Supporting Information

The Gas-Phase Reaction Between CF_2O and $CF_3C(O)OH$: Characterization of $CF_3C(O)OC(O)F$.

*Matias Berasategui, Gustavo A. Argüello and Maxi A. Burgos Paci**

Instituto de Investigaciones en Físico Química de Córdoba (INFIQC) CONICET-UNC, Departamento de Físico Química, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, X5000HUA Córdoba, Córdoba,

*Corresponding Author: mburgos@fcq.unc.edu.ar

Figure S1. Experimental set-up of the reaction cell. It was connected to a vacuum line where the gases were manipulated, and it was placed in the optical path of a Bruker IFS66V FTIR equipment to record the infrared spectra.

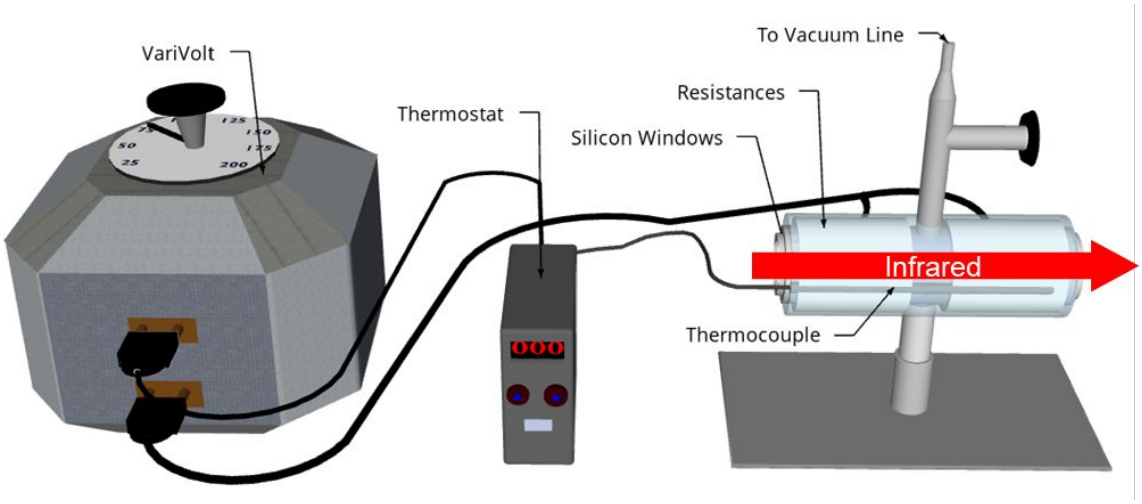

Figure S2. Test for first-order reaction for the CF_2O + $CF_3C(O)OH$ series at constant $[CF_2O]_0$ concentration and τ_{res} at four different temperatures (513, 533, 553 and 573 K). The red straight lines are least-squares fits; correlation coefficients are indicated in the plots.

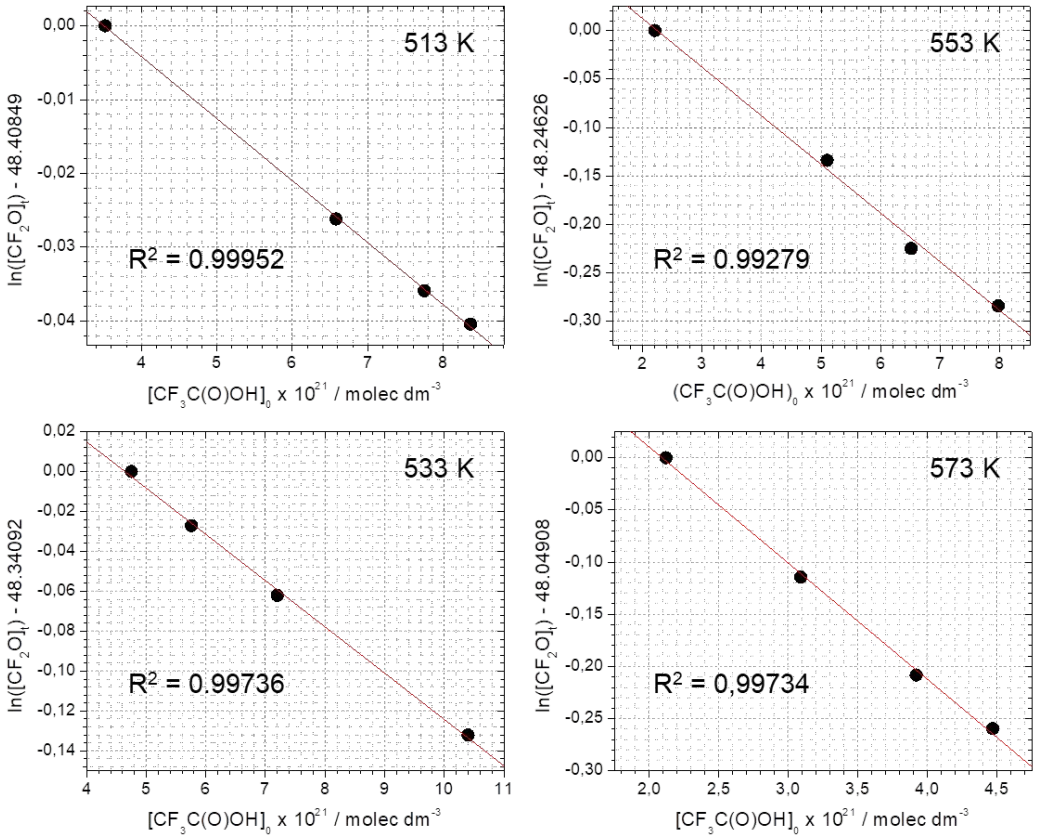

Figure S3. Energy of the hydrogen bond as a function of X – H distance. At the minimum energy, the distance of H - F is 2,26 Å, and the dimer stabilizes at approximately 9.7 kJ mol^{-1}. As alculations were performed at B3LYP/6-31++G(d,p), the energies are not identical to the G4MP2.

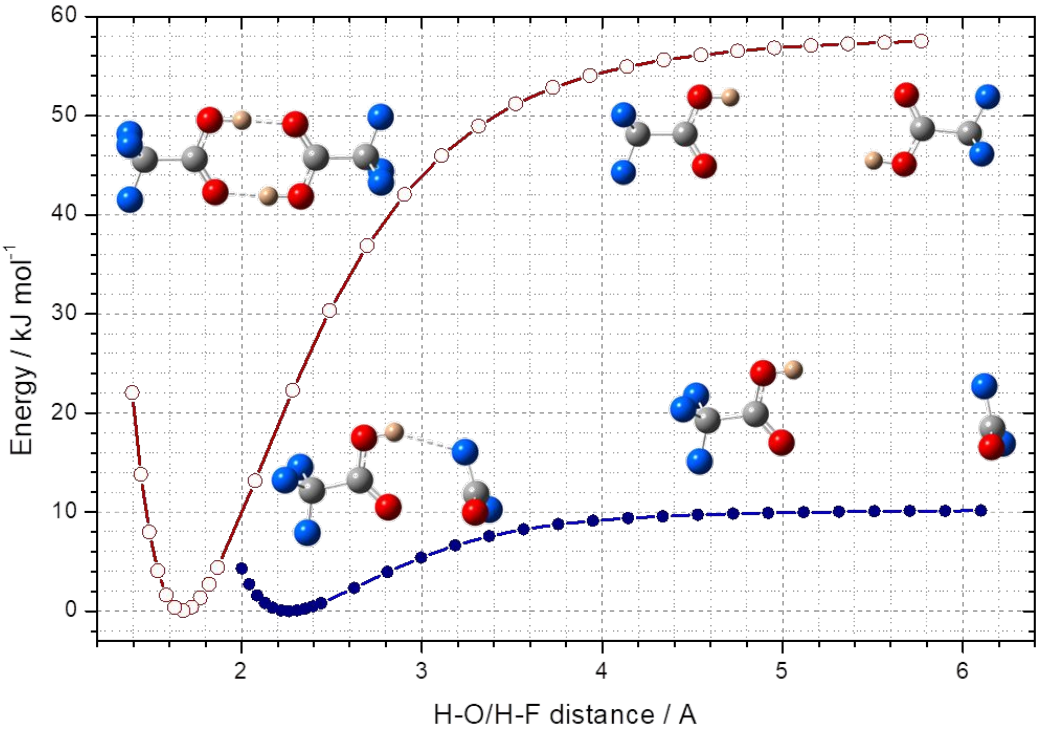

Figure S4. a) Syn conformer, **b)** Anti conformer. The Syn conformer is 3.81 kJ mol^{-1} more stable than anti. The population (from a Boltzmann distribution) at 543 K is 56.3 % syn and 43.7 % anti.

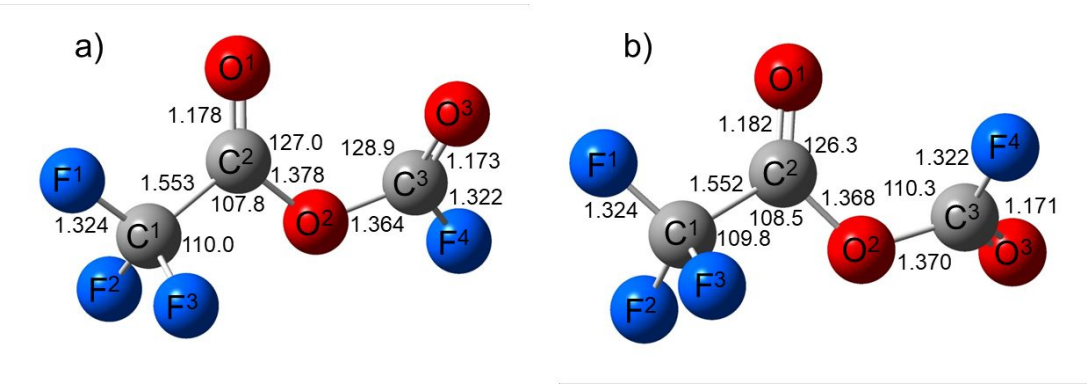

Figure S5. Reaction progression at 543 K and different initial concentrations of HF: a) Under the experimental conditions of section 3.2 ($[CF_2O]_i \approx 1{,}5 \times 10^{17}$ and $[CF_3C(O)OH]i \approx 1{,}5 \times 10^{18}$ molec cm^{-3}). b) Under the conditions of the experiment in section 3.4 ($[CF_2O]_i \approx 2{,}0 \times 10^{19}$ and $[CF_3C(O)OH]_i \approx 2{,}0 \times 10^{18}$ molec cm^{-3}).

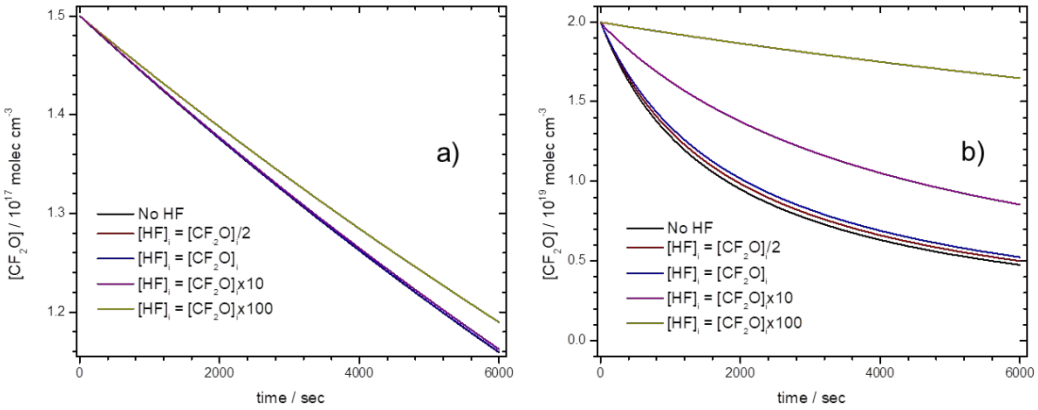

Table S1. Experimental and Calculated Vibrational Wavenumbers for the two more stable conformers (syn and anti) of the $CF_3C(O)OC(O)F$ at B3LYP/6-311++G(3df,2pd) level of theory.

IR Gas[a]	Calculated[b]		assignment/approximate description of mode
	syn	anti	
1953(15)	1960(16)	1952(17)	ν_1 / ν(C=O) sym. stretch
1883(7)	1882(5)	1894(11)	ν_2 / ν(C=O) asym. stretch
	1307(1)	1311(3)	ν_3 / ν(CF_3) umbrella
1229(15)	1228(13)	1228(15)	ν_4 / ν(CF_3) asym. bend
1199(9)	1191(15)		ν_5 / ν(F-C-O) asym. stretch
1171(11)	1168(14)	1171(14)	ν_6 / ν(CF_3) asym. bend
		1164(3)	$\nu_{6'}$ / ν(F-C=O) sym. stretch
1094(41)	1087(28)	1091(31)	ν_7 / ν(C-O-C) asym. stretch
945(<1)	940(2)	937(1)	ν_8 / ν(F-C-O) sym. stretch
	881(1)	883(1)	ν_9 / ν(C-O-C) sym. stretch
	773(1)	768(1)	ν_{10} / ν(C-O-C) twist
	764(<1)	765(1)	ν_{11} / ν(CF_3) sym. stretch
	733(1)	705(1)	ν_{12}
	644(1)	642(1)	ν_{13} / ν(F-C=O) sym. bend
	572(<1)	563(1)	ν_{14} / ν(CF_3) bend
	516(<1)	530(<1)	ν_{15} / ν(CF_3) asym. bend
	481(<1)	507(<1)	ν_{16}
	396(<1)	407(<1)	ν_{17}
	326(<1)	331(<1)	ν_{18}
	252(<1)	251(<1)	ν_{19}
	239(<1)	228(<1)	ν_{20} / ν(C-O-C) sym. bend
	140(<1)	141(<1)	ν_{21}
	84(<1)	64(<1)	ν_{22} / ν(C-O-C) wagg
	44(<1)	55(<1)	ν_{23}
	32(<1)	32(<1)	ν_{24}

[a]Relative absorbance at band maximum in parentheses, [b]Relative IR band intensities in parentheses.