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

SUPPLEMENTARY MATERIAL

The supporting information presented here comprises results of *ab initio* calculations performed on the halide-formic acid complexes. Included are energetics, vibrational data, and structural information in the form of cartesian coordinates predicted using the CCSD(T) method, with aug-cc-pVDZ, TZ, and QZ basis sets, referred to collectively as AVXZ. In addition to computational data, a putative assignment of the presented mass spectrum is also provided.

1 Energetics

Table S1: Energies of the bare formic acid conformers, the halide anions, and the halogen radicals determined from CCSD(T) calculations.

		$E_{CCSD(T)}$ [E_h]	zpe [kJ mol^{-1}]	VDE [eV]	Experimental SO* [eV]	Split [eV]	Literature $^2P_{3/2}$ VDE† [eV]	Shift [eV]
Anti-formic acid	AVDZ	-189.349020						
	AVTZ	-189.511048	87.7					
	AVQZ	-189.560920						
	CBS	-189.589247						
Syn-formic acid	AVDZ	-189.355744						
	AVTZ	-189.517767	88.7					
	AVQZ	-189.567652						
	CBS	-189.596005						
Cl^- | Cl	AVDZ	-459.743800 | -459.618075		3.421		3.385 | 3.494		+0.228
	AVTZ	-459.806627 | -459.677858		3.504		3.468 | 3.578		+0.145
	AVQZ	-459.828395 | -459.695891		3.606		3.570 | 3.679		+0.043
	CBS	-459.841427 | -459.706279		3.677	-0.036 | +0.073	3.641 | 3.750	3.613	-0.028
Br^- | Br	AVDZ	-415.726436 | -415.606190		3.272		3.120 | 3.577		+0.244
	AVTZ	-415.836425 | -415.713279		3.351		3.199 | 3.656		+0.165
	AVQZ	-415.912356 | -415.785328		3.457		3.305 | 3.762		+0.059
	CBS	-415.959933 | -415.830231		3.529	-0.152 | +0.305	3.377 | 3.834	3.364	-0.013
I^- | I	AVDZ	-294.883258 | -294.769062		3.107		2.793 | 3.735		+0.266
	AVTZ	-294.982288 | -294.865413		3.180		2.866 | 3.808		+0.193
	AVQZ	-295.061242 | -294.939975		3.300		2.986 | 3.928		+0.073
	CBS	-295.110115 | -294.985954		3.379	-0.314 | +0.628	3.065 | 4.007	3.059	-0.005

* Values from http://www.nist.gov/pml/data/handbook/index.cfm

† Values from http://webbook.nist.gov

‡ Shift refers to the difference between the predicted and literature Electron Detachment Energy

Table S2: Energetic parameters predicted for the chloride complexes with *anti*- and *syn*-formic acid, determined from CCSD(T) calculations.

		$E_{CCSD(T)}$ [E_h]	D_e [kJ mol^{-1}]	D_0 [kJ mol^{-1}]	VDE [eV]
$Cl^- \cdots$ HCOOH	AVDZ	-649.141967			
Anti-formic acid conformer	AVTZ	-649.368568			
OH bound	AVQZ	-649.439696			
	CBS	-649.480836	131.7	129.6	5.12 | 5.23
$Cl^- \cdots$ HCOOH	AVDZ	-649.133180			
Syn-formic acid conformer	AVTZ	-649.359661			
OH bound	AVQZ	-649.430753			
	CBS	-649.471881	90.4	91.3	4.75 | 4.86
$Cl^- \cdots$ HCOOH	AVDZ	-649.118289			
Syn-formic acid conformer	AVTZ	-649.343127			
CH bound	AVQZ	-649.414337			
	CBS	-649.455499	47.4	46.0	4.19 | 4.30

Table S3: Energetic parameters predicted for the bromide complexes with *anti*- and *syn*-formic acid, determined from CCSD(T) calculations.

		$E_{CCSD(T)}$ [E_h]	D_e [kJ mol^{-1}]	D_0 [kJ mol^{-1}]	VDE [eV]
$Br^- \cdots$ HCOOH	AVDZ	-605.119999			
Anti-formic acid conformer	AVTZ	-605.394379			
OH bound	AVQZ	-605.520357			
	CBS	-605.596485	124.2	121.9	4.63 | 5.08
$Br^- \cdots$ HCOOH	AVDZ	-605.111381			
Syn-formic acid conformer	AVTZ	-605.385591			
OH bound	AVQZ	-605.511444			
	CBS	-605.587497	82.9	83.1	4.24 | 4.70
$Br^- \cdots$ HCOOH	AVDZ	-605.099407			
Syn-formic acid conformer	AVTZ	-605.371713			
CH bound	AVQZ	-605.497055			
	CBS	-605.572725	44.1	42.5	3.84 | 4.29

Table S4: Energetic parameters predicted for the iodide complexes with *anti*- and *syn*-formic acid, determined from CCSD(T) calculations.

		$E_{CCSD(T)}$ [E_h]	D_e [kJ mol^{-1}]	D_0 [kJ mol^{-1}]	VDE [eV]
$I^- \cdots$ HCOOH	AVDZ	-484.271161			
Anti-formic acid conformer	AVTZ	-484.534177			
OH bound	AVQZ	-484.662756			
	CBS	-484.739850	106.3	103.9	4.07 | 5.01
$I^- \cdots$ HCOOH	AVDZ	-484.262638			
Syn-formic acid conformer	AVTZ	-484.525874			
OH bound	AVQZ	-484.654301			
	CBS	-484.731292	66.1	65.8	3.69 | 4.63
$I^- \cdots$ HCOOH	AVDZ	-484.253749			
Syn-formic acid conformer	AVTZ	-484.514794			
CH bound	AVQZ	-484.643135			
	CBS	-484.720052	36.6	35.1	3.41 | 4.36

Table S5: Energetic parameters predicted for the transition states connecting the *anti*- and *syn*-formic acid conformers, both in halide complexes and for the bare formic acid molecule, determined from CCSD(T) calculations.

		$E_{CCSD(T)}$ [E_h]	ΔG^{298K} (from *syn*-formic acid) [kJ mol^{-1}]	ΔG^{298K} (from *anti*-formic acid) [kJ mol^{-1}]
$Cl^- \cdots$ HCOOH	AVDZ	-649.121580		
	AVTZ	-649.348235		
	AVQZ	-649.419201		
	CBS	-649.460252	26.4	47.5
$Br^- \cdots$ HCOOH	AVDZ	-605.099226		
	AVTZ	-605.373671		
	AVQZ	-605.499512		
	CBS	-605.575563	27.5	48.9
$I^- \cdots$ HCOOH	AVDZ	-484.250510		
	AVTZ	-484.513448		
	AVQZ	-484.641867		
	CBS	-484.718866	28.6	49.2
HCOOH	AVDZ	-189.335822		
	AVTZ	-189.497855		
	AVQZ	-189.547574		
	CBS	-189.575821	47.8	31.0

2 Vibrational Data

Table S6: Vibrational frequencies, in cm^{-1}, of the bare formic acid conformers.

	Symmetry	*anti*-formic acid	Symmetry	*syn*-formic acid
ω_1	a'	655	a'	627
ω_2	a'	1114	a'	1132
ω_3	a'	1288	a'	1311
ω_4	a'	1415	a'	1405
ω_5	a'	1843	a'	1803
ω_6	a'	3006	a'	3088
ω_7	a'	3805	a'	3742
ω_8	a''	513	a''	665
ω_9	a''	1029	a''	1051
zpe	87.7 kJ mol^{-1}		88.7 kJ mol^{-1}	

Table S7: Vibrational frequencies, in cm^{-1}, of halide complexes with *anti*-formic acid where the halide anion binds to the acidic hydrogen (OH) portion of the formic acid molecule.

	Symmetry	$Cl^- \cdots$ HCOOH	Symmetry	$Br^- \cdots$ HCOOH	Symmetry	$I^- \cdots$ HCOOH
ω_1	a'	110	a'	92	a'	83
ω_2	a'	250	a'	205	a'	175
ω_3	a'	698	a'	694	a'	689
ω_4	a'	1230	a'	1217	a'	1202
ω_5	a'	1404	a'	1404	a'	1407
ω_6	a'	1466	a'	1443	a'	1414
ω_7	a'	1769	a'	1776	a'	1783
ω_8	a'	2850	a'	3009	a'	3022
ω_9	a'	3014	a'	3039	a'	3193
ω_{10}	a''	166	a''	165	a''	159
ω_{11}	a''	985	a''	935	a''	867
ω_{12}	a''	1074	a''	1074	a''	1070
zpe	89.8 kJ mol^{-1}		90.0 kJ mol^{-1}		90.1 kJ mol^{-1}	

Table S8: Vibrational frequencies, in cm^{-1}, of halide complexes with *syn*-formic acid where the halide anion binds to the acidic hydrogen (OH) portion of the formic acid molecule.

	Symmetry	$Cl^- \cdots$ HCOOH	Symmetry	$Br^- \cdots$ HCOOH	Symmetry	$I^- \cdots$ HCOOH
ω_1	a'	105	a'	87	a'	75
ω_2	a'	254	a'	206	a'	174
ω_3	a'	688	a'	677	a'	666
ω_4	a'	1244	a'	1225	a'	1205
ω_5	a'	1371	a'	1359	a'	1347
ω_6	a'	1416	a'	1417	a'	1418
ω_7	a'	1751	a'	1762	a'	1771
ω_8	a'	2638	a'	2868	a'	2979
ω_9	a'	2955	a'	2975	a'	3097
ω_{10}	a''	175	a''	171	a''	162
ω_{11}	a''	1000	a''	961	a''	904
ω_{12}	a''	1090	a''	1077	a''	1069
zpe	87.8 kJ mol^{-1}		88.4 kJ mol^{-1}		88.9 kJ mol^{-1}	

Table S9: Vibrational frequencies, in cm^{-1}, of halide complexes with *syn*-formic acid where the halide anion binds to the formyl hydrogen (CH) portion of the formic acid molecule.

	Symmetry	$Cl^- \cdots HCOOH$	Symmetry	$Br^- \cdots HCOOH$	Symmetry	$I^- \cdots HCOOH$
ω_1	a'	88	a'	78	a'	71
ω_2	a'	136	a'	110	a'	89
ω_3	a'	625	a'	626	a'	626
ω_4	a'	1088	a'	1094	a'	1101
ω_5	a'	1288	a'	1291	a'	1294
ω_6	a'	1438	a'	1434	a'	1427
ω_7	a'	1744	a'	1751	a'	1758
ω_8	a'	2936	a'	2974	a'	3013
ω_9	a'	3734	a'	3737	a'	3739
ω_{10}	a''	177	a''	176	a''	155
ω_{11}	a''	669	a''	670	a''	669
ω_{12}	a''	1146	a''	1141	a''	1127
zpe	90.1 kJ mol^{-1}		90.2 kJ mol^{-1}		90.1 kJ mol^{-1}	

Table S10: Vibrational frequencies, in cm^{-1}, of the bare formic acid transition state separating the two conformers.

	Symmetry	formic acid
ω_1	a	599i
ω_2	a	670
ω_3	a	915
ω_4	a	1090
ω_5	a	1208
ω_6	a	1392
ω_7	a	1806
ω_8	a	3039
ω_9	a	3827
zpe	83.4 kJ mol^{-1}	

Table S11: Vibrational frequencies, in cm^{-1}, of transition states of halide complexes with formic acid separating the two conformers of formic acid.

	Symmetry	$Cl^- \cdots HCOOH$	Symmetry	$Br^- \cdots HCOOH$	Symmetry	$I^- \cdots HCOOH$
ω_1	a	289i	a	309i	a	342i
ω_2	a	98	a	81	a	68
ω_3	a	267	a	221	a	188
ω_4	a	655	a	564	a	446
ω_5	a	712	a	698	a	691
ω_6	a	1017	a	1005	a	989
ω_7	a	1213	a	1192	a	1171
ω_8	a	1317	a	1304	a	1286
ω_9	a	1406	a	1406	a	1404
ω_{10}	a	1732	a	1748	a	1759
ω_{11}	a	2427	a	2751	a	2967
ω_{12}	a	2939	a	2960	a	3027
zpe	82.4 kJ mol^{-1}		83.3 kJ mol^{-1}		83.7 kJ mol^{-1}	

3 Cartesian Coordinates

Table S12: Cartesian coordinates, in Å, of both conformers of bare formic acid.

Atom	*anti*-formic acid			*syn*-formic acid		
	X	Y	Z	X	Y	Z
C	-0.101716	0.401839	0.000000	0.099296	0.414537	0.000000
O	1.1100912	-0.222732	0.000000	-1.137290	-0.122072	0.000000
H	1.800226	0.442239	0.000000	-1.021372	-1.085165	0.000000
O	-1.136154	-0.201141	0.000000	1.125195	-0.215514	0.000000
H	-0.029800	1.500313	0.000000	0.031033	1.507085	0.000000

Table S13: Cartesian coordinates, in Å, of halide complexes with *anti*-formic acid where the halide anion binds to the acidic hydrogen (OH) portion of the formic acid molecule. (Note: X represents the halide anion).

Atom	$Cl^- \cdots HCOOH$			$Br^- \cdots HCOOH$			$I^- \cdots HCOOH$		
	X	Y	Z	X	Y	Z	X	Y	Z
C	-1.411711	0.269652	0.000000	-2.203649	0.265400	0.000000	-2.744177	0.267335	0.000000
O	-0.721558	-0.856085	0.000000	-1.572430	-0.899363	0.000000	-2.155263	-0.924445	0.000000
H	0.264285	-0.604722	0.000000	-0.585134	-0.700353	0.000000	-1.169890	-0.767274	0.000000
O	-2.628661	0.326533	0.000000	-3.414536	0.379820	0.000000	-3.948643	0.419573	0.000000
H	-0.772163	1.165622	0.000000	-1.516408	1.124697	0.000000	-2.026189	1.100605	0.000000
X	2.031489	0.133519	0.000000	1.372658	0.059525	0.000000	1.054200	0.035707	0.000000

Table S14: Cartesian coordinates, in Å, of halide complexes with *syn*-formic acid where the halide anion binds to the acidic hydrogen (OH) portion of the formic acid molecule. (Note: X represents the halide anion).

Atom	$Cl^- \cdots HCOOH$			$Br^- \cdots HCOOH$			$I^- \cdots HCOOH$		
	X	Y	Z	X	Y	Z	X	Y	Z
C	-1.832226	-0.253232	0.000000	-2.635827	-0.226860	0.000000	-3.204844	-0.208772	0.000000
O	-0.748001	-0.996127	0.000000	-1.579488	-1.015742	0.000000	-2.160438	-1.020638	0.000000
H	0.136367	-0.466230	0.000000	-0.693597	-0.516611	0.000000	-1.282858	-0.531814	0.000000
O	-1.927421	0.958858	0.000000	-2.676292	0.986247	0.000000	-3.215007	1.002963	0.000000
H	-2.726909	-0.901460	0.000000	-3.553140	-0.840473	0.000000	-4.131232	-0.806172	0.000000
X	1.927175	0.143365	0.000000	1.317574	0.057804	0.000000	1.023560	0.032595	0.000000

Table S15: Cartesian coordinates, in Å, of halide complexes with *syn*-formic acid where the halide anion binds to the formyl hydrogen (CH) portion of the formic acid molecule. (Note: X represents the halide anion).

Atom	$Cl^- \cdots HCOOH$			$Br^- \cdots HCOOH$			$I^- \cdots HCOOH$		
	X	Y	Z	X	Y	Z	X	Y	Z
C	1.207720	0.119835	0.000000	2.074034	0.120567	0.000000	2.675414	0.121890	0.000000
O	1.701011	-1.151029	0.000000	2.557929	-1.151794	0.000000	3.146191	-1.152823	0.000000
H	2.664057	-1.039154	0.000000	3.521930	-1.049104	0.000000	4.111385	-1.062625	0.000000
O	1.950153	1.080108	0.000000	2.816239	1.079793	0.000000	3.417927	1.079332	0.000000
H	0.101351	0.126153	0.000000	0.970330	0.131288	0.000000	1.574672	0.139246	0.000000
X	-2.164204	0.017630	0.000000	-1.461957	0.007981	0.000000	-1.125477	0.005070	0.000000

Table S16: Cartesian coordinates, in Å, of of the bare formic acid transition state separating the two conformers.

Atom	HCOOH		
	X	Y	Z
C	0.118900	0.408694	0.012275
O	1.134661	-0.223493	0.002476
H	0.087920	1.506377	0.018142
O	-1.135230	-0.159482	-0.064498
H	-1.494612	-0.294538	0.820024

Table S17: Cartesian coordinates, in Å, of transition states of halide complexes with formic acid separating the two conformers of formic acid. (Note: X represents the halide anion).

Atom	$Cl^- \cdots HCOOH$			$Br^- \cdots HCOOH$			$I^- \cdots HCOOH$		
	X	Y	Z	X	Y	Z	X	Y	Z
C	1.620189	0.166649	0.357719	2.407485	0.138059	0.366133	2.945083	0.109224	0.374931
O	2.236786	-0.736117	-0.170189	2.974970	-0.783599	-0.177574	3.486234	-0.815053	-0.185153
H	1.847843	0.458286	1.399844	2.627717	0.391496	1.418145	3.144508	0.326865	1.437485
O	0.697759	0.934188	-0.211936	1.543096	0.980606	-0.205779	2.127324	1.006863	-0.199077
H	-0.253008	0.511041	-0.183684	0.591157	0.609978	-0.205222	1.178935	0.671874	-0.228196
X	-1.944227	-0.175723	0.016980	-1.322886	-0.073711	0.006534	-1.020347	-0.042435	0.003371

4 Mass Spectral Assignment

Table S18: Putative assignment of mass spectral data presented in main article, associated with a mass spectrum collected from a gas mixture of argon, dibromomethane, and formic acid as well as trace iodomethane.

Spectral Peak [m/z]	Assignment
78.9	$^{79}Br^-$
81.1	$^{81}Br^-$
91.0	$HCOO^- \cdots HCOOH$
92.0	$HCOOH_2^-$
97.0	$^{79}Br^- \cdots H_2O$
99.0	$^{81}Br^- \cdots H_2O$
107.0	$^{79}Br^- \cdots N_2$
109.0	$^{81}Br^- \cdots N_2$
119.0	$^{79}Br^- \cdots Ar$
121.0	$^{81}Br^- \cdots Ar$
123.0	$^{79}Br^- \cdots CO_2$
125.0	$^{79}Br^- \cdots HCOOH$, $^{81}Br^- \cdots CO_2$
127.0	$^{81}Br^- \cdots HCOOH$, I^-
138.0	$HCOOH_3^-$
145.0	$I^- \cdots H_2O$
159.0	$^{79}Br^- \cdots Ar_2$
161.0	$^{81}Br^- \cdots Ar_2$