Hydroxyl Radical Substitution in Halogenated Carbonyls: Oxalic Acid Formation

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Supplementary Table 1: Energies for species of OH + ClC(O)C(O)Cl and resulting reactions. Energies given in kcal·mole^{-1}. Values corrected with zero point energy.

species	MP2 6-31G (d)	MP4 6-311++G (2d,2p)	MP4 6-311++G (2df,2p)	CCSD(T) 6-311++G (2d,2p)	CCSD(T) 6-311++G (2df,2p)
optimized species energies					
ClC(O)C(O)Cl	-1145.288990	-1145.598017	-1145.741063	-1145.584565	-1145.726276
ClC(OH)OC(O)Cl	-1220.815087	-1221.211696	-1221.377080	-1221.204383	-1221.368145
C(O)(OH)C(O)Cl	-761.291746	-761.618837	-761.748621	-761.604991	-761.733562
C(O)(OH)C(OH)ClO	-836.818133	-837.232387	-837.384391	-837.224838	-837.375376
C(O)(OH)C(O)(OH)	-377.297205	-377.645358	-377.762534	-377.631161	-377.747196
ClC(O)(OH)	-648.270028	-648.506899	-648.601642	-648.499270	-648.593242
C(O)(OH)	-188.578252	-188.755911	-188.812086	-188.749929	-188.805694
C(O)OC(O)Cl	-760.624590	-760.939368	-761.067560	-760.929895	-761.056744
OH	-75.514686	-75.605545	-75.624210	-75.606332	-75.624913
Cl	-459.562057	-459.625060	-459.657666	-459.625918	-459.658731
CO	-113.023340	-113.120385	-113.150870	-113.114204	-113.144537
H_2O	-76.177767	-76.287569	-76.307724	-76.286536	-76.306621
optimized transition state energies					
[ClC(O)C(O)Cl + OH → ClC(OH)OC(O)Cl]‡	-1220.772015	-1221.175827	-1221.340069	-1221.172527	-1221.335263
[ClC(OH)OC(O)Cl → C(O)(OH)C(O)Cl + Cl]‡	-1220.809660	-1221.209969	-1221.375249	-1221.205599	-1221.369337
[C(O)(OH)C(O)Cl + OH → C(O)(OH)C(OH)ClO]‡	-836.776437	-837.197512	-837.348171	-837.193810	-837.343141
[C(O)(OH)C(OH)ClO → C(O)(OH)C(O)(OH) + Cl]‡	-836.816200	-837.235013	-837.387039	-837.230770	-837.381424
[ClC(OH)OC(O)Cl → ClC(O)(OH) + CO + Cl]‡	-1220.805013	-1221.206086	-1221.372511	-1221.202056	-1221.366874
[C(O)(OH)C(OH)ClO → C(O)(OH) + ClC(O)(OH)]‡	-836.808236	-837.226409	-837.379311	-837.220835	-837.372322
[C(O)(OH)C(O)Cl + OH → C(O)OC(O)Cl + H_2O]‡	-836.783252	-837.205279	-837.354459	-837.194858	-837.342791

Supplementary Table 2: Vibrational frequencies for species of OH + ClC(O)C(O)Cl and resulting reactions. Frequencies in cm^{-1}.

species	vibrational frequencies MP2 / 6-31G(d)
optimized species energies	
ClC(O)C(O)Cl	1820, 1797, 1123, 798, 726, 629, 507, 440, 394, 298, 214, 34
ClC(OH)OC(O)Cl	3712, 1950, 1405, 1288, 1121, 973, 774, 682, 573, 531, 487, 443, 374, 361, 287, 234, 169, 41
C(O)(OH)C(O)Cl	3683, 1848, 1811, 1414, 1216, 1000, 782, 688, 666, 568, 460, 381, 231, 36
C(O)(OH)C(OH)ClO	3718, 3688, 1870, 1460, 1372, 1294, 1197, 1082, 840, 786, 679, 619, 568, 532, 467, 397, 369, 295, 265, 182, 40
C(O)(OH)C(O)(OH)	3605, 3600, 1869, 1843, 1501, 1373, 1255, 1236, 839, 794, 722, 705, 666, 574, 459, 421, 280, 130
ClC(O)(OH)	3685, 1876, 1370, 1173, 734, 716, 581, 504, 421
C(O)(OH)	3757, 1919, 1276, 1125, 611, 562
C(O)OC(O)Cl	2046, 1832, 1286, 997, 756, 641, 546, 460, 415, 346, 205, 52
OH	3740
Cl	n/a
CO	2125
H_2O	3917, 3775, 1735
optimized transition state energies	
$[ClC(O)C(O)Cl + OH \rightarrow ClC(OH)OC(O)Cl]^{‡}$	3647, 2444, 1693, 1118, 944, 782, 694, 645, 506, 482, 414, 341, 308, 268, 222, 189, 48, 991i
$[ClC(OH)OC(O)Cl \rightarrow C(O)(OH)C(O)Cl + Cl]^{‡}$	3683, 2415, 1433, 1420, 1186, 972, 693, 671, 566, 554, 470, 404, 363, 286, 232, 151, 44, 732i
$[C(O)(OH)C(O)Cl + OH \rightarrow C(O)(OH)C(OH)ClO]^{‡}$	3687, 3656, 1918, 1696, 1394, 1218, 1036, 927, 775, 695, 618, 599, 485, 434, 399, 372, 297, 235, 214, 45, 988i
$[C(O)(OH)C(OH)ClO \rightarrow C(O)(OH)C(O)(OH) + Cl]^{‡}$	3682, 3625, 1846, 1527, 1454, 1373, 1221, 1177, 816, 740, 669, 631, 612, 557, 426, 379, 294, 266, 163, 88, 719i
$[ClC(OH)OC(O)Cl \rightarrow ClC(O)(OH) + CO + Cl]^{‡}$	3752, 1899, 1457, 1286, 1069, 768, 703, 584, 523, 451, 413, 390, 350, 248, 226, 179, 57, 729i
$[C(O)(OH)C(OH)ClO \rightarrow C(O)(OH) + ClC(O)(OH)]^{‡}$	3706, 3641, 1921, 1496, 1360, 1305, 1145, 1044, 710, 683, 646, 513, 475, 429, 390, 353, 311, 232, 167, 68, 754i
$[C(O)(OH)C(O)Cl + OH \rightarrow C(O)OC(O)Cl + H_2O]^{‡}$	3736, 1988, 1812, 1795, 1462, 1231, 981, 826, 765, 646, 573, 492, 426, 400, 272, 235, 220, 135, 73, 30, 2923i

Supplementary Table 3: Energies for species of OH + ClCH(O) and resulting reactions. Energies given in kcal·mole^{-1}. Values corrected with zero point energy.

transition state	MP2 6-31G (d)	MP4 6-311++G (2d,2p)	MP4 6-311++G (2df,2p)	CCSD(T) 6-311++G (2d,2p)	CCSD(T) 6-311++G (2df,2p)
optimized species energies					
ClCH(O)	-573.213900	-573.384424	-573.455279	-573.379272	-573.449548
ClCH(OH)O	-648.740718	-648.997693	-649.090819	-648.998182	-649.090501
CH(O)(OH)	-189.217603	-189.405431	-189.463177	-189.399511	-189.456778
ClC(O)(OH)	-648.266148	-648.505762	-648.600209	-648.497877	-648.591555
OH	-75.514686	-75.605545	-75.624210	-75.606332	-75.624913
Cl	-459.562057	-459.625060	-459.657666	-459.625918	-459.658731
CO	-113.023340	-113.120385	-113.150870	-113.114204	-113.144537
H_2O	-76.177767	-76.287569	-76.307724	-76.286536	-76.306621
H	-0.498233	-0.499818	-0.499818	-0.499818	-0.499818
optimized transition state energies					
$[ClCH(O) + OH \rightarrow ClCH(OH)O]^{\ddagger}$	-648.702305	-648.967311	-649.057375	-648.966999	-649.056050
$[ClCH(OH)O \rightarrow CH(O)(OH) + Cl]^{\ddagger}$	-648.737231	-648.997330	-649.090277	-649.000579	-649.092744
$[ClCH(OH)O \rightarrow ClC(O)(OH) + H]^{\ddagger}$	-648.717143	-648.974753	-649.069504	-648.976221	-649.070253
$[ClCH(O) + OH \rightarrow Cl + CO + H_2O]^{\ddagger}$	-648.715507	-648.984191	-649.074524	-648.985274	-649.074743

Supplementary Table 4: Vibrational frequencies for species of OH + ClCH(O) and resulting reactions. Frequencies in cm^{-1}.

species	vibrational frequencies MP2 / 6-31G(d)
optimized species energies	
ClCH(O)	3154, 1811, 1404, 972, 774, 47
ClCH(OH)O	3724, 3202, 1473, 1328, 1260, 1184, 1041, 668, 574, 476, 357, 297
CH(O)(OH)	3685, 3166, 1843, 1442, 1339, 1157, 1069, 714, 628
ClC(O)(OH)	3743, 1940, 1324, 1175, 708, 682, 490, 476, 424
OH	3740
Cl	n/a
CO	2125
H_2O	3917, 3775, 1735
H	n/a
optimized transition state energies	
$[ClCH(O) + OH \rightarrow ClCH(OH)O]^{\ddagger}$	3679, 3263, 1902, 1276, 1025, 886, 624, 577, 382, 336, 307, 641i
$[ClCH(OH)O \rightarrow CH(O)(OH) + Cl]^{\ddagger}$	3697, 3223, 1502, 1364, 1311, 1188, 1004, 619, 548, 359, 310, 394i
$[ClCH(OH)O \rightarrow ClC(O)(OH) + H]^{\ddagger}$	3697, 1748, 1355, 1148, 852, 808, 745, 654, 513, 432, 388, 1853i
$[ClCH(O) + OH \rightarrow Cl + CO + H_2O]^{\ddagger}$	3719, 2109, 1548, 920, 872, 835, 504, 395, 154, 97, 93, 2533i

Supplementary Table 5: Energies for species of OH + $ClC(O)CH_3$ and resulting reactions. Energies given in kcal·mole^{-1}. Values corrected with zero point energy.

species	MP2 6-31G (d)	MP4 6-311++G (2d,2p)	MP4 6-311++G (2df,2p)	CCSD(T) 6-311++G (2d,2p)	CCSD(T) 6-311++G (2df,2p)
optimized species energies					
$ClC(O)CH_3$	-612.370055	-612.592435	-612.676023	-612.586723	-612.669461
$ClC(OH)OCH_3$	-687.895676	-688.203647	-688.309383	-688.203836	-688.308509
$C(O)(OH)CH_3$	-228.370819	-228.611047	-228.681644	-228.605037	-228.674903
ClC(O)(OH)	-648.270030	-648.506917	-648.601655	-648.499294	-648.593261
$ClC(O)CH_2$	-611.721610	-611.934878	-612.018008	-611.934476	-612.016836
CH_3	-39.642489	-39.713488	-39.724045	-39.714849	-39.725298
OH	-75.514686	-75.605545	-75.624210	-75.606332	-75.624913
Cl	-459.562057	-459.625060	-459.657666	-459.625918	-459.658731
H_2O	-76.177767	-76.287569	-76.307724	-76.286536	-76.306621
optimized transition state energies					
$[ClC(O)CH_3 + OH \rightarrow ClC(OH)OCH_3]^{\ddagger}$	-687.860105	-688.176964	-688.279738	-688.175785	-688.277254
$[ClC(OH)OCH_3 \rightarrow C(O)(OH)CH_3 + Cl]^{\ddagger}$	-687.893119	-688.204057	-688.309641	-688.206672	-688.311210
$[ClC(OH)OCH_3 \rightarrow ClC(O)(OH) + CH_3]^{\ddagger}$	-687.872403	-688.185221	-688.291534	-688.185351	-688.290678
$[ClC(O)CH_3 + OH \rightarrow ClC(O)CH_2 + H_2O]^{\ddagger}$	-687.865573	-688.187447	-688.290881	-688.184835	-688.287326

Supplementary Table 6: Vibrational frequencies for species of OH + $ClC(O)CH_3$ and resulting reactions. Frequencies in cm^{-1}.

species	vibrational frequencies MP2 / 6-31G(d)
optimized species energies	
$ClC(O)CH_3$	3246, 3220, 3127, 1867, 1529, 1527, 1450, 1162, 1085, 1001, 626, 527, 454, 356, 144
$ClC(OH)OCH_3$	3725, 3258, 3233, 3136, 1545, 1542, 1475, 1422, 1301, 1156, 1098, 1015, 872, 625, 529, 475, 428, 399, 296, 271, 262
$C(O)(OH)CH_3$	3695, 3257, 3218, 3132, 1862, 1539, 1537, 1469, 1388, 1240, 1104, 1035, 888, 696, 586, 558, 428, 92
$ClC(O)(OH)$	3683, 1879, 1369, 1173, 733, 715, 582, 503, 421
$ClC(O)CH_2$	3400, 3261, 2310, 1496, 1167, 1034, 716, 626, 574, 456, 375, 199
CH_3	3409, 3409, 3220, 1481, 1481, 406
OH	3740
Cl	n/a
H_2O	3917, 3775, 1735
optimized transition state energies	
$[ClC(O)CH_3 + OH \rightarrow ClC(OH)OCH_3]^{‡}$	3690, 3281, 3223, 3133, 1999, 1535, 1524, 1455, 1127, 1068, 1010, 861, 594, 528, 467, 334, 318, 310, 243, 167, 615i
$[ClC(OH)OCH_3 \rightarrow C(O)(OH)CH_3 + Cl]^{‡}$	3701, 3268, 3231, 3134, 1545, 1538, 1495, 1440, 1376, 1191, 1070, 1047, 847, 585, 537, 432, 409, 332, 261, 238, 625i
$[ClC(OH)OCH_3 \rightarrow ClC(O)(OH) + CH_3]^{‡}$	3704, 3360, 3344, 3177, 1618, 1502, 1486, 1341, 1209, 1055, 854, 832, 672, 584, 462, 431, 405, 278, 270, 236, 799i
$[ClC(O)CH_3 + OH \rightarrow ClC(O)CH_2 + H_2O]^{‡}$	3720, 3287, 3186, 2310, 1511, 1490, 1251, 1157, 1067, 1022, 840, 716, 605, 522, 445, 354, 323, 198, 99, 43, 2367i

Supplementary Table 7: Energies for species of OH + BrCH(O) and resulting reactions. Energies given in kcal·mole^{-1}. Values corrected with zero point energy.

transition state	MP2 6-31G (d)	MP4 6-311++G (2d,2p)	MP4 6-311++G (2df,2p)	CCSD(T) 6-311++G (2d,2p)	CCSD(T) 6-311++G (2df,2p)
optimized species energies					
BrCH(O)	-2683.619443	-2686.210722	-2686.280530	-2686.205086	-2686.274260
CH(O)(OH)	-189.217603	-189.405431	-189.463177	-189.399511	-189.456778
CH(O)(OH)$^{\cdots}$Br (complex)	-2759.207094	-2761.880090	-2761.971152	-2761.874905	-2761.965521
OH	-75.514686	-75.605545	-75.624210	-75.606332	-75.624913
Br	-2569.981463	-2572.470109	-2572.503321	-2572.470775	-2572.504080
CO	-113.023340	-113.120385	-113.150870	-113.114204	-113.144537
H_2O	-76.177767	-76.287569	-76.307724	-76.286536	-76.306621
optimized transition state energies					
[BrCH(O) + OH → complex]‡	-2759.102413	-2761.786928	-2761.877929	-2761.790398	-2761.880611
[BrCH(O) + OH → Br + CO + H_2O]‡	-2759.122757	-2761.811544	-2761.900651	-2761.812431	-2761.900592

Supplementary Table 8: Vibrational frequencies for species of OH + BrCH(O) and resulting reactions. Frequencies in cm^{-1}.

species	vibrational frequencies MP2 / 6-31G(d)
optimized species energies	
BrCH(O)	3146, 1822, 1348, 925, 652, 358
CH(O)(OH)	3685, 3166, 1843, 1442, 1339, 1157, 1069, 714, 628
CH(O)(OH)···Br (complex)	3680, 3191, 1812, 1440, 1352, 1175, 1080, 722, 637, 112, 79, 72
OH	3740
Br	n/a
CO	2125
H_2O	3917, 3775, 1735
optimized transition state energies	
[BrCH(O) + OH → complex]‡	3662, 3162, 1637, 1351, 1107, 954, 655, 495, 352, 286, 238, 984i
[BrCH(O) + OH → Br + CO + H_2O]‡	3707, 2113, 1450, 1051, 871, 645, 792, 332, 190, 147, 67, 2563i

Supplementary Table 9: Energies for species of OH + $BrC(O)CH_3$ and resulting reactions. Energies given in kcal·mole^{-1}. Values corrected with zero point energy.

species	MP2 6-31G (d)	MP4 6-311++G (2d,2p)	MP4 6-311++G (2df,2p)	CCSD(T) 6-311++G (2d,2p)	CCSD(T) 6-311++G (2df,2p)
optimized species energies					
$BrC(O)CH_3$	-2722.777848	-2725.419481	-2725.502035	-2725.413059	-2725.494703
$C(O)(OH)CH_3$	-228.370818	-228.611047	-228.681644	-228.605037	-228.674903
$BrC(O)CH_2$	-2722.129361	-2724.761846	-2724.843844	-2724.760924	-2724.842083
OH	-75.514686	-75.605545	-75.624210	-75.606332	-75.624913
Br	-2569.981463	-2572.470109	-2572.503321	-2572.470775	-2572.504080
H_2O	-76.177767	-76.287569	-76.307724	-76.286536	-76.306621
optimized transition state energies					
$[BrC(O)CH_3 + OH \rightarrow complex]^{\ddagger}$	-2798.261436	-2800.995448	-2801.099025	-2800.997560	-2801.100101
$[BrC(O)CH_3 + OH \rightarrow BrC(O)CH_2 + H_2O]^{\ddagger}$	-2798.275902	-2801.014526	-2801.116998	-2801.011002	-2801.112455

Supplementary Table 10: Vibrational frequencies for species of OH + $BrC(O)CH_3$ and resulting reactions. Frequencies in cm^{-1}.

species	vibrational frequencies MP2 / 6-31G(d)
optimized species energies	
$BrC(O)CH_3$	3241, 3223, 3125, 1891, 1525, 1524, 1443, 1144, 1075, 985, 574, 500, 338, 309, 162
$C(O)(OH)CH_3$	3696, 3257, 3218, 3132, 1862, 1539, 1537, 1469, 1388, 1240, 1104, 1035, 888, 695, 586, 558, 428, 92
$BrC(O)CH_2$	3400, 3256, 2362, 1489, 1143, 1036, 700, 574, 567, 337, 330, 187
OH	3740
Br	n/a
H_2O	3917, 3775, 1735
optimized transition state energies	
$[BrC(O)CH_3 + OH \rightarrow complex]^{‡}$	3653, 3257, 3225, 3127, 1686, 1529, 1528, 1446, 1154, 1065, 975, 949, 602, 517, 371, 346, 319, 273, 261, 229, 970i
$[BrC(O)CH_3 + OH \rightarrow BrC(O)CH_2 + H_2O]^{‡}$	3702, 3287, 3181, 2259, 1536, 1486, 1236, 1147, 1057, 1009, 862, 706, 558, 489, 357, 320, 296, 282, 124, 51, 2376i

Supplementary Table 11: Energies for species of OH + BrC(O)C(O) Br and resulting reactions. Energies given in kcal·mole^{-1}. Values corrected with zero point energy.

species	MP2 6-31G (d)	MP4 6-311++G (2d,2p)	MP4 6-311++G (2df,2p)	CCSD(T) 6-311++G (2d,2p)	CCSD(T) 6-311++G (2df,2p)
optimized species energies					
BrC(O)C(O)Br	-5366.104036	-5371.253138	-5371.393978	-5371.238301	-5371.377679
C(O)(OH)C(O)Br	-2871.698791	-2874.445980	-2874.574540	-2874.431496	-2874.558784
C(O)(OH)C(O)(OH)	-377.297205	-377.645358	-377.762534	-377.631161	-377.747196
C(O)OC(O)Br	-2871.031874	-2873.767001	-2873.893954	-2873.757005	-2873.882547
OH	-75.514686	-75.605545	-75.624210	-75.606332	-75.624913
Br	-2569.981463	-2572.470109	-2572.503321	-2572.470775	-2572.504080
H_2O	-76.177767	-76.287569	-76.307724	-76.286536	-76.306621
optimized transition state energies					
[BrC(O)C(O)Br + OH → complex]‡	-5441.590081	-5446.831179	-5446.993237	-5446.826377	-5446.986785
[C(O)(OH)C(O)Br + OH → complex]‡	-2947.183607	-2950.024136	-2950.173698	-2950.019986	-2950.168158
[C(O)(OH)C(O)Br + OH → C(O)OC(O)Br + H_2O]‡	-2947.190575	-2950.032718	-2950.180749	-2950.021744	-2950.168469

Supplementary Table 12: Vibrational frequencies for species of OH + BrC(O)C(O) Br and resulting reactions. Frequencies in cm^{-1}.

species	vibrational frequencies MP2 / 6-31G(d)
optimized species energies	
BrC(O)C(O)Br	1833, 1801, 1050, 700, 683, 588, 397, 375, 352, 195, 173, 33
C(O)(OH)C(O)Br	3680, 1850, 1820, 1407, 1208, 955, 779, 663, 660, 545, 400, 370, 334, 195, 42
C(O)(OH)C(O)(OH)	3605, 3600, 1869, 1843, 1501, 1373, 1255, 1236, 839, 794, 722, 705, 666, 574, 459, 421, 280, 130
C(O)OC(O)Br	1961, 1829, 1262, 945, 751, 591, 526, 407, 362, 315, 178, 55
OH	3740
Br	n/a
H_2O	3917, 3775, 1735
optimized transition state energies	
[BrC(O)C(O)Br + OH → complex]‡	3606, 2364, 1711, 1051, 948, 686, 663, 618, 459, 395, 374, 333, 256, 223, 190, 155, 48, 991i
[C(O)(OH)C(O)Br + OH → complex]‡	3684, 3640, 1914, 1695, 1388, 1208, 1011, 910, 769, 673, 616, 584, 451, 392, 351, 341, 263, 223, 182, 45, 992i
[C(O)(OH)C(O)Br + OH → C(O)OC(O)Br + H_2O]‡	3737, 1979, 1912, 1795, 1460, 1185, 940, 809, 753, 631, 538, 427, 406, 353, 242, 225, 212, 122, 73, 19, 2951i