

Supporting Information for:
**Atmospheric Reaction of Cl + Methacrolein: A Theoretical
Study on the Mechanism, and Pressure- and
Temperature-Dependent Rate Constants**

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To be published in **The Journal of Physical Chemistry A**.

(Dated: Mar 31, 2014)

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The Cartesian coordinates and vibrational frequencies of all species in the reaction system at the M06-2X/6-31+G(d,p) level of theory

MACR

COORDINATES

C	1.509556	-0.936198	-0.000012
H	1.333487	-2.009326	0.000008
H	2.543072	-0.603081	-0.000042
C	0.487442	-0.073446	0.000003
C	-0.886339	-0.638713	0.000049
O	-1.889058	0.038856	-0.000027
H	-0.946664	-1.746808	-0.000031
C	0.607950	1.420736	0.000002
H	0.107935	1.841773	-0.877091
H	0.108324	1.841735	0.877337
H	1.654656	1.730580	-0.000214

FREQUENCY

141.4156	187.9580	264.6558
398.1312	427.2610	630.5670
715.6357	847.8383	977.1185
991.6038	1019.5718	1038.0082
1074.2827	1345.9925	1396.8318
1424.8078	1458.0774	1480.5388
1495.6640	1740.0747	1849.3240
2989.3210	3071.0553	3139.0659
3165.0139	3170.8349	3259.3168

IM_{add-t}

COORDINATES

C	0.778107	-0.227573	0.880437
H	0.747398	-1.246251	1.269133
H	1.125748	0.456891	1.656324
C	-0.524991	0.193596	0.310079
C	-1.530847	-0.808321	0.056081
O	-2.636627	-0.552765	-0.411147
H	-1.257749	-1.849836	0.311763
C	-0.761345	1.618350	-0.036930
H	-0.011781	1.961241	-0.760508
H	-1.758207	1.746232	-0.459890
H	-0.659700	2.252680	0.852585
Cl	2.067162	-0.209126	-0.402249

FREQUENCY

57.4625	91.2101	154.3495
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245.1375	285.2335	358.7521
424.9757	629.6261	690.9007
836.7804	911.6407	954.2845
1004.8334	1011.8652	1160.9218
1269.6736	1311.7664	1378.1033
1414.3507	1433.4441	1480.9852
1489.3698	1499.6653	1658.4964
3011.9155	3046.6955	3104.9160
3114.8742	3181.9436	3188.1302

TS_{add-t/c}

COORDINATES

C	0.369735	1.183834	1.220025
H	0.487562	0.703917	2.186762
H	0.853498	2.142024	1.065248
C	-0.319814	0.563452	0.206058
C	-1.101502	-0.671245	0.561604
O	-2.026489	-1.058449	-0.106008
H	-0.785149	-1.187353	1.488003
C	-0.653638	1.225722	-1.093742
H	-0.707022	0.485154	-1.892746
H	-1.641344	1.691856	-1.009283
H	0.086183	1.987079	-1.345009
Cl	1.655853	-0.656804	-0.294623

FREQUENCY

-190.8928	106.5329	150.6053
193.7854	234.0160	261.6772
361.1891	394.5823	603.3878
630.7607	830.1418	956.7090
969.7726	1009.5054	1027.3377
1052.5593	1338.6559	1374.4723
1414.7219	1453.0200	1473.4108
1491.1112	1606.5210	1865.4110
3039.1250	3077.2550	3156.0425
3189.0097	3192.0453	3298.0399

IM_{add-c}

COORDINATES

C	0.314892	1.280051	1.205767
H	0.348109	0.902452	2.221218
H	0.682361	2.278657	1.004454
C	-0.010540	0.378564	0.091514
C	-1.098171	-0.603968	0.521363
O	-2.128564	-0.749010	-0.080475
H	-0.870914	-1.171745	1.445179

C	-0.337621	1.076517	-1.212669
H	-0.539997	0.347915	-1.998691
H	-1.232997	1.688791	-1.072033
H	0.495369	1.714984	-1.513928
Cl	1.466778	-0.738586	-0.181073

FREQUENCY

99.0565	226.4194	255.7345
260.7936	293.3859	314.0965
356.8260	378.0964	490.7368
594.4765	654.8557	833.9625
934.5498	1002.9655	1024.2975
1079.5191	1260.8069	1295.3359
1406.8291	1428.6706	1471.3623
1489.2064	1498.1445	1881.4882
3012.0434	3080.8761	3164.5311
3187.1979	3188.4200	3302.5702

The variational transition state in addition channel ($r_{\text{Cl-X}}=3.8 \text{ \AA}$)

COORDINATES

C	0.454731	1.663866	-0.495924
C	0.959262	0.577332	0.102698
C	1.846267	-0.301411	-0.704340
O	2.368472	-1.302026	-0.269087
C	0.711317	0.170700	1.524237
H	0.686161	1.886669	-1.534787
H	-0.196644	2.357812	0.027508
H	2.009518	0.018100	-1.754117
H	0.023519	0.860543	2.017044
H	0.295842	-0.840420	1.561841
H	1.653704	0.142505	2.079168
Cl	-2.779373	-0.392466	-0.164940

FREQUENCY

-55.1379	21.7216	42.5721
161.6862	190.2413	265.4558
402.6214	424.8058	628.4616
711.7938	843.2569	977.7860
993.0687	1017.6194	1037.9609
1076.9406	1346.5418	1397.5602
1423.4058	1463.0931	1479.6258
1501.6446	1739.9410	1847.5820
2973.4790	3080.3340	3149.9221
3173.0801	3174.2548	3264.9380

TS_{absH-CH3} (based on the M06-2X/6-311+g(2df,2dp) level)

COORDINATES

C	-1.630971	-1.567162	-0.519380
C	-1.112351	-0.502486	0.090119
C	-1.546387	0.844495	-0.359484
O	-1.151186	1.863474	0.137024
C	-0.110909	-0.554101	1.180314
H	-2.356316	-1.447053	-1.314831
H	-1.354946	-2.576892	-0.246250
H	-2.270616	0.852335	-1.194790
H	0.050386	-1.554785	1.569972
H	-0.319277	0.164672	1.970979
Cl	2.410510	0.031321	-0.293817
H	0.885302	-0.203013	0.764211

FREQUENCY

-237.7947	37.9546	52.7714
157.6860	211.8445	270.5605
398.3327	422.5678	628.4541
703.8254	851.2996	947.1440
982.2041	1009.2293	1025.5933
1051.0091	1316.6930	1323.6505
1368.1685	1394.2989	1440.2640
1475.7225	1703.1407	1840.7927
2172.2509	2996.4600	3098.9743
3156.0689	3177.3723	3246.7452

TS_{absH-CH3}(1)

COORDINATES

C	1.525840	1.664399	-0.460460
C	1.092841	0.529305	0.107007
C	1.658649	-0.760430	-0.374828
O	1.345612	-1.833107	0.084834
C	0.062197	0.458988	1.170238
H	2.277577	1.641682	-1.245894
H	1.147984	2.636857	-0.160119
H	2.401327	-0.679758	-1.193776
H	-0.148500	1.419448	1.640544
H	0.253848	-0.330988	1.899094
Cl	-2.459438	-0.088532	-0.291083
H	-0.923848	0.129092	0.678153

FREQUENCY

-236.8387	26.4784	49.7534
156.5451	231.8032	264.9681
387.8830	418.4601	625.0609
681.9872	855.4422	942.0485

972.1300	996.8504	1019.6162
1041.5071	1288.1949	1312.2066
1362.8202	1392.2210	1439.8295
1475.1639	1702.6974	1848.3403
2022.6851	3001.6556	3122.2829
3165.1312	3204.0075	3260.1526

IM_{absH-CH3}

COORDINATES

C	1.370334	1.745482	-0.391172
C	1.040920	0.551772	0.129630
C	1.741120	-0.660312	-0.382020
O	1.528154	-1.773341	0.035561
C	0.000728	0.350649	1.152841
H	2.137355	1.825192	-1.157302
H	0.888223	2.663748	-0.070650
H	2.487426	-0.477546	-1.180732
H	-0.273477	1.245621	1.710174
H	0.157197	-0.527908	1.779799
Cl	-2.443494	-0.148951	-0.293329
H	-1.001175	0.064229	0.565133

FREQUENCY

32.5508	65.4717	156.7522
218.3366	284.3293	317.3157
399.0735	433.1379	625.9857
683.0434	858.0358	919.5726
981.1859	999.0588	1025.2649
1035.8889	1158.0017	1255.0086
1338.8039	1392.1980	1445.0852
1480.8672	1595.7074	1730.3402
1855.7389	2986.4902	3135.2445
3178.3626	3224.0557	3273.2888

TS_{absH-CH3(2)}

COORDINATES

C	1.331753	1.759296	-0.379707
C	1.022593	0.555139	0.138795
C	1.740244	-0.645337	-0.381009
O	1.544854	-1.762571	0.032236
C	-0.008231	0.338065	1.151794
H	2.095709	1.855862	-1.146648
H	0.833749	2.667344	-0.054227
H	2.481909	-0.447522	-1.180162
H	-0.313342	1.214917	1.720772
H	0.098230	-0.576489	1.734797

Cl	-2.412561	-0.160626	-0.294987
H	-1.059704	0.074117	0.503112

FREQUENCY

-692.3876	36.7039	75.9245
158.8133	281.4231	368.2972
401.3563	430.2176	516.8762
626.4005	681.6831	868.4334
927.0017	983.4891	994.4239
1019.4163	1038.0953	1168.2406
1261.9652	1371.0861	1395.6241
1447.3197	1481.9658	1681.2394
1857.7638	3006.4308	3141.4567
3175.4220	3238.2620	3271.3864

Com_{absH-CH3}

COORDINATES

C	3.106912	-0.300438	-0.000584
C	1.725764	-0.254823	-0.000034
C	1.115428	1.105475	0.000312
O	-0.075211	1.332866	0.000077
C	0.885112	-1.367691	0.000598
H	3.696264	0.610038	-0.000922
H	3.640657	-1.243564	-0.000819
H	1.835008	1.946857	0.000975
H	1.297388	-2.369538	0.000748
H	-0.191507	-1.253462	0.000762
Cl	-2.875084	-0.231590	-0.000230
H	-1.798992	0.488634	0.000797

FREQUENCY

34.7644	67.3095	132.5552
153.4800	305.1004	397.5756
416.9525	433.3676	459.4247
515.5428	584.6637	612.2888
817.4619	861.0475	903.3375
974.0702	1033.7417	1036.0538
1329.5111	1379.0726	1447.1171
1498.1578	1546.9922	1842.0492
2808.4799	3031.4841	3184.5816
3193.4147	3288.2758	3303.1125

P_{absH-CH3}(CH₂C(CH₂)CHO)

COORDINATES

C	1.590905	-0.816329	-0.000018
H	1.459499	-1.893246	0.000036

H	2.605119	-0.434001	0.000101
C	0.500147	0.029740	-0.000014
C	-0.851615	-0.613655	-0.000001
O	-1.893235	-0.002858	0.000010
H	-0.844658	-1.723108	-0.000010
C	0.557051	1.422363	-0.000013
H	-0.360282	1.997761	0.000006
H	1.507274	1.942752	0.000053

FREQUENCY

154.4837	292.0723	393.8294
449.0842	524.5635	587.1010
609.5105	814.1255	855.5413
898.9895	973.1440	1032.1240
1036.3411	1324.6513	1372.3234
1438.1302	1488.1828	1542.6501
1859.4782	2997.4065	3176.4750
3191.3289	3278.1225	3304.3142

HCl

COORDINATES

Cl	0.000000	0.000000	0.071136
H	0.000000	0.000000	-1.209319

FREQUENCY

3030.0648

TS_{absH-CH2}(H3)

COORDINATES

C	0.065523	-1.259050	-0.022329
H	1.532361	-0.531855	-0.018733
H	0.286742	-2.320344	-0.026479
C	-1.009551	-0.496980	-0.006242
C	-0.871256	0.996219	-0.010301
O	-1.837518	1.720610	-0.000294
H	0.157297	1.397394	-0.023287
C	-2.421630	-1.033343	0.016885
H	-2.934897	-0.660083	0.907003
H	-2.964856	-0.658599	-0.854621
H	-2.435197	-2.123600	0.016437
Cl	2.734129	0.111243	0.007880

FREQUENCY

-355.6041	26.1775	82.1299
135.9451	173.8006	271.4056
351.5346	362.0289	419.7607
616.1794	670.8060	756.7039

820.6629	903.1036	970.8818
1037.0272	1056.6684	1242.2249
1395.9037	1399.8853	1462.8870
1477.4375	1479.9456	1706.2710
1846.5535	3065.4409	3074.7728
3155.3707	3176.5737	3270.8936

TS_{absH-CH2(H4)}
COORDINATES

C	0.121657	-1.013463	0.026349
H	0.175278	-2.096227	0.028599
H	1.657855	-0.449466	0.015778
C	-0.836818	-0.108593	0.013089
C	-2.250755	-0.626072	-0.007916
O	-3.203182	0.113069	-0.021197
H	-2.368735	-1.725621	-0.010723
C	-0.669129	1.384642	0.015532
H	-1.144969	1.807664	-0.873110
H	-1.178066	1.808340	0.885275
H	0.384112	1.665472	0.034903
Cl	2.935897	0.015659	-0.011380

FREQUENCY

-315.8280	13.9614	63.0417
106.2491	168.5179	255.0426
368.4952	389.4085	419.8478
609.3358	657.6458	741.2406
831.8360	894.6536	975.0635
1039.5096	1064.7968	1237.5404
1406.7788	1415.5007	1474.5886
1480.5836	1540.8741	1705.0488
1848.7651	3025.5241	3079.2167
3150.9967	3190.9689	3254.4720

Com_{absH-CH2}
COORDINATES

C	0.076312	-1.121019	0.000160
H	0.076420	-2.203505	0.000183
H	-1.983987	-0.421437	-0.000111
C	0.978028	-0.158808	0.000080
C	2.420890	-0.572526	-0.000058
O	3.323004	0.229200	-0.000136
H	2.614976	-1.661952	-0.000089
C	0.703395	1.319811	0.000111
H	1.162811	1.779332	0.879378
H	1.162616	1.779341	-0.879253

H	-0.367402	1.526411	0.000233
Cl	-3.195366	0.033145	-0.000059

FREQUENCY

18.6276	58.0896	66.0233
127.7349	166.5569	262.4276
266.3076	378.8695	419.5404
562.7732	620.8586	733.5167
829.7068	865.3983	982.6280
1044.9088	1065.0653	1241.1606
1410.3300	1421.1664	1481.8713
1483.7054	1698.9238	1841.3922
2756.2218	3020.8833	3075.7832
3149.7926	3179.1575	3261.1124

P_{absH-CH₂}(CHC(CH₃)CHO)

COORDINATES

C	-1.511221	-1.028694	0.000002
H	-1.556641	-2.110344	0.000287
C	-0.546848	-0.126189	-0.000208
C	0.865532	-0.615922	0.000007
O	1.817230	0.129633	-0.000002
H	0.997742	-1.715484	0.000217
C	-0.746558	1.364828	-0.000019
H	-0.273077	1.804147	0.882371
H	-0.263343	1.805831	-0.876193
H	-1.807951	1.614640	-0.005359

FREQUENCY

139.1721	178.1381	258.5846
367.1878	415.2781	622.5311
742.0097	830.7947	861.1006
988.3194	1043.5388	1065.0876
1254.7335	1409.2326	1418.3026
1481.7118	1484.8533	1696.1950
1837.5908	3008.0478	3074.6725
3145.3030	3182.9439	3266.9723

TS_{absH-CHO}

COORDINATES

C	-0.460435	-1.563346	-0.573870
C	-1.101564	-0.472090	-0.138396
C	-0.497341	0.846373	-0.456301
O	-0.978578	1.907803	-0.144981
C	-2.382976	-0.459908	0.638375
H	0.457601	-1.483797	-1.152138

H	-0.830258	-2.563910	-0.371076
H	0.465098	0.800600	-1.022713
H	-2.242736	0.061284	1.589964
H	-3.153858	0.088663	0.089435
H	-2.734692	-1.474936	0.831166
Cl	2.501257	-0.046853	0.257433

FREQUENCY

-299.8459	39.7931	103.2125
121.7814	142.8271	262.9832
391.7675	405.5469	630.6598
723.7580	842.9731	962.7585
985.4539	997.9670	1036.5592
1071.7848	1339.7968	1379.2589
1419.1464	1456.2157	1476.1046
1496.8447	1720.4574	1847.3923
2776.4087	3071.3633	3141.7699
3161.4510	3167.9372	3252.9854

Com_{abs}H-CHO

COORDINATES

C	0.742942	-1.644645	-0.000195
H	-0.338023	-1.746928	-0.000175
H	1.338097	-2.553005	-0.000277
C	1.327781	-0.442080	0.000045
C	0.439851	0.751803	0.000092
O	0.746118	1.893871	-0.000223
H	-1.526939	0.345676	0.001107
C	2.808513	-0.174641	0.000148
H	3.091842	0.407981	-0.880990
H	3.091696	0.408491	0.880991
H	3.366038	-1.113248	0.000463
Cl	-2.759186	-0.108386	0.000007

FREQUENCY

28.3856	77.9659	86.6687
162.9671	190.2343	243.2896
406.5128	412.2903	505.5810
593.5621	612.3512	752.4173
814.6064	965.4636	1022.3722
1028.1644	1070.7203	1270.4861
1413.7616	1449.4506	1479.3892
1497.0435	1729.8881	1971.1986
2463.5204	3077.7403	3154.5901
3168.4779	3183.7544	3279.5755

P_{abs}H-CHO(CH₂C(CH₃)CO)**COORDINATES**

C	-0.628010	1.660866	0.000000
H	-1.712426	1.706332	0.000000
H	-0.075576	2.595978	0.000000
C	0.000000	0.481263	0.000000
C	-0.854026	-0.743968	0.000000
O	-0.482404	-1.869182	0.000000
C	1.489615	0.272553	0.000000
H	1.793541	-0.301628	0.880048
H	1.793541	-0.301628	-0.880048
H	2.014681	1.230115	0.000000

FREQUENCY

127.3972	179.8617	243.1325
396.4074	450.3961	592.1149
743.3184	807.2910	958.5364
1003.3372	1027.3535	1067.5758
1269.8938	1409.9159	1440.2226
1477.2402	1495.6828	1733.5122
1967.2648	3073.5930	3150.6099
3163.4283	3172.3117	3268.7728

The variational transition state in aldehyde-H abstraction channel ($r_{\text{H-Cl}}=2.8$ Å):**COORDINATES**

C	-0.525972	-1.550399	-0.003030
H	0.555999	-1.436063	-0.006241
H	-0.915532	-2.563909	-0.001360
C	-1.332744	-0.484370	-0.001159
C	-0.695550	0.856754	-0.002669
O	-1.306965	1.897666	-0.000357
H	0.419135	0.853197	-0.007360
C	-2.831750	-0.518414	0.003521
H	-3.219928	0.003325	0.883012
H	-3.225615	0.005364	-0.872222
H	-3.200347	-1.545687	0.003521
Cl	3.079888	-0.018764	0.001384

FREQUENCY

-43.2481	36.5090	55.6844
147.2683	183.8228	265.4879
408.3163	424.2391	628.3950
707.7721	844.1420	974.0556
993.6187	1007.7126	1036.5095

1073.2038	1335.9744	1384.5739
1418.1522	1456.9967	1478.4263
1495.8629	1742.4933	1851.9463
2881.6645	3078.9981	3146.9417
3169.1634	3175.5590	3261.9241

Com_{add-CHO}

COORDINATES

C	2.877300	0.132040	-0.108964
H	3.408296	-0.813981	-0.181889
H	3.474431	1.038492	-0.129786
C	1.543544	0.168137	0.000275
C	0.846572	-1.138887	0.021530
O	-0.354740	-1.288227	0.108856
H	1.503640	-2.028739	-0.044762
C	0.714803	1.412020	0.103497
H	0.031265	1.489879	-0.747025
H	0.092056	1.385076	1.002403
H	1.349929	2.299374	0.132361
Cl	-2.524412	0.205639	-0.058834

FREQUENCY

32.7142	88.4758	152.2748
174.7050	199.6667	281.7159
413.5439	427.2013	629.2291
713.5668	848.2235	984.7236
999.2994	1016.3137	1042.3816
1072.9802	1348.2774	1393.7365
1426.9216	1460.1997	1482.7655
1496.4146	1738.1837	1822.2518
3005.8539	3077.4435	3147.7806
3170.9573	3173.1857	3266.6634

TS_{add-CHO}

COORDINATES

C	1.922814	-1.177381	0.139850
H	1.647580	-2.024765	0.762398
H	2.869232	-1.236264	-0.388604
C	1.128036	-0.108345	0.031136
C	-0.121768	-0.108482	0.832998
O	-0.662966	0.991232	1.195801
H	-0.315487	-1.013526	1.425782
C	1.409017	1.107011	-0.799428
H	0.613436	1.250440	-1.537427
H	1.431598	2.002543	-0.172829
H	2.363143	1.007189	-1.319479

Cl	-1.725551	-0.364252	-0.562563
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FREQUENCY

-390.9027	90.2984	160.8774
172.8438	269.1322	299.8127
401.8717	502.2523	602.9497
729.6679	841.5829	974.6362
985.2167	1007.5620	1045.6530
1077.1015	1325.6476	1336.1051
1420.5839	1437.3939	1473.4862
1485.5819	1504.6509	1743.4494
3077.2046	3105.3030	3149.2664
3172.4739	3174.1034	3264.3009

IM_{add-CHO}

COORDINATES

C	-1.827050	-1.093016	-0.518415
H	-1.535786	-1.714692	-1.359086
H	-2.794999	-1.285996	-0.065965
C	-1.036301	-0.135880	-0.036734
C	0.325022	0.093661	-0.685009
O	0.455618	1.380301	-1.014697
H	0.426945	-0.527505	-1.586128
C	-1.369524	0.763771	1.118020
H	-0.595696	0.698750	1.888863
H	-1.424639	1.806679	0.789502
H	-2.329007	0.482407	1.555494
Cl	1.650315	-0.486663	0.448689

FREQUENCY

63.6035	168.1488	189.3751
246.4432	348.5436	426.4950
462.7789	487.9848	655.7131
766.7672	821.5497	963.0488
982.7523	1014.1607	1070.7292
1094.0050	1124.6985	1211.8630
1287.5213	1415.4394	1458.0969
1482.5355	1500.1065	1748.1594
3068.4254	3070.3525	3141.9271
3166.0320	3180.7018	3271.2366

TS_{abs-CHO}

COORDINATES

C	-1.906032	-1.148218	-0.587843
H	-1.453008	-1.748208	-1.372501
H	-2.915200	-1.420988	-0.275254

C	-1.290959	-0.144064	-0.011104
C	0.658513	0.225159	-0.793318
O	0.677747	1.423547	-0.910689
H	0.466204	-0.500852	-1.592843
C	-1.510065	0.879083	1.022486
H	-0.760524	0.788317	1.814127
H	-1.429238	1.879136	0.588710
H	-2.507553	0.750815	1.458978
Cl	1.615800	-0.588727	0.522528

FREQUENCY

-347.6798	48.1128	137.3246
188.0455	202.1720	291.0264
344.1292	385.3135	445.2751
493.4460	684.6890	895.3873
899.7425	929.1864	971.9328
1059.2771	1107.7866	1297.4176
1395.7058	1426.6500	1461.5815
1483.6890	1692.2723	1794.2291
3059.5730	3107.1648	3126.3827
3141.9771	3160.3210	3217.3427

P_{abs-CHO}(CH₂CCH₃)

COORDINATES

C	1.338153	0.104747	-0.000012
H	2.225384	-0.522982	0.001124
H	1.500668	1.186647	-0.000319
C	0.125953	-0.401396	-0.000409
C	-1.267066	0.080764	0.000088
H	-1.806738	-0.275822	-0.882118
H	-1.804357	-0.272566	0.885095
H	-1.297196	1.180034	-0.001792

FREQUENCY

179.0130	319.2072	513.1233
906.9091	915.1424	946.3788
1050.0835	1111.9352	1395.0421
1429.5581	1467.9043	1482.7349
1773.3238	3021.6888	3091.2843
3109.0545	3138.0261	3221.0219

P_{abs-CHO}(HClCO)

COORDINATES

C	0.672836	0.426402	-0.000008
O	1.575054	-0.338412	0.000002
H	0.749224	1.520914	0.000019

Cl	-1.022745	-0.080708	0.000001
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FREQUENCY

470.4136	755.4976	962.9376
1354.1491	1913.3179	3128.5597

TS_{abs-CH3}

COORDINATES

C	-1.818173	1.777752	-0.000070
H	-2.896682	1.949420	-0.000209
H	-1.179375	2.657192	-0.000052
C	-1.333648	0.547645	0.000167
C	-2.110396	-0.706582	-0.000044
O	-1.640743	-1.816977	-0.000004
H	-3.210621	-0.545942	-0.000308
C	0.672598	0.227922	0.000116
H	0.421757	-0.828195	-0.001305
H	0.675036	0.777440	-0.932592
H	0.674798	0.774836	0.934464
Cl	2.716397	-0.078198	-0.000057

FREQUENCY

-829.4398	93.3654	96.5501
138.1907	151.5005	208.5109
280.7821	331.6387	352.1438
573.0878	603.3145	891.2949
983.8878	1003.7845	1058.6281
1117.8425	1146.7237	1188.1735
1376.2992	1401.1734	1414.2512
1434.4540	1713.0318	1842.3613
2964.1369	3118.0784	3123.6807
3238.7589	3292.0637	3295.8283

P_{abs-CH3}(CH₂CCHO)

COORDINATES

C	-1.820084	0.030799	0.000212
H	-2.034340	1.103181	0.000977
H	-2.674869	-0.639899	0.000231
C	-0.578166	-0.410778	-0.000463
C	0.696907	0.316267	-0.000284
O	1.792788	-0.188032	0.000344
H	0.574958	1.423250	-0.000741

FREQUENCY

103.1643	245.9406	481.1136
561.6727	881.4434	970.3867

1004.5402	1128.6281	1380.1649
1431.3200	1730.6989	1837.6036
2935.7146	3109.2184	3227.6623

P_{abs-CH3}(CH₃Cl)

COORDINATES

C	1.128512	0.000034	0.000001
H	1.473550	-0.230709	1.005879
H	1.473908	0.986502	-0.303183
H	1.473832	-0.756031	-0.702558
Cl	-0.658374	0.000002	-0.000009

FREQUENCY

768.0645	1039.7673	1041.3902
1404.9814	1491.4604	1494.4795
3105.0193	3210.9919	3213.3532

Table S1 The absolute energies (a.u.) at each method/basis set combination for all species

Species	M02-2X/6-31+G(d,p)	HL
MACR	-231.1361884	-230.9708837
Cl	-460.100399	-459.7117000
TS _{CVT-add}	-691.2398056	-690.6846843
IM _{add-t}	-691.2806414	-690.7232319
TS _{add-t/c}	-691.2508595	-690.6944256
IM _{add-c}	-691.2602671	-690.7045075
TS _{absH-CH3}	-691.3411433 ^a	-690.6811505
TS _{absH-CH3(1)}	-691.2357031	-690.6800726
IM _{absH-CH3}	-691.2359535	-690.6793942
TS _{absH-CH3(2)}	-691.2357448	-690.6799889
Com _{absH-CH3}	-691.25544	-690.7057617
P _{absH-CH3(CH₂C(CH₂)CHO)}	-230.4833595	-230.3143343
HCl	-460.7619152	-460.3824901
TS _{absH-CH2(H3)}	-691.2154207	-690.6643954
Com _{absH-CH2}	-691.2170218	-690.6664017
P _{absH-CH2(CHC(CH₃)CHO)}	-230.4503521	-230.2800712
TS _{absH-CH2(H4)}	-691.2149091	-690.6636166
TS _{absH-CHO}	-691.2402384	-690.6843026
Com _{absH-CHO}	-691.254037	-690.7037679
P _{absH-CHO(CH₂C(CH₃)CO)}	-230.4840947	-230.3151758
TS _{CVT-abs}	-691.2391053	-690.6831353
Com _{add-CHO}	-691.244988	-690.6881247
TS _{add-CHO}	-691.2269817	-690.6717747
IM _{add-CHO}	-691.2381505	-690.6799412
TS _{abs-cho}	-691.2107141	-690.6561549
P _{abs-CHO(CH₂CCH₃)}	-117.1684434	-117.0645137
P _{abs-CHO(HClCO)}	-574.041286	-573.5936760
TS _{abs-CH3}	-691.1698283	-690.6168570
P _{abs-CH3(CCH₂CHO)}	-191.1464504	-191.0106076
P _{abs-CH3(CH₃Cl)}	-500.0504121	-499.6339546

^a is based on the M06-2X/6-311+G(2df,2pd) level of theory

Tables of rate constant data and branching ratio data used to create Figures 9 and 10

Table S2 The temperature dependence of the rate constants at 760 Torr for the abstraction channel and the addition channel ($10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

	200	250	300	350	400	450	500
$k_{\text{CVT-add}}$	3.54	2.59	2.14	1.98	1.93	1.93	1.96
$k_{\text{CVT-abs}}$	0.14	0.15	0.16	0.16	0.20	0.23	0.25
$k_{\text{ME-add}}$	3.38	2.49	2.09	0.87	0.86	0.85	0.86

Table S3 The branching ratio of the products at different temperatures

T	200	250	300	350	400	450	500
$\text{IM}_{\text{add-t}}$	0.96	0.94	0.82	0.00	0.00	0.00	0.00
$\text{P}_{\text{absH-CHO}}$	0.04	0.06	0.14	0.72	0.72	0.71	0.70
$\text{P}_{\text{absH-CH}_3}$	0.00	0.00	0.03	0.27	0.28	0.29	0.29
$\text{IM}_{\text{add-c}}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table S4 The rate constants for the addition process versus pressures at different temperatures in the N_2 bath gas ($10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

	1	10	20	50	100	200	300	760
200	3.19	3.47	3.50	3.52	3.53	3.53	3.53	3.54
250	1.99	2.40	2.47	2.53	2.56	2.58	2.58	2.59
300	1.38	1.75	1.86	1.96	2.01	2.05	2.06	2.09

The IRC paths for the Cl atom abstracting the H atom of —CHO , the H atom of —CH_3 , and the H atom of —CH_2

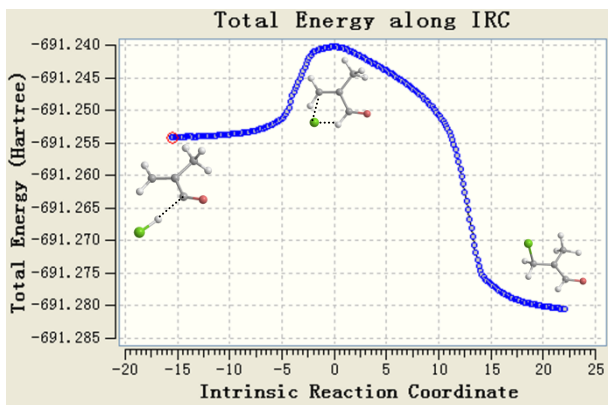


Figure S1a The IRC path for the processes of the Cl atom abstracting the H atom of —CHO

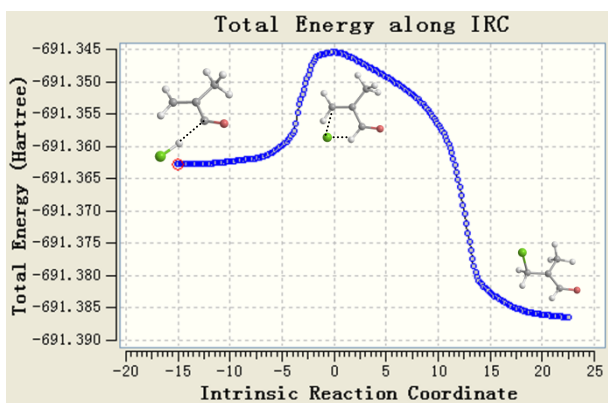


Figure S1b The IRC path for the processes of the Cl atom abstracting the H atom of —CHO (Based on the M06-2X/6-311+G(2df,2pd) level of theory)

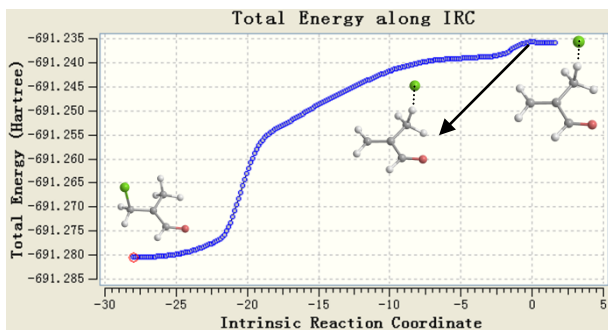


Figure S2a The IRC path for $\text{TS}_{\text{absH-CH}_3}(1)$ in the processes of the Cl atom abstracting the H atom of

—CH₃

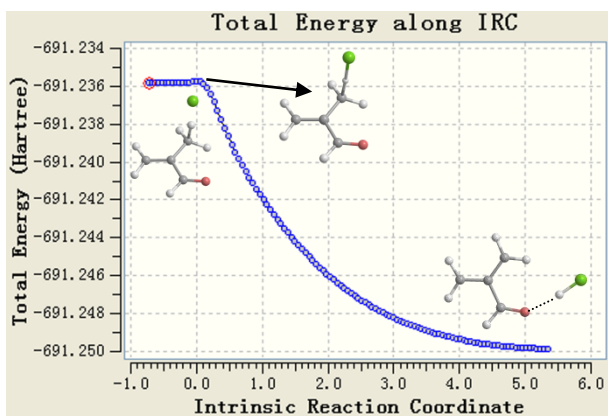


Figure S2b The IRC path for TS_{absH-CH₃}(2) in the processes of the Cl atom abstracting the H atom of —CH₃

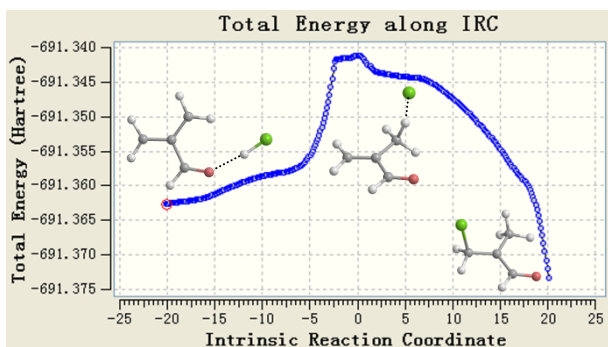


Figure S2c The IRC path for the processes of the Cl atom abstracting the H atom of —CH₃ (Based on the M06-2X/6-311+G(2df,2pd) level of theory)

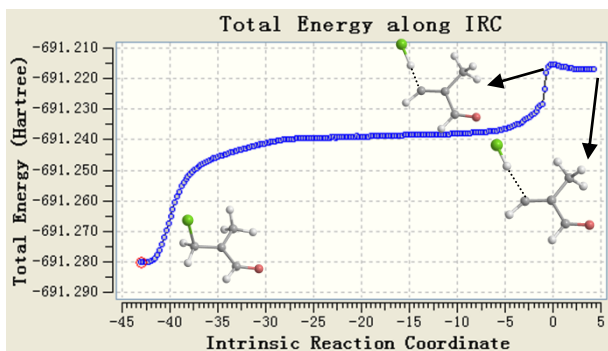


Figure S3a The IRC path for the processes of the Cl atom abstracting the H₃ atom of —CH₂

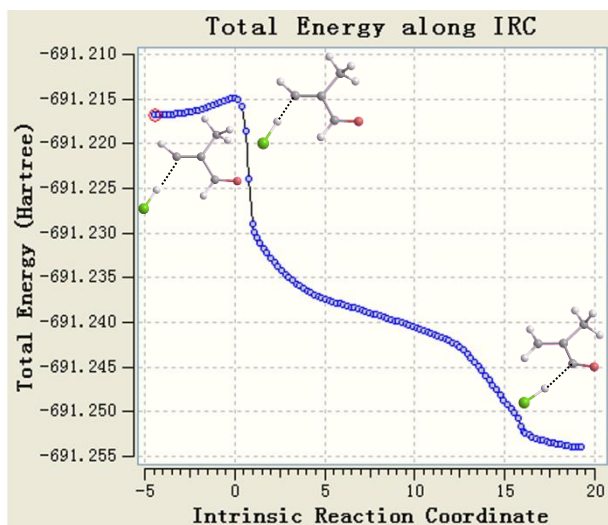


Figure S3b The IRC path for the processes of the Cl atom abstracting the H4 atom of —CH_2

The complete author list of References #29 & 39

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