Ion chemistry of metals in the gas phase: From catalysis to chemi-ionization

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Shaun Ard
Research Physicist
Boston College ISR
Air Force Research Laboratory
Space Vehicles Directorate

Integrity ★ Service ★ Excellence
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AFRL Plasma Chemistry Group

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Overview

1) Fundamental studies of metal ion kinetics

- Experiment
  - T dependences as probe of PES
- Ab initio Calculations
  - Calculation of stationary points
- Statistical Modeling
  - Energetics and mechanistic insight

2) Chemical releases in the ionosphere
   - Analysis of samarium releases
   - Efforts to guide future releases
The Plasma Chemistry group studies the kinetics of charged species

Why does the AF care about ion chemistry?

The AF cares about communications

Communications greatly impacted by Total Electron Content (TEC)

TEC highly dependent on ion chemistry

⇒ The AF cares about plasma chemistry!
Charged Species in the Atmosphere

Ambient and Modified Atmospheric Ion Chemistry: From Top to Bottom
New Directions: Metal Ion Chemistry

Ionospheric Chemistry
- ~2000 MT of meteoric material deposited daily, much of it metallic.
- Metal chemistry can have an outsized effect on the ionosphere.

Fuel Production
- ~7.5 Billion dollars spent annually on jet fuel.
- AF goal of 50/50 blend of alternative jet fuel.
- Metal chemistry figures prominently in solar and biofuel catalysts.

Cluster Chemistry
- Clusters display many properties unique from atomic or bulk phases.
- Kinetics will help characterize and utilize unique characteristics.
Variable Temperature Selected Ion Flow Tube VT- SIFT

Source Gas

Electron Impact Source

Reactant Gas Inlets

Venturi Inlet
Reaction Barriers

\[ A + BC \rightarrow A + B + C \]

- Positive T dependence

\[ e^{-E_a/kT} \]

- Arrhenius behavior (Positive T dep)
- Can fit T dep to find barrier height
Arrhenius Behavior

Arrhenius behavior is typically observed with $E_a \sim 1 \text{ kJ/mol}$. However, in SIFT, this behavior is not usually observed:

- Temperature range 100-700K
- Only reactions with $E_a \leq 10 \text{ kJ/mol}$ will react enough to be seen, $k > 1 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$.
Submerged Barrier

Loose Entrance Channel (lots of available states)

Tight Transition State (only specific states available)

At higher T, reverse reaction wins out \( \rightarrow \) Negative T dependence

Long-lived complex

Stabilized complex
What Do We Learn?

- Temperature dependence of catalytic cycles towards improved effectiveness and efficiency.

- Rate data gives information on the rate limiting step, branching data give relative product info.
Role of Spin in Kinetics

Adiabatic Principle

“A physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum.”

Born-Oppenheimer

\[ \psi_{\text{total}} = \psi_{\text{electronic}} \times \psi_{\text{nuclear}} \]

Spin is Conserved in Complex-Forming Reactions

Or Is It?
Spin Forbidden Reactions

- Many metal ion reactions involve reactants and products of differing ground spin states.
- Spin appears conserved in some cases resulting in low reactivity, while in other cases it is not, resulting highly efficient reactivity.

$$ P = \left(1 + e^{-\frac{\pi\epsilon}{4}}\right)\left(1 - e^{-\frac{\pi\epsilon}{4}}\right), $$

$$ \epsilon = 8 \frac{|\langle \Psi_{HS} | \hat{H}_{SO} | \Psi_{LS} \rangle|^2}{\hbar \sum_{\alpha} g_{\alpha}^* \nu_{\alpha}} $$

- Theoretical treatments such as the Landau-Zener formulism are not currently tractable as calculations remain challenging for metal systems.
Spin Catalyzed Reactions

- Formally spin-allowed, these reactions have excited states which allow a lower energy path to products.
- Two-State Reactivity, as it has been dubbed, has been found to play a role in a wide range of reactions, such as C-H and C-C activation by atomic metal ions hydroxylation and epoxidation by the protein cytochrome P-450.

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3\text{OH} \\
\end{align*}
\]
Modeling Approach

Calculate \textit{ab initio} surface CCSD(T)-F12/AVTZ

Statistical modeling
- Vary energies of rate limiting TS

Exp. rate constants and branching

Vibrational and rotational frequencies
FeO$^+$ + H$_2$

- Model captures the T-dependence over a wide energy range including the isotopic effects.
- Initial spin crossing effective: i.e. takes place on a faster time scale than the rate limiting quartet TS.

Further Insight into the Reaction FeO$^+$ + H$_2$ → Fe$^+$ + H$_2$O: Temperature Dependent Kinetics, Isotope Effects, and Statistical Modeling

Excited State Production

• While the reactant well crossing was effective, the product well crosses with near zero effectiveness producing excited state products.
• Recent trajectory calculations by Jeremy Harvey confirm these results.
To Cross Or Not to Cross

Effective crossing
\( \tau_{\text{crossing}} < \tau_{\text{adiabatic}} \)

Spin Allowed
- \( ^6\text{FeO}^+ + \text{H}_2 \) (Ent well)
- \( ^6\text{FeO}^+ + \text{CH}_4 \) (Ent well)
- \( ^6\text{FeO}^+ + \text{CO} \) (Ent well)
- \( ^6\text{Fe}^+ + \text{CH}_3\text{I} \) (Ent & Prod well)
- \( ^6\text{Fe}^+ + \text{CH}_3\text{Cl} \) (Ent & Prod well)
- \( ^6\text{Fe}^+ + \text{CH}_3\text{Br} \) (Ent & Prod well)
- \( ^4\text{Ti}^+ + \text{O}_2 \)

Spin Forbidden
- \( ^6\text{Fe}^+ + \text{CH}_3\text{OCH}_3 \)
- \( ^4\text{NiO}^+ + \text{CH}_4 \)
- \( ^4\text{Ti}^+ + \text{N}_2\text{O} \)
- \( ^4\text{Ti}^+ + \text{CH}_3\text{OH} \)

Ineffective crossing
\( \tau_{\text{crossing}} > \tau_{\text{adiabatic}} \)

- \( ^6\text{FeO}^+ + \text{H}_2 \) (Prod well)
- \( ^6\text{FeO}^+ + \text{CH}_4 \) (Prod well)

Competitive crossing
\( \tau_{\text{crossing}} \sim \tau_{\text{adiabatic}} \)

- \( ^6\text{Fe}^+ + \text{N}_2\text{O} \) (Ent well)
- \( ^4\text{Ti}^+ + \text{CO}_2 \)


Reactivity from excited state (FeO+):Fe+ + CO sampled through reaction of ground state (FeCO+)Fe+ + N2O. J. Chem. Phys. (2016) 144(23).


Conclusions

- Combined experimental, computational, and statistical approach offers unique insight into reaction dynamics
  - Derived energetics of transition states and intermediates offer computational benchmarks.
  - Gives mechanistic insight, such as the adiabatic or non-adiabatic nature of spin crossings in TSR.
- TSR is Complex!
  - Data on a wider variety of systems is needed to build upon the simple current models to a quantified understanding.
- Detailed Calculations of crossing seams and SOC are greatly needed!
Active Ionospheric Modification
Artificial Ionosphere Efforts

Photo-ionization
- Low IP atomic species (Ba, Cs, Sr, Li,) produce an ion cloud with clear optical signature
- Limited to daytime use

HAARP
- High Frequency Active Auroral Research Program
- Employed high power high frequency waves to produce enhanced densities from excited electron impact
- Requires large non-mobile facility

Chemionization
- Also called associative ionization
- \( M + O \rightarrow MO^+ + e^- \) (M= most lanthanides and a few transition metals)
- Poorly characterized chemistry
Samarium Release Experiments

A few kg of metal, vaporized, ionized, and dispersed, predicted to create “enhanced” ionosphere over areas up to 100 km.

Quickly Reacts with Ambient Oxygen
And Spontaneously Ionizes
To form dense long-lived plasma

Expelled Metal Vapor

Expelled Oxygen

Actual burst-disc release canister
Overview of Field Experiments

- Two sounding rocket experiments: MOSC (Kwajalein, March 2013); AIC (White Sands, Feb 2015); Future launch (PRECISE) in planning stages
- Both campaigns successful! Ionization unambiguously observed, but only ~10% of predicted electron density
Sm$^+$ and SmO$^+$ chemistry

Selected Ion Flow Tube Apparatus (AFRL)

Measured ($ T \geq 300k$):

- $\text{Sm}^+ + O_2 \rightarrow \text{SmO}^+ + O$
  \[ k(300) = 2.8 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \quad k \propto T^{-1} \]
- $\text{Sm}^+ + N_2O \rightarrow \text{SmO}^+ + N_2$
  \[ k(300) = 1.3 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \quad k \propto T^{-4} \]
- $\text{Sm}^+ + \text{NO} \rightarrow \text{No Rxn}$
- $\text{Sm}^+ + \text{C}_2\text{H}_4 \rightarrow \text{No Rxn}$
- $\text{Sm}^+ + \text{CO}_2 \rightarrow \text{No Rxn}$
- $\text{Sm}^+ + \text{SO}_2 \rightarrow \text{SmO}^+ + \text{SO}$
  \[ k(300) = 4 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \quad k \propto T^{-6} \]
- $\text{Sm}^+ + \text{NO}_2 \rightarrow \text{SmO}^+ + \text{NO}$
  \[ k(300) = 6 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \quad k \propto T^{-6} \]
- $\text{SmO}^+ + \text{O}_2 \rightarrow \text{No Rxn}$

$\text{SmO}_2^+$ + e would be an electron sink

SmO$^+$ + N$_2$O + He → SmO(N$_2$O)$^+$ + He
  \[ k_{\text{ter}} = (1.2 \times 10^{-28} \text{ cm}^6\text{s}^{-1}) \]
- SmO$^+$ + SO$_2$ + He → SmO(SO$_2$)$^+$ + He
  \[ k_{\text{ter}} = (1.2 \times 10^{-27} \text{ cm}^6\text{s}^{-1}) \]
- SmO$^+$ + CO$_2$ + He → SmO(CO$_2$)$^+$ + He
  \[ k_{\text{ter}} = (1.1 \times 10^{-28} \text{ cm}^6\text{s}^{-1}) \]
- SmO$^+$ + NO$_2$ + He → SmO(NO$_2$)$^+$ + He
  \[ k_{\text{ter}} = (2.1 \times 10^{-27} \text{ cm}^6\text{s}^{-1}) \]

Implies BDE(\text{SmO}^+) > BDE(\text{SO}_2) = 5.71 eV
Thermochemistry in Doubt

\[ \text{Sm} + \text{O} \rightarrow \text{SmO}^+ + \text{e}^- \quad -\Delta H_{\text{RXN}} = -0.08 \pm 0.07 \text{ eV} \]

Old = -0.35 eV
SmO⁺ Dissociative Recombination

Could SmO⁺ + e → Sm + O be limiting electron density?

- Dissociative recombination is typically a very fast process ($k > 10^{-7}$ cm$^3$ s$^{-1}$)
- Endothermic DR has never been studied
- Estimate of equilibrium constant suggests $k_{DR} \approx 10^3 x k_{chemi-ionization}$ at 1000 K; resulting equilibrium correct order of magnitude to limit $e^-$ density to that observed.
- Can also explain observed red/blue separation in cloud
- Experiments on endothermic DR planned (Cryogenic Storage Ring in Heidelberg) within the year
Most of the rare earth metals have energetics analogous to Sm, but even more favorable!

However, vapor pressure is anti-correlated with chemi-ionization exothermicity.
Chemi-ionization Kinetics

Flow tube
7 cm diameter, 1m long, multiple inlets, temperature variable 100 – 700 K

Signal out
-4 kV

Mass spectrometer
Quadrupole mass filter; in-line detector comprising conversion dynode and Channeltron

Metal atom source
Ar ‘bubbling’ through metal chips in a clamshell oven (up to 1500 K); vapor is entrained in He flow upon exit

O atom source
Standard technique of titrating NO with N (from discharge of N₂)

Distribution A: Cleared for public release; distribution unlimited
Kinetics Data and Results

Chemi-ionization rate constants w/ O

- 5 of 6 systems studied proceed at or near the hard sphere collisional value, increasing as $T^{1/2}$ (as does the collisional rate)

- Sm is an outlier
- Is Sm reactivity state dependent?
P Dependence

- Sm chemi-ionization shows a large P dependence.
- Consistent with excited states being primarily responsible for observed reactivity.
Alternative Release Mechanisms

Burst canister used in MOSC experiment

- Vaporizing pure metal requires a lot of energy
- Mass of thermite required ~2x mass of active material
- Cylinder must withstand high pressure; adds weight
- Ground tests indicate incomplete vaporization

Instead of pure metal, use a compound containing ligands weakly bound to a metal core atom

\[
\begin{align*}
\text{Ln} - \text{R} \\
\text{R} \rightarrow \text{R}
\end{align*}
\]

Decomposition to the bare metal can occur at ambient thermosphere temperatures

- Reduces weight of inactive material
- No high energy material to be transported
- No pressure rating for the vessel required
- Allows for metered release (important for cloud shaping to optimize efficiency of active material)
- But need to ensure carrier material does not inadvertently destroy desired plasma
- Compounds with similar properties are developed for chemical vapor deposition \(\rightarrow\) established community exists that can tailor compounds to meet these requirements
Conclusions

• Progress made towards improving modeling of chemical release experiments and towards identifying ideal candidates for future releases

• Samarium reactivity is unique among studied species; appears to be electronic state-dependent

• Further studies of kinetics and determination of emission spectra for candidate species will be beneficial

• Alternative oxidizers are unlikely to be practical

• Efficiency of the release mechanism may be significantly improved
Questions?