Supporting information

Theoretical Investigation on the Mechanism and Kinetics of Atmospheric Reaction of Methyldichloroacetate with Hydroxyl Radical

M. Gnanaprakasam[a], L. Sandhiya[b] and K. Senthilkumar*[a]

[a]Department of Physics, Bharathiar University, Coimbatore-641 046, India.

[b]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, USA.

*Corresponding author: Fax No: +91-422-2422387, E-Mail: ksenthil@buc.edu.in

Table S1: Harmonic vibrational frequencies of reactant complex, transition states and intermediate complexes for the initial reactions calculated at M06-2X/6-311++G(2df,2p) level of theory.

Species	Vibrational frequencies (cm^{-1})
$CCl_2HC(O)OCH_3$	28, 97, 159, 172, 232, 250, 334, 436, 688, 730, 787, 865, 918, 1099, 1191, 1223, 1257, 1269, 1352, 1492, 1500, 1506, 1863, 3075, 3153, 3196, 3205
RC1	42, 49, 93, 122, 154, 180, 195, 237, 262, 341, 386, 438, 521, 663, 736, 798, 856, 930, 1091, 1193, 1227, 1255, 1300, 1373, 1494, 1500, 1508, 1828, 3087, 3168, 3195, 3206, 3676
RC2	10, 54, 77, 113, 146, 180, 236, 248, 257, 326, 347, 448, 169, 686, 730, 791, 862, 925, 1090, 1190, 1229, 1257, 1277, 1375, 1496. 1507, 1518, 1840, 3080, 3160, 3196, 3206, 3688
RC3	30, 36, 55, 103, 121, 175, 197, 231, 251, 291, 335, 431, 450, 686, 722, 787, 856, 913, 1091, 1191, 1230, 1247, 1333, 1492, 1498, 1511, 1877, 3088, 3174, 3196, 3198, 3747
TS1	1303i, 28, 85, 102, 138, 183, 238, 246, 330, 391, 434, 494, 687, 734, 823, 876, 903, 961, 1094, 1162, 1189, 1228, 1353, 1483, 1494, 1499, 1505, 1840, 3089, 3171, 3192, 3729
TS2	1327i, 19, 51, 132, 143, 171, 248, 251, 330, 349, 384, 440, 684, 727, 769, 806, 861, 906, 925, 1136, 1143, 1246, 1256, 1283, 1344, 1370, 1474, 1502, 1850, 3117, 3203, 3215, 3761
TS3	473i, 54, 61, 91, 124, 159, 167, 187, 201, 238, 325, 422, 496, 672, 752, 821, 911, 976, 1094, 1107, 1185, 1226, 1282, 1345, 1489, 1500, 1504, 1831, 3077,

	3155, 3195, 3226, 3856
TS4	588i, 68, 119, 167, 181, 193, 239, 281, 290, 347, 358, 447, 595, 683, 776, 836, 884, 910, 1100, 1191, 1230, 1241, 1268, 1354, 1468, 1503, 1514, 1551, 3086, 3197, 3199, 3791
TS5	641i, 66, 108, 151, 189, 210, 251, 296, 310, 395, 459, 486, 575, 633, 753, 859, 918, 1044, 1129, 1155, 1184, 1242, 1268, 1364, 1426, 1452, 1494, 1544, 3031, 3101, 3138, 3169.
IC1	13, 67, 79, 109, 133, 166, 183, 197, 261, 263, 334, 341, 428, 470, 484, 737, 793, 980, 1051, 1150, 1190, 1236, 1365, 1493, 1500, 1505, 1652, 1767, 3073, 3152, 3188, 3824, 3975
IC2	14, 52, 101, 125, 139, 185, 193, 234, 260, 285, 332, 341, 365, 445, 478, 694, 718, 781, 850, 909, 1167, 1220, 1254, 1277, 1348, 1480, 1635, 1844, 3192, 3212, 3374, 3843, 3984
IC3	26, 47, 70, 79, 138, 161, 166, 175, 225, 331, 443, 465, 555, 670, 740, 812, 846, 963, 1115, 1188, 1228, 1283, 1350, 1363, 1489, 1495, 1502, 1774, 3081, 3162, 3194, 3281
I1	72, 123, 167, 209, 253, 264, 328, 425, 463, 732, 787, 976, 1043, 1147, 1188, 1231, 1343, 1487, 1501, 1505, 1786, 3080, 3153, 3196
I2	44, 113, 174, 233, 253, 295, 332, 357, 436, 694, 717, 779, 851, 899, 1184, 1217, 1252, 1272, 1326, 1460, 1867, 3198, 3222, 3378
I3	81, 150, 172, 185, 331, 449, 509, 675, 742, 852, 970, 1127, 1189, 1227, 1285, 1370, 1493, 1497, 1505, 1760, 3071, 3146, 3184, 3266
I4	72, 98, 160, 169, 214, 240, 326, 332, 352, 370, 483, 565, 667, 765, 850, 872, 1061, 1091, 1130, 1189, 1190, 1236, 1251, 1304, 1377, 1493, 1507, 1520, 3068, 3144, 3175, 3181, 3879
P1	19, 44, 53, 87, 131, 166, 181, 198, 245, 287, 440, 653, 688, 737, 785, 865, 908, 945, 1040, 1174, 1253, 1267, 1310, 1354, 1405, 1461, 1507, 1851, 2963, 3034, 3122, 3190, 3429
H_2O	1625, 3892, 3997
HOCl	819, 1283, 3867 3766

OH CH_3O	879, 971, 1138, 1390, 1396, 1520, 2971, 3038, 3080

Table S2: Cartesian coordinates of the transition state involved in the studied reactions calculated at M06-2X/6-311++G(2df,2p) level of theory.

Species	**Reaction coordinates**			
MDCA	6	0.739978000	-0.000237000	0.543910000
	17	1.357778000	-1.466111000	-0.233207000
	1	1.073573000	-0.000810000	1.573147000
	17	1.357811000	1.466404000	-0.231649000
	6	-0.782572000	-0.000404000	0.535118000
	8	-1.279587000	0.001053000	-0.688834000
	8	-1.418905000	-0.001895000	1.548715000
	6	-2.706655000	0.000737000	-0.770576000
	1	-3.107140000	-0.887746000	-0.287041000
	1	-3.107720000	0.887395000	-0.284191000
	1	-2.940297000	0.002347000	-1.829122000
TS1	6	0.650459000	-0.015806000	-0.000191000
	17	1.050028000	-0.886590000	1.464783000
	1	1.300487000	0.973369000	0.000323000
	17	1.051225000	-0.887025000	-1.464222000
	6	-0.806746000	0.431527000	-0.000492000
	8	-1.641796000	-0.587519000	-0.000320000
	8	-1.121000000	1.589307000	-0.000874000
	6	-3.032252000	-0.246277000	-0.000015000
	1	-3.271101000	0.334614000	0.887995000
	1	-3.271831000	0.334403000	-0.887976000
	1	-3.564872000	-1.190186000	0.000262000
	1	0.806290000	2.659790000	0.000381000
	8	1.689167000	2.251062000	0.000403000
TS2	6	-1.087256000	0.166688000	0.552139000
	17	-1.315299000	1.676070000	-0.338433000
	1	-1.319110000	0.349651000	1.593539000
	17	-2.156008000	-1.117861000	-0.031666000
	6	0.361222000	-0.284836000	0.458036000

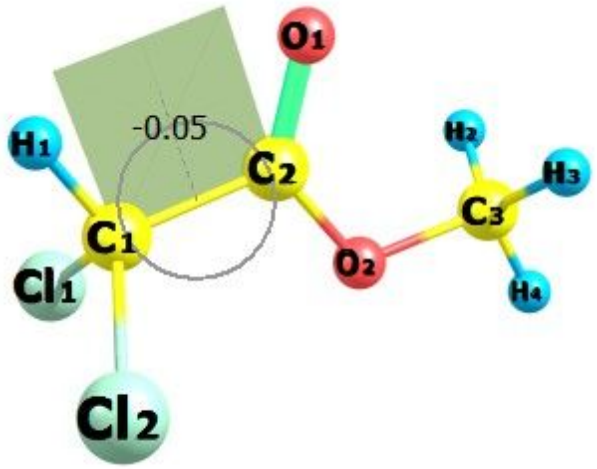
	8	0.740932000	-0.513751000	-0.790679000
	8	1.054435000	-0.409381000	1.427001000
	6	2.066008000	-0.954184000	-0.967244000
	1	2.811847000	-0.108799000	-0.577789000
	1	2.278793000	-1.847952000	-0.385741000
	1	2.234807000	-1.069158000	-2.031616000
	1	3.039375000	0.576251000	1.018578000
	8	3.445466000	0.803688000	0.165820000
TS3	6	-0.030806000	0.743622000	0.712043000
	17	1.686971000	-0.221137000	-0.137612000
	1	0.305089000	0.890485000	1.727700000
	17	-0.222561000	2.187587000	-0.178896000
	6	-1.042526000	-0.340817000	0.554770000
	8	-1.673452000	-0.303901000	-0.610281000
	8	-1.209381000	-1.167144000	1.409559000
	6	-2.602791000	-1.366362000	-0.830746000
	1	-2.094157000	-2.325948000	-0.764548000
	1	-3.395670000	-1.329130000	-0.086473000
	1	-3.001579000	-1.208046000	-1.826298000
	1	2.890464000	-2.097394000	-0.040547000
	8	3.190037000	-1.226239000	-0.329979000
TS4	6	-0.825315000	0.081916000	0.464140000
	17	-1.399685000	1.440348000	-0.494144000
	1	-1.043766000	0.277188000	1.506351000
	17	-1.654161000	-1.425387000	0.020337000
	6	0.673415000	-0.165763000	0.318534000
	8	1.074397000	-0.112524000	-0.936160000
	8	1.272552000	-0.811471000	1.207350000
	6	2.433646000	-0.488925000	-1.168055000
	1	3.092546000	0.122621000	-0.555233000
	1	2.576613000	-1.540573000	-0.930446000
	1	2.610736000	-0.306165000	-2.221912000
	1	1.369992000	1.228714000	2.010829000
	8	1.355400000	1.349057000	1.048487000
TS5	6	-0.899920000	0.049601000	0.522490000
	17	-1.252465000	1.561918000	-0.322944000
	1	-1.336922000	0.129519000	1.513177000
	17	-1.633728000	-1.332985000	-0.278360000

	6	0.610147000	-0.154648000	0.711360000
	8	1.113159000	-0.193001000	-0.948982000
	8	1.090999000	-1.277706000	0.950186000
	6	2.479610000	-0.009706000	-1.148678000
	1	2.912530000	0.689172000	-0.431202000
	1	3.010298000	-0.961646000	-1.149830000
	1	2.554023000	0.423660000	-2.151677000
	1	1.957968000	0.672277000	1.720342000
	8	1.149386000	0.951166000	1.275088000
TS6				
	6	0.415766000	0.281691000	-0.255004000
	17	1.658430000	-0.429658000	-1.139577000
	17	0.568347000	1.929404000	0.146137000
	6	-0.940585000	-0.321304000	-0.408352000
	8	-1.863871000	0.392019000	0.224984000
	8	-1.132267000	-1.354182000	-0.983754000
	6	-3.178299000	-0.169806000	0.202281000
	1	-3.528487000	-0.258313000	-0.823875000
	1	-3.170423000	-1.154120000	0.665532000
	1	-3.800382000	0.516898000	0.765104000
	8	0.726403000	-0.576505000	1.584343000
	8	1.627585000	-1.379287000	1.555449000
TS7				
	6	-0.130277000	0.581447000	0.000220000
	17	-1.193563000	0.783158000	1.368531000
	17	0.199966000	2.133115000	-0.780890000
	6	1.215758000	-0.043309000	0.432116000
	8	1.816266000	-0.583314000	-0.609067000
	8	1.628438000	0.012842000	1.546591000
	6	3.086906000	-1.184959000	-0.332308000
	1	3.775790000	-0.434188000	0.048195000
	1	2.965895000	-1.975100000	0.405061000
	1	3.432255000	-1.586053000	-1.277893000
	8	-0.688691000	-0.286502000	-1.003822000
	8	-1.974608000	-0.154295000	-1.170717000
	1	-2.439743000	-1.198159000	-0.020078000
	8	-1.999773000	-2.110895000	-0.118808000
	8	-0.766302000	-1.940613000	0.137656000
TS8				
	6	-0.396700000	0.791385000	0.328810000
	17	1.918651000	0.745546000	-0.811012000
	17	-0.972177000	2.306514000	-0.141763000
	6	-0.937904000	-0.471372000	-0.365750000

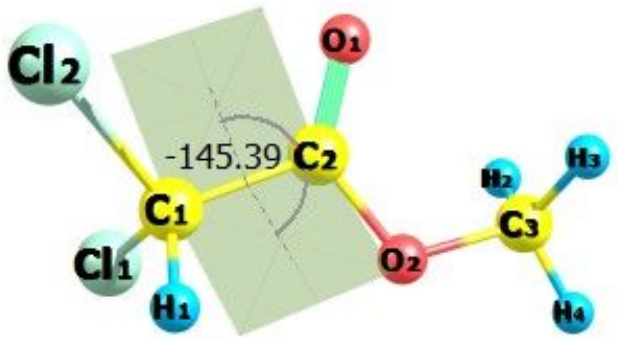
	8	-2.139886000	-0.655521000	0.155333000
	8	-0.411758000	-1.130291000	-1.199448000
	6	-2.820107000	-1.837944000	-0.287077000
	1	-2.968292000	-1.797744000	-1.363610000
	1	-2.229479000	-2.713877000	-0.029390000
	1	-3.768367000	-1.841816000	0.237488000
	8	0.094783000	0.678189000	1.467141000
	8	0.515573000	-0.622060000	1.721304000
	7	2.360714000	-1.006304000	0.414767000
	8	2.101206000	-1.942801000	-0.095152000
TS9				
	6	0.516988000	-0.465029000	-0.115224000
	17	1.691058000	-0.698885000	1.171930000
	17	0.682436000	-1.728847000	-1.342571000
	6	-0.930693000	-0.575535000	0.431492000
	8	-1.754579000	0.031888000	-0.406863000
	8	-1.204891000	-1.180429000	1.415873000
	6	-3.156120000	-0.000900000	-0.104943000
	1	-3.657643000	-0.483070000	-0.939149000
	1	-3.330517000	-0.548056000	0.816054000
	1	-3.491906000	1.027719000	-0.008973000
	8	0.766885000	0.718537000	-0.830263000
	8	0.730307000	2.872719000	-0.785568000
	7	0.464467000	1.919304000	-0.141580000
	8	-0.000428000	1.818349000	0.951330000
TS10				
	6	-0.824737000	-0.325503000	-0.241275000
	17	-1.143425000	-0.756153000	1.606864000
	17	-2.461289000	-0.239833000	-1.005500000
	6	-0.291399000	1.115784000	-0.077484000
	8	1.043785000	1.082935000	0.143912000
	8	-0.918894000	2.123689000	-0.122652000
	6	1.626044000	2.365157000	0.389140000
	1	1.441859000	3.029099000	-0.452164000
	1	1.199099000	2.801358000	1.289807000
	1	2.691427000	2.195720000	0.517047000
	8	-0.068736000	-1.171444000	-0.812595000
	8	1.564739000	-1.585783000	0.466938000
	7	2.402192000	-1.180029000	-0.152496000
TS11				
	8	2.888227000	-0.670252000	-1.042189000
	6	0.581957000	-0.071632000	0.456687000
	17	1.820490000	-1.220966000	-0.009249000
	17	0.904509000	1.655717000	-0.630374000
	6	-0.814696000	-0.461954000	-0.106428000

TS12	8	-1.748118000	0.230937000	0.511010000
	8	-0.967482000	-1.274228000	-0.961903000
	6	-3.083446000	-0.011317000	0.051930000
	1	-3.163526000	0.249666000	-1.001193000
	1	-3.336202000	-1.060662000	0.186158000
	1	-3.720011000	0.622295000	0.658403000
	8	0.689584000	0.551710000	1.528031000
	6	0.208820000	0.731065000	-0.444246000
	17	-0.669938000	0.316434000	1.624920000
	17	0.636310000	2.423107000	-0.372005000
	6	1.395793000	-0.187676000	-0.113200000
	8	1.074225000	-1.445873000	-0.401250000
	8	2.447553000	0.185683000	0.299255000
	6	2.076714000	-2.406350000	-0.060490000
	1	2.999964000	-2.188340000	-0.592563000
	1	2.262350000	-2.379303000	1.011483000
	1	1.679263000	-3.370100000	-0.360002000
	8	-0.687492000	0.394258000	-1.222567000
	8	-2.926892000	-0.045476000	-0.311861000
	7	-2.087447000	-0.794574000	-0.310263000
	8	-1.638112000	-1.825425000	-0.298455000

Figure S1: The orientation of the MDCA rotamer is optimized at M06-2X/6-311++G(2df, 2p) level of theory.



***Cis*-SC1**



***trans*-SC2**

Table S3: The electron density (ρ(r) a.u) and Laplacian of electron density ($\nabla^2\rho(r)$ a.u) of reactant complex (RC) and intermediate complex (IC) calculated through AIM analysis at M06-2X/6-311++G(2df, 2p) level of theory.

Reactive Species	**Bond type with numbering of atoms**	***ρ*(*r*) a.u**	**($\nabla^2\rho$) a.u**
RC1	O1-H5•••O3	0.0220	0.0817
IC1	O1-H5•••O3	0.0202	0.0810
RC2	O1-H5•••O3	0.0202	0.0810
IC2	O1-H5•••O3	0.0194	0.0807
RC3	O2-H5•••O3	0.0170	0.0662
IC3	O2-H5•••O3	0.0238	0.0897

RC4	O1-H5•••O3	0.0146	0.0556

Table S4: The rate constant for the initial reactions calculated using CVT, TST and TST(SCT) methods.

Temp (K)	**I1 (x10^{-13}) cm^3 molecule^{-1} s^{-1}**			**I2 (x10^{-13}) cm^3 molecule^{-1} s^{-1}**		
	CVT	**TST**	**TST(SCT)**	**CVT**	**TST**	**TST(SCT)**
278	5.15	5.14	1.95	0.30	0.27	0.23
288	5.17	5.18	1.99	0.34	0.32	0.26
298	5.19	5.20	2.03	0.37	0.35	0.28
308	5.21	5.22	2.10	0.40	0.38	0.31
318	5.23	5.25	2.14	0.44	0.43	0.33
328	5.27	5.29	2.19	0.48	0.45	0.36
338	5.32	5.32	2.25	0.51	0.50	0.39
348	5.39	5.38	2.27	0.55	0.51	0.42
350	5.39	5.39	2.29	0.56	0.55	0.43