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Consequences of radioiodine transmutation on the capture capabilities of graphite

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Nuclear Disaster Scenario

- ^{131}I is released during nuclear accidents
 - Generated from ^{235}U fission
 - β^- emitter with 8 days of half-life which poses significant danger of thyroid cancer (public health concern)

From M. J. Truex, *et al.* PNNL-24709 rev. 2, (2017)

Nuclear Disaster Scenario – ^{131}I Mitigation

❑ Mitigate ^{131}I release into the atmosphere

- Thought to be released as I_2 , CH_3I , HI , and/or HOI [1]
- Speciation of iodine is unclear
- Usually trapped with a sorbent such as activated carbon or metal-organic frameworks
- Trapped ^{131}I reduce risk for human contamination and incorporation

❑ Goal: model the consequences of ^{131}I radioactive decay in molecules

- Investigated of several radioiodine-bound species: I_2 , CH_3I , HI , HOI , HIO_2 , and HIO_3
- Used *ab initio* molecular dynamic simulations to determine threshold energy required to break bonds in molecules in gas phase and adsorbed on graphite (surrogate for activated carbon)

Processes Involved in ^{131}I Beta-Decay

1. Transmutation ($^{131}\text{I} \rightarrow ^{131}\text{Xe}$)
2. Emission of beta-particle (ionization: $^{131}\text{I} \rightarrow ^{131}\text{Xe}^+$)
3. $^{131}\text{Xe}^+$ daughter recoil (up to ~ 6 eV)

Consequences of Radiolytic Transmutation

□ Gas phase

▪ Transmutation in I_2

Radioactive I_2 molecule

Radiogenic $[IXe]^+$ molecular ion

▪ Transmutation in CH_3I

- Fragmentation doesn't occur for $[CH_3Xe]^+$
- Fragmentation does occur for doubly ionized $[CH_3Xe]^{++}$
- Depending on ^{131}Xe recoil direction bond breaking occurs for 1-4 eV of kinetic energy

- Depending on ^{131}Xe recoil direction bond breaking occurs for 2-4 eV of kinetic energy

Consequences of Radiolytic Transmutation

□ Gas phase

- Simulations of recoil in HI and HIO found not fragmentations for 6 eV recoil in any directions
- Transmutation in HIO₂

- Transmutation in HIO₃

Consequences of Radiolytic Transmutation

❑ Adsorbed on graphite

^{131}Xe recoil of 4 eV toward graphite surface

End-products from transmutation in H_2O

- All molecules are easier to fragment on graphite surface compared to gas phase (recoil energy < 1 eV)
- Due to distant interactions with graphite, I and Xe fragments are likely to freely diffuse on surface (or desorb)
- Molecular fragmentations involving $\text{OH}\cdot$ and $\text{CH}_3\cdot$ radicals from dissociation of XeHO , XeHO_2 , XeHO_3 , and XeCH_3 have the possibility to form covalent bond with substrate
- Overtime, potential to reduce the number of adsorption sites available

Consequences of Radiolytic Transmutation

□ Bader charges

Species	Products	δq^* (e-)	
		Gas phase	Surface
I ₂	Xe	0.36	0.01
	I	0.64	-0.36 (1.35 in substrate)
HI	Xe	0.75	0.01
	H	0.25	0.01 (0.98 in substrate)
HIO	Xe	1.07	0.01
	OH	-0.07	-0.42 (1.41 in substrate)
HIO ₂	XeO	0.76	-0.01
	OH	0.24	-0.45 (1.46 in substrate)
	Xe	0.43	0.01
	HO ₂	0.57	-0.06 (1.05 in substrate)

Species	Products	δq^* (e-)	
		Gas phase	Surface
HIO ₃	XeO ₂	0.76	-0.41
	OH	0.24	-0.41 (1.82 in substrate)
	Xe	0.34	0.01
	O ₂	0.47	-0.03
	OH	0.19	-0.45 (1.47 in substrate)
	XeO	0.59	-0.02
CH ₃ I	HO ₂	0.41	-0.02 (1.04 in substrate)
	Xe	0.57	0.00
	CH ₃	0.43	0.03 (0.97 in substrate)
	Xe	1.00	0.01
	CH ₃	1.00	0.02 (1.98 in substrate)

*Based on charges: H(1e-), Xe(8e-), I(7e-),
O(6e-), C(4e-). $\delta > 0$: less e-. $\delta < 0$: more e-.

Consequences of Radiolytic Transmutation

❑ Fragmentation energetics

Species	Products	Gas phase (eV)	Surface (eV)
I ₂	Xe+I	0.48	-1.16
HI	Xe+H	No Frag.	-1.38
HIO	Xe+OH	No Frag.	-1.82
HIO ₂	XeO+OH	1.17	-1.52
	Xe+HO ₂	-2.73	-4.45
HIO ₃	XeO+HO ₂	-2.54	-3.82
	XeO ₂ +OH	0.71	-2.19
	Xe+O ₂ +OH	-1.55	-5.72
CH ₃ I	Xe+CH ₃	1.44	-1.80
	[Xe+CH ₃] ⁺	-2.17	-1.13

- Product fragments formed at the graphite surface are more favorable than in gas phase. This suggests that the fragments are very reactive in gas phase.
- There is a thermodynamic driving force favoring the formation of HO₂ either in gas phase or adsorbed on graphite.
- For HIO₃, a reaction competitive to the production of HO₂ could involve the formation of O₂.

Conclusions

- ❑ **Radioiodine transmutation has the potential to fragment molecules**
 - AIMD simulations can identify the possible types of fragments
- ❑ **Gas phase molecular species are harder to fragment**
 - HIO_x recoil > 4 eV
 - I_2 is the easiest to fragment (recoil > 2 eV)
 - The fragmentation of Methyl-Iodine (CH_3I) happens only when additional ionizations occur
- ❑ **Gas phase results can provide useful information for atmospheric measurements**
 - Identified fragments can offer new chemical routes to consider in chemical kinetic models
- ❑ **Graphite surface facilitates molecular fragmentation**
 - Recoils less than 1 eV are sufficient to break bonds
 - The positive charge of the molecule is delocalized in the substrate, facilitating bond breaking
- ❑ **Production of reactive fragments at surface can affect adsorption capabilities of sorbents**
 - OH and CH_3 molecular fragments can form covalent bonds with the substrate

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