

Supplementary Material for

Mechanistic Study of the Reaction of CH_2F_2 with Cl Atoms in the Absence and Presence of CH_4 or C_2H_6 : Decomposition of CHF_2OH and Fate of the CHF_2O Radical

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Cartesian coordinates (Å) for optimized minima and transition states (TSs).

CHF₂OH

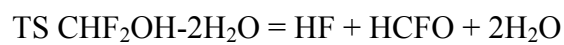
C	0.983347	5.605107	0.079713
H	1.925591	5.150760	-0.233567
F	0.138120	4.650945	0.508832
F	0.384387	6.185211	-0.975607
O	1.236669	6.507551	1.054474
H	0.397952	6.901804	1.322818

TS CHF₂OH = HF + HCFO

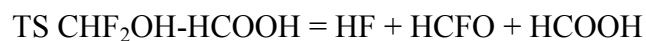
C	-0.267451	0.160954	0.393507
H	-0.269347	-0.023447	1.470117
F	-1.236732	-0.479129	-0.200486
F	1.137190	-0.733270	-0.052136
O	0.207794	1.197234	-0.146510
H	1.107577	0.391446	-0.385479

TS CHF₂OH-H₂O = HF + HCFO + H₂O

C	-0.877040	-0.167203	-0.352817
H	-1.595084	0.157112	-1.106893
F	-1.328467	0.088014	0.876439
F	0.133605	1.206827	-0.466051
O	-0.160377	-1.166099	-0.508935
H	1.049553	-0.855158	0.031345
O	1.841049	-0.147294	0.293829
H	1.950531	-0.132513	1.250766
H	1.165619	0.687353	-0.030957



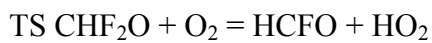
C	-1.272024	-0.341823	-0.008012
H	-2.346927	-0.202648	-0.139915
F	-0.893015	0.136127	1.211004
F	-0.817992	1.006349	-0.868665
O	-0.676229	-1.331572	-0.426437
H	1.637646	0.240234	0.053325
O	1.338158	1.325421	0.027780
H	1.180670	1.594360	0.940363
H	0.351981	1.270630	-0.428924
H	0.739288	-1.297813	-0.111317
O	1.740270	-1.050560	0.065166
H	2.250963	-1.382430	-0.678586



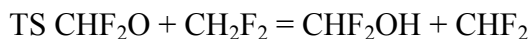
C	-3.356854	6.480425	-0.302825
H	-4.183995	7.087645	-0.679591
F	-3.396069	6.368999	1.001294
F	-2.225866	7.794537	-0.397251
O	-2.858473	5.541107	-0.935430
H	-2.692957	5.768894	-2.167637
H	-1.744969	7.765878	-1.447977
O	-1.306536	7.813116	-2.537130
C	-1.676577	6.994583	-3.405765
H	-1.308410	7.160924	-4.423442
O	-2.430141	5.998183	-3.250511



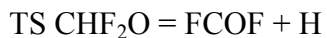
C	0.064782	0.000059	0.291091
H	0.163631	0.000259	1.394777
O	1.328777	0.001542	-0.146980
F	-0.622518	1.075055	-0.109197
F	-0.619987	-1.076494	-0.109190



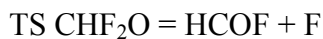
C	0.756568	0.000229	-0.102458
H	-0.297205	-0.000908	0.619591
O	0.177208	0.002508	-1.194811
F	1.433111	-1.076727	0.311847
F	1.433674	1.075198	0.316061
O	-1.751323	-0.001563	0.800983
O	-2.181294	0.000716	-0.313173



C	0.494441	5.773782	0.429699
H	1.038737	5.584822	1.364671
O	1.308058	6.310216	-0.510850
F	-0.534752	6.599255	0.678504
F	-0.030727	4.625244	-0.021888
H	2.532955	6.511653	0.057336
C	3.468204	6.592512	0.795417
H	3.920682	7.584644	0.686010
F	3.003392	6.417690	2.033464
F	4.325847	5.628092	0.499684



C	-1.065830	7.108731	-0.057480
H	-2.344661	7.107066	0.877654
O	-1.712279	7.110838	-1.065677
F	-0.477699	6.043924	0.444781
F	-0.477215	8.171310	0.448914



C	-1.428149	6.875048	0.076122
H	-2.151100	7.062713	0.873890
O	-1.516339	7.273320	-1.065879
F	-0.587935	5.926993	0.408210
F	-0.394161	8.403795	0.355849

Figures illustrating the experimental uncertainties by including error bars

S1: Figure 3 with error bars

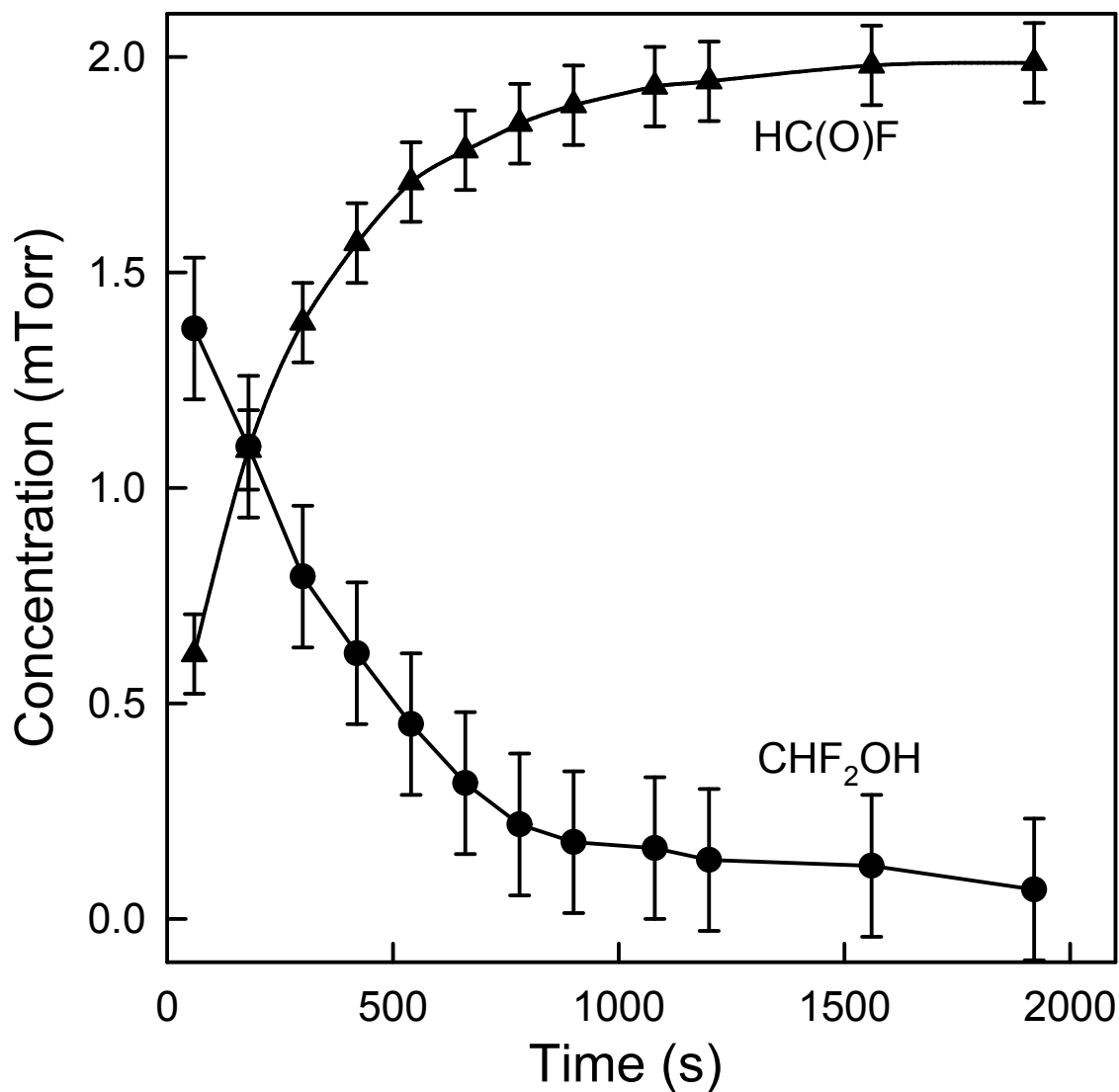


Figure S1: The partial pressures of CHF₂OH (circles) and HC(O)F (triangles) versus time after the UV irradiation of a mixture of CH₂F₂ and Cl₂ with 5 Torr O₂ in a total pressure of 700 Torr made up with N₂ diluent. The lines are drawn through the data to aid visual inspection. All data shown are from Ford. Error bars are representative of the experimental uncertainties.

S2: Figure 4 with error bars

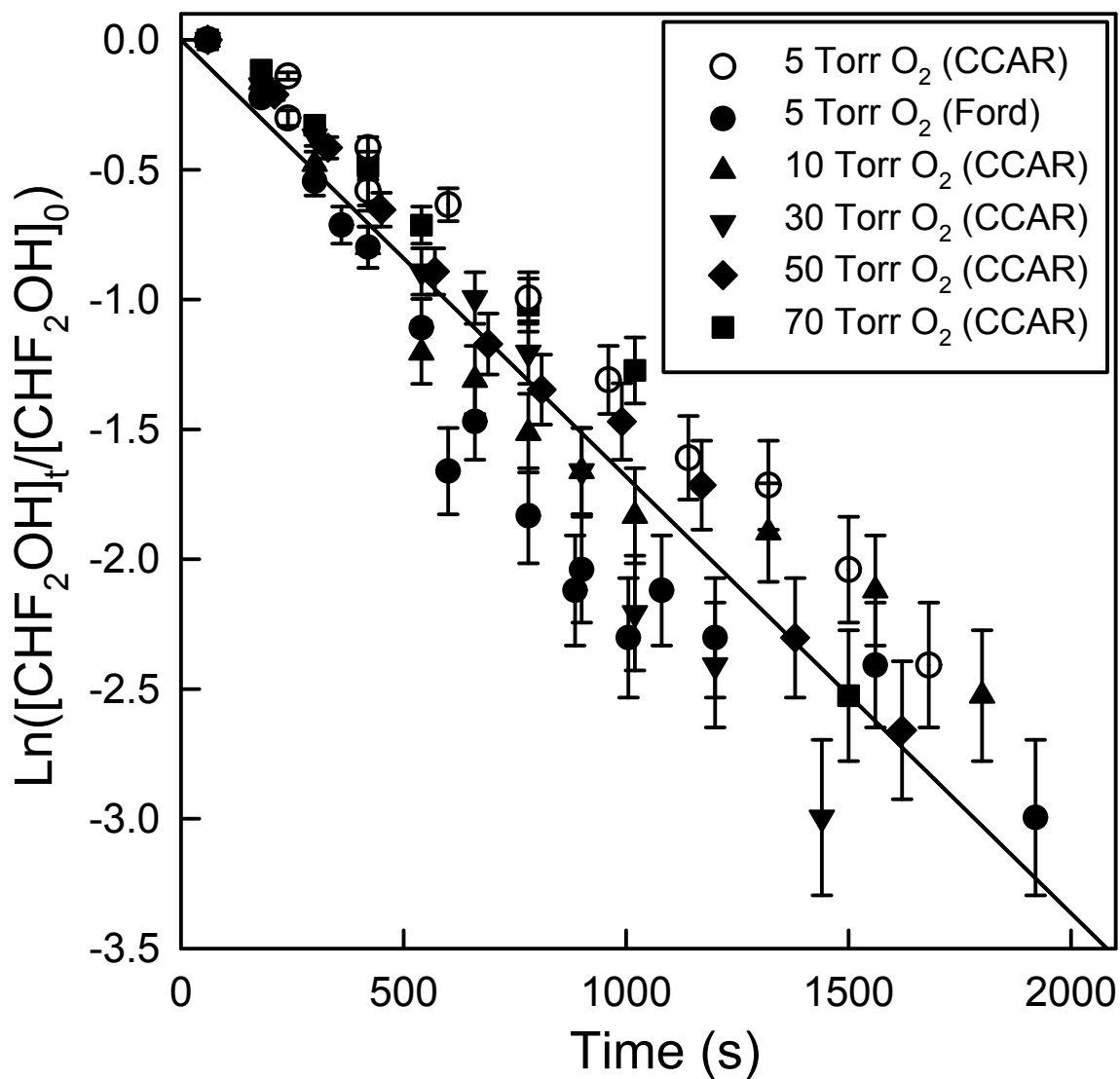


Figure S2: The loss of CHF_2OH versus time for mixtures of CH_2F_2 and Cl_2 in a total pressure of 700 Torr made up with air or N_2 diluent. The shades of the symbols indicate the Ford data (black) and CCAR data (white). The shapes of the symbols indicate the O_2 partial pressure: 5 Torr (circles), 10 Torr (triangles up), 30 Torr (triangles down), 50 Torr (diamonds), and 70 Torr (squares). The line is linear regression fit to the data, see main article text for details. Error bars are representative of the experimental uncertainties for all experiments as shown for the example experiment in Figure S1.