



Towards a stronger halogen bond involving At

– Investigation of halogen-bonded adducts of Atl and Bu_3PO

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Gilles Montavon, Nicolas Galland, Rémi Maurice

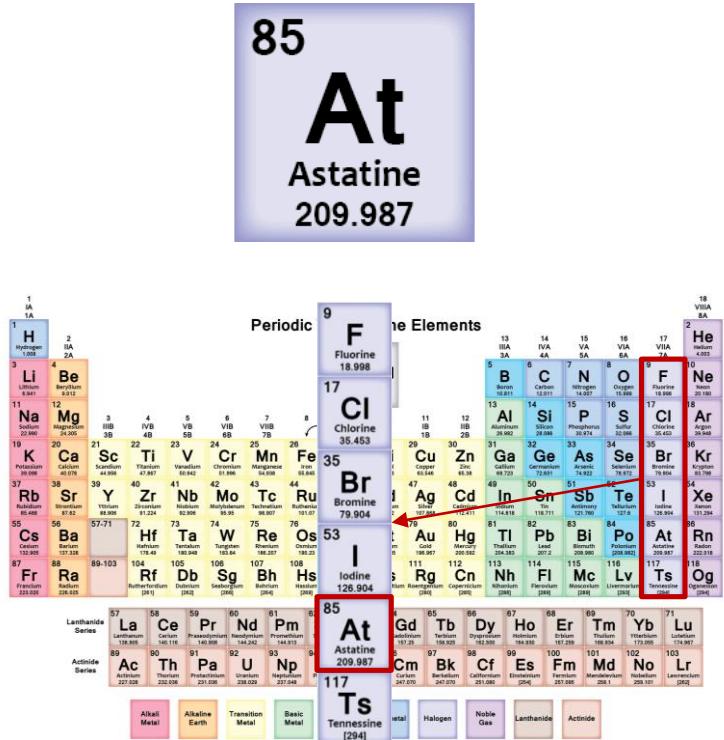
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Astatine



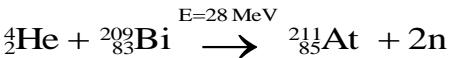
Dale R. Corson, Kenneth Ross MacKenzie, and Emilio Segrè are recognized that discovered and isolated astatine at the University of California, Berkeley in 1940.

□ Astatine << astatos (αστατος)

- Radioelement
- No long-lived isotope ($T_{1/2} \leq 8.1\text{h}$)
- Rarest naturally-occurring element
- Difficult to study
 - Production of its isotopes limited by a cyclotron
 - Available at ultra-trace concentrations
 - No spectroscopic tool applicable

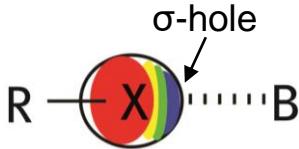
At-211: a promising candidate for nuclear medicine

Production At-211 in Nantes:



Halogen bonds involving At

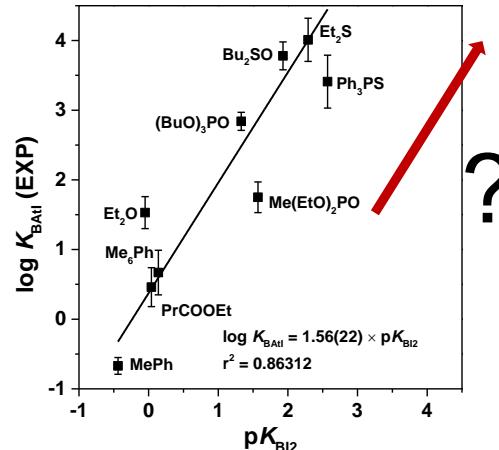
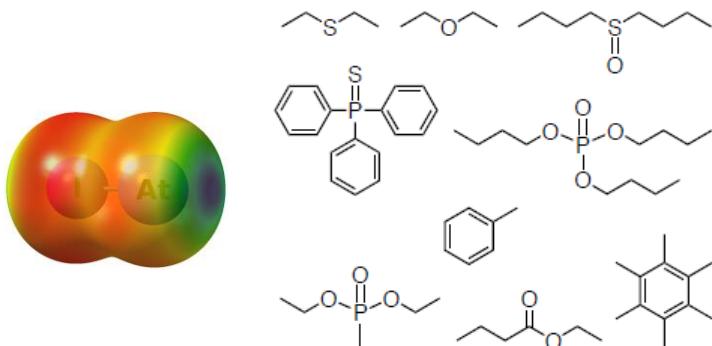
- Halogen bond:



- Halogen bond strength: the basicity scale with diiodine ($pK_{\text{BI}2}$) ¹



- Halogen bonds involving astatine ²



Objective :

Stronger halogen-bond acceptors for AtI

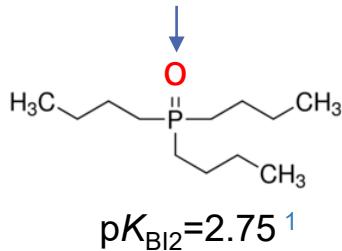
1. Laurence, C. et al. J. Chem. - A Eur. J. 2011, 17 (37), 10431.

2. N. Guo et al., Nat. Chem., 2018, 10 (4), 1-7.

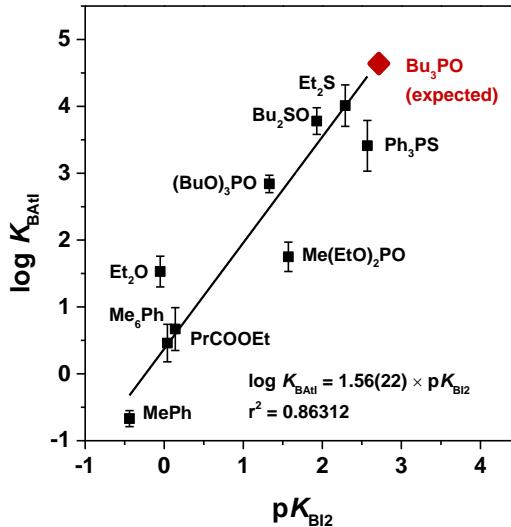
Methodology

- Lewis base: tri-n-butylphosphine oxide (Bu_3PO)

Nucleophilic region

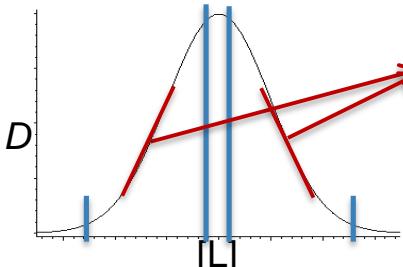


$$\log K_{\text{BAtl}} = 4.29 \text{ expected}$$



- Method: liquid/liquid competition

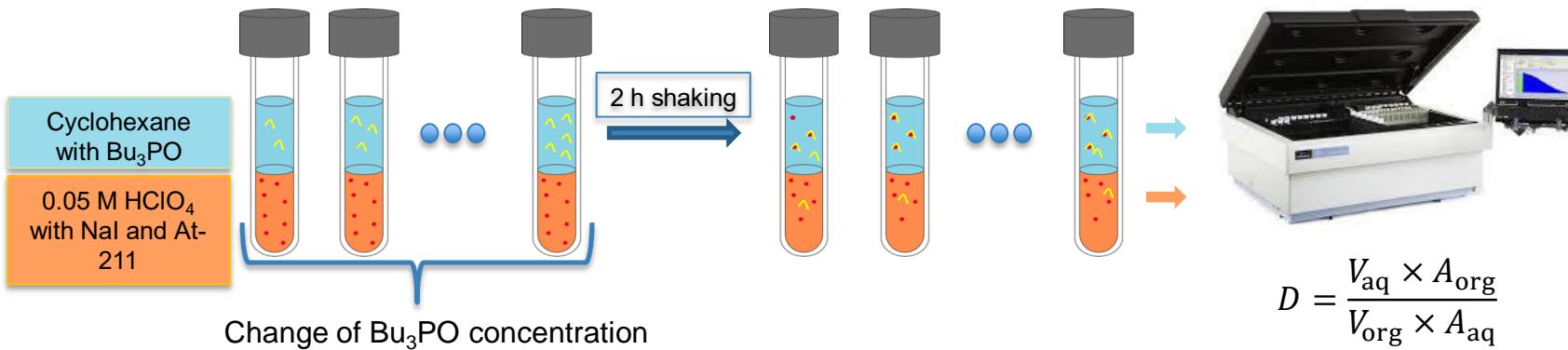
- Principle: change of distribution coefficient of astatine (D) → change of astatine speciation



Information of the stoichiometry and the equilibrium constant

Experimental protocol

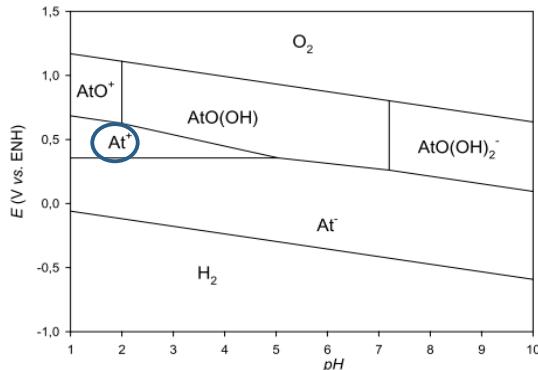
- Organic phase: Cyclohexane with changing concentration of Bu_3PO
- Aqueous phase: 0.05M HClO_4 , $[\text{NaI}]_{\text{fixed}} = 0.01 \text{ M}, 0.05 \text{ M}, 0.07\text{M}, 0.1\text{M}$ and 0.2 M and At-211



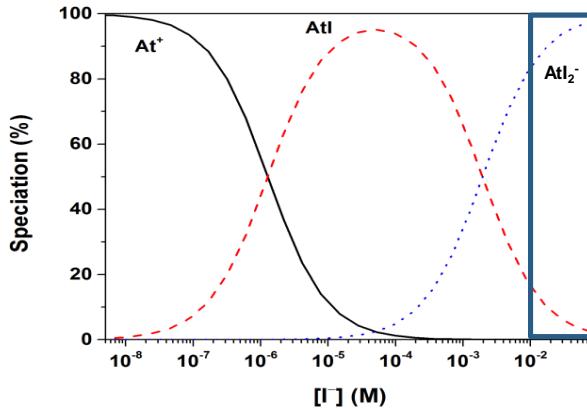
$$D = \frac{V_{\text{aq}} \times A_{\text{org}}}{V_{\text{org}} \times A_{\text{aq}}}$$

Experimental protocol

- Organic phase: Cyclohexane with changing concentration of Bu_3PO
- Aqueous phase: 0.05M HClO_4 , $[\text{NaI}]_{\text{fixed}} = 0.01 \text{ M}, 0.05 \text{ M}, 0.07\text{M}, 0.1\text{M}$ and 0.2 M and At-211
 $\rightarrow \text{pH}=1.35 \pm 0.1$, $E=0.55 \pm 0.05 \text{ vs. NHE}$

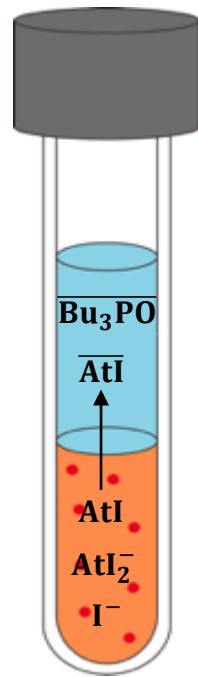


Pourbaix diagram of astatine in non-complexing aqueous medium ¹⁻³



Speciation of $\text{At}(+\text{I})$ in function of $[\text{I}^-]$ ⁴

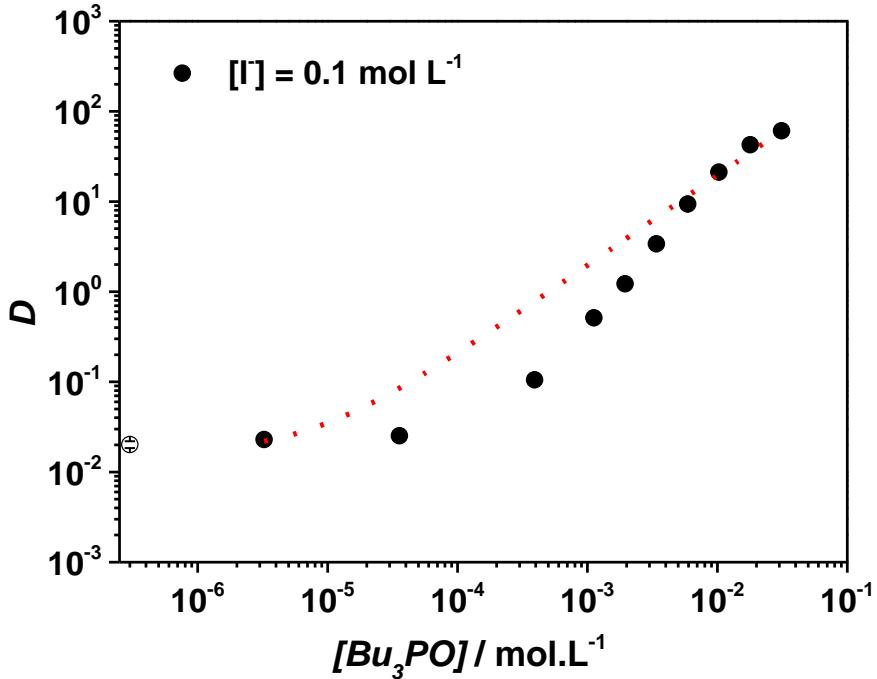
Only AtI is possible to interact with Bu_3PO in the organic phase



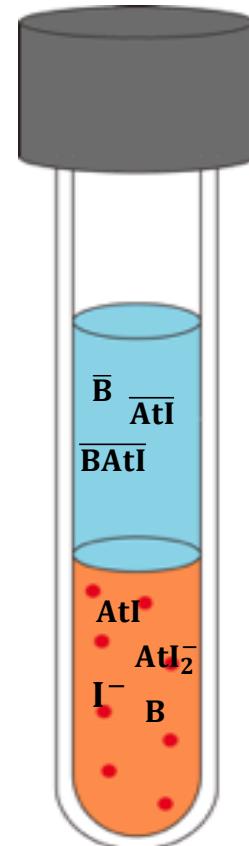
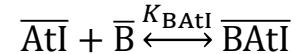
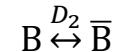
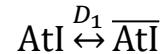
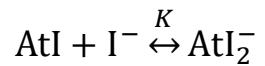
1. J. Champion *et al.*, *J. Phys. Chem. A*, **2010**, *114* (1), 576–582.
2. J. Champion *et al.*, *J. Phys. Chem. A*, **2013**, *117* (9), 1983–1990.
3. D. C. Sergentu *et al.*, *Chem. - A Eur. J.*, **2016**, *22* (9), 2964–2971.
4. N. Guo *et al.*, *Angew. Chemie - Int. Ed.*, **2016**, *55* (49), 15369–15372.

Model of experimental results

Take the example of $[I^-] = 0.1 \text{ M}$

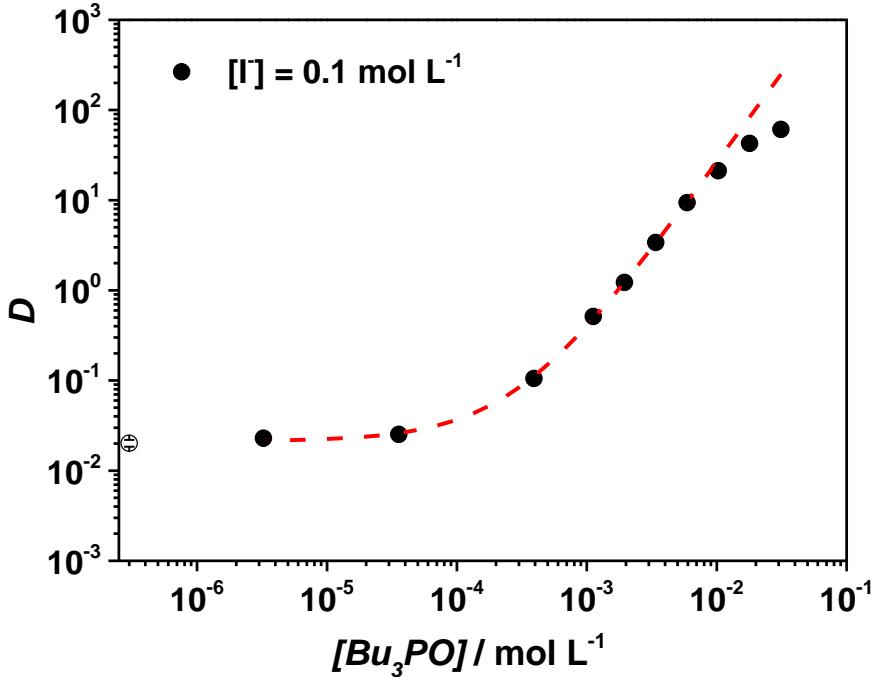


Model

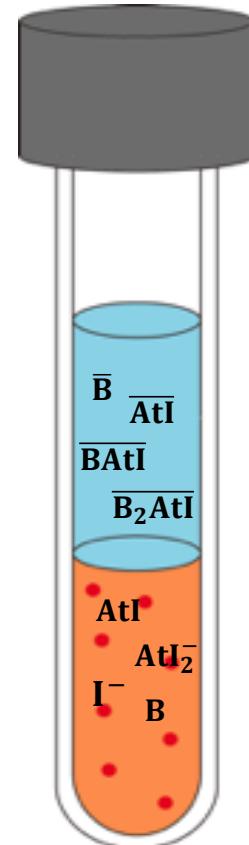
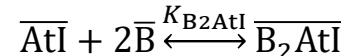
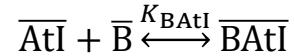
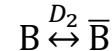
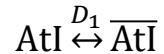
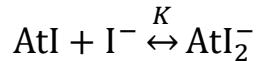


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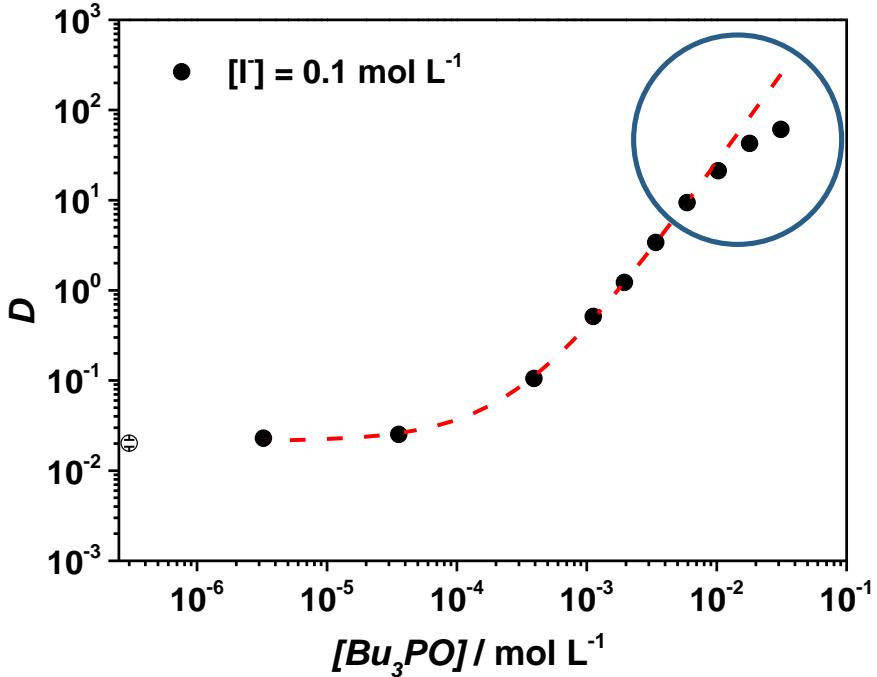


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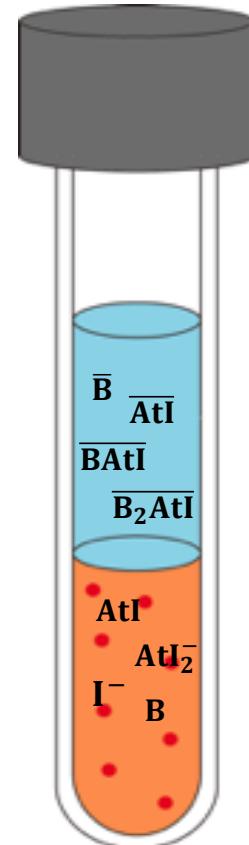
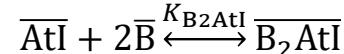
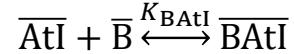
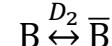
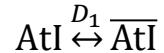
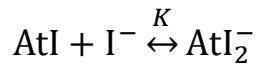


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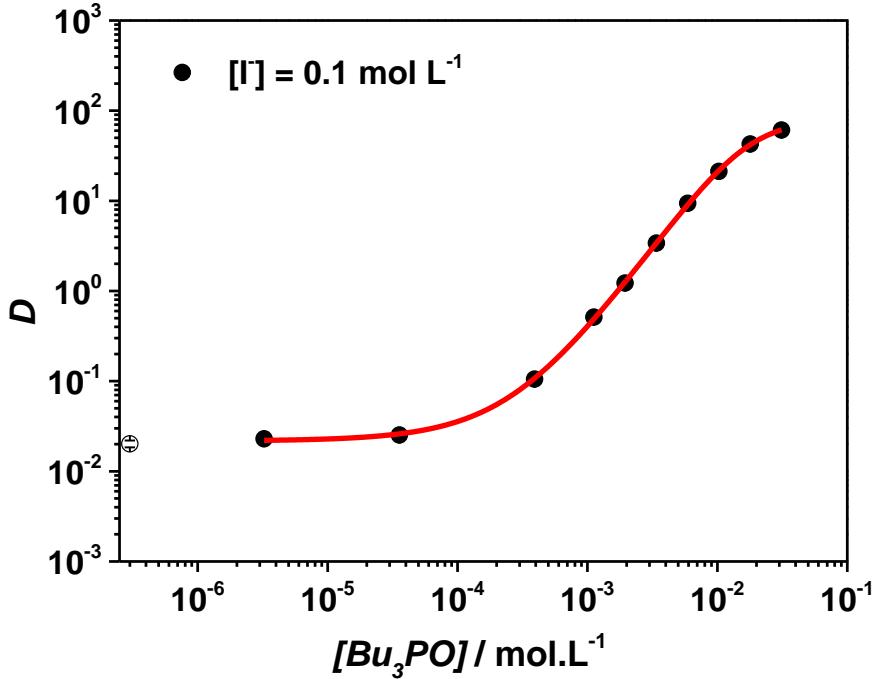


Model

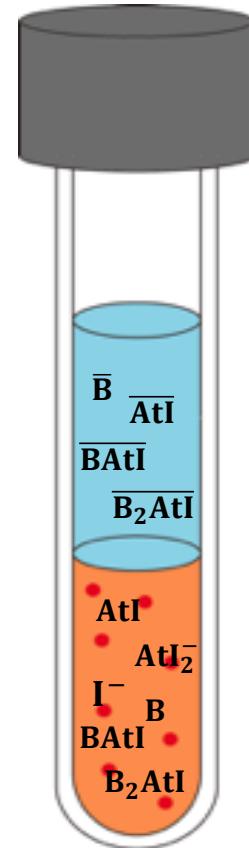
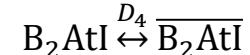
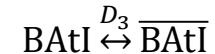
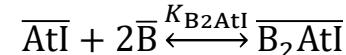
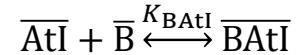
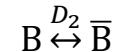
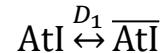
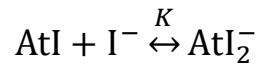


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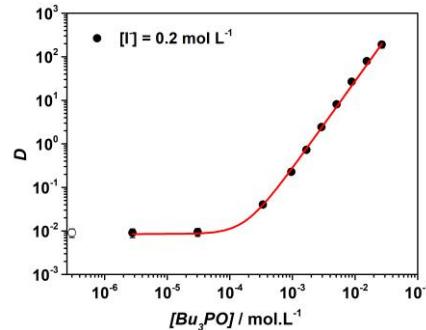
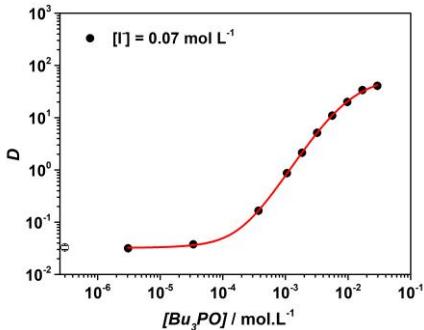
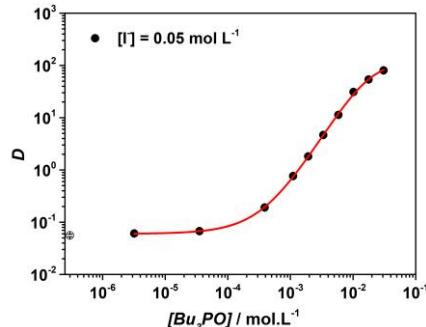
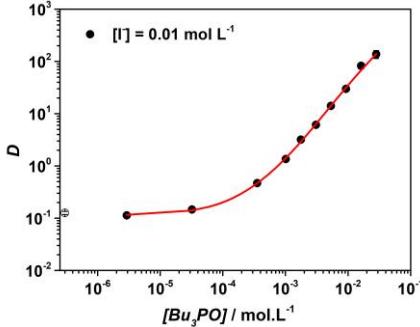


Model

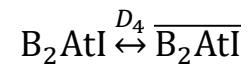
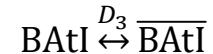
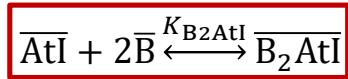
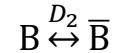
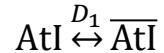
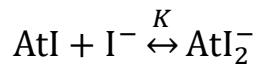


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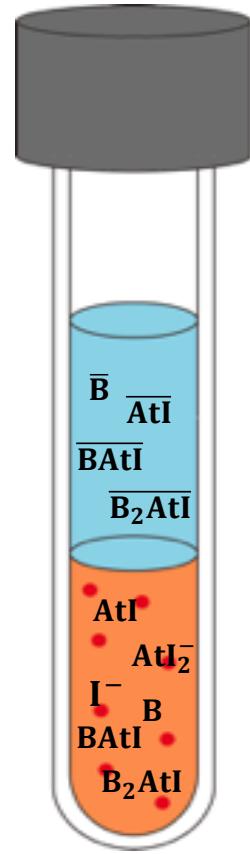


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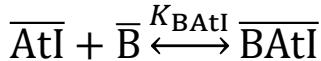


$$\log K_{\text{BAtI}} = 4.16 \pm 0.34$$

$$\log K_{\text{B}_2\text{AtI}} = 8.02 \pm 0.66$$



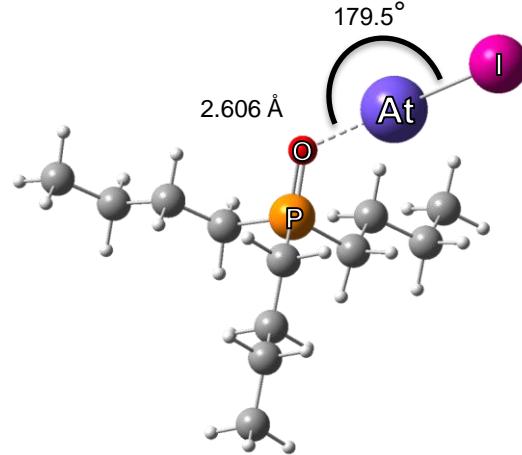
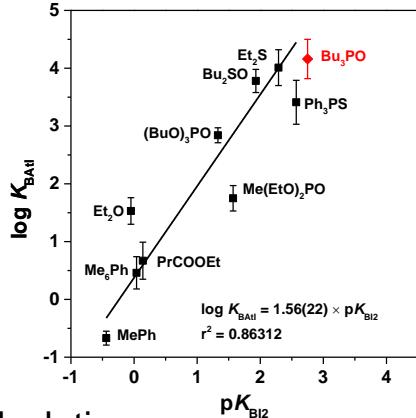
1:1 complex: a stronger halogen bond



$$\log K_{\text{BArI}} = 4.16 \pm 0.34$$

$\text{IAr} \cdots \text{B}$?

	$\log K_{\text{BArI}}$
Experimental	4.16 ± 0.34
dhf-SVPD-2c ¹	4.54
m-aug-cc-pVDZ-PP ¹	4.37



The most stable conformer of BAtI

- Good agreement with theoretical calculations
- Follow the tendency of previous study
- Nearly directional interaction in the calculated structure

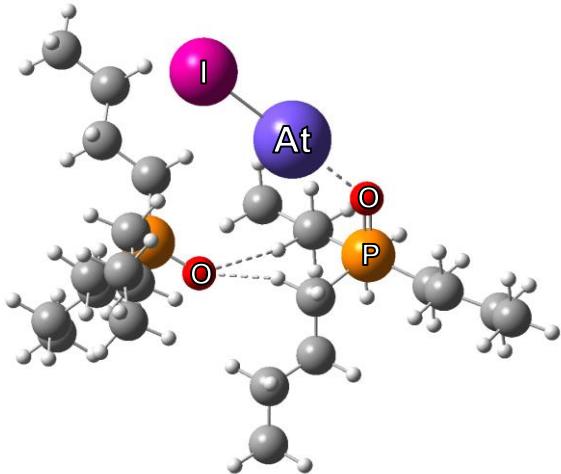
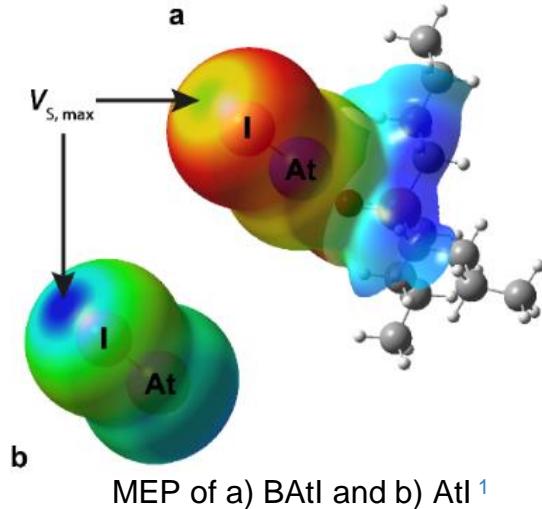
IAt \cdots B

A stronger halogen bond involving astatine than we found before

1. Two-component B3LYP calculations in conjunction with dhf-SVPD-2c and aug-cc-pVDZ-PP (AVDZ) basis set. By Nicolas Galland (CEISAM)

2. Calculated structures at the B3LYP/pVDZ level of theory for the most stable conformer species corresponding to the interaction between AtI and Bu_3PO . By Nicolas Galland (CEISAM)

1:2 complex: what it is ?



- Formation of a halogen bond deactivated the electrophilic site of iodine atom
- 2 hydrogen bonds between two Bu₃PO molecules in B₂AtI² **IAt ··· 2B**

1. Molecular electrostatic potential calculated at the B3LYP/AVDZ level of theory. By **Nicolas Galland (CEISAM)**

2. Calculated structures at the B3LYP/pVDZ level of theory for the most stable conformer species corresponding to the interaction between AtI and Bu₃PO. By **Nicolas Galland (CEISAM)**

Conclusions and perspectives

□ Conclusions

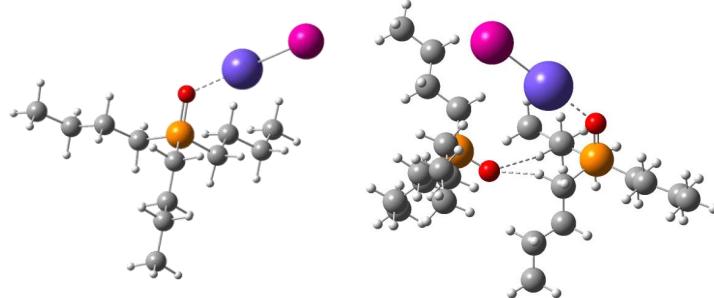
Two equilibria between AtI and Bu_3PO were evidenced

- $\text{AtI} + \bar{\text{B}} \xrightleftharpoons{K_{\text{BA}\text{tI}}} \text{BAtI}$, $\log K_{\text{BA}\text{tI}} = 4.16 \pm 0.34$
- A stronger halogen bond involving astatine
- $\text{AtI} + 2\bar{\text{B}} \xrightleftharpoons{K_{\text{B}_2\text{AtI}}} \text{B}_2\text{AtI}$, $\log K_{\text{B}_2\text{AtI}} = 8.02 \pm 0.66$

→ First 1:2 complex between AtI and Lewis base but **only one halogen bond** involved in

□ Perspectives

- Stronger halogen bond acceptors for AtI
- Possibility to form $\text{B} \cdots \text{AtI} \cdots \text{B}$ complex with Lewis base
- Interaction between AtX and Lewis bases with $\text{X} = \text{Br}$ or Cl





Ning Guo



Rémi Maurice



Gilles Montavon



Julie Champion



Nicolas Galland



Jérôme Graton

Thanks for your attention!