Supporting Information for "Theoretical Modeling of the Hydrogen Abstraction Reaction of Fluoromethane by the Hydroxyl Radical"

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November 27, 2000

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Table S1: Cartesian Coordinates (in angstroms) of the Reactants Calculated at MP2/6-31+G** level

CH$_3$F

Atom	X	Y	Z
F	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.405000
H	1.032620	0.000000	1.744508
H	−0.516310	0.894275	1.744508
H	−0.516310	−0.894275	1.744508

OH

Atom	X	Y	Z
O	0.000000	0.000000	0.108156
H	0.000000	0.000000	−0.865244

Table S2: Cartesian Coordinates (in angstroms) of the Products Calculated at MP2/6-31+G** level

CH$_2$F

Atom	X	Y	Z
C	−0.032754	0.669236	0.000000
F	−0.032754	−0.690500	0.000000
H	0.245654	1.099542	0.947834
H	0.245654	1.099542	−0.947834

H$_2$O

Atom	X	Y	Z
H	0.000000	0.766226	−0.466896
O	0.000000	0.000000	0.116724
H	0.000000	−0.766226	−0.466896

Table S3: Cartesian Coordinates (in angstroms) of the Transition State Calculated at MP2/6-31+G** level

Atom	X	Y	Z
C	−0.597006	0.650131	0.000005
F	−1.238109	−0.580341	−0.000005
H	−0.831232	1.187728	0.913478
H	−0.831257	1.187754	−0.913445
H	0.579516	0.442446	−0.000009
O	1.783951	−0.061528	−0.000009
H	1.536377	−1.003420	0.000063

Table S4: Cartesian Coordinates (in angstroms) of the Reactant Geometry Calculated at MP2/6-311+G** level

CH₃F

Atom	X	Y	Z
C	0.000000	0.635921	0.000000
F	0.000000	−0.752642	0.000000
H	−1.033313	0.986083	0.000000
H	0.516656	0.986084	0.894876
H	0.516656	0.986084	−0.894876

OH

Atom	X	Y	Z
O	0.000000	0.000000	0.107612
H	0.000000	0.000000	−0.860893

Table S5: Cartesian Coordinates (in angstroms) of the Product Geometry Calculated at MP2/6-311+G** level

CH$_2$F

Atom	X	Y	Z
C	−0.030818	0.659121	0.000000
F	−0.030818	−0.684309	0.000000
H	0.231133	1.102029	0.950937
H	0.231123	1.102029	−0.950937

H$_2$O

Atom	X	Y	Z
H	0.000000	0.752977	−0.475738
O	0.000000	0.000000	0.118935
H	0.000000	−0.752977	−0.475738

Table S6: Cartesian Coordinates (in angstroms) of the Transition State Geometry Calculated at MP2/6-311+G** level

Atom	X	Y	Z
C	−0.601311	0.639845	0.000035
F	−1.240880	−0.574785	−0.000036
H	−0.829769	1.187934	0.913678
H	−0.829941	1.188136	−0.913444
H	0.573241	0.439193	−0.000068
O	1.792000	-0.061083	−0.000059
H	1.526260	-0.992599	0.000420

Table S7: Calculated Stationary-Point Vibrational Frequencies (in cm^{-1}) of R1 at MP2/6-31+G** Level.

CH$_3$F	OH	CH$_2$F	H$_2$O	TS
3260.3	3824.5	3414.2	4013.7	3812.1
3260.3		3249.8	3867.0	3298.4
3144.1		1516.3	1623.2	3816.9
1550.9		1201.2		1540.2
1550.9		1163.0		1513.3
1525.1		764.9		1330.8
1213.4				1272.4
1213.4				1195.7
1056.6				1095.0
				862.4
				728.7
				319.8
				118.4
				2124.0 i

Table S8: Calculated Stationary-Point Vibrational Frequencies (in cm^{-1}) of R2 at MP2/6-31+G** Level.

CD$_3$F	OH	CD$_2$F	HDO	TS
2422.5	3824.5	2555.0	3944.6	3811.9
2422.5		2340.7	2860.3	2456.9
2248.1		1211.8	1423.0	2306.9
1174.5		1043.2		1193.4
1126.9		917.9		1123.6
1126.9		600.7		1050.6
1001.8				989.7
926.3				954.7
926.3				922.3
				788.6
				689.6
				238.8
				134.1
				115.0
				1561.7 i

Table S9: Calculated Dual-Level Rate Constants in cm^3 molecule^{-1} s^{-1} of R1 Using MP2/6-31+G** as the Low-Level Theory.

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	6.42(−14)[c]	1.23(−15)	1.71(−15)	1.52(−15)	1.71(−15)
	1.23(−13)[d]	2.18(−15)	2.56(−15)	2.37(−15)	2.56(−15)
250	1.32(−13)	5.60(−15)	6.82(−15)	6.40(−15)	6.82(−15)
	2.21(−13)	8.87(−15).	9.65(−15)	9.26(−15)	9.65(−15)
300	2.23(−13)	1.61(−14)	1.83(−14)	1.76(−14)	1.83(−14)
	3.44(−13)	2.36(−14)	2.48(−14)	2.41(−14)	2.48(−14)
350	3.40(−13)	3.54(−14)	3.89(−14)	3.77(−14)	3.89(−14)
	4.93(−13)	4.92(−14)	5.07(−14)	4.97(−14)	5.07(−14)
400	4.85(−13)	6.58(−14)	7.06(−14)	6.90(−14)	7.06(−14)
	6.70(−13)	8.80(−14)	8.95(−14)	8.82(−14)	8.95(−14)
450	6.59(−13)	1.09(−13)	1.15(−13)	1.13(−13)	1.15(−13)
	8.79(−13)	1.42(−13)	1.43(−13)	1.41(−13)	1.43(−13)
500	8.66(−13)	1.68(−13)	1.75(−13)	1.72(−13)	1.75(−13)
	1.12(−12)	2.12(−13)	2.13(−13)	2.11(−13)	2.13(−13)
600	1.39(−12)	3.34(−13)	3.43(−13)	3.40(−13)	3.43(−13)
	1.73(−12)	4.06(−13)	4.05(−13)	4.02(−13)	4.05(−13)
800	2.99(−12)	8.97(−13)	9.05(−13)	9.00(−13)	9.05(−13)
	3.51(−12)	1.04(−12)	1.03(−12)	1.02(−12)	1.03(−12)
1000	5.46(−12)	1.81(−12)	1.82(−12)	1.81(−12)	1.82(−12)
	6.22(−12)	2.04(−12)	2.01(−12)	2.01(−12)	2.01(−12)

[a]from DeMore's Arrehenius expression.[11]

[b]from Schmolter et al.'s Arrehenius expression.[9]

[c]6.42(−14) means 6.42×10^{-14}.

[d]Upper values are results fitted to experimental rate constants of Ref. 11 at 350K, and the lower values are results fitted to experimental rate constants of Ref. 9 at 250K. See text.

Table S10: Calculated Dual-Level Rate Constants in cm^3 molecule^{-1} s^{-1} of R1 Using MP2/6-31+G** as the Low-Level Theory.[a]

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	2.38(−15)	5.33(−17)	1.52(−16)	1.09(−16)	1.52(−16)
250	9.43(−15)	4.54(−16)	8.76(−16)	7.10(−16)	8.76(−16)
300	2.48(−14)	1.98(−15)	3.11(−15)	2.69(−15)	3.11(−15)
350	5.17(−14)	5.86(−15)	8.16(−15)	7.33(−15)	8.16(−15)
400	9.32(−14)	1.36(−14)	1.75(−14)	1.62(−14)	1.75(−14)
450	1.52(−13)	2.70(−14)	3.29(−14)	3.08(−14)	3.29(−14)
500	2.32(−13)	4.75(−14)	5.57(−14)	5.29(−14)	5.57(−14)
600	4.64(−13)	1.17(−13)	1.30(−13)	1.25(−13)	1.30(−13)
800	1.31(−12)	4.06(−13)	4.31(−13)	4.22(−13)	4.31(−13)
1000	2.82(−12)	9.61(−13)	9.96(−13)	9.82(−13)	9.96(−13)

[a]Using 4.37 (kcal/mol) as the high-level classical barrier height.

Table S11: Calculated Dual-Level Rate Constants in cm^3 molecule^{-1} s^{-1} of R2 Using MP2/6-31+G** as the Low-Level Theory.

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	3.35(−15)[a]	6.58(−16)	9.64(−16)	8.22(−16)	9.64(−16)
	6.42(−15)[b]	1.23(−15)	1.66(−15)	1.44(−15)	1.66(−15)
250	1.21(−14)	3.29(−15)	4.12(−15)	3.78(−15)	4.12(−15)
	2.047(−14)	5.42(−15)	6.47(−15)	6.00(−15)	6.47(−15)
300	3.02(−14)	1.00(−14)	1.17(−14)	1.11(−14)	1.17(−14)
	4.65(−14)	1.53(−14)	1.71(−14)	1.63(−14)	1.71(−14)
350	6.07(−14)	2.32(−14)	2.58(−14)	2.48(−14)	2.58(−14)
	8.80(−14)	3.32(−14)	3.60(−14)	3.48(−14)	3.60(−14)
400	1.07(−13)	4.48(−14)	4.85(−14)	4.71(−14)	4.85(−14)
	1.48(−13)	6.12(−14)	6.51(−14)	6.35(−14)	6.51(−14)
450	1.71(−13)	7.66(−14)	8.15(−14)	7.97(−14)	8.15(−14)
	2.29(−13)	1.01(−13)	1.06(−13)	1.04(−13)	1.06(−13)
500	2.57(−13)	1.20(−13)	1.26(−13)	1.24(−13)	1.26(−13)
	3.34(−13)	1.55(−13)	1.60(−13)	1.58(−13)	1.60(−13)
600	5.06(−13)	2.50(−13)	2.57(−13)	2.54(−13)	2.57(−13)
	6.28(−13)	3.08(−13)	3.15(−13)	3.11(−13)	3.15(−13)
800	1.39(−12)	7.08(−13)	7.18(−13)	7.13(−13)	7.18(−13)
	1.63(−12)	8.29(−13)	8.36(−13)	8.31(−13)	8.36(−13)
1000	2.91(−12)	1.49(−12)	1.50(−12)	1.49(−12)	1.50(−12)
	3.32(−12)	1.69(−12)	1.69(−12)	1.69(−12)	1.69(−12)

[a]7.61(−17) means 7.61×10^{-17}, classical barrier height used is 3.06 kcal/mol.
[b]Classical barrier height used is 2.80 kcal/mol.

Table S12: Calculated Dual-Level Rate Constants[a] in cm^3 molecule^{-1} s^{-1} of R1 Using PM3 as the Low-Level Theory.

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	1.42(−15)	5.10(−17)	6.81(−15)	6.72(−15)	7.83(−15)
250	6.24(−15)	4.64(−16)	1.23(−14)	1.06(−14)	1.33(−14)
300	1.76(−14)	2.11(−15)	2.21(−14)	1.79(−14)	2.31(−14)
350	3.85(−14)	6.48(−15)	3.79(−14)	3.01(−14)	3.89(−14)
400	7.20(−14)	1.55(−14)	6.12(−14)	4.89(−14)	6.23(−14)
450	1.21(−13)	3.11(−14)	9.38(−14)	7.61(−14)	9.49(−14)
500	1.89(−13)	5.56(−14)	1.37(−13)	1.13(−13)	1.38(−13)
600	3.91(−13)	1.39(−13)	2.62(−13)	2.25(−13)	2.63(−13)
800	1.15(−12)	4.90(−13)	6.98(−13)	6.33(−13)	6.99(−13)
1000	2.55(−12)	1.16(−12)	1.44(−12)	1.35(−12)	1.44(−12)

[a]The results are fitted to experimental rate constants at 350 K, See text.

Table S13: Calculated Dual-Level Rate Constants[a] in cm^3 molecule^{-1} s^{-1} of R2 Using PM3 as the Low-Level Theory.

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	7.40(−17)	5.29(−17)	1.38(−15)	9.07(−16)	1.39(−15)
250	5.73(−16)	4.40(−16)	3.25(−15)	2.05(−15)	3.26(−15)
300	2.37(−15)	1.90(−15)	7.28(−15)	4.81(−15)	7.28(−15)
350	6.87(−15)	5.65(−15)	1.48(−14)	1.05(−14)	1.48(−14)
400	1.59(−14)	1.33(−14)	2.74(−14)	2.06(−14)	2.74(−14)
450	3.14(−14)	2.66(−14)	4.68(−14)	3.70(−14)	4.68(−14)
500	5.60(−14)	4.76(−14)	7.49(−14)	6.17(−14)	7.49(−14)
600	1.42(−13)	1.21(−13)	1.65(−13)	1.44(−13)	1.65(−13)
800	5.34(−13)	4.52(−13)	5.34(−13)	4.93(−13)	5.34(−13)
1000	1.36(−12)	1.12(−12)	1.22(−12)	1.16(−12)	1.22(−12)

[a]Classical barrier height used is 4.58 kcal/mol, same as in Table S11.

Table S14: Calculated Rate Constants in cm^3 molecule^{-1} s^{-1} of R1 at MP2/6-31+G**
Single Level

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	1.58(−21)	7.83(−23)	2.49(−20)	2.66(−20)	3.43(−20)
250	1.03(−19)	9.30(−21)	3.41(−19)	2.59(−19)	3.84(−19)
300	1.74(−18)	2.35(−19)	2.90(−18)	1.88(−18)	3.03(−18)
350	1.38(−17)	2.44(−18)	1.58(−17)	1.01(−17)	1.61(−17)
400	6.73(−17)	1.45(−17)	6.20(−17)	4.11(−17)	6.26(−17)
450	2.39(−16)	5.97(−17)	1.91(−16)	1.32(−16)	1.92(−16)
500	6.76(−16)	1.89(−16)	4.89(−16)	3.55(−16)	4.90(−16)
600	3.44(−15)	1.12(−15)	2.18(−15)	1.71(−15)	2.19(−15)
800	3.11(−14)	1.17(−14)	1.72(−14)	1.47(−14)	1.72(−14)
1000	1.35(−13)	5.36(−14)	6.87(−14)	6.21(−14)	6.87(−14)

Table S15: Calculated Rate Constants in cm^3 molecule^{-1} s^{-1} of R2 at MP2/6-31+G**
Single Level

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	7.51(−23)	4.28(−23)	4.12(−21)	1.77(−21)	4.28(−21)
250	8.76(−21)	5.53(−21)	6.97(−20)	3.91(−20)	7.10(−20)
300	2.21(−19)	1.48(−19)	8.02(−19)	4.70(−19)	8.07(−19)
350	2.32(−18)	1.61(−18)	5.44(−18)	3.44(−18)	5.45(−18)
400	1.41(−17)	9.91(−18)	2.50(−17)	1.70(−17)	2.50(−17)
450	5.95(−17)	4.19(−17)	8.67(−17)	6.30(−17)	8.68(−17)
500	1.93(−16)	1.36(−16)	2.44(−16)	1.87(−16)	2.45(−16)
600	1.21(−15)	8.38(−16)	1.26(−15)	1.04(−15)	1.26(−15)
800	1.41(−14)	9.33(−15)	1.17(−14)	1.05(−14)	1.17(−14)
1000	7.07(−14)	4.47(−14)	5.17(−14)	4.80(−14)	5.17(−14)

Table S16: Calculated Rate Constants in cm^3 molecule^{-1} s^{-1} of R1 at PM3 Single Level

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	9.62(−19)	4.79(−19)	7.60(−16)	1.23(−15)	1.33(−15)
250	1.95(−17)	1.16(−17)	1.40(−15)	1.87(−15)	2.08(−15)
300	1.54(−16)	1.02(−16)	2.79(−15)	3.03(−15)	3.59(−15)
350	7.11(−16)	5.01(−16)	5.55(−15)	5.15(−15)	6.48(−15)
400	2.34(−15)	1.71(−15)	1.06(−14)	8.95(−15)	1.17(−14)
450	6.15(−15)	4.57(−15)	1.90(−14)	1.54(−14)	2.03(−14)
500	1.37(−14)	1.03(−14)	3.23(−14)	2.59(−14)	3.37(−14)
600	4.92(−14)	3.64(−14)	7.99(−14)	6.53(−14)	8.16(−14)
800	2.92(−13)	2.02(−13)	3.12(−13)	2.71(−13)	3.15(−13)
1000	9.89(−13)	6.35(−13)	8.36(−13)	7.56(−13)	8.39(−13)

Table S17: Calculated Rate Constants in cm^3 molecule^{-1} s^{-1} of R2 at PM3 Single Level

T(K)	TST	CVT	CVT/SCT	CVT/LCT	CVT/μOMT
200	3.32(−20)	2.87(−20)	4.97(−17)	6.78(−17)	7.56(−17)
250	1.31(−18)	1.16(−18)	1.29(−16)	1.17(−16)	1.58(−16)
300	1.62(−17)	1.45(−17)	3.56(−16)	2.41(−16)	3.90(−16)
350	1.04(−16)	9.33(−17)	9.35(−16)	5.65(−16)	9.74(−16)
400	4.36(−16)	3.94(−16)	2.24(−15)	1.35(−15)	2.28(−15)
450	1.39(−15)	1.25(−15)	4.86(−15)	3.07(−15)	4.91(−15)
500	3.61(−15)	3.26(−15)	9.66(−15)	6.45(−15)	9.72(−15)
600	1.63(−14)	1.46(−14)	3.06(−14)	2.26(−14)	3.07(−14)
800	1.27(−13)	1.12(−13)	1.66(−13)	1.38(−13)	1.66(−13)
1000	5.04(−13)	4.33(−13)	5.40(−13)	4.80(−13)	5.40(−13)

Table S18: Estimated $s_{1/2}$ (in bohrs) by Intermediate-Level[a] Calculation

	$s_{1/2}$
R1	−1.08
R2	−1.25

[a]The intermediate level is QCISD(T)/6-311+G**//MP2/6-31+G**.

Table S19: Range Parameters L Used in the Dual-Level Calculation

	R1		R2	
Low Level	SECKART	SIL-2	SECKART	SIL-2
PM3	0.300		0.360	
MP2/6-31+G** ($\Delta V^{\neq} = 2.80$)[a]		0.569		0.643
MP2/6-31+G** ($\Delta V^{\neq} = 3.06$)[a]		0.575		0.636

[a]High-level classical barrier height used in kcal/mol.