Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Thermal Decomposition of $FC(O)OCH_3$ and $FC(O)OCH_2CH_3$.

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Supporting Information

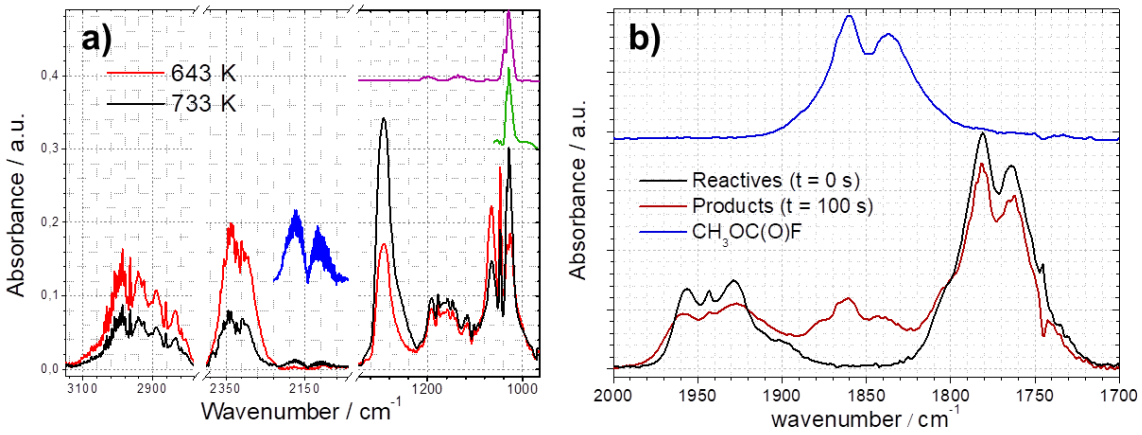

Figura S1. a) Products of the thermal decomposition after 400 seconds of $FC(O)OCH_3$ at two different temperatures: 643 and 733 K. A SiF_4 spectra (purple solid line) is compared with the difference of 643 and 733 K spectra (green solid line). **b)** Reactives (CF_2O + $CH_3OC(O)OCH_3$) and products after 100 seconds of the thermal reaction at ~800K. $FC(O)OCH_3$ spectra from our own database.

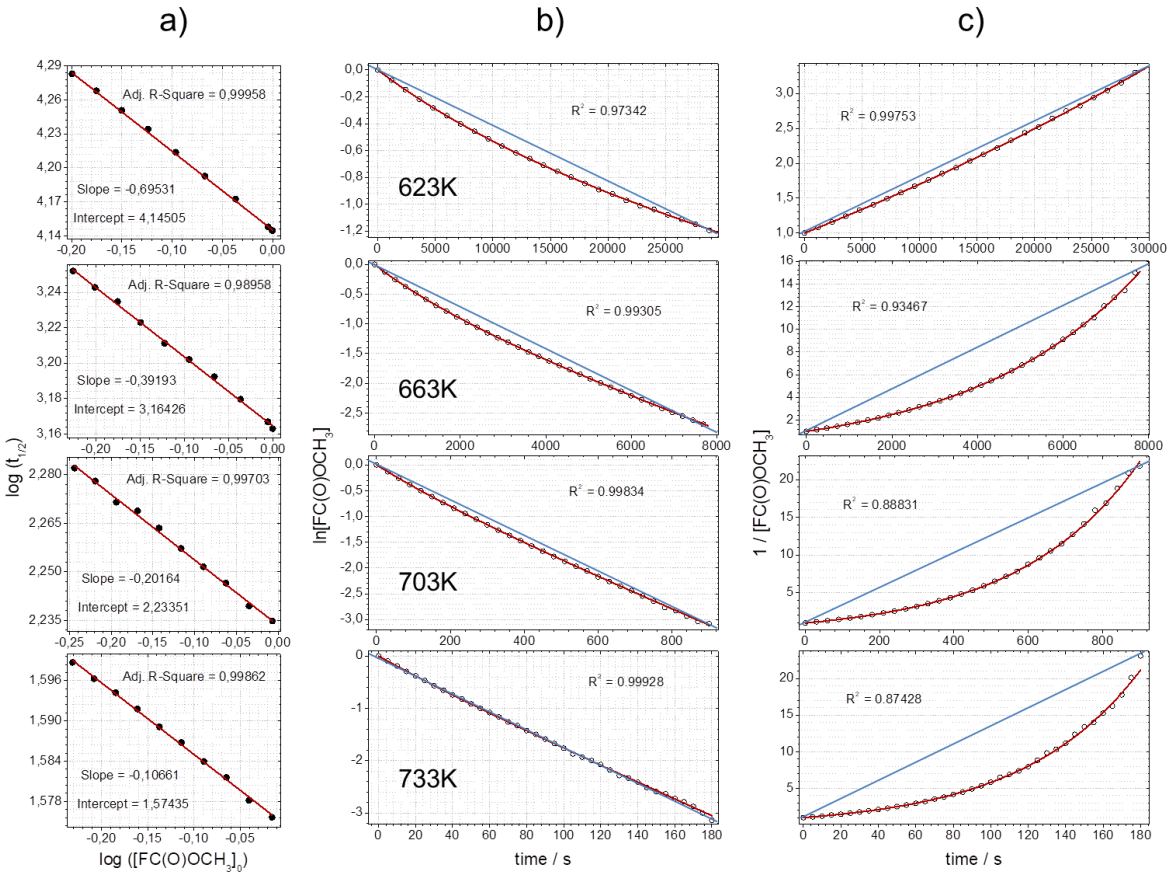

Figura S2. a) Determination of the reaction order (*n*) using Half-life method for different temperatures. The slope is equal to -(n-1). **b)** first-order treatment for the concentration of $FC(O)OCH_3$ as a function of time. R-squared tends to 1 at higher temperatures. **c)** second-order treatment for the concentration of $FC(O)OCH_3$ as a function of time. R-squared tends to 1 at lower temperatures.

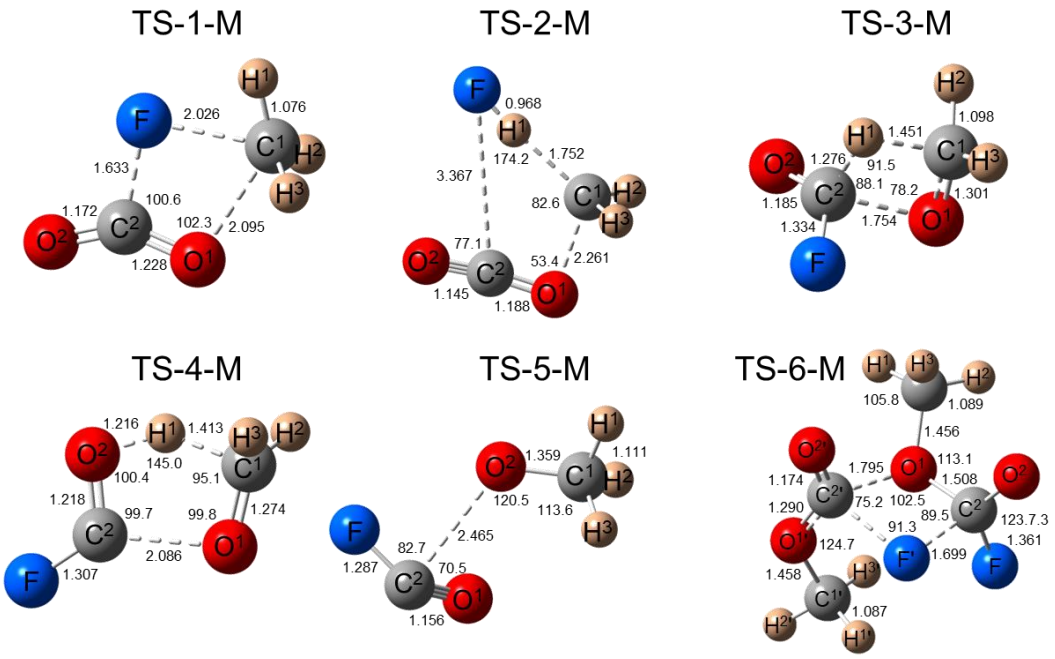

Figura S3. Transition States for the thermal decomposition of $FC(O)OCH_3$. Optimizations are made at B3LYP/6-311++G(3df,2pd) and only one imaginary frequency was obtained for each TS.

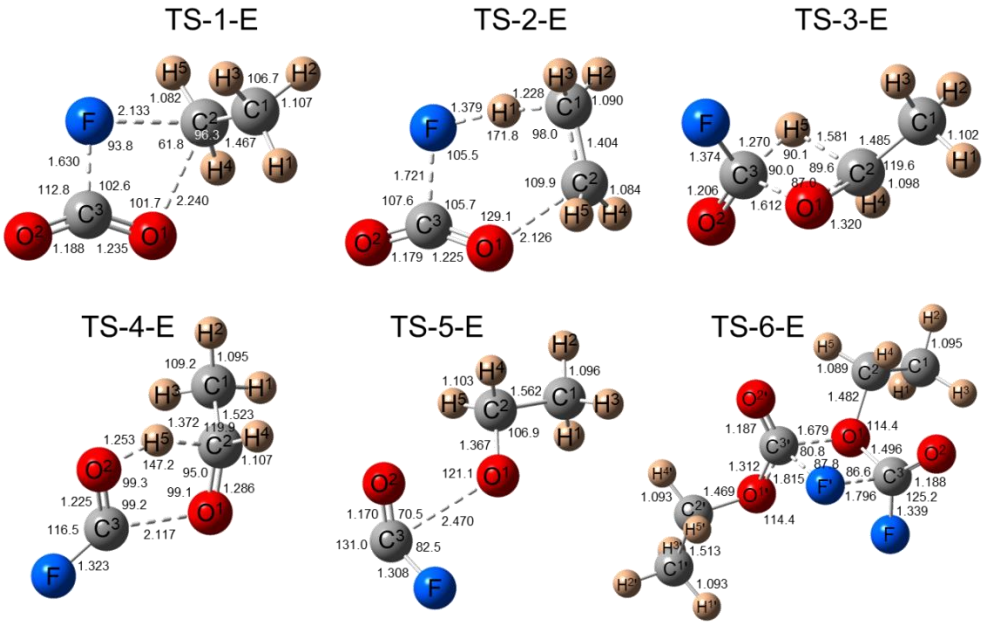

Figura S4. Transition States for the thermal decomposition of $FC(O)OCH_2CH_3$. Optimizations are made at B3LYP/6-311++G(3df,2pd) and only one imaginary frequency was obtained for each TS.

Table S1. Uni- and bi-molecular rate constants obtained from the kinetic fitting of the thermal decomposition of $FC(O)OCH_3$ at different temperatures. (The rate constants obtained from a first-order treatment are presented as well).

Temperature / K	**N_2 pressure / mbar**	**From kinetic fitting**		**First-order treatment k(T) / s^{-1}**
		First-order k(T) / s^{-1}	**Second-order k(T) / cm^3 s^{-1} $molec^{-1}$**	
733 ± 1	0	1.58×10^{-2}	7.71×10^{-21}	1.63×10^{-2}
728 ± 1	372			1.14×10^{-2}
723 ± 1	0	9.56×10^{-3}	5.72×10^{-21}	9.86×10^{-3}
718 ± 1	980			8.48×10^{-3}
713 ± 1	0	5.80×10^{-3}	4.04×10^{-21}	5.98×10^{-3}
708 ± 1	372			5.01×10^{-3}
703 ± 1	0	3.05×10^{-3}	2.88×10^{-21}	3.70×10^{-3}
698 ± 1	980			2.94×10^{-3}
693 ± 1	0	1.63×10^{-3}	1.97×10^{-21}	2.31×10^{-3}
688 ± 1	372			1.55×10^{-3}
683 ± 1	0	9.02×10^{-4}	1.46×10^{-21}	1.30×10^{-3}
678 ± 1	980			1.01×10^{-3}
673 ± 1	0	5.04×10^{-4}	9.63×10^{-22}	0.78×10^{-3}
668 ± 1	980			0.64×10^{-3}
663 ± 1	0	2.56×10^{-4}	6.33×10^{-22}	0.47×10^{-3}
643 ± 1	0	6.23×10^{-5}	2.67×10^{-22}	0.17×10^{-3}
623 ± 1	0	1.26×10^{-5}	1.08×10^{-22}	0.68×10^{-4}
603 ± 1	0	0.22×10^{-5}	4.10×10^{-23}	0.30×10^{-4}
583 ± 1	0	0.56×10^{-6}	1.53×10^{-23}	0.16×10^{-4}
563 ± 1	0	0.09×10^{-6}	5.63×10^{-23}	0.07×10^{-4}

Table S2. Rate constants for the thermal decomposition of $FC(O)OCH_2CH_3$ at different temperatures.

Temperature / K	k(T) / s^{-1}	Standard Error[a]
623 ± 1	8.90×10^{-1}	9.0×10^{-3}
603 ± 1	1.37×10^{-1}	2.8×10^{-3}
583 ± 1	1.13×10^{-1}	6.4×10^{-4}
573 ± 1	4.92×10^{-2}	2.9×10^{-4}
563 ± 1	2.12×10^{-2}	1.7×10^{-4}
553 ± 1	5.38×10^{-3}	6.2×10^{-5}
513 ± 1	1.32×10^{-3}	2.6×10^{-5}
503 ± 1	7.40×10^{-4}	1.8×10^{-5}
488 ± 1	1.16×10^{-4}	3.0×10^{-6}
473 ± 1	7.45×10^{-5}	1.3×10^{-6}
453 ± 1	8.14×10^{-6}	1.1×10^{-7}
433 ± 1	5.72×10^{-7}	1.6×10^{-8}
[a]Standard deviation from the linear regression.		