Table S 1: MP2 structural parameters for reactants, intermolecular complexes, transition states and products for the *hydrogen abstraction reaction* of OH radical with acetone (distances in Å, angles in degrees)

coordinate	OH+acetone		**MC1a**		**MC1b**	**TS1a**		**TS1b**	**MC4a**		**MC4b**	acetonyl+H_2O	
	6-31G**/6-31++G**		6-31G**/6-31++G**		6-31G**	6-31G**/6-31++G**		6-31G**	6-31G**/6-31++G**		6-31G**	6-31G**/6-31++G**	
O_2H_1			2.535	2.863		1.240	1.266		0.962	0.963		0.961	0.963
O_1H_7			1.933	1.923		2.117	2.211		1.928	1.886			
C_1O_1	1.227	1.231	1.233	1.235	1.228	1.229	1.232	1.216	1.215	1.219	1.207	1.203	1.207
C_1C_2	1.513	1.512	1.508	1.501	1.512	1.507	1.507	1.514	1.469	1.470	1.474	1.476	1.477
C_1C_3	1.513	1.512	1.508	1.507	1.512	1.509	1.508	1.509	1.510	1.509	1.514	1.514	1.513
O_2H_2					2.636			1.288	2.355	2.387	0.962		
C_2H_1	1.086	1.086	1.085	1.086	1.086	1.226	1.213	1.085	3.727	4.097	1.078		
C_2H_2	1.090	1.091	1.090	1.095	1.089	1.089	1.089	1.205	1.079	1.079	3.859	1.079	1.080
C_2H_3	1.090	1.091	1.090	1.092	1.091	1.088	1.088	1.088	1.079	1.079	1.079	1.078	1.079
C_3H_4	1.086	1.086	1.086	1.086	1.086	1.086	1.087	1.085	1.084	1.085	1.085	1.085	1.085
C_3H_5	1.090	1.091	1.090	1.092	1.090	1.090	1.090	1.089	1.090	1.091	1.088	1.090	1.091
C_3H_6	1.090	1.091	1.090	1.092	1.091	1.090	1.091	1.091	1.090	1.091	1.091	1.090	1.091
O_2H_7	0.972		0.980	0.982	0.973	0.975	0.977	0.972	0.972	0.976	0.962	0.961	0.963
$C_2C_1O_1$	121.8	121.7	122.2	121.9	121.9	121.8	121.5	121.0	121.7	121.6	121.7	121.4	121.2
$C_3C_1O_1$	121.8	121.7	120.7	120.9	122.0	121.6	121.9	123.1	121.6	121.7	122.6	122.8	122.7
$H_1C_2C_1$	109.6	109.8	110.2	110.6	109.6	107.6	107.8	112.1	85.2	82.2	117.6		
$H_2C_2C_1$	110.2	110.0	109.7	110.2	109.4	111.6	111.6	105.8	118.1	118.8	102.1	122.1	121.8
$H_3C_2C_1$	110.2	110.0	109.7	109.1	110.1	113.5	113.6	112.3	121.1	120.7	121.6	118.0	118.2
$H_4C_3C_1$	109.6	109.8	109.8	110.0	109.6	109.6	109.8	109.5	109.4	109.5	109.2	109.2	109.4
$H_5C_3C_1$	110.2	110.0	110.0	109.2	109.7	110.3	110.4	109.5	109.9	109.7	111.1	109.9	109.7
$H_6C_3C_1$	110.2	110.0	110.0	110.4	110.2	109.5	109.2	109.6	109.6	109.5	108.1	109.9	109.7
$C_1O_1H_7$			117.1	123.3		100.3	100.5		113.1	114.7			
$O_1H_7O_2$			165.9	170.9		132.1	128.4		160.9	159.4			
$H_7O_2H_1$									103.6	106.1		103.8	105.3
$O_2H_2C_2$					152.7			166.7			54.2		
$H_7O_2H_2$					92.7			99.1			104.3		
$H_1C_2C_1O_1$	0.0	0.0	0.1	−8.0	- 1.0	17.7	18.8	- 7.6	-11.7	1.0	4.0		
$H_2C_2C_1O_1$	−120.9	−121.0	−121.2	−130.2	- 122.4	−98.0	−96.6	- 124.2	- 0.1	-0.8	- 144.6	0.0	0.0
$H_3C_2C_1O_1$	120.9	121.0	121.4	112.4	119.8	136.2	137.0	120.1	179.5	178.3	- 173.2	180.0	179.9
$H_4C_3C_1O_1$	0.0	0.0	0.0	−8.2	- 0.9	4.9	7.6	2.7	0.9	0.6	16.3	0.0	0.0
$H_5C_3C_1O_1$	120.9	121.0	121.1	112.1	120.2	126.5	129.5	124.5	122.1	121.9	140.0	120.9	121.0
$H_6C_3C_1O_1$	−120.9	−121.0	−121.1	−130.2	- 121.9	−115.5	−112.6	- 117.9	-120.0	-120.3	-102.3	−120.9	−121.0
$C_3C_1O_1C_2$	180.0	180.0	180.0	180.0	- 179.4	−179.0	−179.4	179.9	180.0	179.9	178.8	180.0	180.0
$C_2C_1O_1H_7$			0.0	3.0		−10.1	−12.4		-4.1	-6.6			
$C_1O_1H_7O_2$			−0.1	6.6		−3.1	−1.8		19.2	-1.3			
$O_2H_2C_2C_1$					- 10.5			- 86.9	3.2	11.5			
$H_7O_2H_2C_2$					149.7			- 50.7	0.8	- 12.9			

Table S 2: MP2 structural parameters for intermolecular complexes, transition states and products for the *OH-addition/ CH_3-elimination* pathway of the OH+acetone reaction system (distances in Å, angles in degrees).

coordinate	**MC 2**	**TS 2**		Adduct $CH_3CO(OH)CH_3$		**TS3**	**MC3**	$CH_3COOH + CH_3$
	6-31G**	6-31G**/6-31++G**		6-31G**/6-31++G**		6-31G**	6-31G**	6-31G**
O_2C_1	3.238	1.836	1.837	1.419	1.426	1.390	1.365	1.362
O_1H_7	2.012	2.133	2.160	2.413	2.422	2.264	2.276	2.278
C_1O_1	1.232	1.252	1.257	1.378	1.379	1.244	1.217	1.217
C_1C_2	1.507	1.511	1.509	1.536	1.536	1.897	4.071	
C_1C_3	1.510	1.511	1.509	1.523	1.522	1.521	1.501	1.502
C_2H_1	1.086	1.086	1.086	1.089	1.090	1.079	1.075	1.074
C_2H_2	1.091	1.086	1.087	1.087	1.088	1.081	1.075	1.074
C_2H_3	1.090	1.091	1.092	1.087	1.088	1.079	1.075	1.074
C_3H_4	1.087	1.085	1.085	1.087	1.088	1.088	1.084	1.084
C_3H_5	1.091	1.087	1.088	1.087	1.088	1.086	1.088	1.088
C_3H_6	1.088	1.091	1.091	1.087	1.087	1.085	1.088	1.088
O_2H_7	0.977	0.975	0.977	0.966	0.968	0.970	0.971	0.971
O_2H_1							2.582	
$C_2C_1O_1$	121.4	120.0	119.8	105.0	105.1	96.3	131.3	
$C_3C_1O_1$	121.1	119.9	119.8	109.8	109.8	122.2	126.6	126.4
$H_1C_2C_1$	109.9	109.4	109.7	110.0	110.1	103.1	33.2	
$H_2C_2C_1$	109.5	111.5	111.5	108.0	107.7	99.9	129.1	
$H_3C_2C_1$	110.2	107.7	107.2	111.0	110.8	105.5	103.7	
$H_4C_3C_1$	109.5	109.0	109.3	109.2	109.3	106.5	109.3	109.3
$H_5C_3C_1$	107.7	111.5	111.4	109.1	108.9	111.7	109.7	109.6
$H_6C_3C_1$	112.2	107.5	107.2	110.1	110.0	109.8	109.3	109.6
$C_1O_1H_7$	104.3	79.3	79.8	53.1	53.5	56.1	55.3	55.1
$O_1H_7O_2$	147.7	79.7	78.2	73.3	72.9	78.8	77.0	76.9
$H_1C_2C_1O_1$	- 1.9	−31.1	−32.2	−58.6	−58.7	-57.9	-106.4	
$H_2C_2C_1O_1$	- 122.8	−153.8	−155.1	−177.2	−177.3	-176.7	167.1	
$H_3C_2C_1O_1$	119.5	86.9	85.8	62.1	62.2	62.6	18.4	
$H_4C_3C_1O_1$	- 32.2	30.9	30.6	60.6	59.2	74.6	3.1	0.1
$H_5C_3C_1O_1$	85.1	153.3	153.2	179.4	178.0	- 166.8	124.3	121.0
$H_6C_3C_1O_1$	- 155.0	−87.6	−88.0	−59.9	−61.3	- 43.4	-117.6	-120.9
$C_3C_1O_1C_2$	- 177,3	157.5	157.3	121.5	121.8	107.6	101.5	
$C_2C_1O_1H_7$	124.7	88.1	89.5	99.9	100.5	102.5	77.9	
$C_1O_1H_7O_2$	- 29.1	29.9	28.1	30.1	29.3	6.9	0.2	0.0
$O_2C_1C_2C_3$	- 99.5	- 107.0	- 107.3					

Table S 3: MP2 structural parameters for intermolecular complexes, transition states and products for the *CH_3-elimination* reaction *from the water-acetonyl complexes* of the OH+acetone reaction system (distances in Å, angles in degrees).

	MC4a		**MC4b**	**TS4a**	**TS4b**	**MC5a**	**MC5b**	**TS5**a	**MC6**a	$CH_3COOH + CH_3$
	6-31G**	6-31++G**	6-31G**	6-31G**	6-31G**	6-31G**	6-31G**	6-31G**	6-31G**	6-31G**
O_2H_1	0.962	0.963		0.962		0.963		0.971	0.971	
O_1H_7	1.928	1.886		2.196		2.949		2.079		
O_1H_1						2.969		3.083		
C_1O_1	1.215	1.219	1.207	1.192	1.183	1.183	1.181	1.181	1.219	1.217
C_1C_2	1.469	1.470	1.474	1.328	1.338	1.318	1.320	1.412	1.501	1.502
C_1C_3	1.510	1.509	1.514	1.998	1.960	3.533	3.453	3.871	4.136	
O_2H_2			0.962	2.613	0.963	2.738	0.963	2.584		
C_2H_1	3.727	4.097	1.078		1.081		1.076			
C_2H_2	1.079	1.079	3.859	1.082		1.075		1.085	1.088	1.088
C_2H_3	1.079	1.079	1.079	1.070	1.070	1.076	1.077	1.083	1.084	1.084
C_3H_4	1.084	1.085	1.085	1.079	1.081	1.075	1.075	1.075	1.075	1.074
C_3H_5	1.090	1.091	1.088	1.078	1.079	1.075	1.075	1.075	1.075	1.074
C_3H_6	1.090	1.091	1.091	1.081	1.080	1.075	1.075	1.075	1.075	1.074
C_2H_7									1.088	1.088
O_2H_7	0.972	0.976	0.962	0.965	0.963	0.963	0.963	1.230		
$C_2C_1O_1$	121.7	121.6	121.7	155.5	154.4	178.9	179.3	150.2	126.5	126.4
$C_3C_1O_1$	121.6	121.7	122.6	104.9	106.2	87.3	87.8	70.4	53.6	
$H_1C_2C_1$	85.2	82.2	117.6		114.8		118.6	57.9		
$H_2C_2C_1$	118.1	118.8	102.1	113.6		118.1		113.2	109.5	109.6
$H_3C_2C_1$	121.1	120.7	121.6	124.5	123.8	118.9	119.3	114.3	109.5	109.3
$H_4C_3C_1$	109.4	109.5	109.2	97.2	95.1	55.9	98.1	37.0	27.2	
$H_5C_3C_1$	109.9	109.7	111.1	113.4	111.1	108.4	88.2	115.6	117.7	
$H_6C_3C_1$	109.6	109.5	108.1	94.8	99.5	107.7	85.9	114.1	117.6	
$H_1O_2C_1$									105.4	
$C_1O_1H_7$	113.1	114.7		96.0		79.7		19.3		
$O_1H_7O_2$	160.9	159.4		140.3		90.2		66.6		
$H_7O_2H_1$	103.6	106.1		103.2		103.5		113.7		
$O_2H_2C_2$			54.2	121.7	76.1	107.1	83.4	63.9		
$H_7O_2H_2$			104.3	84.6	104.2	111.5	104.3	38.8		
$H_1C_2C_1O_1$	-11.7	1.0	4.0	- 26.1	21.5	162.8	24.5	- 178.9	180.0	
$H_2C_2C_1O_1$	- 0.1	-0.8	- 144.6	- 17.5		178.2		131.9	121.0	121.0
$H_3C_2C_1O_1$	179.5	178.3	- 173.2	162.8	- 164.6	- 2.0	- 156.8	- 1.3	- 0.1	0.1
$H_4C_3C_1O_1$	0.9	0.6	16.3	53.1	48.6	- 0.5	50.3	5.3	0.1	
$H_5C_3C_1O_1$	122.1	121.9	140.0	175.4	169.1	113.7	170.7	112.1	103.0	
$H_6C_3C_1O_1$	-120.0	-120.3	-102.3	- 63.5	- 67.6	- 115.2	- 68.7	- 103.1	- 103.0	
$C_3C_1O_1C_2$	180.0	179.9	178.8	- 165.8	167.3	- 2.5	- 162.6	2.4	- 0.1	
$C_2C_1O_1H_7$	-4.1	-6.6		4.5		167.0		117.1		
$C_1O_1H_7O_2$	19.2	-1.3		37.2		50.5		121.6		
$O_2H_2C_2C_1$	3.2	11.5		9.0	- 85.3	- 0.1	- 95.5	48.1		
$H_7O_2H_2C_2$	0.8	- 12.9		11.7	- 93.7	56.4	-95.8	54.2		
$O_2C_1O_1C_2$									180.0	

Table S 4: Harmonic vibrational frequencies (in cm^{-1}) for the intermolecular complexes found on the PES of the OH + acetone reaction system. In brackets the IR line intensities are given (in km mol^{-1}). Both have been calculated at the MP2/6-31G** level of theory and the frequencies are scaled by 0.95.

	MC1a	**MC1b**	**MC2**	**MC3**	**MC4a**	**MC4b**	**MC5a**	**MC5b**	**MC6a**
1	36(0.1)	14(13.2)	11(4.1)	18(1.0)	55(2.9)	29(4.9)	9(0.0)	9(6.4)	25(0.6)
2	45(0.0)	51(11.4)	75(1.8)	55(1.1)	93(0.3)	65(187.8)	36(1.5)	38(22.4)	55(1.8)
3	78(6.7)	70(116.3)	104(7.5)	67(0.0)	130(17.7)	75(25.8)	36(8.0)	47(19.4)	63(0.3)
4	128(1.0)	91(10.2)	141(0.7)	83(0.1)	166(7.9)	97(49.9)	45(68.7)	56(2.5)	89(0.8)
5	167(4.6)	99(70.2)	161(5.3)	104(0.2)	181(101.7)	104(5.6)	59(0.6)	60(32.2)	102(0.5)
6	374(3.9)	119(80.0)	365(5.9)	113(0.3)	309(28.3)	118(77.4)	68(10.1)	85(15.2)	127(0.0)
7	465(0.8)	167(8.4)	381(108.3)	209(2.8)	352(70.0)	152(21.6)	96(20.8)	108(4.0)	232(3.2)
8	523(93.6)	366(2.5)	464(24.0)	405(3.5)	384(8.2)	308(1.1)	116(13.1)	127(29.5)	408(7.5)
9	531(118.3)	468(0.3)	509(111.2)	445(76.6)	520(3.2)	382(6.3)	137(0.1)	139(34.0)	472(87.4)
10	534(136.1)	508(14.8)	517(173.9)	526(21.0)	529(19.1)	505(12.6)	161(0.1)	142(271.7)	526(17.2)
11	782(0.4)	775(1.1)	776(0.7)	553(45.5)	665(238.8)	516(5.1)	258(363.2)	201(8.6)	557(45.3)
12	873(0.1)	874(1.0)	867(1.1)	653(118.9)	681(63.3)	651(41.7)	292(0.1)	279(31.1)	656(118.6)
13	888(2.7)	884(3.3)	909(3.7)	839(5.3)	805(0.1)	792(1.4)	400(2.2)	425(1.7)	843(2.7)
14	1062(0.1)	1060(0.4)	1056(0.3)	979(69.5)	897(10.5)	895(14.5)	421(87.4)	446(105.2)	984(65.3)
15	1093(2.5)	1095(4.6)	1089(4.6)	1044(7.6)	1012(9.4)	1013(11.2)	505(81.1)	507(46.7)	1044(5.5)
16	1233(53.9)	1218(56.5)	1226(63.0)	1167(191.7)	1059(11.0)	1058(5.6)	567(59.1)	612(71.9)	1172(205.5)
17	1370(17.6)	1363(10.2)	1364(10.5)	1304(43.9)	1254(91.6)	1230(100.3)	956(18.2)	974(7.6)	1314(54.0)
18	1377(53.6)	1371(63.4)	1372(63.9)	1389(60.5)	1369(45.0)	1369(41.0)	1107(6.3)	1115(2.9)	1392(62.9)
19	1446(3.3)	1448(0.1)	1445(16.7)	1414(1.0)	1439(33.1)	1438(27.8)	1366(15.5)	1393(13.7)	1414(1.2)
20	1447(0.0)	1454(2.6)	1448(8.7)	1423(0.6)	1448(8.2)	1454(13.8)	1413(2.5)	1415(1.3)	1429(0.5)
21	1454(23.6)	1456(19.7)	1454(5.0)	1458(10.2)	1456(8.9)	1461(8.7)	1416(1.1)	1428(1.3)	1456(10.2)
22	1468(19.8)	1472(12.1)	1468(13.3)	1460(6.7)	1636(67.3)	1590(69.8)	1598(54.4)	1588(66.4)	1463(6.9)
23	1691(116.8)	1705(93.7)	1693(106.8)	1766(235.6)	1970(1133.3))	1991(854.9)	2120(385.6)	2124(394.3)	1756(265.8)
24	2973(0.3)	2973(3.0)	2973(1.2)	2995(1.4)	2979(0.2)	2979(2.8)	3075(0.0)	3069(3.2)	2995(2.3)
25	2978(3.7)	2977(4.5)	2979(2.3)	3072(2.2)	3065(4.3)	3070(4.6)	3132(28.2)	3111(72.2)	3067(7.6)
26	3055(0.2)	3058(1.9)	3055(4.9)	3083(1.6)	3092(15.8)	3098(5.2)	3248(12.1)	3225(32.8)	3082(3.0)
27	3061(9.8)	3064(8.7)	3072(4.3)	3120(3.2)	3117(5.5)	3113(4.5)	3261(4.1)	3254(5.9)	3122(0.7)
28	3105(4.8)	3100(9.2)	3096(7.9)	3258(5.0)	3225(3.9)	3230(0.7)	3263(2.7)	3261(0.5)	3253(7.0)
29	3110(3.1)	3101(4.7)	3104(6.0)	3264(0.3)	3564(259.0)	3690(13.1)	3686(10.6)	3684(13.0)	3259(0.8)
30	3510(280.5)	3641(15.0)	3572(110.5)	3621(62.9)	3777(69.7)	3820(50.5)	3811(44.9)	3815(49.4)	3624(64.0)