

# Redox Chemistry of Bromine

- Bromine in the +VII oxidation state is a very strong oxidizer
- Br(VII) compounds have been difficult to prepare, compared to Cl(VII) and I(VII)

Reason: **d-block contraction**

For bromine:

- Electrons have been filled into the poorly shielding d-orbitals of the n-1 shell
- Build-up of a large effective nuclear charge
- Leading to a contraction of the atom and increase of the ionization energy

# Interhalogen Compounds

**Table 51** Halogens X<sub>2</sub> and Interhalides XY<sup>a)</sup>.

<p><b>FF</b> (1886, Moissan) colorless gas m.p. <math>-219.62^{\circ}\text{C}</math> b.p. <math>-188.14^{\circ}\text{C}</math></p>			
<p><b>ClF</b> (1928, Ruff) colorless gas m.p. <math>-155.6^{\circ}\text{C}</math> b.p. <math>-101.1^{\circ}\text{C}</math> <math>\Delta H_f -56.5 \text{ kJ mol}^{-1}</math></p>	<p><b>ClCl</b> (1774, Scheele) yellow-green gas m.p. <math>-101.00^{\circ}\text{C}</math> b.p. <math>-34.06^{\circ}\text{C}</math></p>		
<p><b>BrF</b> (1933, Ruff) bright red gas m.p. <math>\approx -33^{\circ}\text{C}</math> b.p. <math>\approx +20^{\circ}\text{C}</math>(dispr.) <math>\Delta H_f -58.6 \text{ kJ mol}^{-1}</math></p>	<p><b>BrCl</b> (1930, Lux) dark red liquid m.p. <math>-66^{\circ}\text{C}</math> b.p. ca. <math>+5^{\circ}\text{C}</math>(decomp.) <math>\Delta H_f +14.6 \text{ kJ mol}^{-1}</math></p>	<p><b>BrBr</b> (1826, Balard) deep brown liquid m.p. <math>-7.25^{\circ}\text{C}</math> b.p. <math>+58.78^{\circ}\text{C}</math></p>	
<p><b>IF</b> (1960, Schmeisser) white powder (<math>-78^{\circ}\text{C}</math>) dispr. above <math>-14^{\circ}\text{C}</math> <math>\Delta H_f -95.4 \text{ kJ mol}^{-1}</math></p>	<p><math>\alpha</math>-<b>ICl</b><sup>a)</sup> (1814, Davy)<sup>b)</sup> ruby-red needles m.p. <math>+27.38^{\circ}\text{C}</math><sup>c)</sup> b.p. <math>+94.4^{\circ}\text{C}</math> (decomp.) <math>\Delta H_f -23.8 \text{ kJ mol}^{-1}</math></p>	<p><b>IBr</b> (1826, Balard) black crystals m.p. <math>+41^{\circ}\text{C}</math> b.p. <math>+116^{\circ}\text{C}</math> (decomp.) <math>\Delta H_f -10.5 \text{ kJ mol}^{-1}</math></p>	<p><b>I<sub>2</sub></b> (1812, Courtois) grayish-black flakes m.p. <math>+113.60^{\circ}\text{C}</math> b.p. <math>+185.24^{\circ}\text{C}</math></p>

- a) Dissociation energies: F<sub>2</sub>: 157.9; ClF: 252.5; BrF: 248.6; IF: ca. 277 Cl<sub>2</sub>: 121.7; BrCl: 215.1; ICl: 207.7; Br<sub>2</sub>: 193.9; IBr: 175.4; I<sub>2</sub>: 152.5 [kJ mol<sup>-1</sup>]
- b) Discovered independently by Gay-Lussac.
- c) ICl occurs also in a second, metastable modification ( $\beta$ -ICl) in the form of red-brown rhomboidal flakes, m.p.  $+13.9^{\circ}\text{C}$ .

# Interhalogen Compounds

<b>ClF<sub>3</sub></b> (1930, Ruff) <i>colorless gas</i> m.p. $-76.3^{\circ}\text{C}$ b.p. $+11.75^{\circ}\text{C}$ $\Delta H_f -164.8 \text{ kJ mol}^{-1}$	<b>ClF<sub>5</sub></b> (1963, Smith) <i>colorless gas</i> m.p. $-103^{\circ}\text{C}$ b.p. $-13.1^{\circ}\text{C}$ $\Delta H_f -255 \text{ kJ mol}^{-1}$	<b>ClF<sub>6</sub><sup>+</sup></b> (1972, Christ e) <sup>b)</sup> counterions e.g. BF <sub>4</sub> <sup>-</sup> , PtF <sub>6</sub> <sup>-</sup>
<b>BrF<sub>3</sub></b> (1905, Lebeau) <i>colorless liquid</i> m.p. $+8.77^{\circ}\text{C}$ b.p. $+125.75^{\circ}\text{C}$ $\Delta H_f -301 \text{ kJ mol}^{-1}$	<b>BrF<sub>5</sub></b> (1931, Ruff) <i>colorless liquid</i> m.p. $-60.5^{\circ}\text{C}$ b.p. $+41.3^{\circ}\text{C}$ $\Delta H_f -458.6 \text{ kJ mol}^{-1}$	<b>BrF<sub>6</sub><sup>+</sup></b> (1974, Gillespie) counterions e.g. AsF <sub>6</sub> <sup>-</sup> , Sb <sub>2</sub> F <sub>11</sub>
<b>IF<sub>3</sub></b> (1960, Schmeisser) <i>yellow powder (<math>-78^{\circ}\text{C}</math>)</i> dispr. above $-28^{\circ}\text{C}$ $\Delta H_f \approx -486 \text{ kJ mol}^{-1}$	<b>IF<sub>5</sub></b> (1870, Gore) <i>colorless liquid</i> m.p. $+9.42^{\circ}\text{C}$ b.p. $+104.48^{\circ}\text{C}$ $\Delta H_f -843 \text{ kJ mol}^{-1}$	<b>IF<sub>7</sub></b> (1930, Ruff) <i>colorless gas</i> m.p. $+6.45^{\circ}\text{C}$ b.p. $+4.77^{\circ}\text{C}$ $\Delta H_f -962.5 \text{ kJ mol}^{-1}$

- Only with iodine is the heptafluoride known. WHY?

BrF<sub>6</sub><sup>-</sup> anion: octahedral

Stereochemically inactive lone pair

IF<sub>6</sub><sup>-</sup> anion: distorted octahedral

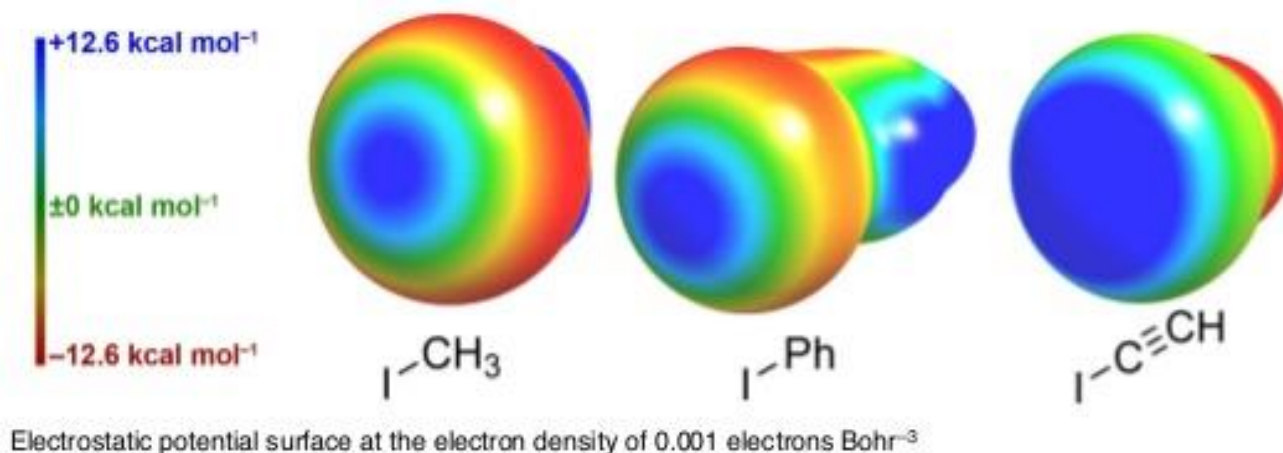
Stereochemically active lone pair

- WHY?

# Halogen Bonding

## Halogen Bonding: Size of $\sigma$ -Hole Increases with Lower Hybridization of XB Donor

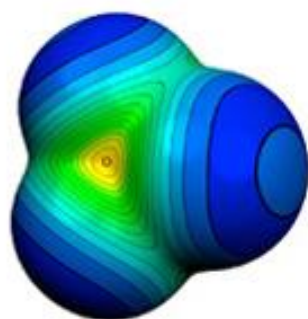
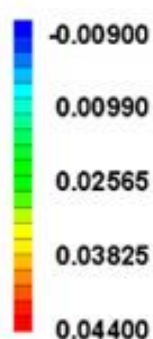
- The size of the  $\sigma$ -hole on iodine increases with decreasing hybridization state of the C atom of the XB donor ( $sp > sp^2 > sp^3$ )
- In parallel, the electronegative area decreases from C( $sp^3$ ) to C( $sp^2$ ) and changes to an electroneutral surface potential for C( $sp$ )



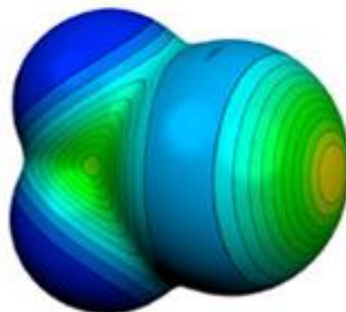
O. Dumele, D. Wu, N. Trapp, N. Goroff, F. Diederich, *Org. Lett.* **2014**, *18*, 4722-4725.

- $\sigma$ -hole opposite to the (electronegative) ligand

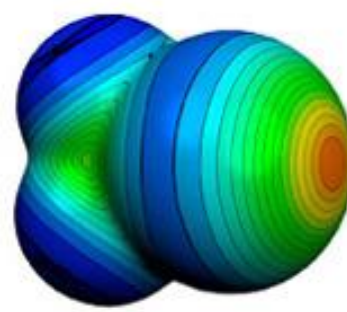
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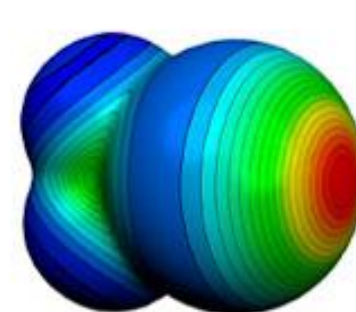
CF<sub>4</sub>



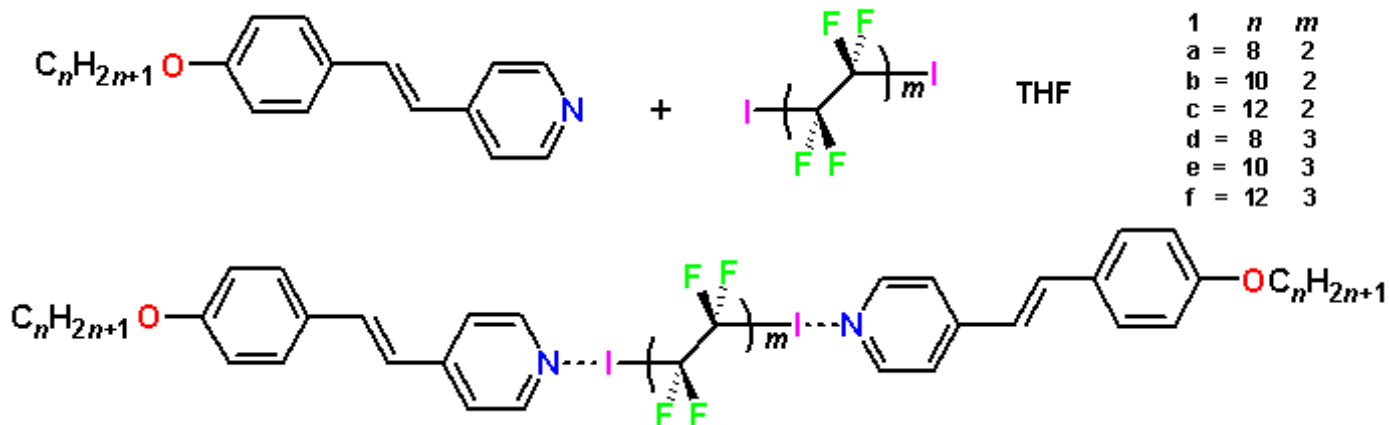
CF<sub>3</sub>Cl



CF<sub>3</sub>Br



CF<sub>3</sub>I



- Iodine compounds are halogen bond donors
- The pyridyl group is a halogen bond acceptor

# Halogen Bonding

- Analogously, there are chalcogen bonds, pnictogen bonds and tetrel bonds
- Mainly electrostatic interactions with little covalency

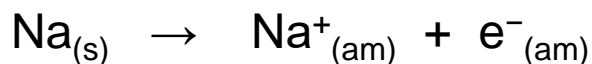
# Non-aqueous Solvents

- Protic solvents, examples:  $\text{H}_2\text{O}$ ,  $\text{aHF}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{OH}$
- Aprotic solvents, examples:  $\text{N}_2\text{O}_4$ ,  $\text{BrF}_3$ ,  $\text{BrF}_5$ ,  $\text{SO}_2$
- Coordinating solvents, examples:  $\text{CH}_3\text{CN}$ ,  $\text{Et}_2\text{O}$

Solvent	m.p. ( $^{\circ}\text{C}$ )	b.p. ( $^{\circ}\text{C}$ )	Dielectric constant	Comments
$\text{H}_2\text{O}$	0	100	78	
Anhydrous HF	-83.6	19.5	175	Superacidic, toxic, oxidative resistant
$\text{SO}_2$	-72	-10	17.6	
$\text{SO}_2\text{ClF}$	-124.7	7.1		
$\text{BrF}_5$	-61.30	40.25		Oxidatively resistant, can react explosively with organic materials
$\text{BrF}_3$	8.6	134	107	Significant autoionization
$\text{CFCl}_3$	-110.48	23.77	2.3	Good for non-polar molecules
Anhydrous $\text{NH}_3$	-77.73	-33.34	25	Basic, good for work in highly reducing environments
Supercritical $\text{CO}_2$				Remarkable solvation properties, but special apparatus are needed to allow for the high pressure

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- Low conc.: deep blue
- High conc.: golden



- Solvolyzed electrons in liquid ammonia (NOT NH<sub>3(aq)</sub>): highly reducing

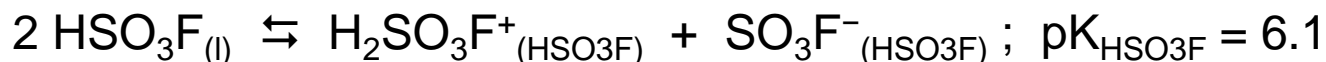


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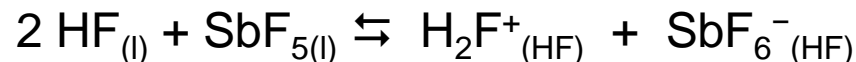
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- Anhydrous HF is a superacid (more acidic than H<sub>2</sub>SO<sub>4</sub>); stable for the most oxidizing species

Autoprotolysis equilibria:



Acidification by SbF<sub>5</sub>:



# Non-aqueous Solvents

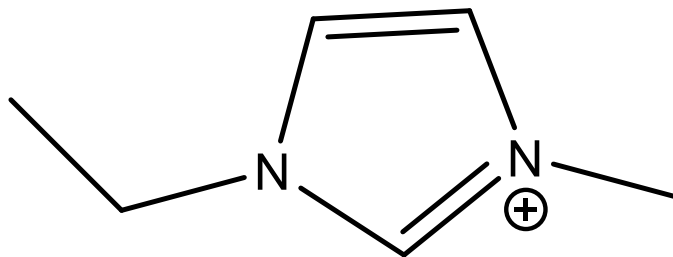
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# Non-aqueous Solvents

## Ionic liquids

- Ionic compounds (salts) that have a low melting point, preferably below RT
- Use large cations that do not pack nicely in the solid state:

*e.g.*, ethylmethylimidazolium cation



# Mechanochemistry

- Some reactions are not carried out in a solvent
- It is possible to grind solid reagents together (typically in a ball mill):  
Allows reaction to occur because the surface contact is greatly increased
- In recent years this approach has become more popular
- Environmentally friendly because of not solvent waste.

# Pseudohalogen

**Table 17.7** Pseudohalides, pseudohalogens, and corresponding acids

Pseudohalide	Pseudohalogen	$E^{\ominus}/V$	Acid	$pK_a$
$CN^-$	NCCN	+0.27	HCN	9.2
Cyanide	Cyanogen		Hydrogen cyanide	
$NCS^-$	NCSSCN	+0.77	HNCS	-1.9
Thiocyanate	Dithiocyanogen		Hydrogen thiocyanate	
$NCO^-$			HNCO	3.5
Cyanate			Isocyanic acid	
$CNO^-$			HCNO	3.66
Fulminate			Fulminic acid	
$NNN^-$			HNNN	4.92
Azide			Hydrazoic acid	