Introduction to Theories of Chemical Reactions

Graduate Course Seminar
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FHI
I. Overview

What kind of reactions?

- gas phase / surface
- unimolecular / bimolecular
- thermal / photochemical
What kind of information?

- structure of reactants, products
- $\Delta E_{\text{react}}$
- mechanism
- TS, $E_a$
- $k$
- $\tau$, lifetime of intermediates
What kind of theoretical approach?

- **MO and VB theory**
  almost without calculation, based on symmetry arguments

- **Quantum Chemistry**
  Born-Oppenheimer approximation
  solution of electronic Schrödinger equation
  optimization of stationary points of PES
  follow IRC
  TD data $\rightarrow$ TS theory
• **Molecular Dynamics**
  
  semiempirical potential
  
or calculation of forces ‘on the fly’ (CPMD)
  \( T \geq 0 \)

• **beyond BO (wave-packet dynamics)**
  
  more than one PES (photochemistry!)
  solution of nuclear SE
  real-time evolution of a chemical reaction
  related to “pump-probe“ spectroscopy or ”femtosecond chemistry”

• **statistical mechanics**
  
  many particles
An attempt to summarize the approaches ...

\[ \psi(\{a, x, X, t\}) \]

\[ \psi(x, x, X) \]

\[ \psi(x, X) \]

Born Oppenheimer approximation or method

\[ \psi(x) \]

\[ \psi_X(x) \]

f(t)

\[ k(t) \]

classical mechanics

quantum mechanics

reaction mechanism

statistical mechanics


a: number of particles

x: electronic coordinates

X: nuclear coordinates

t: time
II. Example Reaction: Chelate Ring Inversion

experimentally $\Delta E_a$ 62 kJ/mol from $^1$H NMR

H. Köpf, Angew. Chem. 83, 146-147, (1971)

$\Delta \nu$ between signals of H at the two $\text{C}_5\text{H}_5$-rings

approximate formula

coalescence temp. $T_C$ (~ 20 °C)

M. Hesse, H. Meier, B. Zeeh
Spektroskopische Methoden in der organischen Chemie Thieme Verlag 1991
Stabilizing and destabilizing effects of folding

Lewis structure
III. Application of MO Theory

Ring opening and closing of ozone - A forbidden reaction
molecular plane $\sigma$ preserved in the reaction
levels of MOs with different symmetry w. r. t. $\sigma$ are crossing
computed* kinetic persistence of the cyclic isomer

life time of the intermediate

\[ k = Ae^{-\frac{E_a}{RT}} \quad \text{Arrhenius equation} \]

\[ \tau \sim \frac{1}{k} \]
unimolecular reaction

\[
\begin{align*}
\text{first-order rate law} & \quad \frac{dx}{dt} = k[c_0 - x] \\
\ln \frac{c_0}{c_0 - x} & = kt \\
x & = \frac{1}{2} c_0 \\
t & = \tau
\end{align*}
\]

half-life time \( \tau = \ln 2k^{-1} \)
Fill in numbers

assume preexponential factor of $10^{15} \text{s}^{-1}$ (unimolecular reaction)
calculated barrier 23 kcal/mol = 95.7 kJ/mol (the lower one)
room temperature 25ºC

$$k = A e^{-\frac{E_a}{R T}}$$

$$k = 10^{15} \text{s}^{-1} e^{-\frac{95.7 \text{kJmol}^{-1}}{8.31 \text{JK}^{-1}\text{mol}^{-1}298 \text{K}}}$$

$$k = 0.64 \cdot 10^{-2} \text{s}^{-1}$$

$$\tau = \ln 2 k^{-1}$$

$$\tau = 44 \text{ s}$$
Use cyclic ozone as a ligand

6 π electron donor
Some Predicted Complexes

applied an ‘18-electron strategy’

Woodward - Hoffmann Rules

to explain stereoselectivity of cycloadditions
different symmetry elements remain, depending on the mechanism

disrotatory antidomino antitrophic

conrotatory domino cistrophic
correlation diagram: level-crossing for disrotatory path

coefficients of Hückel solutions (π systems) correspond to particle-in-a-box solutions
A Conversation on VB vs MO Theory: A Never-Ending Rivalry?

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ABSTRACT
Quantum mechanics has provided chemistry with two general theories, valence bond (VB) theory and molecular orbital (MO) theory. The two theories were developed at about the same time.

SS: I still remember, Roald, when I was at the University of Washington, the Walker—Ames lectures. After inviting all the students to drink.

RH: I think I was experimenting for a while.

SS: ... I of course was too... enough to ask you about science. I think will be the major developmental chemistry in years to come. You said, VB theory would come back.

RH: Did I say that? I don’t remember.

SS: Yes, you did! As an aside, I was shocked — how could someone so busy come up with this? Blasphemy! After all, during my student time as a dead end. And lo and behold, a discovering VB theory with en in your lab, you were very kind of me, even though I had not researched you intended me to...
IV. Application of Quantum Chemistry

use Born-Oppenheimer approximation

$$\Psi_k(x, R) = \Psi_n^{(el)}(x, R) \chi_{v,J,...}^{(n)}(R) , \quad k \equiv \{n, v, J \ldots\}$$

and solve the electronic Schrödinger equation (for fixed $R$)

$$\hat{H}_{el}\Psi_n^{(el)}(x, R) = E_n(R)\Psi_n^{el}(x, R)$$
ideally: determine electronic properties as functions of nuclear coordinates - i.e. determine the PES

Potential Energy Surface, PES:

• governs nuclear motion, forces on the nuclei $F_x = -\partial E/\partial x$

• stationary points correspond to (meta)stable species (local or global minima) and to transition states (saddle points)

• shape of PES around stationary points determines vibrational spectra

• electronic transitions correspond to transitions from one PES to another

• minimum energy path corresponds to reaction coordinate
in reality: Calculated PES only available for very small systems, for example H+H$_2$ in colinear arrangement

without Coulomb interactions
H. Eyring, M. Polanyi, 1931

with Coulomb interactions
M. Karplus et al. 1968
in practice: stationary points of PES, their characterization (frequency calculations), and maybe the reaction path (IRC calculation)
Transition State Theory

Eyring equation

\[ k = \frac{k_b T Q^{TS}}{h \frac{Q^R}{Q^R}} e^{-\frac{E_a}{k_b T}} \]


partition function

\[ Q = \sum_{\text{levels}} g_j e^{-\frac{\varepsilon_j}{k_b T}} \]

\[ \varepsilon_{vib} = \left( n + \frac{1}{2} \right) h \nu \]
Example: Study of a Radical Clock Rearrangement on a Surface

FTIR: ring modes at 1393 cm\(^{-1}\) and 1434 cm\(^{-1}\) vanish and C=C stretch mode emerges at 1645 cm\(^{-1}\)

Cyclopropylmethoxide and 3-butenyloxide on Mo(110)


$$\Delta E_{\text{total}} = 31 \text{ kJ/mol}$$
Alternative mechanisms already for the isolated molecule
Which is the rate-determining step?

... the one with the highest activation energy (not the one with the highest barrier)

V. Molecular Dynamics

nuclei have kinetic energy \( T_K > 0 \)

\[
\mathbf{H} = T_K + \mathbf{U} \\
T_K = \frac{1}{2} \sum P_I^2 / M_I
\]

\( U: T_e(\mathbf{r}) + V_{ek}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}) + V_{KK}(\mathbf{R}) \)

\( P_I: \) classical momentum

classical equations of motion

\[
\dot{\mathbf{R}_I} = \frac{\partial \mathbf{H}}{\partial \mathbf{P}_I} \\
\dot{\mathbf{P}_I} = -\frac{\partial \mathbf{H}}{\partial \mathbf{R}_I}
\]

solutions \( \mathbf{R}_I(t) \) and \( \mathbf{P}_I(t) \) are the trajectories of the nuclei
VI. Wave-Packet Dynamics

treat also the nuclei quantum-mechanically

\[
H \Phi(R,t) = i\hbar \frac{\partial}{\partial t} \Phi(R,t)
\]

\[
H = T_K + U + [H_{\text{extern}}]
\]

\[
T_K = \frac{\hbar^2}{2} \sum \frac{\nabla^2}{M_I}
\]

simulations only for intervals of a few picoseconds

very fast reactions: e.g. laser-induced isomerizations
Ultrafast cis-trans photoswitching: A model study

Susanne Hahn and Gerhard Stock\textsuperscript{a)}

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\[ \varphi \]

\[ \lambda_c \]

\[ \lambda_t \]

\[ \text{trans} \]

\[ \text{cis} \]

\[ 0 \quad \pi/2 \quad \pi \quad 3\pi/2 \varphi \]

\[ \text{population} \]

\[ \text{time [ps]} \]
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Arthur Koestler