RRK model

Rice–Ramsperger–Kassel model → Unimolecular reaction rates

Later elaborated by R.A. Marcus, into the RRKM theory

An early statistical model developed in the 1920s to describe unimolecular reaction rates.

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Key ideas of RRK theory:

A molecule undergoing a unimolecular reaction absorbs energy through a collision.

That energy is assumed to randomize instantly across all the molecule's vibrational degrees of freedom, following a classical picture.

Reaction occurs when enough energy becomes localized along the reaction coordinate, such as the bond that needs to break.

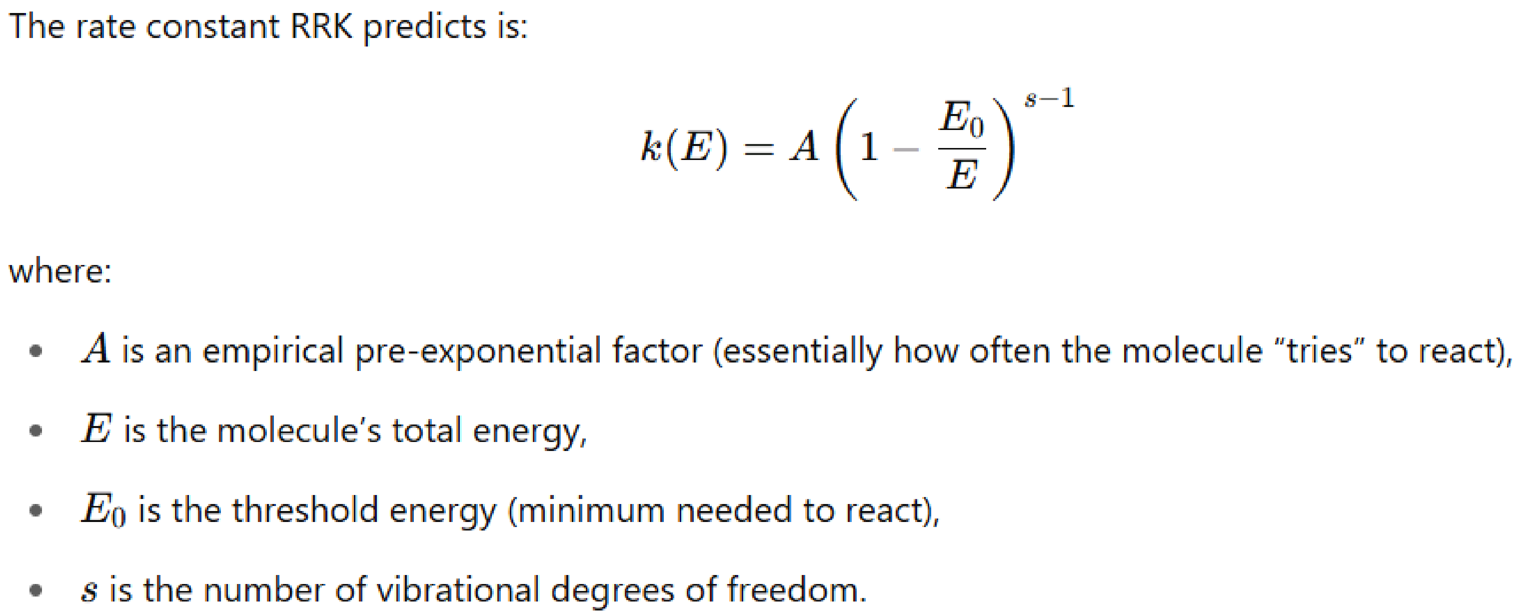
The probability of reaction is based on how much energy is available and how many modes are available to share it.

RRK model

Rice–Ramsperger–Kassel model → Unimolecular reaction rates

Elaborated by R.A. Marcus, into the ‘RRKM model’

RRK gives a formula for the rate constant as a function of the molecule’s total internal energy.



The rate constant RRK predicts is:

$$k(E) = A\left(1 - \frac{E_0}{E}\right)^{s-1}$$

where:

- A is an empirical pre-exponential factor (essentially how often the molecule “tries” to react),
- E is the molecule’s total energy,
- E_0 is the threshold energy (minimum needed to react),
- s is the number of vibrational degrees of freedom.

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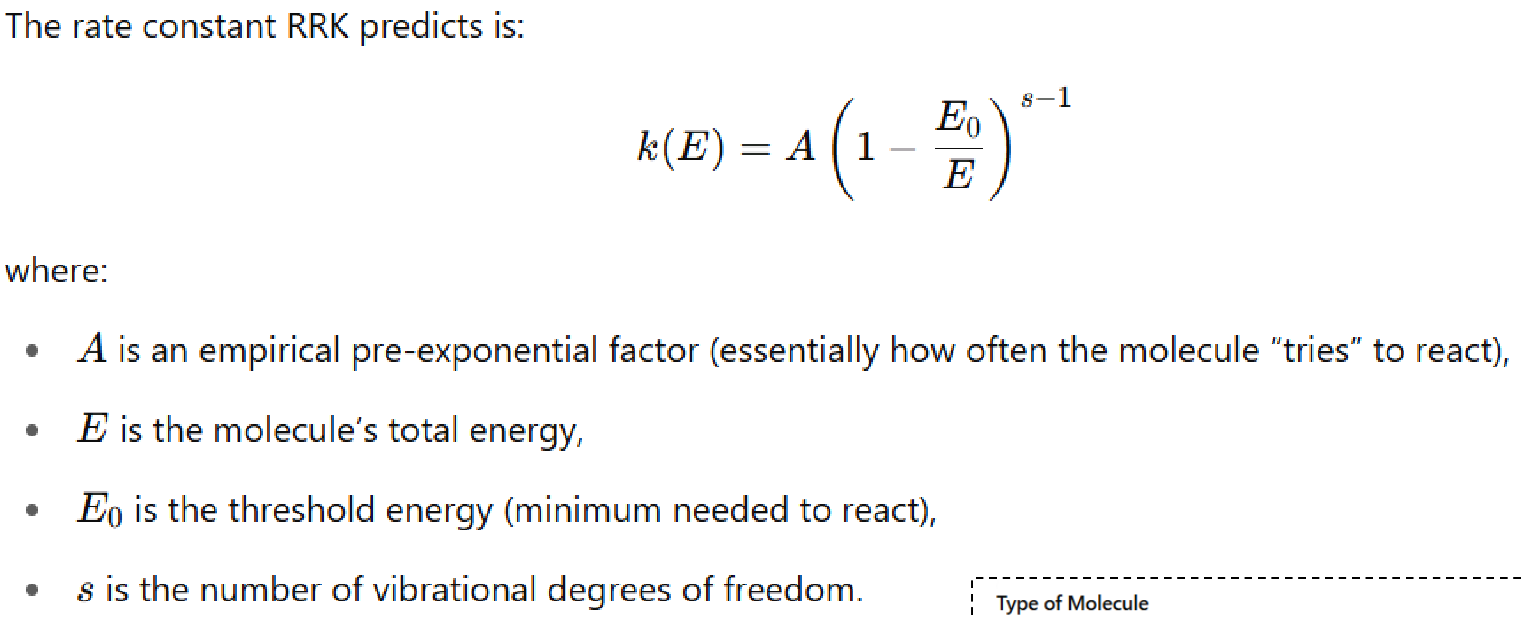

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- E is the molecule's total energy,
- E_0 is the threshold energy (minimum needed to react),
- s is the number of vibrational degrees of freedom.

Type of Molecule	Formula for s
Nonlinear molecule	$s = 3N - 6$
Linear molecule	$s = 3N - 5$

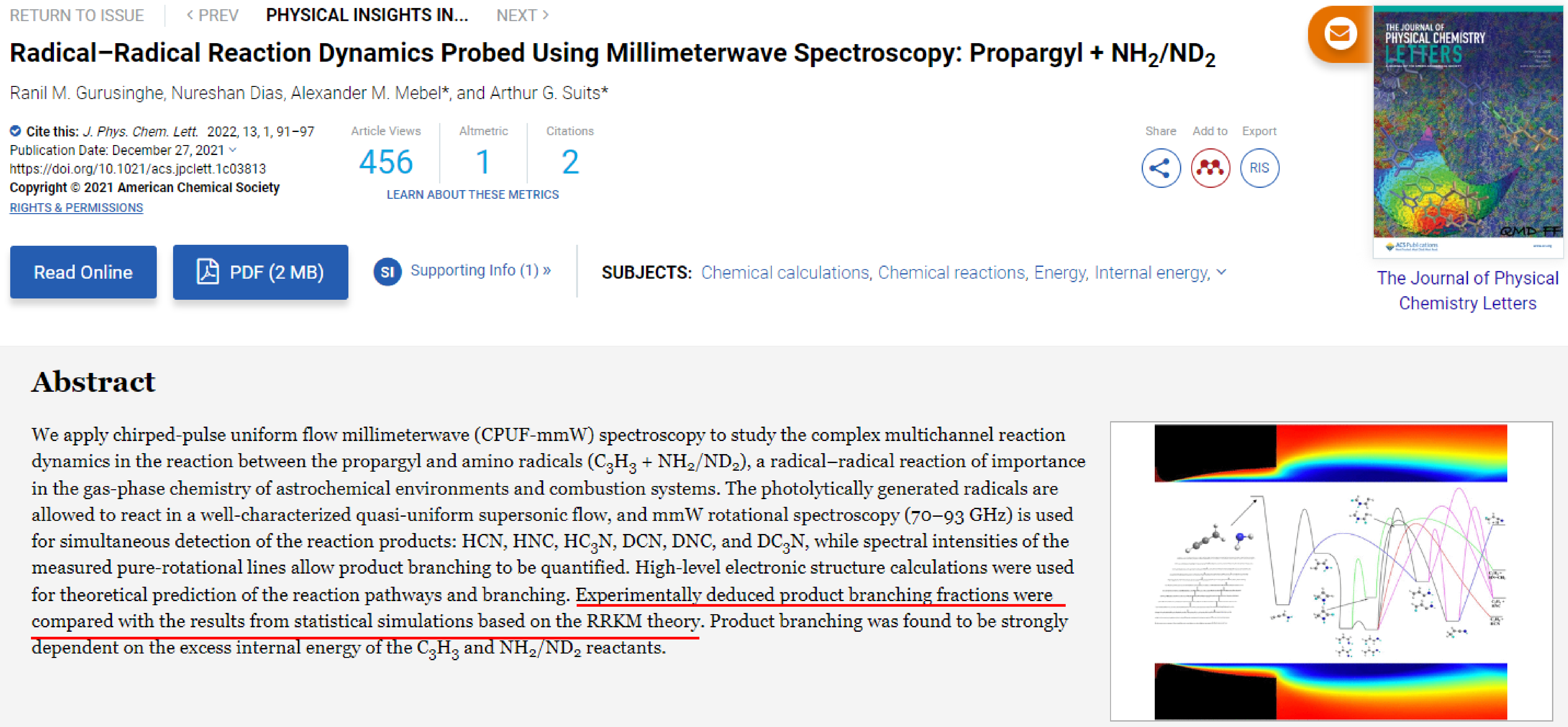
RRK model

Rice–Ramsperger–Kassel model

Elaborated by R.A. Marcus, into the 'RRKM model'

RRKM theory (Rice–Ramsperger–Kassel–Marcus theory) is an improved version of RRK theory that gives a more accurate prediction of unimolecular reaction rates (energy-resolved), especially by including quantum mechanics and transition state theory ideas.

- Energy levels are treated as quantized, not continuous (unlike the purely classical RRK)
- Instead of simply assuming how likely a bond is to break, RRKM counts the number of quantum states available at the transition state compared to all the states in the molecule.



Radical–Radical Reaction Dynamics Probed Using Millimeterwave Spectroscopy: Propargyl + NH_2/ND_2

Ranil M. Gurusinghe, Nureshan Dias, Alexander M. Mebel*, and Arthur G. Suits*

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SUBJECTS: Chemical calculations, Chemical reactions, Energy, Internal energy,

Abstract

We apply chirped-pulse uniform flow millimeterwave (CPUF-mmW) spectroscopy to study the complex multichannel reaction dynamics in the reaction between the propargyl and amino radicals (C_3H_3 + NH_2/ND_2), a radical–radical reaction of importance in the gas-phase chemistry of astrochemical environments and combustion systems. The photolytically generated radicals are allowed to react in a well-characterized quasi-uniform supersonic flow, and mmW rotational spectroscopy (70–93 GHz) is used for simultaneous detection of the reaction products: HCN, HNC, HC_3N, DCN, DNC, and DC_3N, while spectral intensities of the measured pure-rotational lines allow product branching to be quantified. High-level electronic structure calculations were used for theoretical prediction of the reaction pathways and branching. Experimentally deduced product branching fractions were compared with the results from statistical simulations based on the RRKM theory. Product branching was found to be strongly dependent on the excess internal energy of the C_3H_3 and NH_2/ND_2 reactants.

III. All possible reaction pathways for $C_3H_3 + NH_2$ reaction

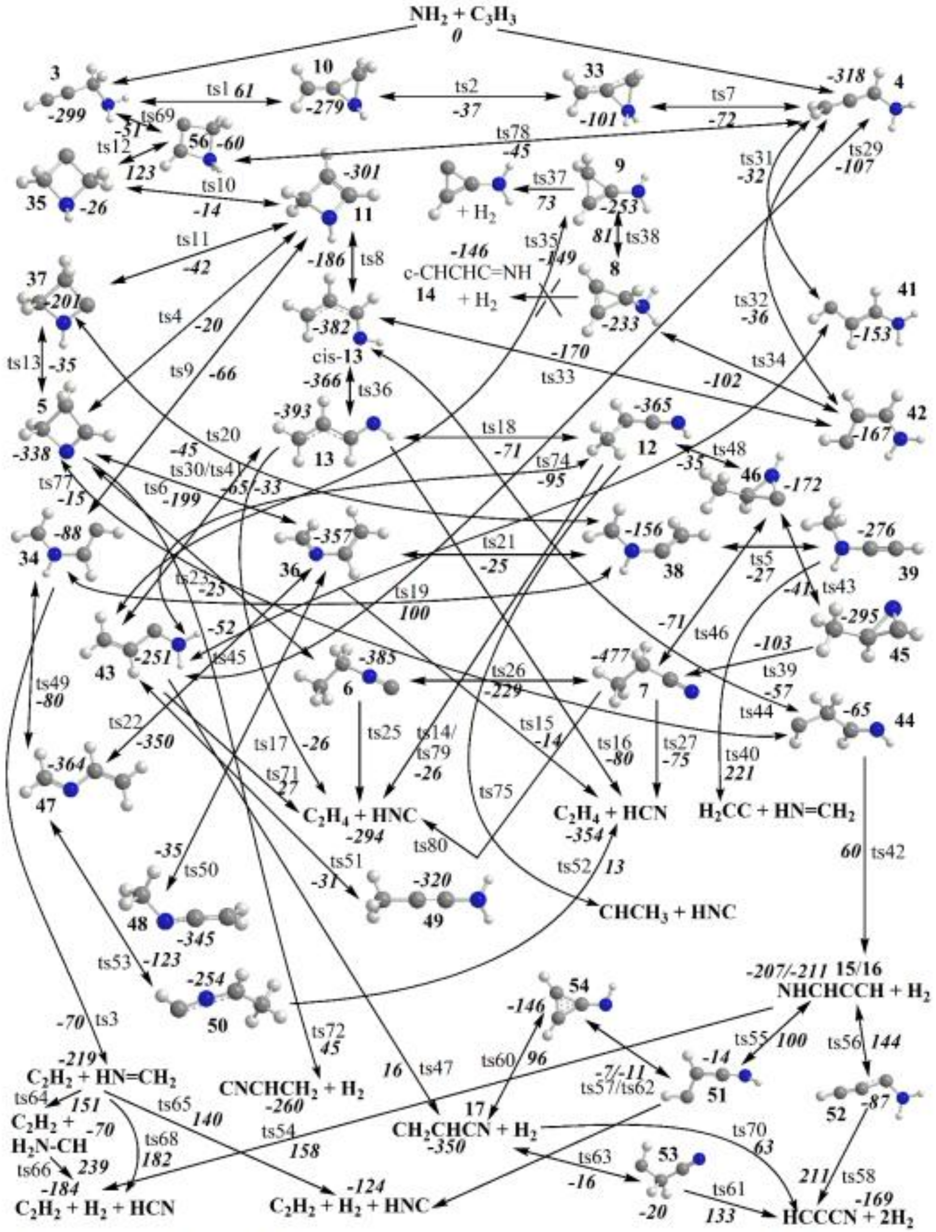

Figure S1a. A map of all possible reaction pathways for $C_3H_3 + NH_2$ reaction calculated at CCSD(T)-F12/cc-pvqz-f12//B3LYP/6-311G**+ ZPE(B3LYP/6-311G**) level of theory. Bold italic numbers show relative energies (in kJ/mol) of various species, including intermediates, transition states, and products with respect to $NH_2 + C_3H_3$.

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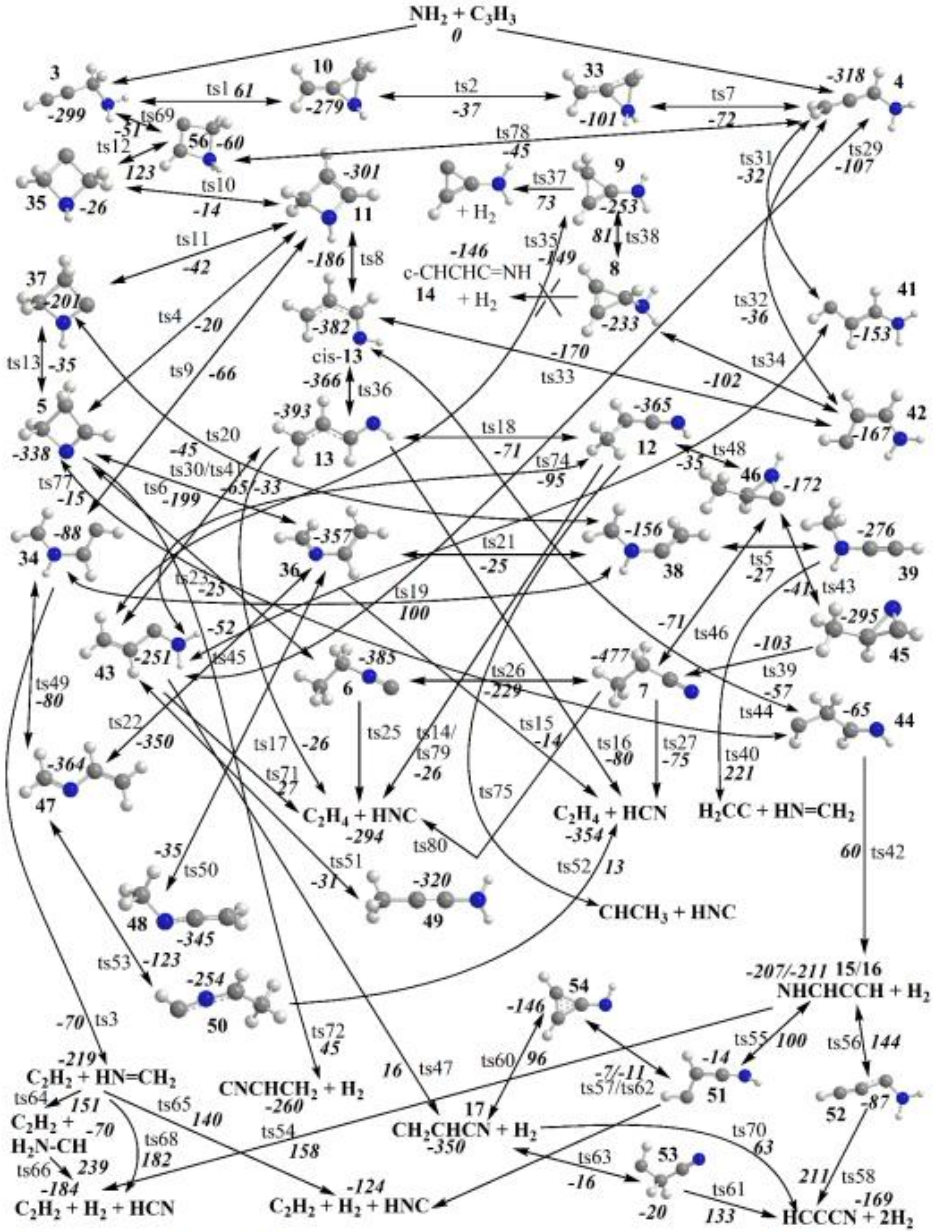

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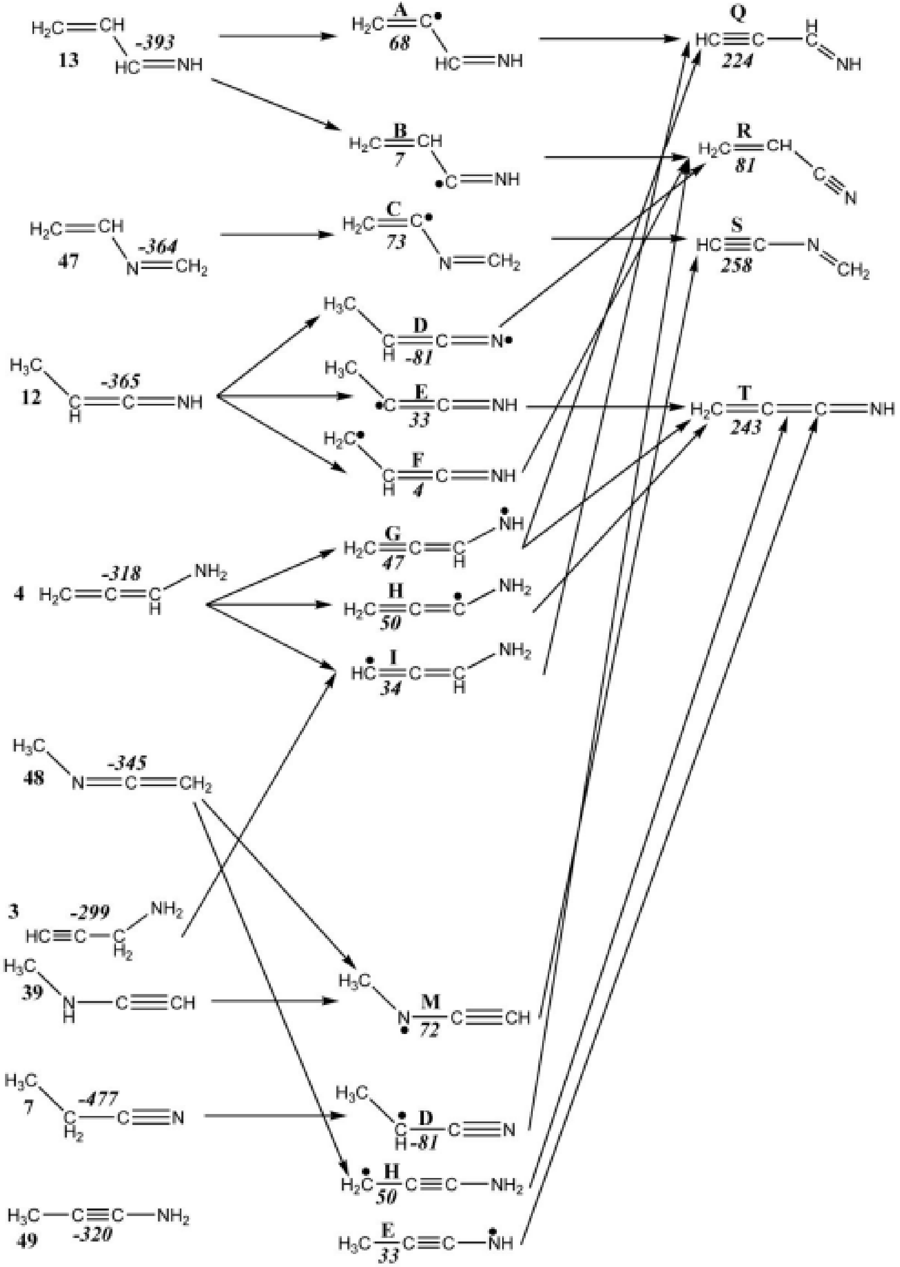


Figure S1b. H elimination pathways in the $C_3H_3 + NH_2$ reaction leading to various C_3NH_4 radicals followed by a second H loss to C_3NH_3 calculated at CCSD(T)-F12/cc-pvqz-f12//B3LYP/6-311G**+ ZPE(B3LYP/6-311G**) level of theory. Only one resonance form of the resonance stabilized radicals is shown here. Bold italic numbers show relative energies (in kJ/mol) of various species with respect to $NH_2 + C_3H_3$.

Focus 18: Reaction Dynamics

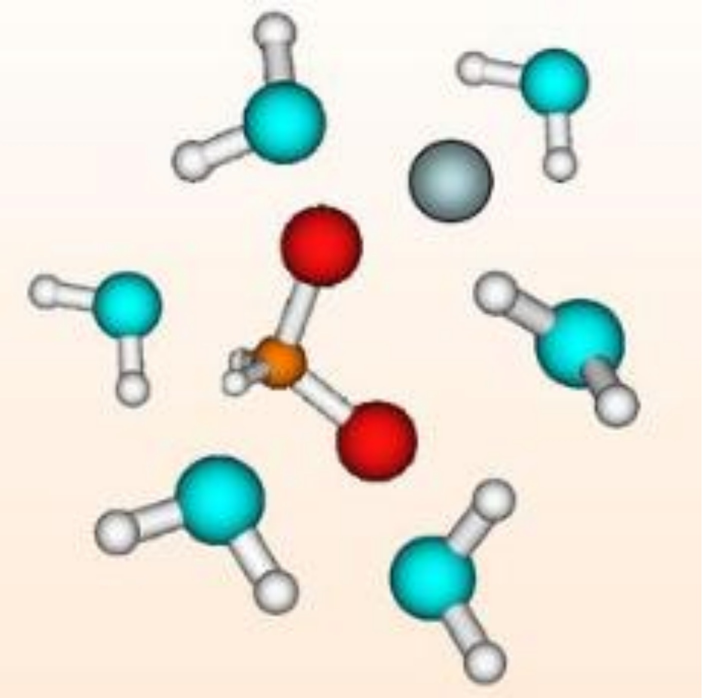
- Collision theory
- Diffusion-controlled reactions and transition-state
- The dynamics of molecular collisions
- Electron transfer in homogeneous systems

Diffusion controlled reactions

Chemical reactions in which the rate is limited by how quickly the reactants can diffuse through the medium (usually a liquid or gas) to find each other, not by the energy barrier for the reaction itself.

Diffusion controlled reactions

Cage effect – reactants surrounded by a solvent cage



Diffusion controlled vs Activation controlled

$$A + B \rightarrow AB \quad \upsilon = k_d[A][B]$$

Diffusion controlled vs Activation controlled

$$A + B \rightarrow AB \quad v = k_d[A][B]$$

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$$\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}] - k'_{\mathrm{d}}[\mathrm{AB}] - k_{\mathrm{a}}[\mathrm{AB}] = 0$$

Diffusion controlled vs Activation controlled

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB} \qquad v = k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]$$

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$$[\mathrm{AB}] = \frac{k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{a}} + k'_{\mathrm{d}}}$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{a}}[\mathrm{AB}] = k_{\mathrm{r}}[\mathrm{A}][\mathrm{B}] \qquad k_{\mathrm{r}} = \frac{k_{\mathrm{a}}k_{\mathrm{d}}}{k_{\mathrm{a}} + k'_{\mathrm{d}}}$$

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$$A + B \rightarrow AB \quad \upsilon = k_d[A][B]$$

$$AB \rightarrow A + B \quad \upsilon = k_d'[AB]$$

$$AB \rightarrow P \quad \upsilon = k_a[AB]$$

$$\frac{d[AB]}{dt} = k_d[A][B] - k_d'[AB] - k_a[AB] = 0$$

$$[AB] = \frac{k_d[A][B]}{k_a + k_d'}$$

$$\frac{d[P]}{dt} = k_a[AB] = k_r[A][B] \qquad k_r = \frac{k_a k_d}{k_a + k_d'}$$

Diffusion-controlled limit

$$k_d'[AB] << k_a[AB]$$

Diffusion controlled vs Activation controlled

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB} \qquad v = k_\mathrm{d}[\mathrm{A}][\mathrm{B}]$$

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Diffusion-controlled limit

$$k_\mathrm{d}'[\mathrm{AB}] \ll k_\mathrm{a}[\mathrm{AB}]$$

$$k_\mathrm{r} \approx \frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{a}} = k_\mathrm{d}$$

Diffusion controlled vs Activation controlled

$$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{AB}\qquad v=k_\mathrm{d}[\mathrm{A}][\mathrm{B}]$$

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$$[\mathrm{AB}]=\frac{k_\mathrm{d}[\mathrm{A}][\mathrm{B}]}{k_\mathrm{a}+k'_\mathrm{d}}$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}=k_\mathrm{a}[\mathrm{AB}]=k_\mathrm{r}[\mathrm{A}][\mathrm{B}]\qquad k_\mathrm{r}=\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{a}+k'_\mathrm{d}}$$

Diffusion-controlled limit $\quad k'_\mathrm{d}[\mathrm{AB}]\ll k_\mathrm{a}[\mathrm{AB}]$

$$k_\mathrm{r}\approx\frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{a}}=k_\mathrm{d}$$

$$\Downarrow$$

$$k_\mathrm{d}=4\pi R^{*}DN_\mathrm{A}$$

Comes from Smoluchowski theory, which models how often two diffusing molecules come into contact close enough to react.

This expression gives the maximum rate at which A and B can react, limited only by how fast they can find each other via diffusion

Diffusion controlled vs Activation controlled

$$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{AB}\qquad v=k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]$$

$$\mathrm{AB}\rightarrow\mathrm{A}+\mathrm{B}\qquad v=k'_{\mathrm{d}}[\mathrm{AB}]$$

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$$[\mathrm{AB}]=\frac{k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{a}}+k'_{\mathrm{d}}}\qquad k_{\mathrm{r}}=\frac{k_{\mathrm{a}}k_{\mathrm{d}}}{k_{\mathrm{a}}+k'_{\mathrm{d}}}$$

Diffusion-controlled limit $k'_{\mathrm{d}}[\mathrm{AB}]\ll k_{\mathrm{a}}[\mathrm{AB}]$

$$k_{\mathrm{r}}\approx\frac{k_{\mathrm{a}}k_{\mathrm{d}}}{k_{\mathrm{a}}}=k_{\mathrm{d}}$$

↓

$$k_{\mathrm{d}}=4\pi R^{*}DN_{\mathrm{A}}$$

↓

critical distance for reaction

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Diffusion-controlled limit $\quad k_\mathrm{d}'[\mathrm{AB}] \ll k_\mathrm{a}[\mathrm{AB}]$

$$k_\mathrm{r} \approx \frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{a}} = k_\mathrm{d}$$

↓

$$k_\mathrm{d} = 4\pi R^* D N_\mathrm{A}$$

↓

critical distance for reaction

$D = D_\mathrm{A} + D_\mathrm{B}$; diffusion constants

Diffusion controlled vs Activation controlled

$$A + B \rightarrow AB \qquad v = k_d[A][B]$$

$$AB \rightarrow A + B \qquad v = k'_d[AB]$$

$$AB \rightarrow P \qquad v = k_a[AB]$$

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$$[AB] = \frac{k_d[A][B]}{k_a + k'_d} \qquad k_r = \frac{k_a k_d}{k_a + k'_d}$$

Diffusion-controlled limit $k'_d[AB] \ll k_a[AB]$

$$k_r \approx \frac{k_a k_d}{k_a} = k_d$$

$$\Downarrow$$

$$k_d = 4\pi R^* D N_A$$

$$\Downarrow$$

critical distance for reaction

$$D = D_A + D_B \qquad J_i = -D_i \frac{d\varphi}{dx}$$

Diffusion controlled vs Activation controlled

$$\mathrm{A}+\mathrm{B}\rightarrow\mathrm{AB}\qquad v=k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]$$

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$$[\mathrm{AB}]=\frac{k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{a}}+k'_{\mathrm{d}}}\qquad k_{\mathrm{r}}=\frac{k_{\mathrm{a}}k_{\mathrm{d}}}{k_{\mathrm{a}}+k'_{\mathrm{d}}}$$

Diffusion-controlled limit $k'_{\mathrm{d}}[\mathrm{AB}]\ll k_{\mathrm{a}}[\mathrm{AB}]$

$$k_{\mathrm{r}}\approx\frac{k_{\mathrm{a}}k_{\mathrm{d}}}{k_{\mathrm{a}}}=k_{\mathrm{d}}$$

$$\Downarrow$$

$$k_{\mathrm{d}}=4\pi R^{*}DN_{\mathrm{A}}$$

$$\Downarrow$$

critical distance for reaction

$$D=D_{\mathrm{A}}+D_{\mathrm{B}}\qquad J_i=-D_i\frac{d\varphi}{dx}$$

Fick's First Law of Diffusion.

Molecules move from regions of high concentration to low concentration, and the flux is proportional to the concentration gradient

Diffusion controlled vs Activation controlled

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$$AB \rightarrow A + B \quad v = k_d'[AB]$$

$$AB \rightarrow P \quad v = k_a[AB]$$

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Diffusion-controlled limit

$$k_d'[AB] \ll k_a[AB]$$

$$k_r \approx \frac{k_a k_d}{k_a} = k_d$$

⬇

$$k_d = 4\pi R^* D N_A$$

⬇

critical distance for reaction

$$D = D_A + D_B, \qquad J_i = -D_i \frac{d\varphi}{dx}$$

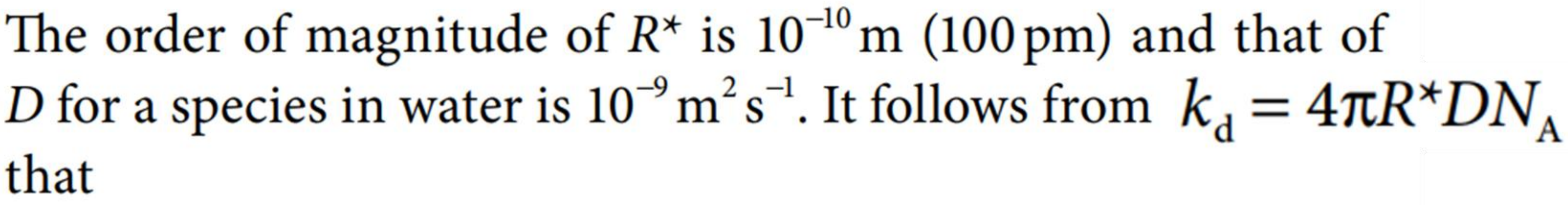
J - diffusion flux - the rate at which species ii is transported (amount per unit area per unit time).

D - diffusion coefficient (diffusivity)

φ - concentration

x - position

Diffusion controlled vs Activation controlled



The order of magnitude of R^* is $10^{-10}\,\mathrm{m}$ (100 pm) and that of D for a species in water is $10^{-9}\,\mathrm{m^2\,s^{-1}}$. It follows from $k_\mathrm{d} = 4\pi R^* D N_\mathrm{A}$ that

Diffusion controlled vs Activation controlled

The order of magnitude of R^* is 10^{-10} m (100 pm) and that of D for a species in water is $10^{-9}\,\mathrm{m^2\,s^{-1}}$. It follows from $k_\mathrm{d} = 4\pi R^* D N_\mathrm{A}$ that

$$\begin{aligned} k_\mathrm{d} &\approx 4\pi \times (10^{-10}\,\mathrm{m}) \times (10^{-9}\,\mathrm{m^2\,s^{-1}}) \times (6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \\ &\approx 8 \times 10^{5}\,\mathrm{m^3\,mol^{-1}\,s^{-1}} \end{aligned}$$

about $10^{9}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$

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$$AB \rightarrow A + B \quad v = k_d'[AB]$$

$$AB \rightarrow P \quad v = k_a[AB]$$

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$$[AB] = \frac{k_d[A][B]}{k_a + k_d'} \qquad k_r = \frac{k_a k_d}{k_a + k_d'}$$

Diffusion-controlled limit $k_d'[AB] \ll k_a[AB]$

$$k_r \approx \frac{k_a k_d}{k_a} = k_d$$

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$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB} \qquad v = k_\mathrm{d}[\mathrm{A}][\mathrm{B}]$$

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Diffusion-controlled limit $k_\mathrm{d}'[\mathrm{AB}] \ll k_\mathrm{a}[\mathrm{AB}]$

$$k_\mathrm{r} \approx \frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{a}} = k_\mathrm{d}$$

Activation-controlled limit $k_\mathrm{a}[\mathrm{AB}] \ll k_\mathrm{d}'[\mathrm{AB}]$

Diffusion controlled vs Activation controlled

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Activation-controlled limit

$$k_\mathrm{a}[\mathrm{AB}] \ll k_\mathrm{d}'[\mathrm{AB}]$$

$$k_\mathrm{r} \approx \frac{k_\mathrm{a}k_\mathrm{d}}{k_\mathrm{d}'} = k_\mathrm{a}\frac{K}{c^\ominus}$$

K is the equilibrium constant for $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}$.

Kinetic isotopic effect

Decrease in the rate of a chemical reaction upon replacement of one atom in a reactant by a heavier isotope

Kinetic isotopic effect

Decrease in the rate of a chemical reaction upon replacement of one atom in a reactant by a heavier isotope

Primary kinetic isotope effect

Secondary kinetic isotope effect

Kinetic isotopic effect

Decrease in the rate of a chemical reaction upon replacement of one atom in a reactant by a heavier isotope

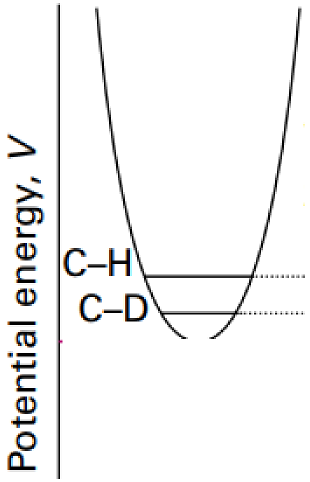
Primary kinetic isotope effect
Occurs when the bond to the isotopically labeled atom is broken or formed in the rate-determining step of the reaction.

Secondary kinetic isotope effect
Occurs when the isotope substitution is not at the site of bond-breaking/forming, but still influences the reaction rate, often due to changes in hybridization or geometry near the reaction center.

Kinetic isotopic effect

Decrease in the rate of a chemical reaction upon replacement of one atom in a reactant by a heavier isotope

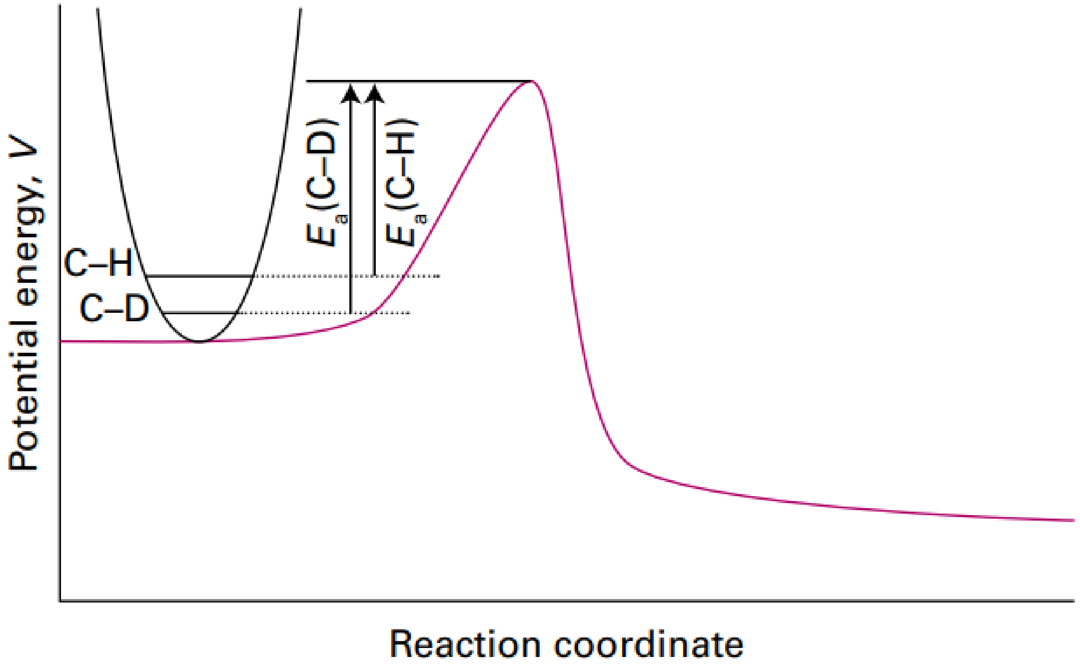
Primary and secondary kinetic isotope effects



Kinetic isotopic effect

Decrease in the rate of a chemical reaction upon replacement of one atom in a reactant by a heavier isotope

Primary and secondary kinetic isotope effects



Effect of deuteration on the activation energy

$$E_a(\text{C–D}) - E_a(\text{C–H}) = N_A\left\{\tfrac{1}{2}\hbar\omega(\text{C–H}) - \tfrac{1}{2}\hbar\omega(\text{C–D})\right\}$$

$$= \tfrac{1}{2}N_A\hbar\{\omega(\text{C–H}) - \omega(\text{C–D})\}$$

Effect of deuteration on the activation energy

$$E_a(\mathrm{C{-}D}) - E_a(\mathrm{C{-}H}) = N_A\left\{\tfrac{1}{2}\hbar\omega(\mathrm{C{-}H}) - \tfrac{1}{2}\hbar\omega(\mathrm{C{-}D})\right\}$$

$$= \tfrac{1}{2}N_A\hbar\{\omega(\mathrm{C{-}H}) - \omega(\mathrm{C{-}D})\}$$

$$\omega(\mathrm{C{-}D}) = (\mu_{\mathrm{CH}}/\mu_{\mathrm{CD}})^{1/2}\omega(\mathrm{C{-}H})$$

Effect of deuteration on the activation energy

$$E_{\mathrm{a}}(\mathrm{C{-}D}) - E_{\mathrm{a}}(\mathrm{C{-}H}) = N_{\mathrm{A}}\left\{\tfrac{1}{2}\hbar\omega(\mathrm{C{-}H}) - \tfrac{1}{2}\hbar\omega(\mathrm{C{-}D})\right\}$$

$$= \tfrac{1}{2}N_{\mathrm{A}}\hbar\{\omega(\mathrm{C{-}H}) - \omega(\mathrm{C{-}D})\}$$

$$\omega(\mathrm{C{-}D}) = (\mu_{\mathrm{CH}}/\mu_{\mathrm{CD}})^{1/2}\omega(\mathrm{C{-}H})$$

$$E_{\mathrm{a}}(\mathrm{C{-}D}) - E_{\mathrm{a}}(\mathrm{C{-}H}) = \tfrac{1}{2}N_{\mathrm{A}}\hbar\omega(\mathrm{C{-}H})\left\{1 - \left(\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}}\right)^{1/2}\right\}$$

Effect of deuteration on the rate constant

$$\frac{k_\mathrm{r}(\mathrm{C{-}D})}{k_\mathrm{r}(\mathrm{C{-}H})} = \mathrm{e}^{-\{E_\mathrm{a}(\mathrm{C{-}D}) - E_\mathrm{a}(\mathrm{C{-}H})\}/RT} = \mathrm{e}^{-\{E_\mathrm{a}(\mathrm{C{-}D}) - E_\mathrm{a}(\mathrm{C{-}H})\}/N_\mathrm{A}kT} \qquad \text{where } R = N_\mathrm{A}k.$$

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where $R = N_\mathrm{A}k$.

$$E_\mathrm{a}(\mathrm{C{-}D}) - E_\mathrm{a}(\mathrm{C{-}H}) = \tfrac{1}{2}N_\mathrm{A}\hbar\omega(\mathrm{C{-}H})\left\{1 - \left(\frac{\mu_\mathrm{CH}}{\mu_\mathrm{CD}}\right)^{1/2}\right\}$$

Effect of deuteration on the rate constant

$$\frac{k_r(\mathrm{C{-}D})}{k_r(\mathrm{C{-}H})} = \mathrm{e}^{-\{E_a(\mathrm{C{-}D})-E_a(\mathrm{C{-}H})\}/RT} = \mathrm{e}^{-\{E_a(\mathrm{C{-}D})-E_a(\mathrm{C{-}H})\}/N_A kT} \qquad \text{where } R = N_A k$$

$$E_a(\mathrm{C{-}D})-E_a(\mathrm{C{-}H}) = \tfrac{1}{2}N_A\hbar\omega(\mathrm{C{-}H})\left\{1-\left(\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}}\right)^{1/2}\right\}$$

$$\frac{k_r(\mathrm{C{-}D})}{k_r(\mathrm{C{-}H})} = \mathrm{e}^{-\zeta}$$

Effect of deuteration on the rate constant

$$\frac{k_\mathrm{r}(\mathrm{C{-}D})}{k_\mathrm{r}(\mathrm{C{-}H})} = \mathrm{e}^{-\{E_\mathrm{a}(\mathrm{C{-}D})-E_\mathrm{a}(\mathrm{C{-}H})\}/RT} = \mathrm{e}^{-\{E_\mathrm{a}(\mathrm{C{-}D})-E_\mathrm{a}(\mathrm{C{-}H})\}/N_\mathrm{A}kT}$$

where $R = N_\mathrm{A}k$

$$E_\mathrm{a}(\mathrm{C{-}D}) - E_\mathrm{a}(\mathrm{C{-}H}) = \tfrac{1}{2} N_\mathrm{A}\hbar\omega(\mathrm{C{-}H})\left\{1-\left(\frac{\mu_\mathrm{CH}}{\mu_\mathrm{CD}}\right)^{1/2}\right\}$$

$$\frac{k_\mathrm{r}(\mathrm{C{-}D})}{k_\mathrm{r}(\mathrm{C{-}H})} = \mathrm{e}^{-\zeta}$$

$$\zeta = \frac{\hbar\omega(\mathrm{C{-}H})}{2kT}\left\{1-\left(\frac{\mu_\mathrm{CH}}{\mu_\mathrm{CD}}\right)^{1/2}\right\}$$

Calculation

From infrared spectra, the fundamental vibrational wavenumber $\tilde{\nu}$ for stretching of a C–H bond is about $3000\,\text{cm}^{-1}$.

Calculate the ratio

$$\frac{k_\text{r}(\text{C–D})}{k_\text{r}(\text{C–H})}$$

Calculation

From infrared spectra, the fundamental vibrational wavenumber $\tilde{\nu}$ for stretching of a C–H bond is about 3000 cm^{-1}.

Calculate the ratio $\dfrac{k_r(\text{C–D})}{k_r(\text{C–H})}$

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$$\omega = 2\pi c\tilde{\nu},$$

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$$\zeta = \frac{\hbar\omega(\text{C–H})}{2kT}\left\{1 - \left(\frac{\mu_{\text{CH}}}{\mu_{\text{CD}}}\right)^{1/2}\right\}$$

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$$\omega = 2\pi c\tilde{\nu},$$

$$\begin{aligned}\omega &= 2\pi \times (2.998\times10^{10}\,\mathrm{cm\,s^{-1}})\times(3000\,\mathrm{cm^{-1}})\\ &= 5.65\ldots\times10^{14}\,\mathrm{s^{-1}}\end{aligned}$$

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$$\frac{\mu_{\text{CH}}}{\mu_{\text{CD}}} = \left(\frac{m_{\text{C}}m_{\text{H}}}{m_{\text{C}}+m_{\text{H}}}\right)\times\left(\frac{m_{\text{C}}+m_{\text{D}}}{m_{\text{C}}m_{\text{D}}}\right)$$

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From infrared spectra, the fundamental vibrational wavenumber $\tilde{\nu}$ for stretching of a C–H bond is about $3000\,\mathrm{cm^{-1}}$.

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$$\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}} = \left(\frac{m_{\mathrm{C}} m_{\mathrm{H}}}{m_{\mathrm{C}} + m_{\mathrm{H}}}\right) \times \left(\frac{m_{\mathrm{C}} + m_{\mathrm{D}}}{m_{\mathrm{C}} m_{\mathrm{D}}}\right)$$

$$= \left(\frac{12.01 \times 1.0078}{12.01 + 1.0078}\right) \times \left(\frac{12.01 + 2.0140}{12.01 \times 2.0140}\right)$$

$$= 0.539\ldots$$

$$\frac{k_r(\mathrm{C{-}D})}{k_r(\mathrm{C{-}H})} = \mathrm{e}^{-\zeta}$$

$$\zeta = \frac{\hbar\omega(\mathrm{C{-}H})}{2kT}\left\{1 - \left(\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}}\right)^{1/2}\right\}$$

Calculation From infrared spectra, the fundamental vibrational wavenumber $\tilde{\nu}$ for stretching of a C–H bond is about 3000 cm^{-1}.

Calculate the ratio $\dfrac{k_r(\text{C–D})}{k_r(\text{C–H})}$

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$$\begin{aligned}\omega &= 2\pi \times (2.998\times10^{10}\,\text{cm s}^{-1}) \times (3000\,\text{cm}^{-1})\\ &= 5.65\ldots\times10^{14}\,\text{s}^{-1}\end{aligned}$$

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$$\frac{k_r(\text{C–D})}{k_r(\text{C–H})} = \text{e}^{-\zeta}$$

$$\zeta = \frac{\hbar\omega(\text{C–H})}{2kT}\left\{1-\left(\frac{\mu_{\text{CH}}}{\mu_{\text{CD}}}\right)^{1/2}\right\}$$

$$\zeta = \frac{(1.055\times10^{-34}\,\text{J s})\times(5.65\ldots\times10^{14}\,\text{s}^{-1})}{2\times(1.381\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})}\times(1-0.539\ldots^{1/2})$$

$$= 1.92\ldots$$

Calculation

From infrared spectra, the fundamental vibrational wave-number $\tilde{\nu}$ for stretching of a C–H bond is about 3000 cm^{-1}.

Calculate the ratio $\dfrac{k_{\mathrm{r}}(\mathrm{C–D})}{k_{\mathrm{r}}(\mathrm{C–H})}$

$$\omega = 2\pi c\tilde{\nu},$$

$$\begin{aligned}\omega &= 2\pi \times (2.998\times 10^{10}\,\mathrm{cm\,s^{-1}}) \times (3000\,\mathrm{cm^{-1}})\\ &= 5.65\ldots \times 10^{14}\,\mathrm{s^{-1}}\end{aligned}$$

$$\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}} = \left(\frac{m_{\mathrm{C}}m_{\mathrm{H}}}{m_{\mathrm{C}}+m_{\mathrm{H}}}\right)\times\left(\frac{m_{\mathrm{C}}+m_{\mathrm{D}}}{m_{\mathrm{C}}m_{\mathrm{D}}}\right)$$

$$= \left(\frac{12.01\times 1.0078}{12.01+1.0078}\right)\times\left(\frac{12.01+2.0140}{12.01\times 2.0140}\right)$$

$$= 0.539\ldots$$

$$\frac{k_{\mathrm{r}}(\mathrm{C–D})}{k_{\mathrm{r}}(\mathrm{C–H})} = \mathrm{e}^{-\zeta}$$

$$\zeta = \frac{\hbar\omega(\mathrm{C–H})}{2kT}\left\{1-\left(\frac{\mu_{\mathrm{CH}}}{\mu_{\mathrm{CD}}}\right)^{1/2}\right\}$$

$$\zeta = \frac{(1.055\times 10^{-34}\,\mathrm{J\,s})\times(5.65\ldots\times 10^{14}\,\mathrm{s^{-1}})}{2\times(1.381\times 10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}\times(1-0.539\ldots^{1/2})$$

$$= 1.92\ldots$$

$$\frac{k_{\mathrm{r}}(\mathrm{C–D})}{k_{\mathrm{r}}(\mathrm{C–H})} = \mathrm{e}^{-1.92\ldots} \quad = 0.146$$

Focus 18: Reaction Dynamics

Collision theory

Diffusion-controlled reactions and transition-state

The dynamics of molecular collisions

Electron transfer in homogeneous systems