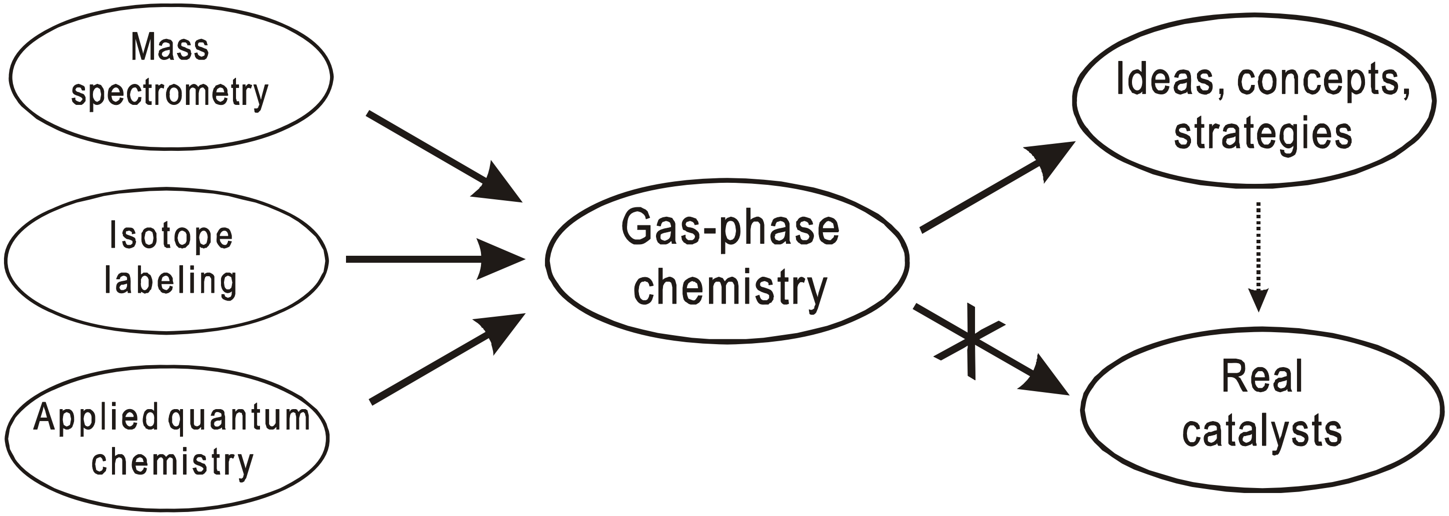
Atomistic models of megaton processes

Or: Using mass spectrometers as chemical laboratories



⇒ Reactivity concepts for model systems

Challenges in selective oxidation

☞ **Methane oxidation** $CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH$

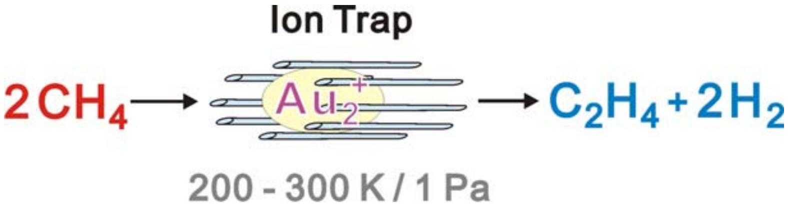
Well-developed, stepwise process

$CH_4 \rightarrow CO/H_2 \rightarrow CH_3OH$

Only economic in large scale

What about "small" sources?

- ☞ **Methane coupling** $2\ CH_4 + O_2 \rightarrow C_2H_4 + 2\ H_2O$



- ☞ **Epoxidation** $C_2H_4 + ½\ O_2 \rightarrow c\text{-}C_2H_4O$

"atom economic"

Key objectives

☞ ***Combustion to be avoided!***

- Principles of C-H bond activation ⇒ basic understanding
- Follow-up reactions ⇒ prevention of overoxidation
- Reactivity/selectivity dilemma ⇒ practical realization
- Spin- and stoichiometry problems ⇒ re-oxidation with O_2

Selective Activation of Alkanes by Gas-Phase Metal Ions
J. Roithová, D. Schröder, *Chem. Rev.* **2010**, *110*, 1170

Overview

⇒ **I. Principles (Example: BMA process)**
Ion/molecule reactions in FTICR-MS
Kinetics & thermochemistry
ab initio studies

⇒ **II. Partial oxidation of methane**
Mononuclear systems
Metal-oxide clusters

⇒ **III. Epoxidation of olefins**
Conceptual problem
Classical methods and uses of epoxides
Contact process

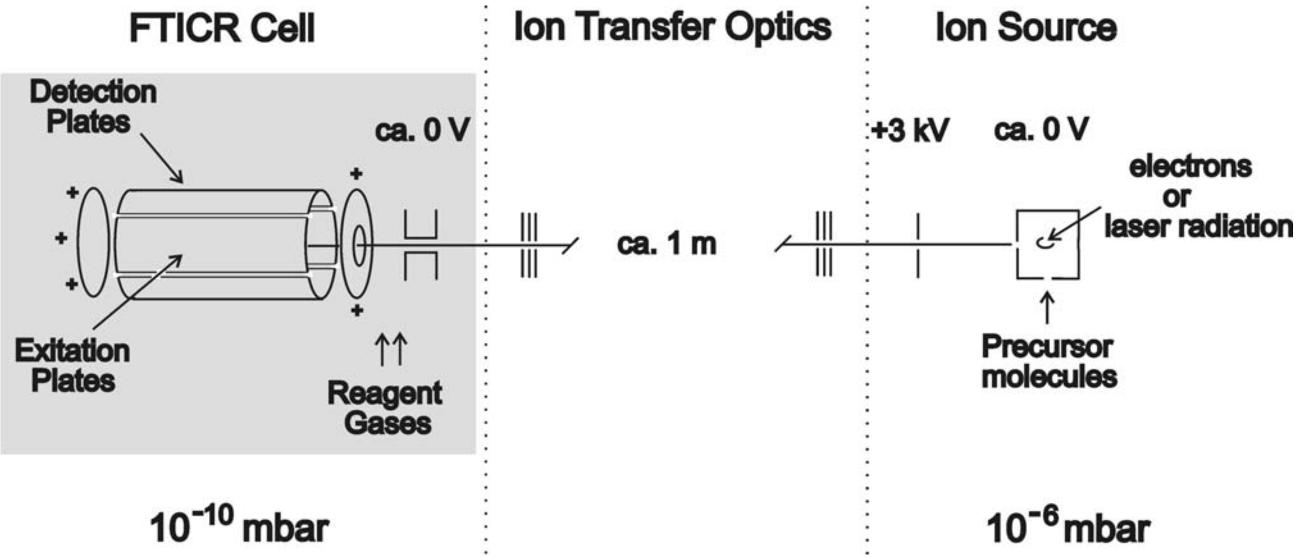
⇒ **IV. Conclusions**

I. Measuring procedure - Example: BMA process

BMA: *Blausäure aus Methan und Ammoniak* [DEGUSSA- and ANDRUSSOW processes]

$$CH_4 + NH_3 \rightarrow HCN + 3\,H_2 \quad \textit{(endothermic)}$$

Fourier-transform ion cyclotron-resonance (FTICR) mass spectrometry
i.e. storage of ions in electromagnetic fields



Procedure

1. Ion generation	here: LD/LI of platinum
2. Transfer to the ICR cell and isolation	here: $^{195}Pt^+$
3. Thermalization	here: collisions with argon
4. Gas pulse for the generation of reactants	here: $Pt^+ + CH_4 \rightarrow PtCH_2^+ + H_2$
5. Isolation of the reactant ion	here: $^{195}PtCH_2^+$
6. Reaction with a neutral gas	here: ammonia
7. Detection and data processing	here: mass spectra

➦ **Intensitities as a function of reaction time** ☞ **Kinetics**

A. Reaction kinetics

Primary reactions in the $Pt^+/CH_4/NH_3$ system

$Pt^+ + CH_4 \rightarrow PtCH_2^+ + H_2$ $k_{CH_4} = 8.2 \cdot 10^{-10}\ cm^3\ s^{-1}$

$Pt^+ + NH_3 \rightarrow Pt(NH_3)^+$ $k_{NH_3} = 5.0 \cdot 10^{-13}\ cm^3\ s^{-1}$

➪ Pt^+ is selective for methane, $S > 99.9\%$ (in UHV)

$PtCH_2^+ + CH_4 \rightarrow PtC_2H_4^+ + H_2$ $k_{CH_4} = 0.9 \cdot 10^{-10}\ cm^3\ s^{-1}$

$PtCH_2^+ + NH_3 \rightarrow PtCH + NH_4^+$ $k_{NH_3} = 0.3 \cdot 10^{-10}\ cm^3\ s^{-1}$

$\rightarrow PtH + CH_2NH_2^+$ $k_{NH_3} = 4.3 \cdot 10^{-10}\ cm^3\ s^{-1}$

$\rightarrow PtCHNH_2^+ + H_2$ $k_{NH_3} = 1.6 \cdot 10^{-10}\ cm^3\ s^{-1}$

➪ $PtCH_2^+$ is selective for ammonia, $S_{C\text{-}N} > 80\%$ (1:1 mixture)

(*Angew. Chem.* **1994**, *106*, 1232 & *Angew. Chem.* **1998**, *110*, 858)

B. Subsequent reactions

Collision-induced dissociation: Dehydrogenation

$PtCHNH_2^+ + E \rightarrow PtCNH^+ + H_2$ then: $PtCNH^+ + E \rightarrow Pt^+ + HCN$

similarly: $PtCDNH_2^+ \rightarrow PtCNH^+ + HD$

Formation of aminocarbene complexes

$PtCH_2^+ + NH_3 \rightarrow PtCHNH_2^+ + H_2$

$PtCHNH_2^+ + NH_3 \rightarrow PtC(NH_2)_2^+ + H_2$

similarly: $PtCD_2^+ \rightarrow \rightarrow PtC(NH_2)_2^+$

Formation of immonium ions

$PtCH_2^+ + NH_3 \rightarrow PtH + CH_2NH_2^+$

$CH_2NH_2^+ + NH_3 \rightarrow NH_4^+ + CH_2NH$

cf. *PA*(CH_2NH) = 203.8 kcal/mol vs. *PA*(NH_3) = 204.0 kcal/mol

similarly: $PtCD_2^+ \rightarrow CD_2NH_2^+ \rightarrow NH_4^+$

C. Comparison of different metals

☞ Model reaction: $MCH_2^+ + NH_3 \rightarrow$ Products

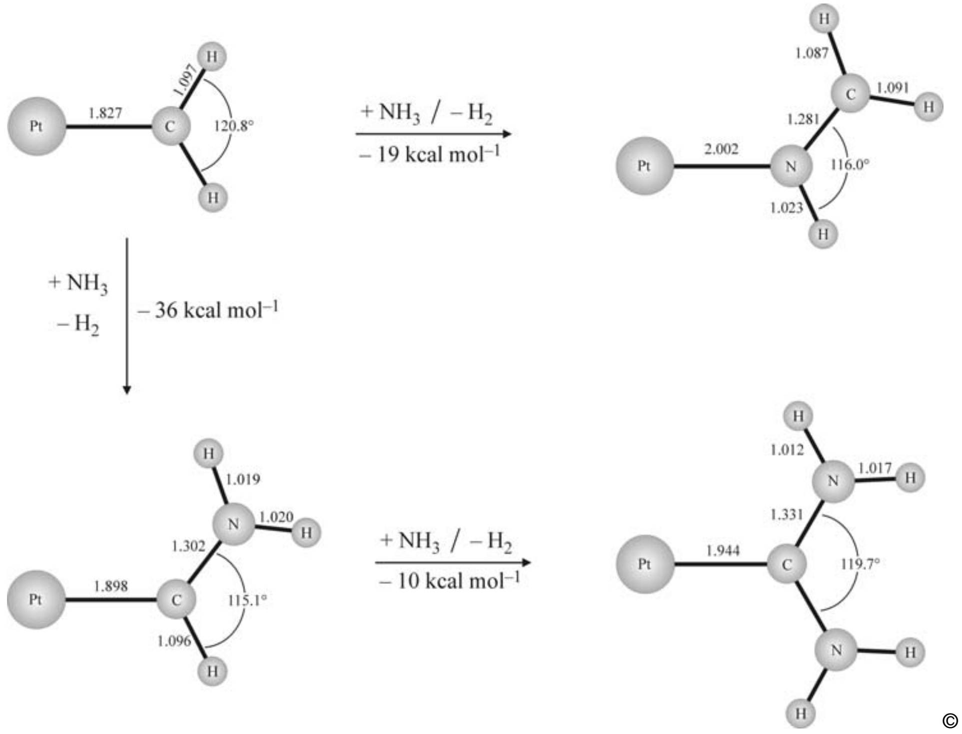
	k_r/k_c	NH_4^+	$CH_2NH_2^+$	CH_3NH_2	$MC(H)NH_2^+$	ϕ_{BMA}
$FeCH_2^+$	0.0		no reaction			0%
$CoCH_2^+$	0.0		no reaction			0%
$RhCH_2^+$	0.1			75	25	0%
$TaCH_2^+$	$0.5^{a,b}$			5	65	20%
WCH_2^+	0.1^{b}				100	10%
$OsCH_2^+$	0.2	45			55	20%
$IrCH_2^+$	0.4	60			40	40%
$PtCH_2^+$	**0.3**	**5**	**70**		**25**	**100%**
$AuCH_2^+$	0.6		**100**			0%

[a] In addition 30% metathesis to $TaNH^+ + CH_4$ [b] Pronounced oxide formation with background water

☞ Kinetic control of C–N-coupling

D. *Ab initio* studies

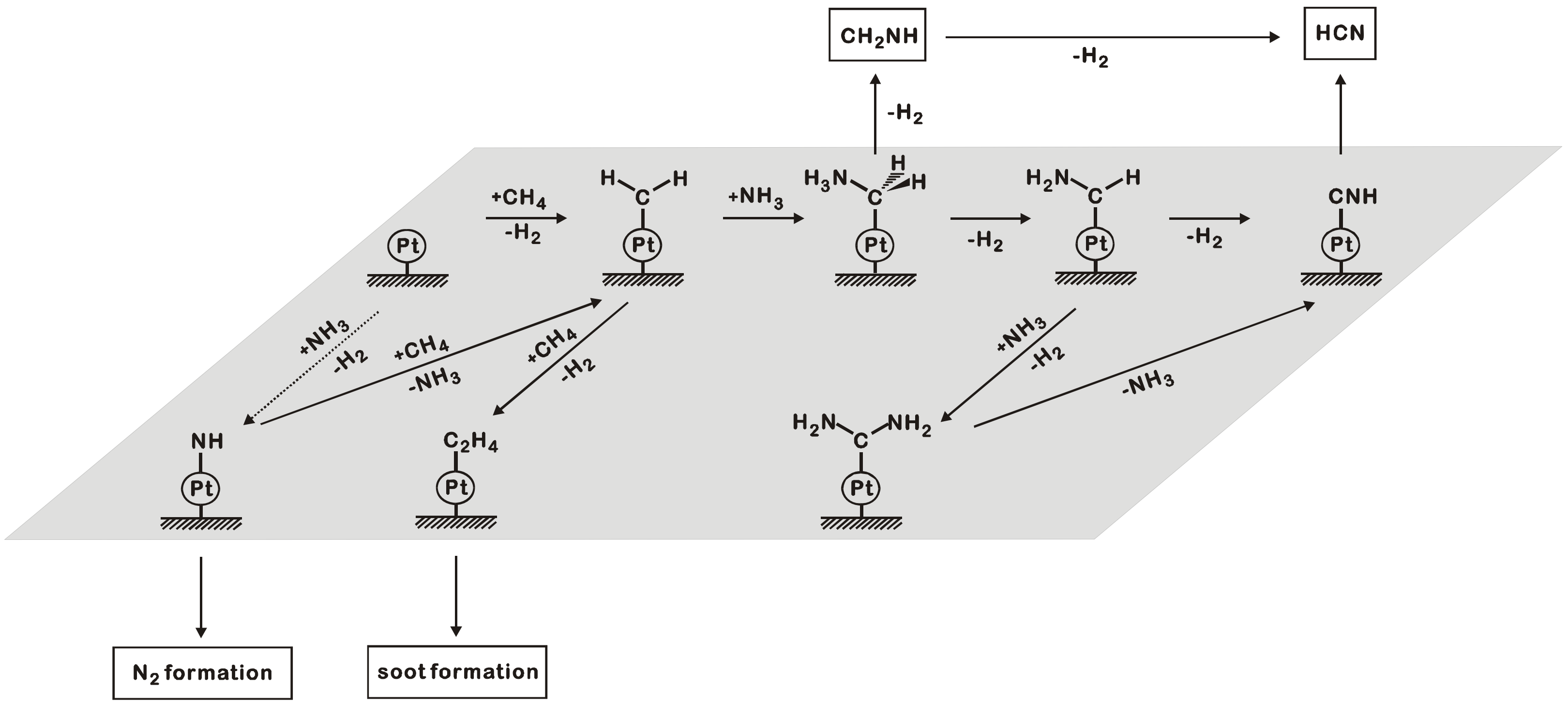
☞ Density functional theory (B3LYP)



☞ Formation of aminocarbene complexes

(*Angew. Chem.* **1998**, *110*, 858)

Result: Model for surface reaction



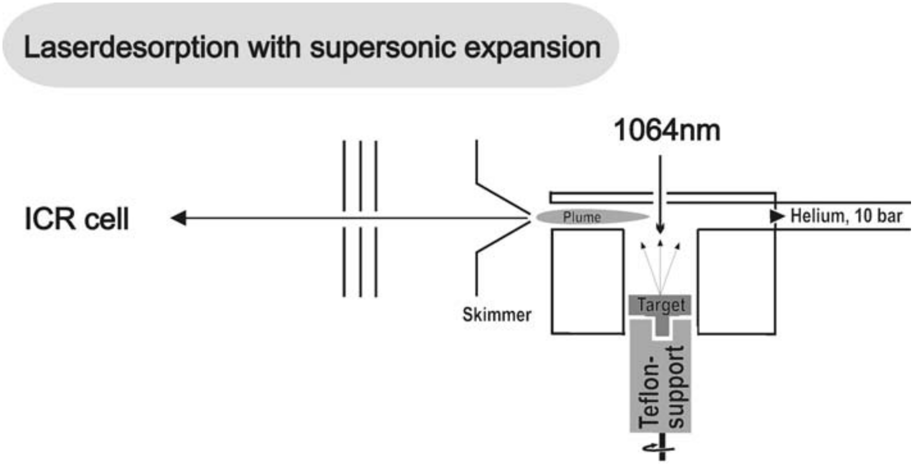
☞ Two separate pathways to HCN (proof in real BMA catalysis in 2004)

ANDRUSSOW: additional combustion of methane

(*J. Am. Chem. Soc.* **1999**, *121*, 10614)

Next step: Reactivity of cluster ions

Cluster source: Laservaporization according to *Smalley*



☛ Neutral and ionic clusters

- ♦ Cooling and aggregation in He-puls
- ♦ Fine tuning via pulse sequence, He-pressure, laser power etc.

1. Step: Activation of methane

$Pt_n^+ + CH_4 \rightarrow Pt_nCH_2^+ + H_2$

Rate constants (in 10^{-10} cm^{-3} s^{-1})

n =	1	2	3	4	5	6	7
	5.0	8.2	6.0	0.15	8.8	13[a]	11[a]

[a] U. Achatz et al. *Chem. Phys. Lett.* **2000**, *320*, 53

☞ Reactivity shows little dependence for cluster size

Pt_4^+ appears as an exception

2. Step: Activation of ammonia

$$Pt_{n}CH_2^+ + NH_3 \rightarrow [Pt_{n}CNH_3]^+ + H_2$$

Rate constants (in 10^{-10} cm^{-3} s^{-1})

n =	1	2	3	4	5
	1.6[a]	9.7	9.6	17	12

[a] A side reaction leads to $CH_2NH_2^+$ + PtH.

☞ Behavior similar to the monomer

Rates increase with cluster size

➢ ***More efficient C–N-coupling with clusters***

BUT:

Labeling $Pt_{n}CD_2^{+} + NH_3 \rightarrow [Pt_{n}CNH_3]^{+} + D_2$

CID $[Pt_{n}CNH_3]^{+} \rightarrow Pt_{n}C^{+} + NH_3$

Ionic products $[Pt_{n}CNH_3]^{+}$ consitute carbide complexes of the type $CPt_{n}(NH_3)^{+}$, rather than $Pt_{n}C(H)NH_2^{+}$ or $Pt_{n}(CH_2NH)^{+}$

☞ ***No C–N-coupling***

Negligible BMA-activity of Pt_n^{+}-clusters

NB: Importance of labeling studies

Possible solution: combination of two metals

- $PtAu^+$ instead of Pt_2^+

$AuCH_2^+$ rapidly reacts with NH_3, whereas methane is not activated at all by gaseous Au_n^+ ions

(*J. Am. Chem. Soc.* **1999**, *121*, 10614)

$$PtAu^+ + CH_4 \rightarrow PtAuCH_2^+ + H_2$$

$$PtAuCH_2^+ + NH_3 \rightarrow [PtAuCNH_3]^+ + H_2$$ (HD from $PtAuCD_2^+$)

$$[PtAuCNH_3]^+ \rightarrow [PtAuCNH]^+ + H_2$$

☞ ***C–N-coupling with a heterometallic cluster***
Correlation with Au-doped BMA catalysts

(*J. Am. Chem. Soc.* **2003**, *125*, 3676)

Further: Pt_n^+, $PtCu^+$, $PtAg^+$, $Pt_mAu_n^+$, $PtRh^+$

Organometallics **2003**, *22*, 3809, *Chem. Phys. Chem.* **2003**, *4*, 1233, *Angew. Chem. Int. Ed.* **2004**, *43*, 121, *Int. J. Mass Spectrom.* **2004**, *237*, 19.

Exkursus: *"Chemical laundry"* of $PtAu^+$

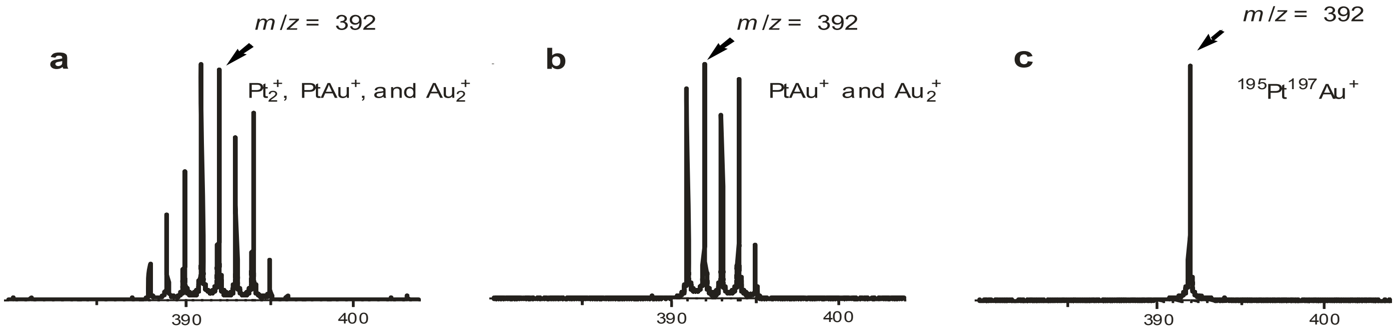
- Platinum: ^{194}Pt (33%), ^{195}Pt (34%), ^{196}Pt (25%), ^{198}Pt (7%)
- Gold: Pure element ^{197}Au (100%)

Laserdesorption auf Pt/Au target

Abundant $PtAu^+$ cluster is isobaric with Pt_2^+

Removal of Pt_2^+ by reaction with O_2 followed by *rf*-pulse

$Pt_2^+ + O_2 \rightarrow Pt^+ + PtO_2$



☞ ***Isobaric overlaps are avoided, pure $^{195}Pt^{197}Au^+$***

(*J. Am. Chem. Soc.* **2003**, *125*, 3676)

II. Partial oxidation of methane

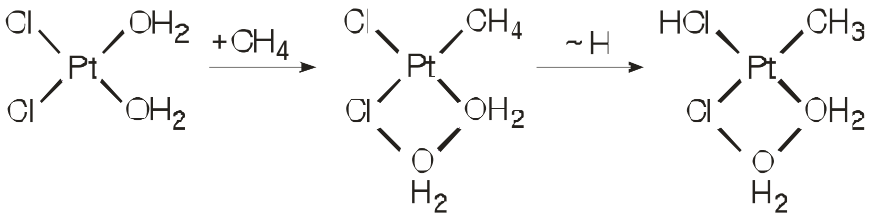
Shilov systems

- Pt^{II}-salt, water, acid
- Attractive selectivity *e.g. $CH_3 > CH_2$ in propane*

Proposed mechanism

- radical-type abstraction? 👎 *selectivity*
- oxidative addition? 👎 *unlikely (solvent effects, Pd-analog)*

σ-complex followed by σ-bond metathesis



$\Delta G^{\neq}$ = 20 kcal/mol

P. E. M. Siegbahn, R. H. Crabtree *J. Am. Chem. Soc.* **1996**, *118*, 4442

Gas-phase studies of methane activation with Pt

- Many studies of Pt^+	(Beauchamp, Schwarz, Bondybey, Armentrout)
- Some studies of $Pt^{0/-}$	(Kaldor, Niedner-Schatteburg, Ervin)
- Reactivity of Pt_n^+ clusters	(Schwarz, Bondybey, Uggerud)
- Mixed $Pt_nM_m^+$ clusters	(Schwarz)
- Miscellaneous PtX^+ ions	(X = CH_2, NH, O etc., Schwarz, Bondybey)

Methane activation frequently observed

But: Pt^{I} and Pt^{III} are rather uncommon oxidation states

"normal": Pt^0, Pt^{II}, Pt^{IV}, and Pt^{VI}

Problem: How to generate PtX^+ ions with formal Pt^{II}?

Good model might be $PtCl^+$

Gas-phase experiment

desired: $Pt^+ + R{-}X \rightarrow PtX^+ + R^\bullet$

real: atom transfer associated with ET
$Pt^+ + R{-}X \rightarrow PtX + R^+$

exception $Pt^+ + X_2 \rightarrow PtX^+ + X^\bullet$ X = Cl, Br *(not suited for reactivity)*

Theory

DFT $PtX^+ + CH_4 \rightarrow PtCH_3{}^+ + HX$ (ok for X = Cl, F)
predicted *IEs* of neutral PtX much above 10 eV

☹ **No access to the ions of interest**

New approach to ions of interest

Electrospray ionization of strongly acidic solutions

- conductivity of solution *(discharge via syringe)*
- breakdown of spray *(droplet model)*
- corrosion of capillary *(metal parts)*

Often: "ESI does not work below pH = 3"

However, reality is the probe

☞ Replacement of steel capillary by one of fused-silica

It shouldn't work, but it does ☺

Likewise: Cu^{II} & Fe^{III} salts, HCl at pH = 0, even $KMnO_4$ and H_2O_2

Ion chemistry of H_2PtCl_6 in $MeOH/H_2O$ upon ESI

Anions: $PtCl_6^{2-}$ dianion prevails

Cations	Soft ionization	$[H_3PtCl_6(CH_3OH)_n]^+$
		$\downarrow$ - CH_3OH
	Increasing energy	$[H_3PtCl_6(CH_3OH)_3]^+$
		$\downarrow$ - 3 HCl
		$[PtCl_3(CH_3OH)_3]^+$
		$\downarrow$ - CH_3OH
		$[PtCl_3(CH_3OH)_2]^+$
		$\downarrow$
	Hard ionization	$PtCl_n^+$, $Pt(OCH_3)_n^+$, $Pt(OCH)_n^+$
	Very hard ESI	Pt^+, PtH^+, $PtCH^+$

Good to reasonable yields, MeOH required for stable spray, care for isotope patterns needed

Ion/molecule reactions with methane

reaction	products	x_i	k_{rel}	ϕ_i
$Pt^+ + CH_4$	$PtCH_2^+ + H_2$	100	40	35%
$PtH^+ + CH_4$	$PtCH_3^+ + H_2$	100	50	45%
$PtCHO^+ + CH_4$	(H/D exchange)		< 1	
$PtCl^+ + CH_4$	$PtCH_3^+ + HCl$	100	70	65%
$PtCl_2^+ + CH_4$	$ClPtCH_3^+ + HCl$	100	60	55%
$PtBr^+ + CH_4$	$BrPtCH_2^+ + H_2$	15	100	90%
	$PtCH_3^+ + HBr$	85		
$PtCl_3^+ + CH_4$			< 1	

Reaction efficiency ϕ_i derived from $k_{abs}(Pt^+)_{ICR} = 4.8 \bullet 10^{-10}$ cm^3 s^{-1}

Isotope effects

reaction	products	*KIE*	
$Pt^+ + CH_4$	$PtCH_2^+ + H_2$	1.70 ± 0.04	ICR: 1.6 ± 0.1
$PtH^+ + CH_4$	$PtCH_3^+ + H_2$	1.11 ± 0.05	
$PtCl^+ + CH_4$	$PtCH_3^+ + HCl$	1.16 ± 0.04	
$PtCl_2^+ + CH_4$	$ClPtCH_3^+ + HCl$	1.38 ± 0.04	
$PtBr^+ + CH_4$	$BrPtCH_2^+ + H_2$	1.25 ± 0.08	
	$PtCH_3^+ + HBr$	1.03 ± 0.03	

☞ **C–H bond activation appears rather facile (rates & KIEs)**

Thermochemistry?

► P. B. Armentrout and coworkers *J. Phys. Chem. A* **2003**, *107*, 10303

$D_0(Pt^+\text{-}Cl) = 58.8 \pm 3.5$ kcal/mol

$D_0(ClPt^+\text{-}Cl) = 61.5 \pm 4.5$ kcal/mol

NB. First bond weaker than the second ("prepared state")

$PtCl^+ + D_2 \rightarrow PtD^+ + DCl \quad \Delta H_r = -35$ kcal/mol

$PtCl^+ + CH_4 \rightarrow PtCH_3^+ + HCl \quad \Delta H_r = -2$ kcal/mol

► Thermochemically, all bond activations are feasible

☞ **Large rates and low *KIEs* due to thermochemical control**

Transition-metal oxides

☞ Central units in oxidases (P450, MMO etc.)

Gas phase: FeO^+ cation is a highly potent oxidant

Oxidation of alkanes:	$R{-}H \rightarrow R{-}OH$	(even CH_4)
O-transfer to alkenes:	$C_2H_4 \rightarrow CH_3CHO$	(rearrangement to aldehyde)
Oxidation of arenes:	$Ar{-}H \rightarrow Ar{-}OH$	(arene oxide involved)
Robust substrates:	$C_6F_6 \rightarrow C_6F_5O^{\bullet}$	(perfluoroalkanes are unreactive)

(Reviews: *Angew. Chem.* **1995**, *107*, 2126; *Struct. Bond.* **2000**, *97*, 91)

- ➢ Mostly with change of spin along the reaction coordinate

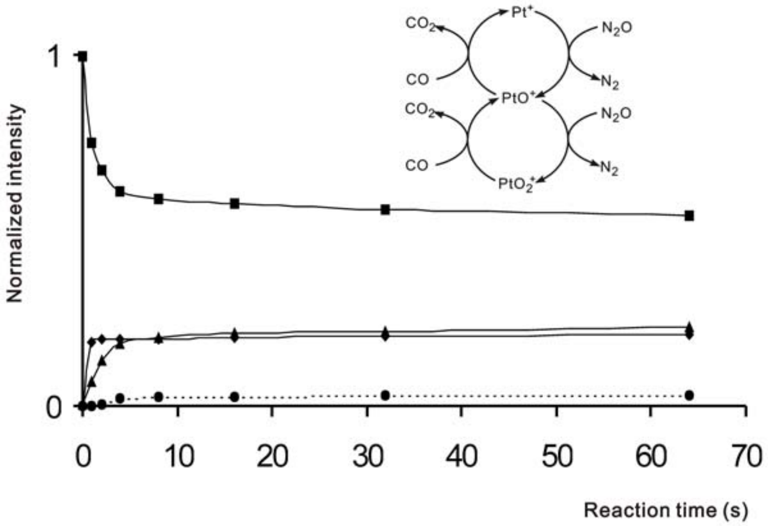
  Two-State Reactivity

(*Acc. Chem. Res.* **2000**, *33*, 139)

Example for a "real" gas-phase catalysis: Oxidations with PtO_2^+

- PtO_2^+ cation as highly efficient oxidant
  e.g. H_2, CO, CH_4, C_2H_4

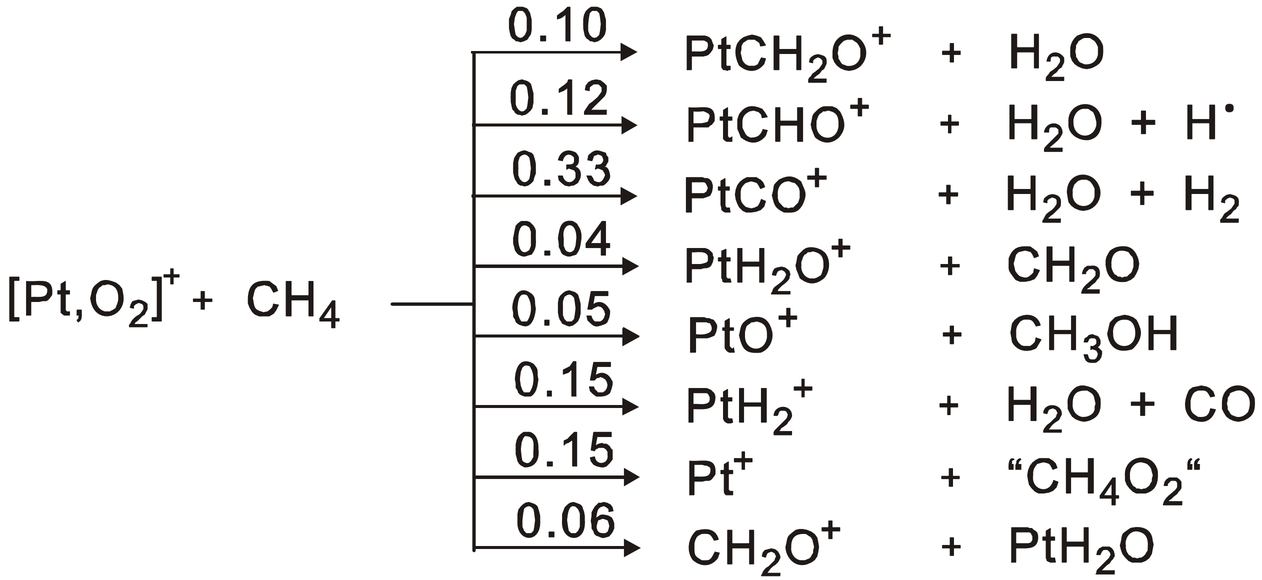
"Real" gas-phase catalysis, *TON* limited by impurities



(*J. Am. Chem. Soc.* **2001**, *123*, 142)

Problem: Low selectivity of metal oxides

Example: Methane/PtO_2^+



$[Pt,O_2]^+ + CH_4$

$\xrightarrow{0.10} PtCH_2O^+ + H_2O$

$\xrightarrow{0.12} PtCHO^+ + H_2O + H^\bullet$

$\xrightarrow{0.33} PtCO^+ + H_2O + H_2$

$\xrightarrow{0.04} PtH_2O^+ + CH_2O$

$\xrightarrow{0.05} PtO^+ + CH_3OH$

$\xrightarrow{0.15} PtH_2^+ + H_2O + CO$

$\xrightarrow{0.15} Pt^+ +$ “CH_4O_2“

$\xrightarrow{0.06} CH_2O^+ + PtH_2O$

☞ Poor selectivity → **complete oxidation**

Possible solution: Modulation of reactivity by ligands

Oxidation of the ligands requires "inverted" approach

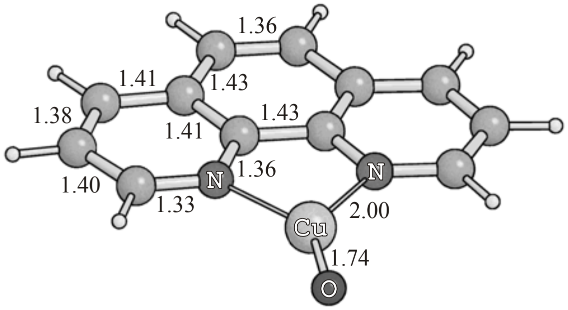
first: $M^+ + L \rightarrow M(L)^+$ then: $M(L)^+ + [O] \rightarrow (L)MO^+$

- (arene)FeO^+ epoxidizes olefines and permits selective C–H activations (e.g. dealkylation of *N,N*-dimethylaniline)

(*Can. J. Chem.* **1999**, *77*, 774)

However: **Reactivity is lowered too much**

☞ ***Alternative approach*** *(ligand needs to be resistant against oxidation)*

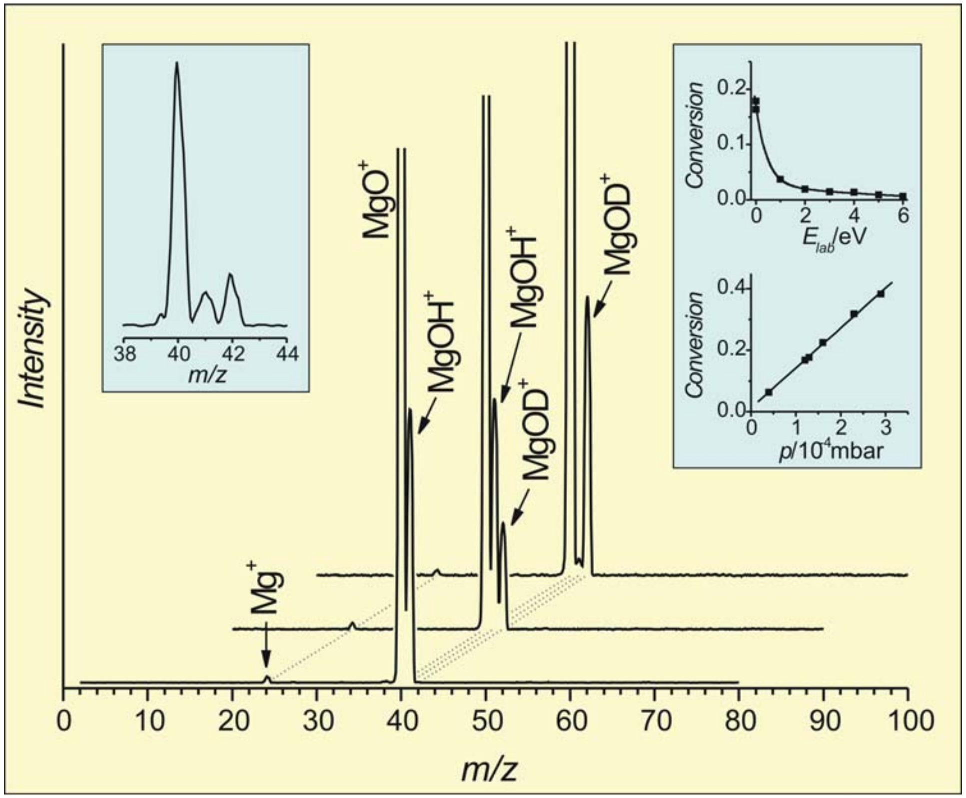


(1,10-phenanthroline)CuO^+

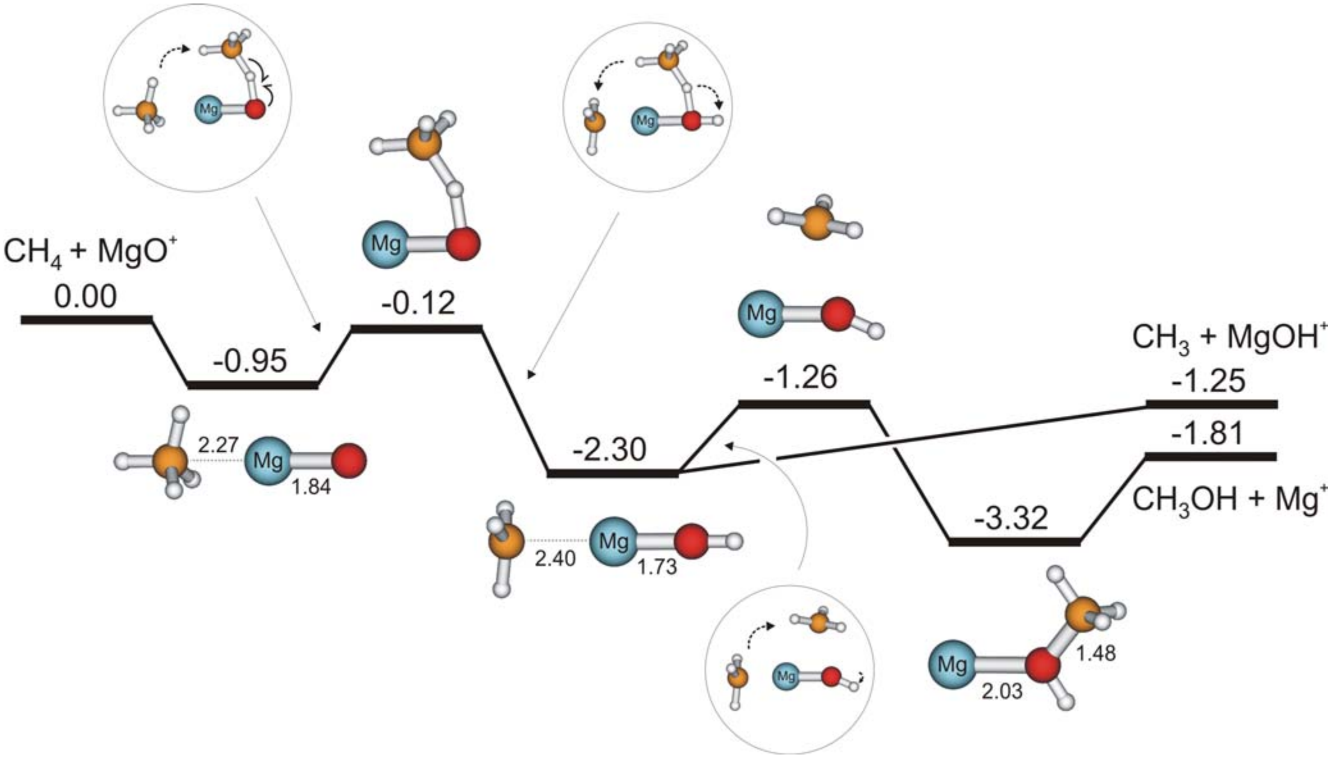
(*J. Phys. Chem. B* **2004**, *108*, 14407)

Do we really need a transition metal?

MgO^+ cation activates methane efficiently



How does it work?



Close analogy to Li/Mg/O in applied catalysis

Low-temperature activation of methane: It also works without a transition metal!
D. Schröder, J. Roithová, *Angew. Chem. Int. Ed.* **2006**, *45*, 5705

III. Epoxidation of olefines

$C_2H_4 \xrightarrow{\text{Oxidation}} c\text{-}C_2H_4O$ (ethylene oxide, EO)

Uses: polymers
antifreezing
food additives

Classical route:

$NaCl_{aq} \xrightarrow{\text{current}} NaOH + \frac{1}{2}\,Cl_2$

$2\,NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$

$NaOCl + C_2H_4 \rightarrow NaCl + C_2H_4O$

👎 electricity consumption
👎 "salt load"
👎 chlorinated waste, mercury

"Dream reaction": $\mathbf{C_2H_4 + \frac{1}{2}\,O_2 \rightarrow c\text{-}C_2H_4O}$

Megaton process on silver contact

Atom-economic process

High selectivity (no byproducts)

Almost completely replaced Cl-route

Remaining problems

- 👎 significant amount of total combustion
- 👎 heat removal
- 👎 safety issues

Recall: +1% product = -1% waste = +2% profit

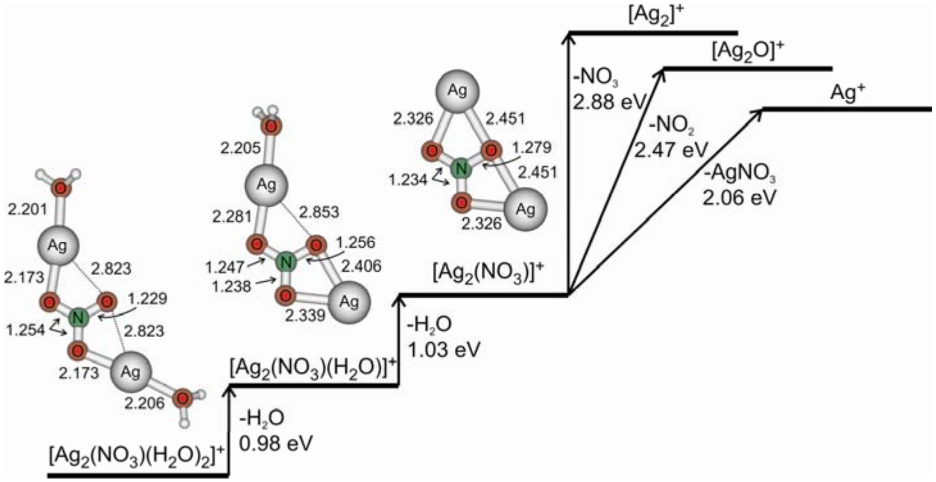
Can gas-phase chemistry contribute?

Gas-phase model

1st task: Make it!

Electrospray ionization of aqueous $AgNO_3$ gives solvated ions

$[Ag(H_2O)_n]^+$, $[Ag_2(NO_3)(H_2O)_n]^+$, $[Ag_3(NO_3)_2(H_2O)_n]^+$ etc.



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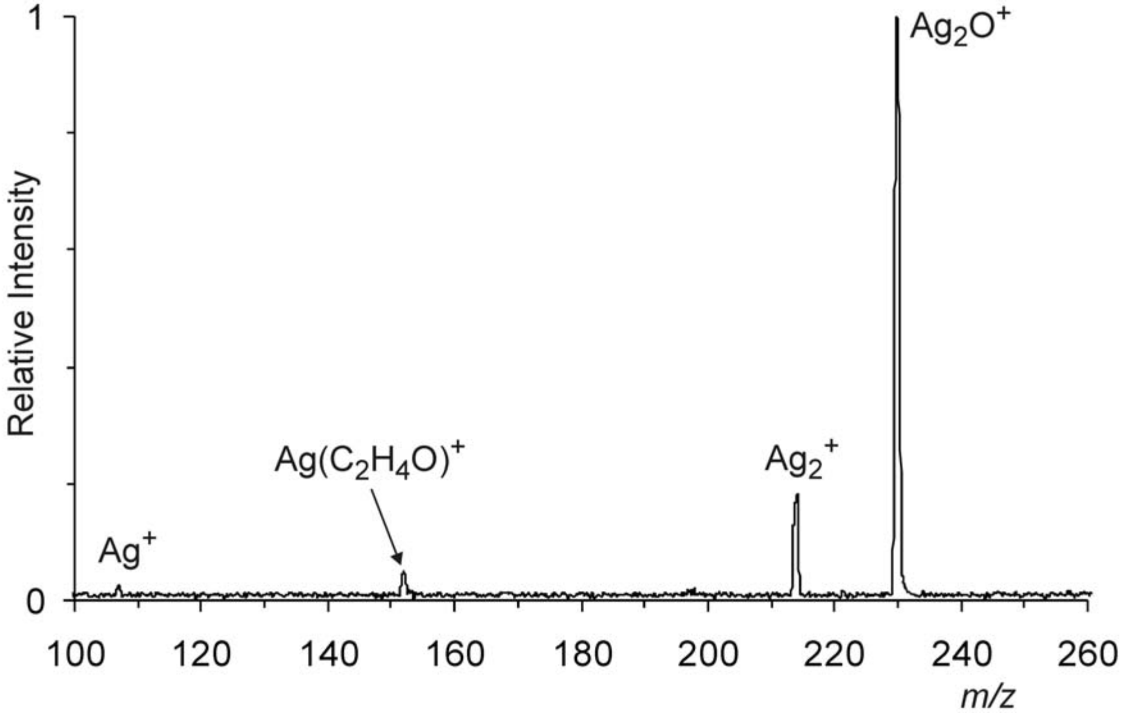
👍 **Reasonable yields of triatomic Ag_2O^+**

2nd task: React it!

Interaction of mass-selected $^{107}Ag_2{}^{16}O^+$ with ethylene



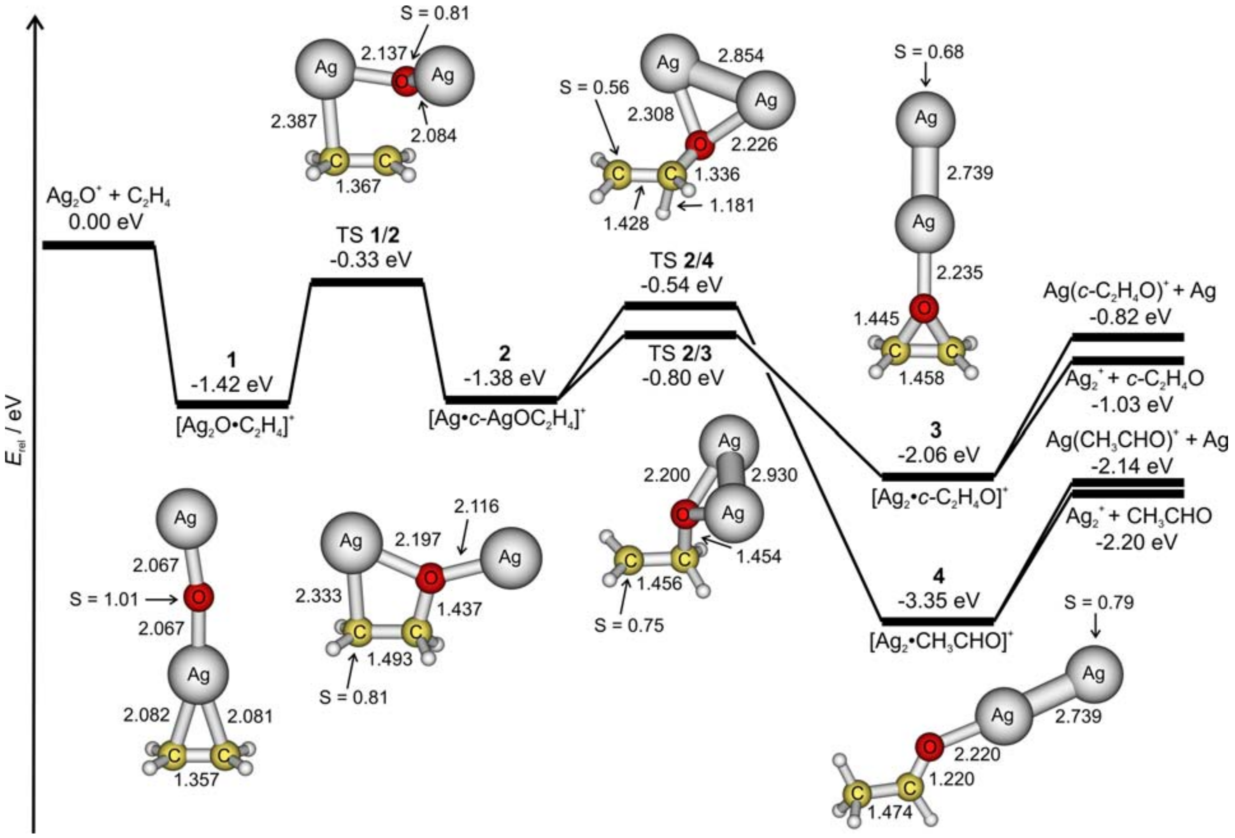
Two major channels:

$$Ag_2O^+ + C_2H_4 \rightarrow Ag_2^+ + C_2H_4O$$
$$\rightarrow Ag(C_2H_4O)^+ + Ag$$

$k_r = 4.4 \cdot 10^{-10}\ cm^3\ s^{-1}$, $\phi = 45\ \%$

👍 **Efficient oxygen-atom transfer**

3rd task: Understand it!

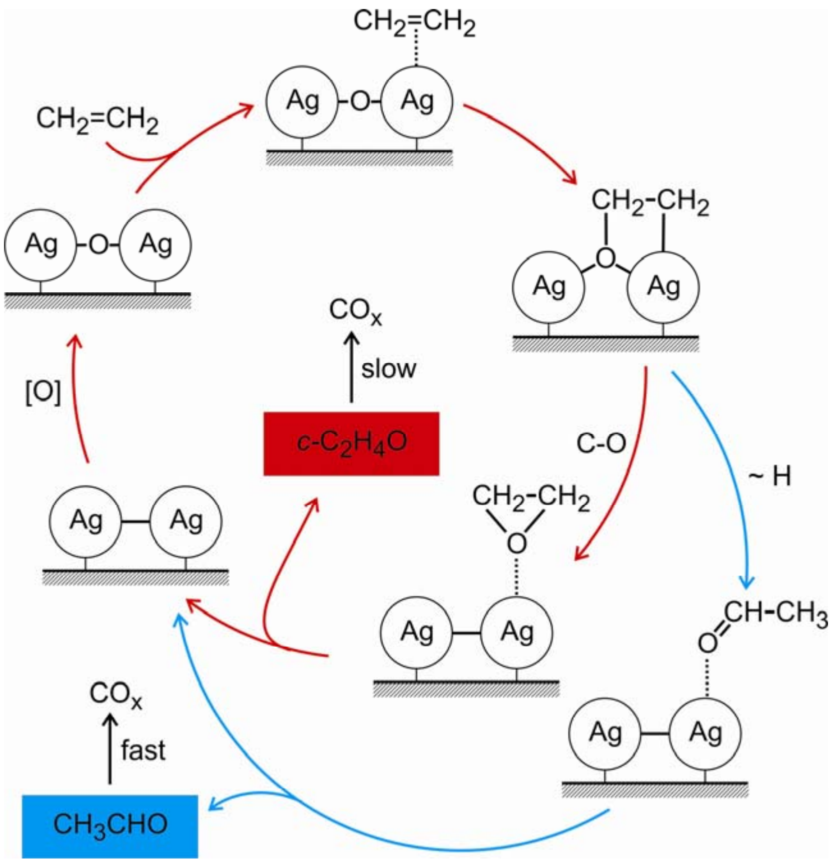


👍 **Kinetic control of epoxidation**

Result

Reactions of Ag_2O^+ generated via ESI combined with ab initio calculations provide a functional model for the surface reaction

"Triatomic model for megaton process"



Gas-phase Models for Catalysis: Alkane Activation and Olefin Epoxidation by the Triatomic Cation Ag_2O^+

J. Roithová, D. Schröder, *J. Am. Chem. Soc.* **2007**, *129*, 15311

IV. Conclusions

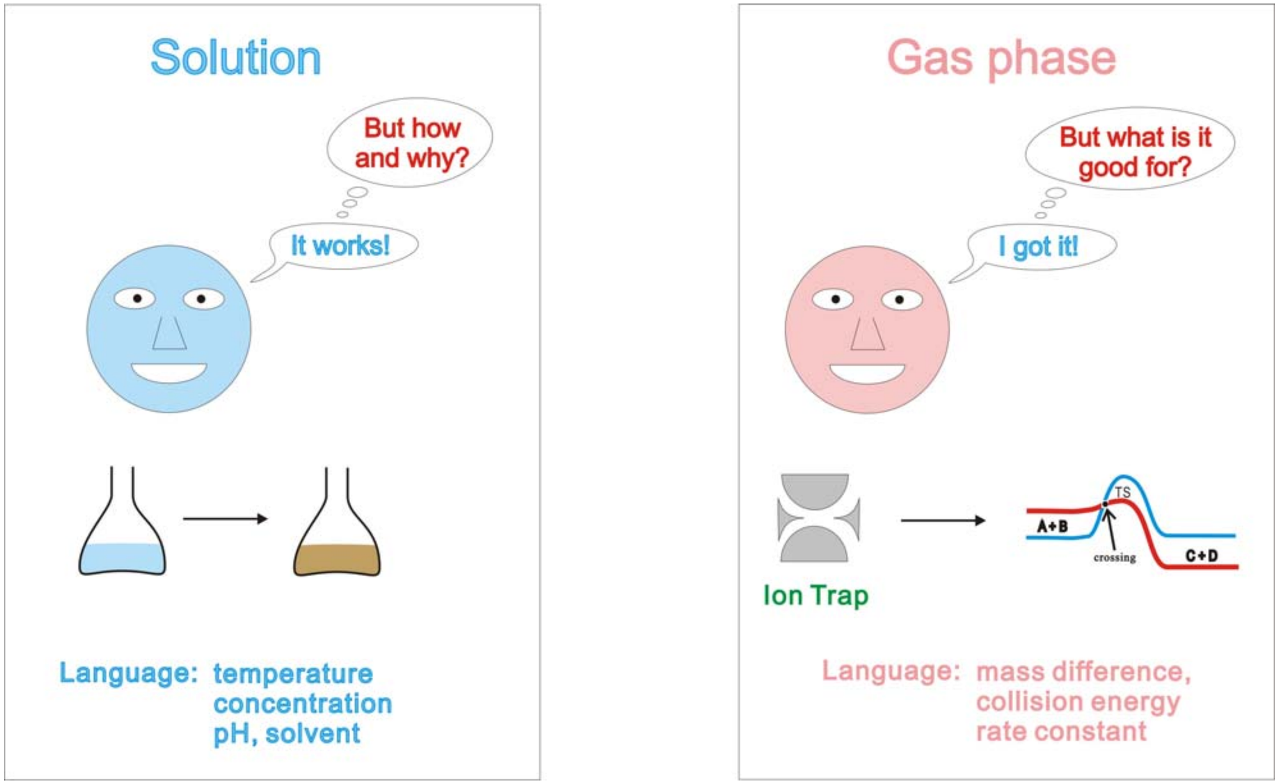
- **BMA activity of Pt_n^+ ions**
  - C–N-coupling only for the Pt^+-monomer and the mixed $PtAu^+$ cluster
  - Impact in applied catalysis (PCT/EP2004/001516)
- **CH_4 activation by Shilov-type Pt^{II} ions**
  - Cationic mechanism in solution?
- **No transition metal is required!**
  - Methane activation by MgO^+
- **Epoxidation of ethylene on silver contacts**
  - Triatomic model for a large-scale industrial process

M. Brönstrup, M. Diefenbach, K. Koszinowski, P. Milko
K. P. De Jong (Utrecht), M. C. Holthausen (Marburg), J. Roithová (Prague), H. Schwarz (Berlin)

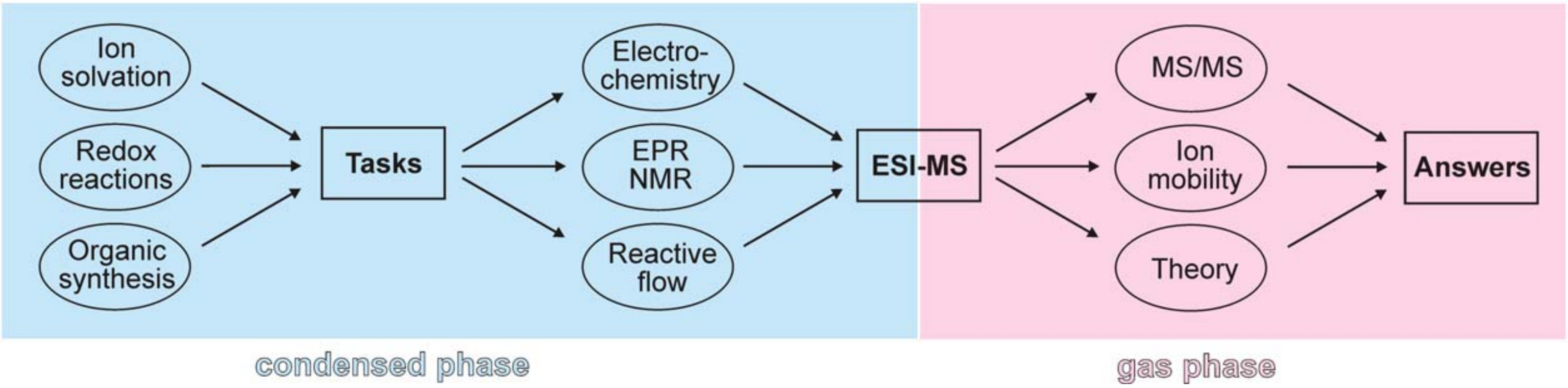
ERC, GAAV, GAČR, TNA/EU

ERC Advanced Grant HORIZOMS

"Language barriers" in current chemistry



Linkage of gas phase and "real" chemistry



Ion solvation

Redox reactions

Organic synthesis

Tasks

Electro-chemistry

EPR NMR

Reactive flow

ESI-MS

MS/MS

Ion mobility

Theory

Answers

condensed phase

gas phase

EPR: electron paramagnetic resonance. NMR: nuclear magnetic resonance. ESI: electrospray ionization. MS: mass spectrometry