Supporting information for

Kinetics of the reaction of methyl radical with hydroxyl radical and methanol decomposition

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Table S1. RHF-RQCISD(T)/*X*//B3LYP/6-311+G** energies

Species	*X* = cc-pVDZ	cc-pVTZ	cc-pVQZ	CBS[a]
OH	-75.5593358	-75.6376935	-75.6615705	-75.6781355
CH_3	-39.7159114	-39.7609310	-39.7723812	-39.7803249
H_2O	-76.2411086	-76.3323070	-76.3599079	-76.3790564
$^1CH_2$	-39.0223296	-39.0614248	-39.0719425	-39.0792394
$^3CH_2$	-39.0413233	-39.0776681	-39.0871287	-39.0936922
H_2	-1.1634841	-1.1723350	-1.1737929	-1.1748043
H_2CO	-114.2189730	-114.3343759	-114.3695359	-114.3939288
c-HCOH	-114.1283803	-114.2445617	-114.2793846	-114.3035436
t-HCOH	-114.1357647	-114.2520060	-114.2869485	-114.3111905
H	-0.4992784	-0.4998098	-0.4999456	-0.5000398
CH_2OH	-114.7641707	-114.8882218	-114.9248241	-114.9502175
CH_3O	-114.7550934	-114.8749035	-114.9102612	-114.9347913
Stationary point				
CH_3 + OH	-115.2752472	-115.3986245	-115.4339516	-115.4584604
CH_3OH	-115.4203504	-115.5510446	-115.5892001	-115.6156712
CH_3OH[b]	-115.4180211	-115.5492855	-115.5875600	-115.6141136
SP1: $^1CH_2$-H_2O	-115.2848188	-115.4130255	-115.4499807	-115.4756189
vdW: $^1CH_2\cdots H_2O$	-115.2896467	-115.4177101	-115.4548876	-115.4806802
$^1CH_2$ + H_2O	-115.2634382	-115.3937318	-115.4318504	-115.4582958
SP2: H_2CO-H_2	-115.2656424	-115.3970186	-115.4360037	-115.4630502
H_2 + H_2CO	-115.3824571	-115.5067109	-115.5433288	-115.5687331
SP3: c-HCOH-H_2	-115.2760156	-115.4019435	-115.4390875	-115.4648568
H_2 + c-HCOH	-115.2918644	-115.4168968	-115.4531775	-115.4783479
SP4: t-HCOH-H_2	-115.2803103	-115.4064046	-115.4436852	-115.4695492
H_2 + t-HCOH	-115.2992488	-115.4243410	-115.4607414	-115.4859947
H + CH_2OH	-115.2543718	-115.3880316	-115.4247697	-115.4502573
H + CH_3O	-115.2543718	-115.3747133	-115.4102068	-115.4348310
SP5: $^3CH_2$ + H_2O	-115.2614764	-115.3870993	-115.4230916	-115.4480618
$^3CH_2$ + H_2O	-115.2824319	-115.4099751	-115.4470366	-115.4727486

[a]Complete basis set limit, extrapolated from the cc-pVTZ and cc-pVQZ basis sets.
[b]Eclipsed, relaxed.

Table S2. B3LYP/6-311+G** rotational constants

Species	Rotational constants, cm^{-1}		
OH	18.663		
CH_3	9.550	9.550	4.775
H_2O	27.488	14.344	9.426
$^1CH_2$	19.711	11.250	7.162
$^3CH_2$	58.107	8.381	7.324
H_2	60.410		
H_2CO	9.466	1.301	1.144
c-HCOH	9.377	1.213	1.074
t-HCOH	9.703	1.217	1.081
CH_2OH	6.456	0.996	0.870
CH_3O	5.243	0.934	0.927
CH_3OH	4.273	0.822	0.794
CH_3OH[a]	4.290	0.818	0.789
SP1: $^1CH_2$-H_2O	4.473	0.543	0.526
vdW: $^1CH_2 \cdots H_2O$	4.184	0.569	0.545
SP2: H_2CO-H_2	3.468	0.919	0.850
SP3: c-HCOH-H_2	3.049	0.828	0.763
SP4: t-HCOH-H_2	3.193	0.831	0.771
SP5: $^3CH_2$ + H_2O	6.063	0.327	0.321

[a]Eclipsed, relaxed.

Table S3. B3LYP/6-311+G** frequencies

Species	ZPE, kcal/mol	Frequencies, cm^{-1}											
OH	5.30	3707											
CH_3	18.6	536	1402	1402	3103	3283	3283						
H_2O	13.4	1603	3817	3922									
$^1CH_2$	10.4	1385	2900	2966									
$^3CH_2$	10.8	1040	3119	3363									
H_2	6.32	4418											
H_2CO	16.6	1202	1260	1531	1815	2883	2941						
c-HCOH	16.1	1007	1199	1322	1468	2755	3528						
t-HCOH	16.7	1097	1216	1320	1504	2858	3717						
CH_2OH	23.2	407	533	1050	1198	1351	1480	3127	3273	3843			
CH_3O	22.6	691	957	1103	1353	1365	1510	2890	2965	3009			
Stationary point													
$CH_3 + OH$	23.9												
CH_3OH	32.0	291	1042	1070	1167	1356	1480	1493	1505	2990	3037	3113	3851
CH_3OH[a]	31.7	-303	1038	1075	1176	1339	1483	1486	1511	3009	3070	3077	3884
SP1: $^1CH_2$-H_2O	27.2	-680	326	452	686	925	1068	1400	1525	2741	3017	3104	3811
vdW: $^1CH_2 \cdots H_2O$	29.3	76	345	608	632	1052	1121	1399	1651	2932	2997	3786	3865
$^1CH_2 + H_2O$	23.7												
SP2: H_2CO-H_2	26.3	-2138	865	904	1148	1177	1250	1453	1499	1947	2273	2933	2974
$H_2 + H_2CO$	22.9												
SP3: c-HCOH-H_2	25.6	-775	573	656	916	1041	1223	1239	1422	1501	2718	2920	3682
H_2 + c-HCOH	22.4												
SP4: t-HCOH-H_2	26.0	-874	576	675	974	1060	1184	1279	1444	1560	2637	3012	3781
H_2 + t-HCOH	23.1												
$H + CH_2OH$	23.2												
$H + CH_3O$	22.6												
SP5: $^3CH_2 + H_2O$	22.9	-1140	111	351	433	513	781	1125	1184	1309	3133	3306	3760
$^3CH_2 + H_2O$	24.1												

[a]Eclipsed, relaxed.

Table S4. B3LYP/6-311+G** optimized geometries in Å

Species	Atom #	Atom type	x	y	z
OH	1	O	0.000000	0.000000	-0.108453
	2	H	0.000000	0.000000	0.867620
CH_3	1	C	0.000000	0.000000	0.000000
	2	H	0.000000	1.080585	0.000000
	3	H	0.935814	-0.540292	0.000000
	4	H	-0.935814	-0.540292	0.000000
H_2O	1	O	0.000000	0.000000	0.117071
	2	H	0.000000	0.763505	-0.468285
	3	H	0.000000	-0.763505	-0.468285
$^1CH_2$	1	C	0.000000	0.000000	0.176074
	2	H	0.000000	0.862313	-0.528222
	3	H	0.000000	-0.862313	-0.528222
$^3CH_2$	1	C	0.000000	0.000000	0.102502
	2	H	0.000000	0.998966	-0.307506
	3	H	0.000000	-0.998966	-0.307506
H_2	1	H	0.000000	0.000000	0.372080
	2	H	0.000000	0.000000	-0.372080
H_2CO	1	O	0.000000	0.000000	0.674310
	2	C	0.000000	0.000000	-0.527490
	3	H	0.000000	0.939912	-1.114767
	4	H	0.000000	-0.939912	-1.114767
c-HCOH	1	C	0.121783	0.742104	0.000000
	2	O	0.121783	-0.565665	0.000000
	3	H	-0.950863	1.071821	0.000000
	4	H	-0.754094	-0.999120	0.000000
t-HCOH	1	C	0.010859	0.742803	0.000000
	2	O	0.010859	-0.568766	0.000000
	3	H	-1.078708	0.979193	0.000000
	4	H	0.926683	-0.885887	0.000000
CH_2OH	1	C	-0.685073	0.027820	-0.059544
	2	O	0.670404	-0.125533	0.021465
	3	H	1.102811	0.729932	-0.063715
	4	H	-1.119885	0.995991	0.158918
	5	H	-1.235722	-0.888578	0.090344

Table S4. B3LYP/6-311+G** optimized geometries in Å (continued)

Species	Atom #	Atom type	x	y	z
CH_3O	1	C	-0.011333	-0.574352	0.000000
	2	O	-0.011333	0.791260	0.000000
	3	H	1.059187	-0.866356	0.000000
	4	H	-0.450261	-1.008807	0.910425
	5	H	-0.450261	-1.008807	-0.910425
CH_3OH	1	C	-0.046440	0.666002	0.000000
	2	O	-0.046440	-0.757998	0.000000
	3	H	-1.090912	0.978435	0.000000
	4	H	0.438901	1.078649	0.893071
	5	H	0.438901	1.078649	-0.893071
	6	H	0.863266	-1.067765	0.000000
CH_3OH[a]	1	C	0.048387	0.668020	0.000000
	2	O	0.048387	-0.760143	0.000000
	3	H	-0.963890	1.083449	0.000000
	4	H	0.571721	1.032922	0.888755
	5	H	0.571721	1.032922	-0.888755
	6	H	-0.856963	-1.076265	0.000000
SP1: $^1CH_2$-H_2O	1	C	-1.021886	-0.003267	0.137029
	2	H	-1.201743	0.979296	-0.320347
	3	H	-1.256614	-0.755080	-0.625540
	4	O	0.883007	-0.096775	-0.079286
	5	H	1.191925	0.817431	-0.027643
	6	H	0.333690	-0.247847	0.785640
vdW: $^1CH_2\cdots H_2O$	1	C	-1.022358	-0.000206	-0.192763
	2	H	-1.209539	-0.860780	0.476528
	3	H	-1.209076	0.862318	0.474226
	4	O	0.807114	-0.000176	0.128925
	5	H	1.047817	-0.762015	-0.413872
	6	H	1.048039	0.763124	-0.411704
SP2: H_2CO-H_2	1	C	0.020395	-0.104622	-0.049759
	2	O	-0.026911	0.014129	1.274096
	3	H	0.959133	0.120451	-0.582589
	4	H	-0.871527	0.140784	-0.649815
	5	H	0.017376	-1.490735	-0.386217
	6	H	-0.014488	-1.212896	0.564640

Table S4. B3LYP/6-311+G** optimized geometries in Å (continued)

Species	Atom #	Atom type	x	y	z
SP3: c-HCOH-H_2	1	C	-0.510079	-0.328552	-0.190244
	2	O	0.730354	0.146251	-0.077297
	3	H	-0.818323	-0.883026	0.719309
	4	H	1.128979	0.018960	0.796604
	5	H	-1.463389	0.661024	-0.263553
	6	H	-1.629626	1.004351	0.507480
SP4: t-HCOH-H_2	1	C	0.516878	-0.265587	-0.247493
	2	O	-0.729020	0.036657	0.152584
	3	H	0.945577	-0.936654	0.513661
	4	H	-1.169035	0.528526	-0.551727
	5	H	1.380979	0.763750	-0.265228
	6	H	1.573368	0.944642	0.567581
SP5: $^3CH_2 + H_2O$	1	H	-0.006609	0.051541	0.014925
	2	C	0.002958	-0.022613	1.244738
	3	H	0.975590	-0.020189	1.717973
	4	H	-0.938080	-0.268751	1.717833
	5	O	-0.046112	0.354024	-1.208713
	6	H	-0.170724	1.314841	-1.143939

[a]Eclipsed, relaxed.