

**A FIRST STUDY OF THE PYROLYSIS OF A HALOGENATED ESTER:
METHYL CHLOROACETATE**

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Supplementary Description

- 1) *Experimental setup***
- 2) *Temperature profiles in the TR***
- 3) *Carbon, oxygen and chlorine atom balances in the TR***
- 4) *SCF energy, zero-point corrected electronic energy, frequencies and geometry of molecules, radicals and transition states, calculated at the CBS-QB3 level of theory.***
- 5) *Comparison of the kinetic parameters of reaction R30 in Table 1 with literature data.***
- 6) *Experimental mole fractions of species in a tabular form***

1) Experimental setup

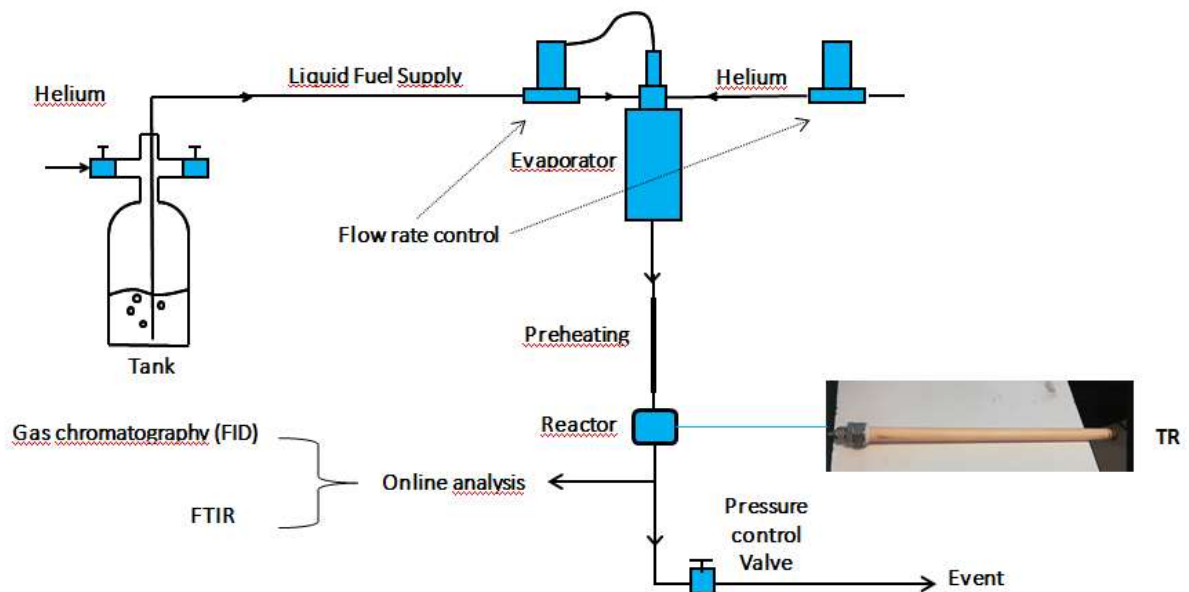


Figure S1: Scheme of the experimental setup used for running pyrolysis experiments.

2) Temperature profiles in the TR

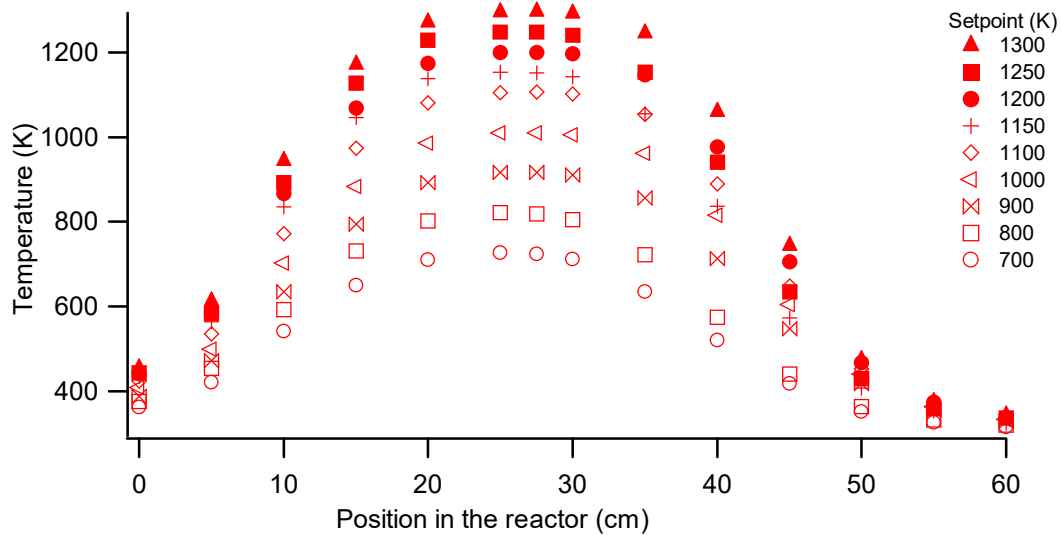


Figure S2 : Measured temperature profile in TR in absence of reaction.

3) Carbon, oxygen and chlorine atom balances in the TR

The deviation was calculated as follow:

$$\text{deviation(in \%)} = \frac{\text{number of atom } i \text{ at the inlet} - \text{number of atom } i \text{ at the outlet}}{\text{number of atom } i \text{ at the inlet}} \times 100$$

Table S1 : Carbon, oxygen and chlorine atom balances in the TR

T(°C)	T(K)	Carbone balance (%)	Oxygen balance (%)	Chlorine balance (%)
300	573	0,0	0,0	0,0
400	673	0,7	0,7	0,7
450	723	7,3	7,3	7,3
600	873	-4,2	-4,6	-3,8
650	923	-1,6	-0,3	-10,3
675	948	3,7	3,0	-7,1
700	973	-0,3	0,5	-9,7
712	985	12,6	15,6	5,1
725	998	9,8	13,2	9,9
750	1023	14,7	17,5	25,6
775	1048	7,3	6,5	27,3

4) SCF energy, zero-point corrected electronic energy, frequencies and geometry of molecules, radicals and transition states, calculated at the CBS-QB3 level of theory.

Species	E(SCF) [Hartrees]	CBSQB3 (OK) [Hartrees]	Frequencies [cm ⁻¹]			Geometry				
						N°	Atom N°	XYZ Coordinates [Angstroms]		
<i>CH₃OCOCH₂Cl</i>	-725.852347	-727.128713	41.4326	114.2958	158.5069	1	6	-1.275594	0.073426	-0.017976
						2	1	-0.639558	-0.121356	0.844454
						3	1	-1.679495	-0.875173	-0.369285
						4	6	-0.445613	0.709176	-1.124673
						5	8	0.550262	-0.143446	-1.438593
						6	8	-0.624176	1.774510	-1.642017
						7	17	-2.637476	1.103582	0.508751
						8	6	1.444135	0.298586	-2.480203
						9	1	2.170926	-0.501631	-2.596314
						10	1	0.894713	0.459199	-3.408600
						11	1	1.935624	1.227708	-2.189134
<i>CH₃OCOCH₂</i>	-266.303314	-267.321655	124.2255	174.7838	284.7932	1	6	0.722245	-0.926031	-0.009521
						2	1	1.795253	-0.867880	-0.126547
						3	6	-0.096510	0.265942	-0.041294
						4	1	0.231200	-1.877380	0.134895
						5	8	0.649632	1.386508	-0.229677
						6	6	-0.090780	2.615691	-0.273641
						7	8	-1.306279	0.281662	0.083090
						8	1	0.649687	3.397610	-0.427631
						9	1	-0.628322	2.775023	0.663121
						10	1	-0.811085	2.602114	-1.093910
<i>HCl</i>	-460.100058	-460.348216	2931.4825			1	17	0.000000	0.000000	0.071259
						2	1	0.000000	0.000000	-1.211399

$CH_3OCOCHCl$	-725.231742	-726.484934	101.9264	129.1181	162.6581	1	6	0.314432	0.074057	-0.004076
			183.1055	312.5299	436.7165	2	1	0.033667	-0.966813	-0.054626
			523.3051	664.3568	720.1359	3	6	-0.694421	1.090218	-0.240999
			824.5856	934.1311	1070.8418	4	8	-0.233679	2.351794	-0.154156
			1173.2861	1208.9293	1267.5389	5	6	-1.211891	3.381035	-0.383872
			1329.9995	1472.8736	1482.6595	6	8	-1.845814	0.791939	-0.494185
			1499.6754	1706.7768	3048.1333	7	1	-0.673724	4.319633	-0.275556
			3118.7685	3160.0524	3241.7706	8	1	-2.018167	3.312302	0.348149
						9	1	-1.632866	3.291601	-1.386596
						10	17	1.944212	0.412833	0.356491
CH_2OCOCH_2Cl	-725.218671	-726.471197	33.4425	95.3704	151.4535	1	6	1.351287	-0.219589	-0.020502
			180.9379	290.7876	310.9951	2	1	1.215096	-0.313075	1.056431
			395.7732	562.1804	667.4933	3	6	0.280518	0.694862	-0.587564
			794.2732	874.7033	931.4086	4	8	0.398581	1.905340	0.044328
			1095.4366	1177.6589	1187.1574	5	6	-0.472422	2.904391	-0.296145
			1213.8239	1319.5547	1437.3521	6	8	-0.531652	0.448520	-1.427305
			1450.9377	1850.0385	3085.4458	7	1	-0.284483	3.835525	0.209221
			3136.0499	3182.9098	3345.9364	8	1	-1.188350	2.721752	-1.080181
						9	17	1.312157	-1.854302	-0.738381
						10	1	2.333579	0.213912	-0.206467
H_2	-1.132955	-1.166083	4419.2598			1	1	-0.730352	0.274390	0.000000
						2	1	-1.474526	0.274390	0.000000
CH_3	-39.576435	-39.744796	505.1758	1403.1570	1403.1712	1	6	-2.055314	-0.629625	0.000001
			3104.1993	3283.2781	3283.3235	2	1	-2.056890	-1.710074	0.000004
						3	1	-2.056891	-0.089411	-0.935704
						4	1	-2.054447	-0.089413	0.935709
CH_4	-40.355896	-40.465297	1341.6165	1341.6165	1341.6165	1	6	0.000000	0.000000	0.000000
			1563.5772	1563.5772	3039.2754	2	1	0.630364	0.630364	0.630364
			3153.2315	3153.2315	3153.2315	3	1	-0.630364	-0.630364	0.630364
						4	1	-0.630364	0.630364	-0.630364
						5	1	0.630364	-0.630364	-0.630364

CH_3Cl	-499.139907	-499.562037	708.2450	1026.1341	1026.4132	1	6	-0.602940	0.697406	0.000000
			1381.4430	1479.8686	1479.9441	2	1	-0.229271	1.189408	0.894333
			3072.7596	3171.7106	3172.0424	3	1	-0.229271	1.189408	-0.894333
						4	1	-1.689624	0.673181	0.000000
						5	17	-0.001808	-1.002827	0.000000
$COCH_2Cl$	-611.275124	-612.095201	174.7089	216.4721	573.7920	1	6	-0.352822	0.884316	-0.007512
			647.4199	789.3375	829.4286	2	8	-0.892512	1.004380	-1.041667
			1180.3678	1258.4000	1415.3662	3	6	0.147175	-0.295700	0.756767
			1972.9222	3090.0306	3144.7702	4	17	-0.106086	-1.927245	-0.037281
						5	1	1.217640	-0.171840	0.919894
						6	1	-0.356608	-0.318242	1.722955
CH_2Cl	-498.507950	-498.905997	155.8240	824.7556	996.2595	1	6	1.759770	0.677247	-0.258610
			1409.1347	3167.9616	3324.1861	2	1	2.322682	1.390308	-0.838369
						3	1	0.764472	0.840168	0.121236
						4	17	2.499756	-0.825262	0.081410
CO	-112.777311	-113.182057		2219.9667		1	6	-0.779342	0.187113	-0.004865
						2	8	-1.271775	0.011330	-1.003174
$TS1^{**}$	-726.324795	-727.614442	-785.3707	51.9075	106.3150	1	6	-1.489829	-0.038214	-0.008542
			110.6546	122.7757	155.9199	2	1	-1.335565	0.420420	0.961125
			222.5019	277.5717	407.1537	3	1	-1.587640	-1.118299	0.028504
			588.9840	678.4753	770.4773	4	6	-0.469110	0.437397	-1.005216
			845.0227	913.3711	1027.5802	5	8	-0.453669	-0.350933	-2.093074
			1102.1380	1173.1823	1196.3540	6	8	0.241829	1.396318	-0.842846
			1212.9808	1286.4955	1453.7595	7	6	0.457998	0.044741	-3.136212
			1474.7273	1483.6248	1497.9867	8	1	0.325921	-0.687455	-3.928922
			1802.0831	3051.4606	3124.1738	9	1	0.213854	1.046725	-3.491606
			3130.0706	3162.7544	3219.7288	10	1	1.484846	0.035409	-2.767977
						11	1	-4.940599	1.037429	-0.865880
						12	17	-3.222025	0.574847	-0.569925

TS2**	-726.319354	-727.616333	-1320.2069	59.2646	106.0586	1	6	-0.166960	-0.278983	0.025663
			149.2749	183.3656	294.1167	2	1	-0.411954	-1.315830	-0.188554
			307.6654	339.5198	394.4756	3	6	0.667217	0.373209	-1.046060
			669.0082	691.5603	815.5799	4	8	1.559004	-0.530108	-1.498866
			901.6592	959.1163	1022.5029	5	8	0.591232	1.512470	-1.415850
			1167.6262	1172.9330	1194.8450	6	17	-1.595015	0.626282	0.501413
			1212.1004	1315.1264	1327.8344	7	6	2.490151	-0.042972	-2.486549
			1347.8594	1471.6984	1482.8690	8	1	3.132434	-0.888569	-2.719769
			1498.6230	1821.7578	3052.5444	9	1	1.956609	0.294071	-3.376100
			3126.1886	3147.5294	3163.3358	10	1	3.072976	0.785486	-2.082004
						11	1	1.179630	-0.457463	1.866230
						12	1	0.579712	-0.357031	1.031859
TS3**	-726.314606	-727.611183	-1315.8873	44.4661	93.1432	1	6	-1.346989	0.721257	-0.002375
			138.7443	182.0936	309.6166	2	1	-0.727324	0.250586	0.759801
			320.1137	398.1265	546.3679	3	1	-1.892765	-0.058676	-0.532640
			567.7184	679.5196	793.2656	4	6	-0.460858	1.466637	-0.986188
			886.3695	937.1358	1054.5870	5	8	0.435331	0.571455	-1.491503
			1109.0626	1164.6728	1190.5183	6	8	-0.509170	2.621750	-1.285521
			1199.0943	1271.2699	1283.4654	7	17	-2.530012	1.786323	0.806741
			1326.9693	1449.9538	1454.5653	8	6	1.331021	1.040426	-2.464043
			1519.3978	1852.0135	3087.7412	9	1	2.162235	0.346293	-2.538408
			3098.1560	3139.3105	3208.7339	10	1	1.588572	2.090399	-2.348618
						11	1	0.267754	0.915609	-4.485363
						12	1	0.728848	0.978798	-3.648535

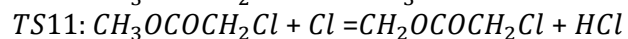
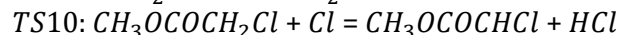
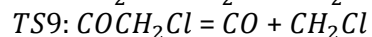
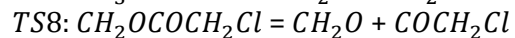
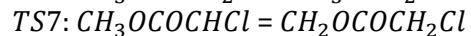
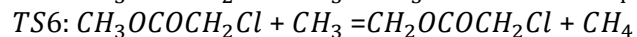
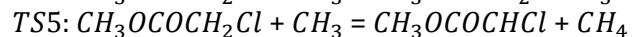
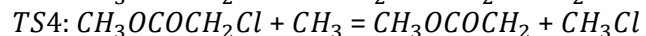
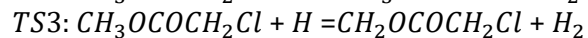
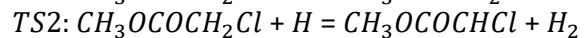
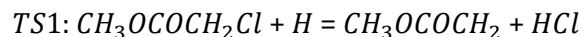
TS4**	-765.385214	-766.851062	-497.9081	37.8819	47.9494	1	6	-0.365700	0.164910	-0.000713
			59.8218	92.1782	113.4940	2	1	-0.098793	0.158296	1.047801
			133.1146	194.3760	281.0710	3	1	-0.778424	-0.756753	-0.391607
			356.3835	411.7001	652.8769	4	6	0.641266	0.836155	-0.860006
			657.8207	661.4368	744.9410	5	8	0.452529	0.532397	-2.162443
			791.3675	876.3097	1018.3677	6	8	1.516159	1.564715	-0.456242
			1034.5514	1064.8456	1078.5948	7	6	1.352846	1.173320	-3.081804
			1172.9892	1210.5327	1270.8506	8	1	1.055431	0.827760	-4.069258
			1427.8759	1428.4319	1449.4914	9	1	1.261957	2.258449	-3.010268
			1474.2125	1482.8322	1499.3384	10	1	2.384810	0.889113	-2.868979
			1778.7649	3046.6339	3097.6616	11	6	-3.865235	2.614562	0.101874
			3116.6896	3148.5296	3156.3651	12	1	-4.390425	2.150751	0.926561
			3250.1660	3257.8780	3258.3902	13	1	-3.439034	3.591185	0.290742
						14	1	-4.277574	2.450408	-0.885168
						15	17	-2.046539	1.384152	0.006692
TS5**	-765.388977	-766.860103	-1504.6707	41.8900	49.4536	1	6	-0.190582	-0.001836	-0.002017
			75.0046	114.3828	126.2223	2	1	-0.785363	-0.903555	-0.117385
			177.3669	194.2284	301.1334	3	6	0.715598	0.268171	-1.164222
			384.1527	441.5660	514.7643	4	8	1.203785	-0.912504	-1.610392
			563.2960	703.0711	722.2301	5	8	1.019078	1.342209	-1.610048
			816.6491	910.9654	987.4951	6	17	-1.201600	1.361363	0.475167
			1032.4815	1124.9792	1170.9241	7	6	2.155337	-0.820305	-2.687620
			1173.6880	1209.4009	1278.1917	8	1	2.438432	-1.845802	-2.913163
			1366.0685	1378.5349	1428.4032	9	1	1.699712	-0.346184	-3.557979
			1429.2716	1471.3686	1482.8747	10	1	3.025685	-0.238791	-2.379756
			1499.8474	1812.6470	3049.8279	11	6	1.409285	-0.568538	2.111154
			3067.4101	3121.8142	3149.7540	12	1	1.983641	0.345842	2.226929
			3158.6009	3213.3139	3214.0364	13	1	0.689368	-0.762322	2.900514
						14	1	1.974316	-1.432742	1.774817
						15	1	0.578550	-0.264290	0.989866

TS6**	-765.381715	-766.852294	-1647.4526	24.0904	47.7518	1	6	-0.659987	-0.078005	0.000692
			60.3112	69.0554	177.8952	2	1	-0.630807	-1.156972	0.146474
			186.4028	304.4491	336.2418	3	1	-1.559744	0.169699	-0.561397
			380.4287	488.1217	552.8363	4	6	0.565197	0.358356	-0.788745
			601.5253	660.1154	709.2085	5	8	0.556287	-0.313174	-1.966239
			791.4701	894.2792	936.8594	6	8	1.397575	1.152368	-0.459234
			1044.9596	1143.0694	1156.5407	7	17	-0.767123	0.704525	1.603821
			1186.7282	1191.3168	1234.2291	8	6	1.623355	-0.057742	-2.860079
			1325.2767	1387.0867	1403.2379	9	1	1.346318	-0.457680	-3.831142
			1441.5463	1445.6776	1450.4527	10	1	1.931180	0.985864	-2.859787
			1468.2608	1839.9222	3058.6215	11	6	3.763743	-1.441946	-1.960133
			3087.7410	3089.7438	3139.7357	12	1	3.406649	-2.464520	-1.864467
			3190.5851	3194.5390	3198.0564	13	1	4.538468	-1.313353	-2.712240
						14	1	3.981219	-0.955009	-1.013304
						15	1	2.679489	-0.736662	-2.450682
TS7**	-725.153366	-726.431030	-1755.0658	66.7827	162.0636	1	6	-0.890982	0.654510	-0.012210
			209.0958	413.6509	500.8508	2	1	-1.366725	-0.203533	0.458785
			572.6063	623.4435	693.2730	3	6	-1.538751	1.068041	-1.327631
			814.4165	884.9661	943.4130	4	8	-2.350475	2.154759	-1.116838
			1004.5092	1094.3089	1166.8028	5	6	-2.262115	2.671084	0.190320
			1175.3448	1242.8600	1390.6610	6	8	-1.409643	0.558194	-2.394305
			1484.8060	1724.9701	1891.4471	7	1	-1.812363	3.660984	0.217886
			3082.2710	3129.2766	3186.3001	8	1	-1.326664	1.735840	0.620972
						9	1	-3.181481	2.546531	0.757787
						10	17	0.849568	0.445246	-0.064977

TS8**	-725.152572	-726.423620	-545.9469	57.2806	135.6529	1	6	-0.061971	1.843812	0.000743
			202.5468	221.1492	304.5695	2	1	-0.776077	1.031305	-0.119995
			403.8114	501.0335	510.0091	3	6	-0.407487	2.917824	-0.938137
			605.1684	863.6161	910.4591	4	8	0.237349	4.403156	-0.023281
			1032.8824	1173.2631	1235.3422	5	6	0.475351	5.376697	-0.748300
			1248.7151	1421.5807	1438.9441	6	8	-0.371478	3.085025	-2.110265
			1575.4873	1890.0407	3013.1061	7	1	0.551784	5.249510	-1.834030
			3113.8272	3126.6900	3201.6426	8	1	0.573429	6.369872	-0.302590
						9	17	1.614771	1.057168	-0.307816
						10	1	-0.037037	2.205295	1.021869
TS9**	-611.259683	-612.074460	-336.3080	65.9764	117.5353	1	6	-0.843213	0.159740	0.011311
			349.2776	545.3971	752.1996	2	8	-1.344131	-0.005599	-0.999551
			937.9691	1046.2653	1413.9038	3	6	-0.142486	-1.578982	1.066662
			2082.4778	3131.9626	3258.7063	4	17	-0.454532	-3.041410	0.188508
						5	1	0.905955	-1.316054	1.120599
						6	1	-0.741660	-1.469407	1.961221
TS10**	-1185.293496	-1186.817684	-967.6139	42.6637	62.7187	1	6	0.097609	-0.036669	0.004684
			109.5297	122.0990	149.7613	2	1	0.902688	-0.227909	0.707791
			194.2565	300.2245	370.2901	3	6	0.591753	0.390124	-1.352118
			443.7855	621.9509	706.7267	4	8	-0.382676	0.503982	-2.248058
			820.8391	887.0549	908.0244	5	8	1.760655	0.618050	-1.537508
			984.3081	1044.5658	1142.4528	6	17	-1.149010	-1.240936	0.081924
			1173.0979	1210.7508	1269.5790	7	6	0.019676	0.948711	-3.563027
			1292.7647	1474.6408	1485.3813	8	1	-0.899501	1.000224	-4.139871
			1495.3738	1782.9981	3057.2955	9	1	0.493183	1.928537	-3.496805
			3133.9593	3169.5893	3173.7996	10	1	0.715889	0.234815	-4.004024
						11	1	-0.429388	1.081102	0.498719
						12	17	-0.923076	2.389898	1.122691

TS11**	-1185.297764	-1186.816397	-702.8621	30.3833	47.6144	1	6	-0.435465	1.000573	0.002828
			57.1110	180.5524	187.1926	2	1	0.115997	0.353435	0.683758
			312.6404	387.9509	410.9552	3	1	-1.047701	0.374010	-0.646845
			534.0788	558.2673	668.0225	4	6	0.538297	1.780577	-0.853204
			796.9612	856.8942	927.5284	5	8	1.417956	0.864128	-1.416753
			933.0008	962.1832	1082.1107	6	8	0.590161	2.951498	-1.050433
			1173.1579	1187.7184	1194.0440	7	17	-1.511598	2.057204	0.953289
			1232.5273	1324.4251	1445.5980	8	6	2.316561	1.328264	-2.341984
			1448.9981	1876.4978	3083.7041	9	1	3.147485	0.641213	-2.457310
			3105.1062	3136.1299	3235.2350	10	1	2.500286	2.398857	-2.321114
						11	1	1.698388	1.189175	-3.638688
						12	17	1.052026	1.022148	-4.933098

* Transition state and associated reactions:



5) Comparison of the kinetic parameters of reaction R30 in Table 1 with literature data.

Figure S1 displays the comparison of the kinetic constant calculated for reaction R30 ($COCH_2Cl = CO + CH_2Cl$) with kinetic constants calculated at different level of theory by Mereau et al. (Mereau et al., 2001). Kinetic parameters are given in Table S1.

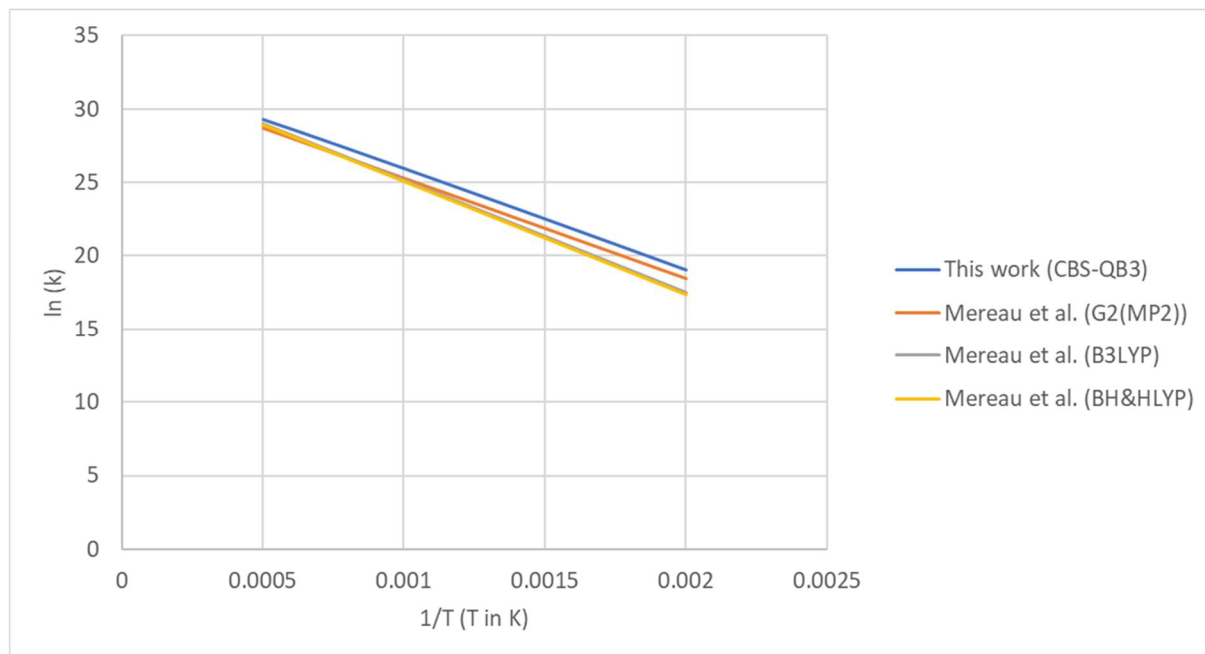


Figure S1: Comparison of the kinetic constant calculated for reaction R30 ($COCH_2Cl = CO + CH_2Cl$) with kinetic constants calculated at different level of theory by Mereau et al. (Mereau et al., 2001).

Table S1: Kinetic parameters of reaction R30.

	this work	Mereau et al., 2001		
A (s^{-1})	2.32E+15	9.20E+13	1.80E+14	1.70E+14
n	-0.33			
Ea (cal/mol)	14186	13599	15201	15296

Mereau, R., Rayez, M.T., Rayez, J.C., Caralp, F., Lesclaux, R., 2001. Theoretical study on the atmospheric fate of carbonyl radicals: kinetics of decomposition reactions. *Phys. Chem. Chem. Phys.* 3, 4712–4717. <https://doi.org/10.1039/b105824j>

6) Experimental mole fractions of species in a tabular form

$x_{inlet} = 0.01$

residence time = 2 s

P = 1.067 bar

T (K)	GC Data										
	Methyl chloroacetate	Chloromethane	Chloroethane	Dichloromethane	Methane	Ethylene	Ethane	Propene	1,3-butadiene	Methyl formate	Acetic acid
573	1.00E-02	0	0	0	0	0	0	0	0	0	0
673	9.93E-03	0	0	0	0	0	0	0	0	0	0
723	9.27E-03	0	0	0	0	0	0	0	0	0	0
873	1.02E-02	8.99E-05	1.11E-05	0	3.33E-05	4.96E-06	0	0	0	0	0
923	8.93E-03	6.21E-04	1.27E-04	3.77E-05	4.12E-04	7.71E-05	3.62E-06	0	0	0	0
948	7.27E-03	9.21E-04	2.01E-04	4.20E-05	5.94E-04	1.29E-04	5.44E-06	3.42E-06	0	0	0
973	5.47E-03	2.05E-03	3.82E-04	4.93E-05	1.31E-03	3.38E-04	1.38E-05	1.00E-05	0	3.09E-05	0
985	2.84E-03	2.67E-03	4.56E-04	3.77E-05	1.92E-03	6.39E-04	1.99E-05	1.30E-05	4.01E-06	7.34E-05	2.46E-05
998	1.35E-03	3.42E-03	4.75E-04	4.93E-05	2.65E-03	9.54E-04	2.65E-05	1.47E-05	8.39E-06	1.19E-04	5.07E-05
1023	1.95E-04	3.14E-03	3.75E-04	3.12E-05	3.09E-03	1.39E-03	2.14E-05	1.30E-05	1.68E-05	1.51E-04	1.31E-04
1048	2.49E-05	2.79E-03	2.36E-04	2.94E-05	3.37E-03	1.79E-03	1.59E-05	1.22E-05	2.75E-05	1.31E-04	1.94E-04

FTIR Data					
T (K)	HCl	Methane	CO	CO ₂	Formaldehyde
573	0	0	0	0	0
673	0	0	0	0	0
723	0	0	0	0	0
873	7.18E-05	0	4.72E-04	0	2.37E-05
923	1.27E-03	5.45E-05	2.09E-03	0	1.05E-04
948	2.24E-03	4.28E-04	4.08E-03	9.57E-06	7.45E-04
973	2.98E-03	1.32E-03	7.56E-03	1.41E-04	1.08E-03
985	3.44E-03	1.68E-03	9.70E-03	3.05E-04	7.23E-04
998	3.67E-03	2.71E-03	1.28E-02	5.52E-04	5.01E-04
1023	3.67E-03	3.50E-03	1.39E-02	8.06E-04	1.12E-04
1048	4.16E-03	4.08E-03	1.58E-02	1.15E-03	4.42E-06