
        389.6733
```

```
        776.0953
        956.1352
        1175.3106
        1181.7938
        1225.6315
        1470.5068
        1492.1729
        1496.7755
        1909.5486
        3092.8521
        3179.1821
           3207.4870
    ZeroEnergy[1/cm]      0
    ElectronicLevels[1/cm]    1
     0     2
   End
  Fragment      H2O
   RRHO
         Geometry[angstrom]              3
         O           0.00000000    0.00000000    0.11600300
         H           0.00000000    0.76532600   -0.46401400
         H           0.00000000   -0.76532600   -0.46401400
         Core    RigidRotor
          SymmetryFactor                 2
         End
         Frequencies[1/cm]               3
         1597.3541
         3866.1715
         3974.4742
    ZeroEnergy[1/cm]      0
    ElectronicLevels[1/cm]     1
     0     1
   End
  GroundEnergy[kcal/mol]                          -15.80228555 !-17.677+1.187
 End
!Barriers
 Barrier B1  W1  R                          # MF~OH = MF + OH
```

```
RRHO
  Stoichiometry  C2H5O3
  Core      PhaseSpaceTheory
    FragmentGeometry[angstrom]      8
            C       0.82527400    0.43152500   -0.00003200
            O       1.28292500   -0.67192200    0.00001900
            O      -0.47256700    0.72765200    0.00007300
            C      -1.35372100   -0.39789900   -0.00004400
            H      -1.18674500   -1.00537100    0.88835000
            H      -1.18254800   -1.00855600   -0.88541200
            H      -2.35896200    0.01115500   -0.00308400
            H       1.41607100    1.35518200   -0.00013300
    FragmentGeometry[angstrom]      2
            O         0.00000000    0.00000000    0.10815400
            H         0.00000000    0.00000000   -0.86523400
    SymmetryFactor                1
    PotentialPrefactor[au]         13.96048875 !13.60473028
    PotentialPowerExponent          6.
  End
  Frequencies[1/cm]                              19
  91.3023
  318.5380
  350.6410
  792.5903
  985.1802
  1067.7163
  1184.5877
  1204.2954
  1272.8776
  1405.5534
  1475.2131
  1487.0945
  1500.4241
  1850.7900
  3077.6375
  3102.3855
  3157.1877
```

```
    3184.8780
    3738.6669
    ZeroEnergy[kcal/mol]            1.874495963
    ElectronicLevels[1/cm]    1
     0     2
  End

 Barrier B2  W1  P1                   # MF~OH -> TS -> P2
  RRHO
    Geometry[angstrom]              10
    C      0.14400800    0.49404000   -0.00033400
    O     -0.38311600    1.55743200    0.00022600
    O     -0.44866500   -0.69211700   -0.00037700
    C     -1.88370400   -0.65937800    0.00018300
    H      1.30518200    0.32847200   -0.00065500
    H     -2.24303100   -0.14358400   -0.88867100
    H     -2.24233700   -0.14338300    0.88919900
    H     -2.20254500   -1.69644700    0.00040900
    O      2.53545300   -0.37396500   -0.00000200
    H      2.19153000   -1.28382700    0.00185800
    Core RigidRotor
     SymmetryFactor      1.
    End
    Frequencies[1/cm]               23
    95.8609
    100.6793
    161.1072
    167.3333
    314.1870
    391.5209
    669.6510
    762.0822
    953.7332
    993.5146
    1027.5409
    1186.9036
    1200.4409
```

```
    1251.2415
    1477.1568
    1495.8540
    1505.1790
    1688.3705
    1894.2250
    3086.6694
    3167.2821
    3207.4579
    3758.9903
    Tunneling        Eckart
     ImaginaryFrequency[1/cm]      792.2006
     WellDepth[kcal/mol]          3.635950298
     WellDepth[kcal/mol]          19.43823585
    End
     ZeroEnergy[kcal/mol]                          3.635950298
     ElectronicLevels[1/cm]                  1
                  0          2
  End
End
```