

Kinetics of Cations with C₂ Hydrofluorocarbon Radicals

Justin P. Wiens,¹ Oscar Martinez Jr., Shaun G. Ard, Brendan C. Sweeny, Albert A. Viggiano, and Nicholas S. Shuman*

Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, NM 87117, USA

* Corresponding author

¹Present address: Central New Mexico Community College, 525 Buena Vista SE, Albuquerque, NM 87106, USA

Supporting Information

The fits to the data shown in Figures 2 and 3 to determine the rate coefficients and product branching of O₂⁺ + C₂F₅ and O₂⁺ + C₂F₅I may be reproduced by standard modeling of the kinetics occurring in the afterglow assuming the set of reactions shown in Table 1. Both experiments had a reaction time of 8.1 ms, an ambipolar diffusion rate of 275 s⁻¹, and an initial O₂ concentration of 3.1 × 10¹³ cm⁻³. The VENDAMS data in Figure 2 was taken with an initial C₂F₅I concentration of 8 × 10¹⁰ cm⁻³. The data in Figure 3 was taken with an initial electron concentration of 10⁹ cm⁻³.

Table S1. Reaction scheme used for modeling data shown in Figures 2 and 3.

Reactants		Products ^a	k (×10 ⁻¹⁰ cm ³ s ⁻¹)
Ar ⁺ + O ₂	→	O ₂ ⁺ + Ar	0.46
O ₂ ⁺ + C ₂ F ₅ I	→	C ₂ F ₅ I ⁺ + O ₂	10
	→	C ₂ F ₅ ⁺ + O ₂ + I	3.5
O ₂ + C ₂ F ₅	→	C ₂ F ₅ ⁺ + O ₂	8
	→	CF ₃ ⁺ + CF ₂ + O ₂	2
C ₂ F ₅ I ⁺ + C ₂ F ₅ I	→	C ₃ F ₅ ⁺ + CF ₄ + I ₂ + F	1.5
CF ₃ ⁺ + C ₂ F ₅ I	→	C ₂ F ₄ I ⁺ + CF ₄	6
Ar ⁺ + C ₂ F ₅ I	→	C ₂ F ₄ I ⁺ + F + Ar	6
	→	CF ₃ ⁺ + CF ₂ I + Ar	2
	→	I ⁺ + C ₂ F ₅ + Ar	1
Ar ⁺ + C ₂ F ₅	→	C ₂ F ₄ ⁺ + F + Ar	7
	→	C ₂ F ₅ ⁺ + Ar	2
	→	CF ⁺ + CF ₄ + Ar	1
O ₂ ⁺ + e ⁻	→	O + O	1900
C ₂ F ₅ I + e ⁻	→	C ₂ F ₅ + I	1500
Ar ⁺ + I	→	Ar + I	170
	→	Ar + I ⁺ + e ⁻	20
CF ₃ ⁺ + I	→	CF ₃ + I	100
C ₂ F ₃ ⁺ + I	→	C ₂ F ₃ + I	450
C ₂ F ₅ ⁺ + I	→	C ₂ F ₅ + I	300
C ₂ F ₅ I ⁺ + I	→	C ₂ F ₅ I + I	400

$C_2F_4I^+ + I$	\rightarrow	$C_2F_4I + I$	350
$C_3F_5^+ + I$	\rightarrow	$C_3F_5 + I$	400
$O_2^+ + I$	\rightarrow	$O_2 + I$	200

^a Neutral products are inferred based on thermochemistry, not observed. In some cases, particularly mutual neutralization reactions, multiple sets of neutral co-products in addition to those shown are energetically accessible.

At the thermal energies of these experiments, reactions that are endothermic to any significant extent will not occur. Identifying which reaction channels are endo- or exothermic aids interpretation of the VENDAMS data. Unfortunately, no experimental or calculated thermochemistry exists for many of the fluoro- and iodo-containing radicals and ions relevant to these systems. Because the number of species with undetermined thermochemistry is large and only coarse accuracy is required in most cases to determine whether a channel is energetically accessible or not, we calculate the needed enthalpies of formation using density functional theory. Zero-point corrected 298 K atomization enthalpies were calculated at the B3LYP/6-311++G(d,p) level of theory. 298 K enthalpies of formation ($\Delta H_{f,298K}^0$) were derived from the atomization enthalpies of the unknown species relative to those for species with well-determined literature enthalpies of formation through isodesmic reaction schemes where possible, or through bond-dissociation schemes where not possible. The uncertainty (indicating 2σ) in the calculated atomization enthalpies is approximately ± 35 kJ mol⁻¹.^{1,2} The resulting uncertainty in enthalpies of formation derived from bond-dissociation processes is estimated at ± 60 kJ mol⁻¹. For those derived from isodesmic reactions, errors in the atomization enthalpies are assumed to cancel to a large degree and the uncertainty in the enthalpies of formation are estimated at ± 50 kJ mol⁻¹. Calculated values are reported in Table 2. Ancillary values used in those calculations are reported in Table 3.

Table S2. Enthalpies of formation ($\Delta H_{f,298K}^0$) at the B3LYP/6-311++G(d,p) level determined by isodesmic reaction where possible.

Species	$\Delta H_{f,298K}^0$ (kJ mol ⁻¹)	E+ZPE+H _{298K} (Hartree)	Reaction Scheme
CHF ⁺	1126	-138.065979	CHF ⁺ + CH ₄ → CH ₂ ⁺ + CH ₃ F
CFH ₂ ⁺	862	-138.751078	CFH ₂ ⁺ + e ⁻ → CFH ₂
CF ₂ H ⁺	626	-238.040868	CF ₂ H ⁺ + e ⁻ → CF ₂ H
CF ₂ CH ₂ ⁺	645	-276.739157	CF ₂ CH ₂ ⁺ + CH ₄ → C ₂ H ₄ + CH ₂ F ₂
C ₂ F ₃	-233	-375.688449	C ₂ F ₃ + CH ₄ → C ₂ H ₃ + CF ₃ H
C ₂ F ₃ ⁺	751	-375.309631	C ₂ F ₃ ⁺ + e ⁻ → C ₂ F ₃
C ₂ F ₃ H ⁺	482	-376.002771	C ₂ F ₃ H ⁺ + CH ₄ → C ₂ H ₄ ⁺ + CF ₃ H
CH ₂ FCF ₂	-467	-376.942612	CH ₂ FCF ₂ + CH ₄ → C ₂ H ₅ + CF ₃ H
CH ₂ FCF ₂ ⁺	359	-376.627908	CH ₂ FCF ₂ ⁺ + e ⁻ → CH ₂ FCF ₂
CF ₃ CO ⁺	227	-450.675746	CF ₃ CO ⁺ → CF ₃ ⁺ + CO
CHF ₂ CF ₂	-685	-476.220082	CHF ₂ CF ₂ + CH ₄ → C ₂ H ₅ + CF ₄
CHF ₂ CF ₂ ⁺	209	-475.879668	CHF ₂ CF ₂ ⁺ → CHF ₂ CF ₂
C ₂ F ₅ ⁺	37	-575.150915	C ₂ F ₅ ⁺ + e ⁻ → C ₂ F ₅

CF ₂ CF ₂ ⁺	81	-613.274749	C ₃ F ₅ ⁺ + C ₂ H ₆ → C ₃ H ₅ ⁺ + C ₂ F ₅ H
CI ⁺	1364	-6957.14929	CI ⁺ + CH ₄ → CH ⁺ + CH ₃ I
CHI ⁺	1272	-6957.773759	CHI ⁺ + CH ₄ → CH ₂ ⁺ + CH ₃ I
CH ₂ I ⁺	1028	-6958.446592	CH ₂ I ⁺ + CH ₄ → CH ₃ ⁺ + CH ₃ I
C ₂ H ₅ I ⁺	911	-6998.362203	C ₂ H ₅ I ⁺ + e ⁻ → C ₂ H ₅ I
CFI	142	-7057.398647	CFI + CF ₂ H ₂ → CH ₂ + CF ₃ I
CFI ⁺	1050	-7057.05278	CFI ⁺ + CF ₂ H ₂ → CH ₂ ⁺ + CF ₃ I
C ₂ FI ⁺	1128	-7095.147211	C ₂ FI ⁺ + CH ₂ F ₂ → C ₂ H ₂ ⁺ + CF ₃ I
CF ₂ I ⁺	-118	-7156.99807	CF ₂ I ⁺ + CH ₃ F → CH ₃ ⁺ + CF ₃ I
C ₂ F ₂ I ⁺	830	-7195.035726	C ₂ F ₂ I ⁺ + CFH ₃ → C ₂ H ₃ ⁺ + CF ₃ I
C ₂ H ₂ F ₂ I ⁺	529	-7196.319028	CH ₂ CF ₂ I ⁺ + CH ₃ F → C ₂ H ₅ ⁺ + CF ₃ I
C ₂ F ₃ I	-400	-7295.296865	C ₂ F ₃ I + CH ₃ F → C ₂ F ₄ + CH ₃ I
C ₂ F ₃ I ⁺	497	-7294.95506	C ₂ F ₃ I ⁺ → C ₂ F ₃ I
CF ₂ ICHF ⁺	406	-7295.566885	C ₂ F ₃ HI ⁺ + CH ₄ → C ₂ H ₅ ⁺ + CF ₃ I
CF ₃ CH ₂ I	-649	-7296.551705	C ₂ F ₃ H ₂ I + CH ₄ → C ₂ H ₆ + CF ₃ I
CF ₃ CH ₂ I ⁺	317	-7296.176019	C ₂ F ₃ H ₂ I ⁺ + e ⁻ → C ₂ F ₃ H ₂ I
CF ₃ CFI	-610	-7395.160610	C ₂ F ₄ I + CH ₃ F → C ₂ F ₅ + CH ₃ I
CF ₃ CFI ⁺	242	-7394.836016	C ₂ F ₄ I ⁺ → C ₂ F ₄ I
CHF ₂ CF ₂ I	-805	-7395.81219	C ₂ F ₄ HI + CH ₄ → CFH ₂ CH ₃ + CF ₃ I
CHF ₂ CF ₂ I ⁺	201	-7395.42899	C ₂ F ₄ HI ⁺ + e ⁻ → C ₂ F ₄ HI
C ₂ F ₅ I	-1000	-7495.085748	C ₂ F ₅ I + CH ₄ → CHF ₂ CH ₃ + CF ₃ I
C ₂ F ₅ I ⁺	22	-7494.696159	C ₂ F ₅ I ⁺ + e ⁻ → C ₂ F ₅ I

Table S3. Ancillary 298 K enthalpies of formation and 298 K enthalpies calculated at B3LYP/6-311++G(d,p) of species used in the determination of values reported in Table 2.

Species	$\Delta H_{f,298K}^0$ (kJ mol ⁻¹)	E+ZPE+H _{298K} (Hartree)	Ref.
CH ₄	-74.520 ± 0.057	-40.485591	a
CH ₃ F	-235.80 ± 0.23	-139.748509	a
CH ₂ F ₂	-450.73 ± 0.36	-239.029669	a
CHF ₃	-695.87 ± 0.43	-338.319839	a
CF ₄	-933.39 ± 0.25	-437.604837	a
CF ₃ I	-589.87 ± 0.54	-7257.240914	a
CH ₃ I	14.94 ± 0.17	-6959.4157	a
C ₂ H ₂ ⁺	1328.18 ± 0.14	-76.912305	a
C ₂ H ₃	296.91 ± 0.33	-77.888642	a
C ₂ H ₃ ⁺	1115.75 ± 0.57	-77.569092	a
C ₂ H ₄	52.45 ± 0.13	-78.564763	a
C ₂ H ₄ ⁺	1068.07 ± 0.13	-78.181495	a
C ₂ H ₅	119.86 ± 0.28	-79.121146	a
C ₂ H ₅ ⁺	902.95 ± 0.32	-78.819106	a
C ₂ H ₆	-83.91 ± 0.14	-79.777846	a
C ₂ F ₄	-674.93 ± 0.57	-475.638403	a
C ₂ F ₅ H	-1110.6 ± 3.2	-576.182226	b
C ₂ H ₅ F	-272.16 ± 0.37	-179.050978	a
C ₂ H ₅ I	-7.16 ± 0.49	-6998.712196	a
CF ₃ ⁺	405.93 ± 0.51	-337.309033	a

CO	-110.523 ± 0.026	-113.340707	a
CH ⁺	1623.102 ± 0.057	-38.080041	a
CH ₂ ⁺	1393.95 ± 0.13	-38.762966	a
CFH ₂	-31.2 ± 1.6	-139.091193	c
C ₂ F ₅	-894.4 ± 2.8	-575.504411	d

^a ref. 3 ^b ref. 4 ^c ref. 5 ^d ref. 6

1. Bakowies, D., Assessment of Density Functional Theory for Thermochemical Approaches Based on Bond Separation Reactions. *J. Phys. Chem. A* **2012**, *117*, 228-243.
2. Ruscic, B., Uncertainty quantification in thermochemistry, benchmarking electronic structure computations, and Active Thermochemical Tables. *Quantum Chemistry* **2014**, *114*, 1097-1101.
3. Ruscic, B.; Bross, D. H. Active Thermochemical Tables (ATcT) based on ver. 1.122 of the Thermochemical Network (2016); available at ATcT.anl.gov. (accessed June 6).
4. Nagy, B.; Csontos, B.; Csontos, J.; Szakacs, P.; Kallay, M., High-Accuracy Theoretical Thermochemistry of Fluoroethanes. *J. Phys. Chem. A* **2014**, *118*, 4824-4836.
5. Csontos, J.; Rolik, Z.; Das, S.; Kallay, M., High-Accuracy Thermochemistry of Atmospherically Important Fluorinated and Chlorinated Methane Derivatives. *J. Phys. Chem. A* **2010**, *114*, 13093-13103.
6. Ganyecz, A.; Kallay, M.; Csontos, J., Accurate Theoretical Thermochemistry for Fluoroethyl Radicals. *J. Phys. Chem. A* **2017**, *121*, 1153-1162.