

## Lecture 4 Ion Thermochemistry

### Reminmder of terms and quantities

#### Thermochemical parameters

|                    |   |
|--------------------|---|
| AE                 | Appearance Energy                       |
| EA                 | Electron Affinity                       |
| IE                 | Ionization Energy                       |
| PA                 | Proton Affinity (enthalpic)             |
| GB                 | Gas Phase Basicity (free energy)        |
| -G <sub>acid</sub> | Gas Phase Acidity (free energy acidity) |
| -H <sub>acid</sub> | Gas Phase Acidity (enthalpic quantity)  |
| RE                 | Recombination Energy                    |
| HA                 | Hydride Affinity                        |

#### Rationale for Thermochemistry

Mass Spectrometry is a major method of determining thermochemical values for ions & neutrals  
Thermochemical information is essential to predict ionization will occur.

In large molecules, thermochemical information indicates where ionization/reaction will occur

Thermochemical information indicates internal excitation of ionization process

Thermochemical information predicts unimolecular dissociation (and its rate) (from above)

Thermochemical information is needed to predict bimolecular reactions e.g. proton transfer

Thermochemical information is useful in characterizing ion structure

#### GLOSSARY – THERMOCHEMISTRY

##### Adiabatic

No heat transferred between system and surroundings; for a chemical reaction (ionization, dissociation, etc) this usually means the lowest energy product state is formed (eg. adiabatic dissociation, adiabatic ionization energy).

##### Vertical

Used to describe an electronic transition or ionization (neutralization) occurring at the Born-Oppenheimer limit, i.e., with no change in nuclear coordinates of the molecule (eg. vertical excitation, vertical ionization energy).

##### Ionization energy (IE)

Also ionization potential (IP), energy required to remove an electron:  $M \rightarrow M^+ + e$ ; strictly refers to 0 K; may be adiabatic or vertical (recombination energy (RE) is energy released when electron added to an ion)

##### Heat of formation of a positive ion ( $\Delta H_f^\circ(M^+)$ )

Sum of the heat of formation of a neutral molecule and its adiabatic ionization potential:

$$\Delta H_f^\circ(M^+) = \Delta H_f^\circ(M) + IE(K) \text{ (at 0 K)}$$

##### Electron affinity (EA)

Negative of the energy of the reaction in which a negative ion is formed (electron is attached)

$$\text{EA} = -[\Delta H_{\text{rxn}}] = -[\Delta H_f^\circ(\text{M}^-) + \Delta H_f^\circ(\text{e}^-) - \Delta H_f^\circ(\text{M})] = -[\Delta H_f^\circ(\text{M}^-) - \Delta H_f^\circ(\text{M})] \\ = \Delta H_f^\circ(\text{M}) - [\Delta H_f^\circ(\text{M}^-)]$$

So EA is positive when  $\Delta H_f^\circ(\text{M})$  is greater than  $\Delta H_f^\circ(\text{M}^-)$ , i.e. **when the anion is more stable than the neutral.. Many molecules do have metastable anions, i.e. they have -ve EA's but are relatively long lived**

EA is also equal to the energy required to remove an electron from a negative ion:  $\text{M}^- \rightarrow \text{M} + \text{e}^-$ ; strictly refers to 0 K; may be adiabatic or vertical.

Most molecules with stable anions have EA's from 0 - 5 eV

Heat of formation of a negative ion ( $\Delta H_f^\circ(\text{M}^-)$ )

Heat of formation of a neutral molecule **less** its adiabatic electron affinity:

$$\Delta H_f^\circ(\text{M}^-) = \Delta H_f^\circ(\text{M}) - \text{EA(K)} \text{ (at 0 K)}$$

“Stationary electron” convention

Sometimes referred to as the “ion convention”; the integrated heat capacity of the electron is taken as zero.

Appearance energy (AE)

Also appearance potential (AP); mass spectrometrically determined amount of energy required to form an ion from a neutral molecule,

this is approximately equal to the heat of reaction:  $\text{AB} \rightarrow \text{A}^+ + \text{B} + \text{e}^-$  (or  $\text{e}^- + \text{AB} \rightarrow \text{A}^- + \text{B}$ )  
[ if there is a barrier for the reaction, then the approximation will not be exact]

Bond dissociation energy

BDE,  $D[\text{A}-\text{B}]$ ,  $D[\text{A}^+-\text{B}^-]$ , etc.

Energy required to break a bond in a molecule; may be homolytic or heterolytic.

$D_0^\circ[\text{A}-\text{B}]$  or  $D_0[\text{A}-\text{B}]$  at 0 K  $D_{298}^\circ[\text{A}-\text{B}]$  or  $D_{298}[\text{A}-\text{B}]$  at 298K

Approx. given by the energy difference  $\text{AE} - \text{IE}$

Also known as the critical energy (min energy for formation of a particular product, usually lowest energy)

Bond dissociation enthalpy

$\text{DH}[\text{A}-\text{B}]$ ,  $\text{DH}^\circ[\text{A}-\text{B}]$   $\text{DH}_{298}^\circ[\text{A}-\text{B}]$ , etc.

Enthalpy of homolytic or heterolytic bond cleavage; usually differs from bond energy by RT.

Proton affinity (PA)

Enthalpy change for the reaction:  $\text{BH}^+ \rightarrow \text{B} + \text{H}^+$ ; usually pertains to 298K

Equivalent definition is **negative of enthalpy change for addition of a proton**

**Note: all “affinity” definitions are analogous, most important are methyl cation affinity, hydride affinity; metal ion affinity (methyl cation affinities correlates with PA; hydride affinity of cation is inverse with cation stability; metal ion affinity correlates with Lewis acidity).**

Gas phase basicity (GB)

Free energy change for the reaction:  $\text{BH}^+ \rightarrow \text{B} + \text{H}^+$

$$\text{GB} = \text{PA} - T\Delta S_{\text{ioniz}}$$

$\Delta S_{\text{ioniz}}$  is  $\Delta S$  for ionization reaction, i.e.  $\Delta S_{\text{ioniz}} = \Delta S(\text{B}) + \Delta S(\text{H}^+) - \Delta S(\text{BH}^+)$   
 $\sim S(\text{H}^+) = 26 \text{ e.u (cal K}^{-1} \text{ mol}^{-1})$

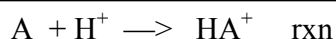
Hence  $\text{GB} - \text{PA} = 7.7 \text{ kcal/mol @ 298K}$

Gas phase acidity ( $\Delta G_{\text{acid}}$  or  $\Delta H_{\text{acid}}$ )

Free energy or enthalpy change, respectively, for the reaction:

$\text{AH} \rightarrow \text{A}^- + \text{H}^+$ ; enthalpy change pertains to 298K

$\Delta H_{\text{acid}}(\text{HA}) = \text{PA}(\text{A}^-)$ ;  $\Delta G_{\text{acid}} = \Delta H_{\text{acid}} - T\Delta S_{\text{acid}}$



Gas Phase Basicity (GB):  $-\Delta G_{\text{rxn}}$

Proton Affinity (A) :  $-\Delta H_{\text{rxn}}$

$\Delta H_{\text{acid}}(\text{HA}^+) = \text{PA}(\text{A})$  **reln between acid and conjugate base**

Methyl cation affinity (MCA)

Enthalpy change for the reaction:

$\text{BCH}_3^+ \rightarrow \text{B} + \text{CH}_3^+$ ; usually pertains to 298K

Hydride (ion) affinity (HA or HIA)

Enthalpy change (298K) for the reaction

$\text{AH} \rightarrow \text{A} + \text{H}^-$  or  $\text{RH} \rightarrow \text{R}^+ + \text{H}^-$

Solvation Energy

Energy released on solvation (enthalpy usually)

## Measuring Thermochemical Properties

Main methods are

### 1. **Equilibrium**

Rates of forward and reverse; positions of equilibrium

### 2. **Thermokinetic**

a. Bracketing – does a rxn occur; best to use a series of systems

b. Threshold – EI, PI, CID, etc

c. Kinetic method

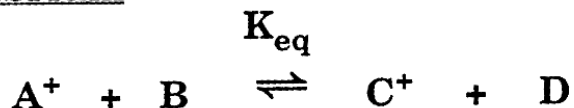
### 3. **Spectroscopic**

### 4. **Calculations**

NOTE : most methods are relative not absolute

Hence the importance of scales of values, e.g. Proton Affinities

### \* equilibrium

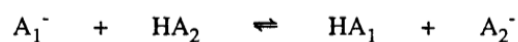


$$\Delta G_T = -RT \ln K_{eq}$$

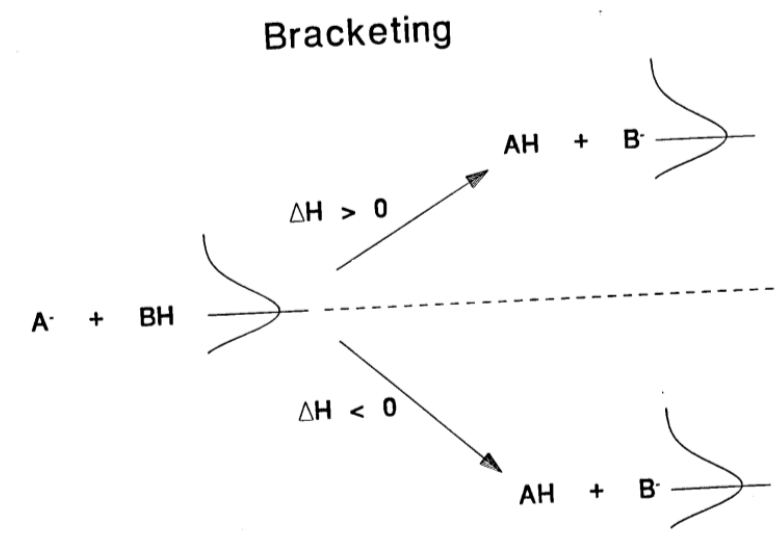
measure  $K_{eq}$  as  $f(T) \Rightarrow$  get  $\Delta H$  &  $\Delta S$

**High Pressure Mass Spectrometry (HPMS)**  
**Ion Cyclotron Resonance (ICR)**

**Proton transfer equilibrium**



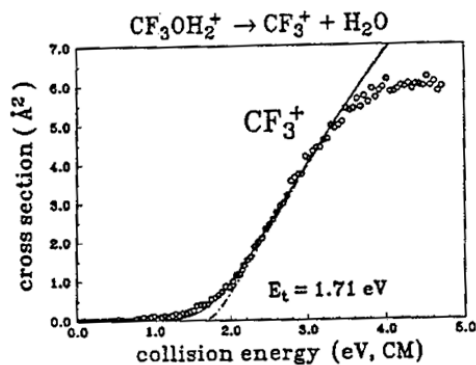
**Thermokinetic**



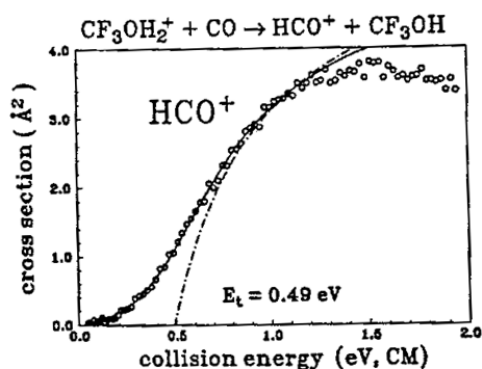
**Example Determination of Thermochemistry by Threshold Methods**

**Example: Determination of Acidity of Chloroform by Bracketing Method**

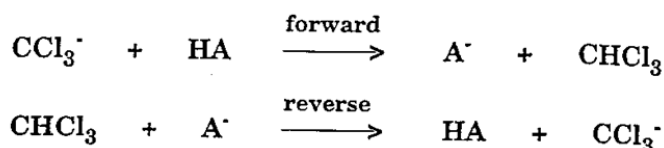
\* collision-induced dissociation thresholds:



\* ion/molecule reaction onsets:



Chyall, Squires *J. Phys. Chem.*, submitted

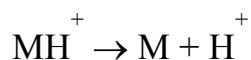


| HA  | $\Delta G_{\text{acid}}(\text{HA})$<br>kcal/mol | forward | reverse |
|---|---|---------|---------|
| PhCOCH <sub>3</sub>                                 | 354.5 ± 2.0                                     | -       | -       |
| CF <sub>3</sub> CH <sub>2</sub> OH                  | 354.1 ± 2.0                                     | -       | +       |
| CF <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> OH | 353.5 ± 2.0                                     | -       | +       |
| (Me <sub>3</sub> Si) <sub>2</sub> NH                | 352.9 ± 2.0                                     | -       | +       |
| HCONH <sub>2</sub>                                  | 352.8 ± 2.0                                     | -       | -       |
| Et <sub>3</sub> SiOH                                | 351.5 ± 2.0                                     | +       | +       |
| pyrrolidine   | 350.9 ± 2.0                                     | +(slow) | +(fast) |
| (CH <sub>3</sub> ) <sub>2</sub> CHNO <sub>2</sub>   | 350.0 ± 2.0                                     | +(slow) | +(fast) |
| CH <sub>3</sub> NO <sub>2</sub>                     | 349.7 ± 2.0                                     | +(fast) | +(slow) |
| CH <sub>3</sub> CH <sub>2</sub> SH                  | 348.9 ± 2.0                                     | +       | -       |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH  | 347.9 ± 2.0                                     | +       | -       |
| 1,3-cyclopentadiene                                 | 347.7 ± 2.0                                     | +       | -       |
| (CH <sub>3</sub> ) <sub>2</sub> CHSH                | 347.1 ± 2.0                                     | +       | -       |

Paulino, Squires *J. Am. Chem. Soc.* 1991, 113, 5574

### Cooks' Kinetic Method:

#### Thermochemistry for Protonation Reactions



- Proton Affinity:

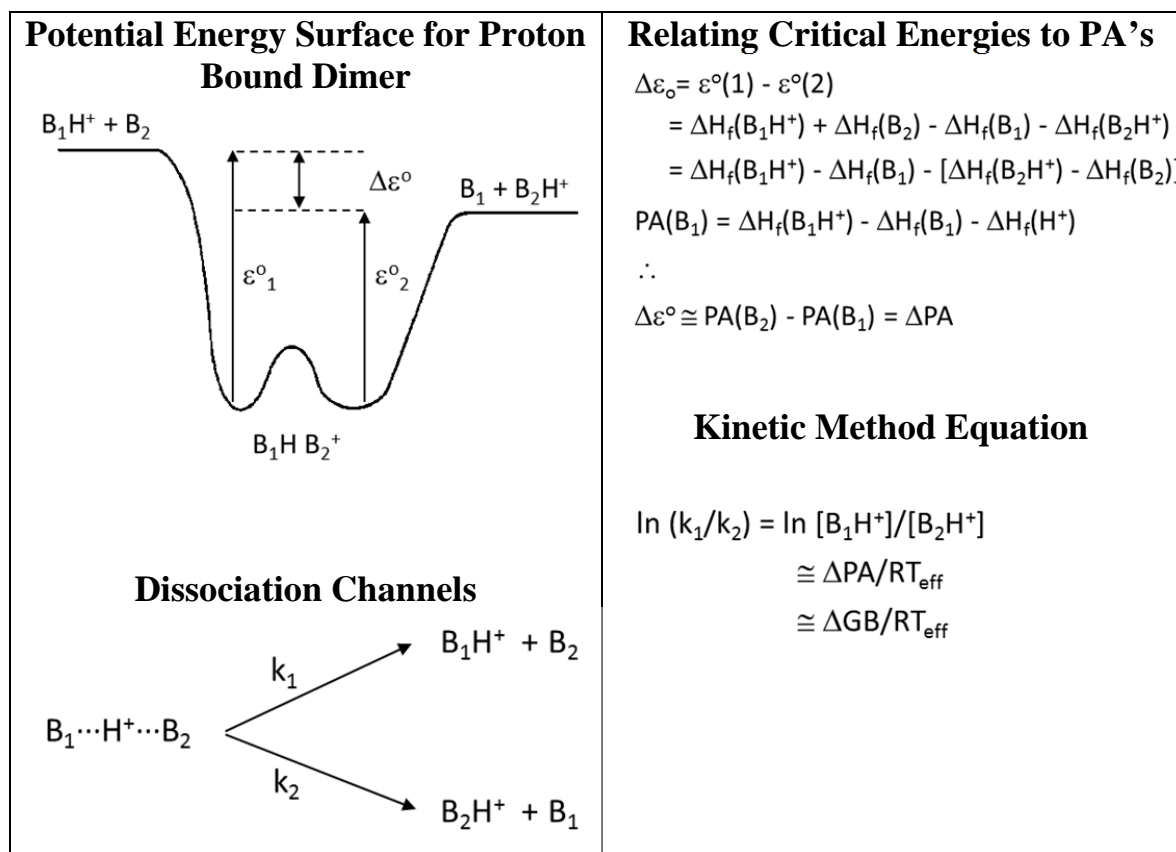
$$\text{PA}(\text{M}) = \Delta H_{\text{rxn}} = \Delta H_{\text{f}}(\text{H}^+) + \Delta H_{\text{f}}(\text{M}) - \Delta H_{\text{f}}(\text{MH}^+)$$

- Entropy of Protonation:

$$\Delta S_{\text{rxn}} = S^\circ(\text{H}^+) + S^\circ(\text{M}) - S^\circ(\text{MH}^+)$$

- Gas-Phase Basicity:

$$\text{GB}^{\text{T}}(\text{M}) = \Delta G_{\text{rxn}}^{\text{T}} = \Delta H_{\text{rxn}}^{\text{T}} - T\Delta S_{\text{rxn}}^{\text{T}}$$



## Kinetic Method Derivation:

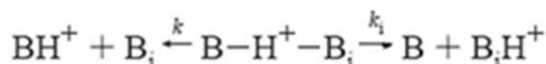
### Cooks' Kinetic Method—thermochemical Determination

Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279.

Cooks, R. G.; Patrick, J. S.; Kotiaho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1994**, *13*, 287.

Cooks, R. G.; Wong, P. S. H. *Acc. Chem. Res.* **1998**, *31*, 379.

Tao, W. A.; Zhang, D.; Nikolaev, E. N.; Cooks, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 10598.



**Unimolecular reaction theory**

$$\ln((k_i/k)) = \ln([\text{B}_i\text{H}^+]/[\text{BH}^+]) \approx \ln(Q_i^*/Q^*) + \frac{\Delta\epsilon_0}{RT_{\text{eff}}}$$

$Q_i^*$  and  $Q^*$ : the partition functions of the transition states  
 effective temperature  $T_{\text{eff}}$ : characteristic temperature of the activated complexes

**Assumption I: the reverse activation energies are negligible**

$$\begin{aligned} \Delta\epsilon_0 &= \epsilon_0(1) - \epsilon_0(2) = \Delta H_f(\text{B}_i\text{H}^+) + \Delta H_f(\text{B}_2) - \Delta H_f(\text{B}_1) \\ &\quad - \Delta H_f(\text{B}_2\text{H}^+) \\ &= \Delta H_f(\text{B}_i\text{H}^+) - \Delta H_f(\text{B}_1) - [\Delta H_f(\text{B}_2\text{H}^+) - \Delta H_f(\text{B}_2)] \\ PA(\text{B}_1) &= \Delta H_f(\text{B}_1\text{H}^+) - \Delta H_f(\text{B}_1) + \Delta H_f(\text{H}^+) \quad (2a) \\ \therefore \Delta\epsilon_0 &\approx PA(\text{B}_2) - PA(\text{B}_1) = \Delta PA. \end{aligned}$$

then: 
$$\ln((k_i/k)) = \ln([\text{B}_i\text{H}^+]/[\text{BH}^+]) \approx \ln(Q_i^*/Q^*) + \frac{PA(\text{B}_i) - PA(\text{B})}{RT_{\text{eff}}}$$

the term  $\ln(Q_i^*/Q^*)$  is equivalent to the difference in reaction entropy between the two dissociation channels

$$\ln((k_i/k)) = \ln([\text{B}_i\text{H}^+]/[\text{BH}^+]) \approx \frac{PA(\text{B}_i) - PA(\text{B})}{RT_{\text{eff}}} + \frac{\Delta(\Delta S)}{R}$$

**Assumption II: if only structurally similar reference and unknown species are involved,  $\Delta(\Delta S)/R$  can be canceled.**

➡ Standard form of the kinetic method

$$\ln((k_i/k)) = \ln([\text{B}_i\text{H}^+]/[\text{BH}^+]) \approx \frac{PA(\text{B}_i) - PA(\text{B})}{RT_{\text{eff}}}$$

Advantage: high sensitivity—isotopic substitution  
 rapid measurement

### **Recap of derivation:**

The kinetic method derivation is based on transition state theory with the unimolecular rate constant given as:

$$k_i = \frac{k_B T}{h} \left( \frac{\sum Q_{i,j}^*}{\sum Q_{i,j}} \right) e^{\left( \frac{-\varepsilon_i^\circ}{RT} \right)}$$

For the two dissociation channels, the natural log of the branching ratio is given as:

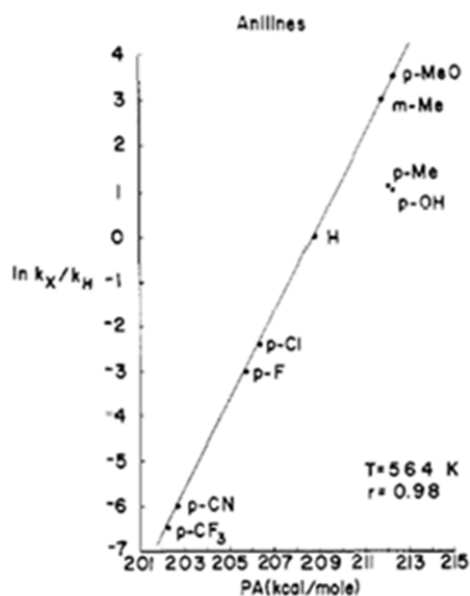
$$\ln \left( \frac{k}{k_i} \right) = \ln \left( \frac{Q^*}{Q_i^*} \right) + \frac{\varepsilon_i^\circ - \varepsilon^\circ}{RT}$$

As previously demonstrated,  $\Delta\varepsilon^\circ$  can be replaced by  $\Delta PA$  and  $T$  is replaced with  $T_{\text{eff}}$  in recognition that the ion population is a microcanonical ensemble

$$\ln \left( \frac{k}{k_i} \right) = \ln \left( \frac{Q^*}{Q_i^*} \right) + \frac{\Delta PA}{RT_{\text{eff}}}$$

For clusters composed of two bases of similar structure, the partition function term will cancel, leaving:

$$\ln \left( \frac{k}{k_i} \right) = \frac{\Delta PA}{RT_{\text{eff}}}$$



Logarithm of relative rates of dissociation from proton-bound dimers of a series of substituted anilines vs. proton affinity. All rates  $k_X$  where X represents the substituent are relative to aniline.

JACS, 1981, 103, 1313

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if the reference bases chosen are dissimilar in structure to the unknown peptides but remain structurally similar among themselves, the entropic term  $\Delta(\Delta S)/R$  is not negligible, but will likely remain constant.

Extended version of the kinetic method

$$\ln(k_i/k) = \ln\left(\frac{[B_iH^+]}{[BH^+]}\right) \approx \frac{PA(B_i) - PA(B)}{RT_{\text{eff}}} + \frac{\Delta(\Delta S)}{R}$$

a plot of  $\ln(k_i/k)$  versus  $PA(B_i)$  should still yield a straight line. Moreover, the slopes and intercepts of the linear regressions derived from a series of such plots provide values for the effective temperature  $T_{\text{eff}}$  and apparent gas-phase basicity  $GB_{\text{app}}(B)$ .

$$\frac{GB^{\text{app}}(B)}{RT_{\text{eff}}} \approx \frac{PA(B)}{RT_{\text{eff}}} - \frac{\Delta(\Delta S)}{R}$$

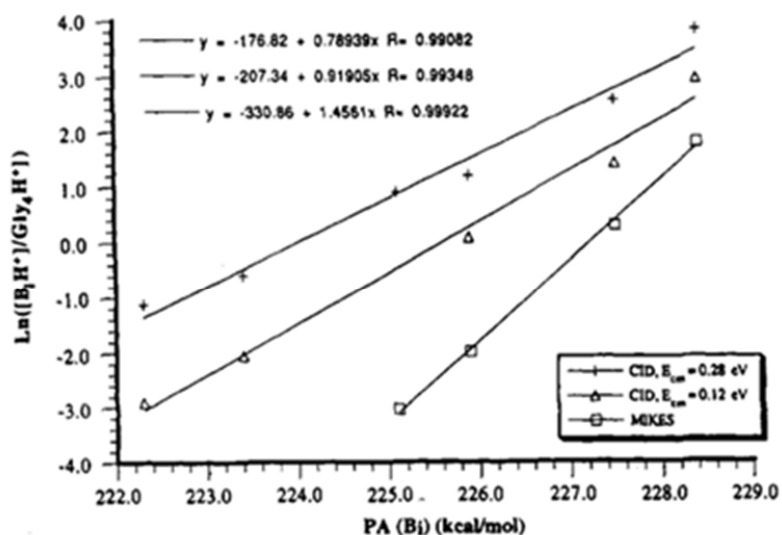
To extract the values of enthalpy ( $PA(B)$ ) and reaction entropy difference  $\Delta(\Delta S)$ , a second plot was constructed by plotting the negative of the intercepts versus the slopes obtained from a series of experiments performed at different collision energies (equivalent to  $GB_{\text{app}}(B)/RT_{\text{eff}}$  versus  $1/RT_{\text{eff}}$  at several values of  $T_{\text{eff}}$ ).

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**Example: Extended kinetic method**

**Plot I**

Slope:  $1/RT_{\text{eff}}$   
 Intercept:  $-GB_{\text{app}}(\text{B})/RT_{\text{eff}}$



Plot of the logarithms of the ratios of product ions from dissociation of proton-bound dimers containing Gly<sub>4</sub> and monoamines against PAs of the monoamines for experiments done at collision energies 0.28, 0.12, and 0.0 eV in the center-of-mass frame.

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|   |   |
|---|---|
| <p><b><u>Ionization Energy</u></b></p> $M_1M_2^{\bullet+} \begin{cases} \xrightarrow{k_1} M_1^{\bullet+} + M_2 \\ \xrightarrow{k_2} M_1 + M_2^{\bullet+} \end{cases}$         | $\ln \frac{[M_1^{\bullet+}]}{[M_2^{\bullet+}]} \approx \frac{-\Delta IE}{RT}$ |
| <p><b><u>Electron Affinity</u></b></p> $M_1 \cdots e^- \cdots M_2 \begin{cases} \xrightarrow{k_1} M_1^{\bullet-} + M_2 \\ \xrightarrow{k_2} M_1 + M_2^{\bullet-} \end{cases}$ | $\ln \frac{[M_1^{\bullet-}]}{[M_2^{\bullet-}]} \approx \frac{\Delta EA}{RT}$  |

### Internal Energy Distributions:

Breakdown curve: internal energy independent form of mass spectrum – more fundamental information

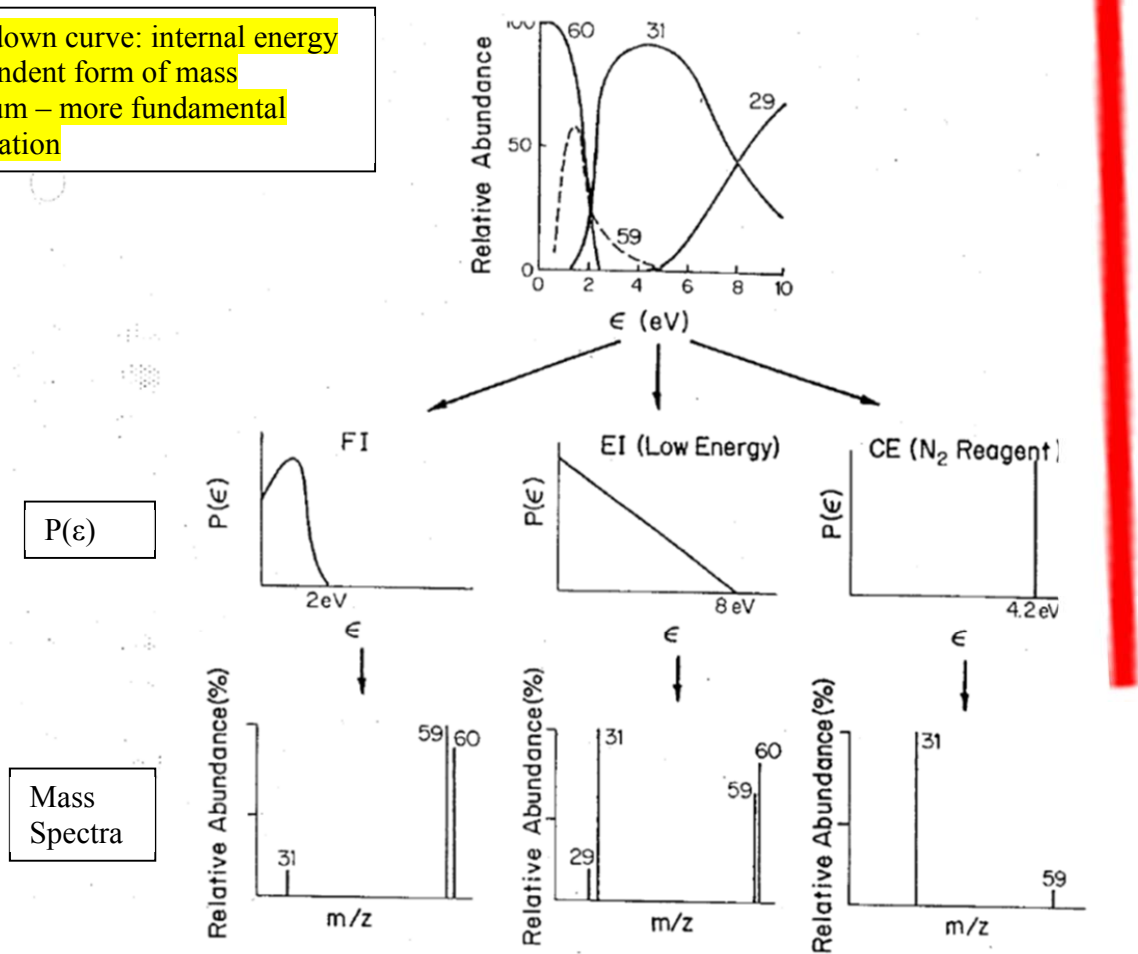


Figure 14-29 Convolution of the breakdown curve (top, an intrinsic property) with the internal energy distribution ( $P[\epsilon]$ ) resulting from different ionization techniques under particular experimental conditions to produce mass spectra of 1-propanol. FI indicates field ionization, a soft ionization method used for vapor phase samples.

**Thermometer ion method: determination of P(e)**

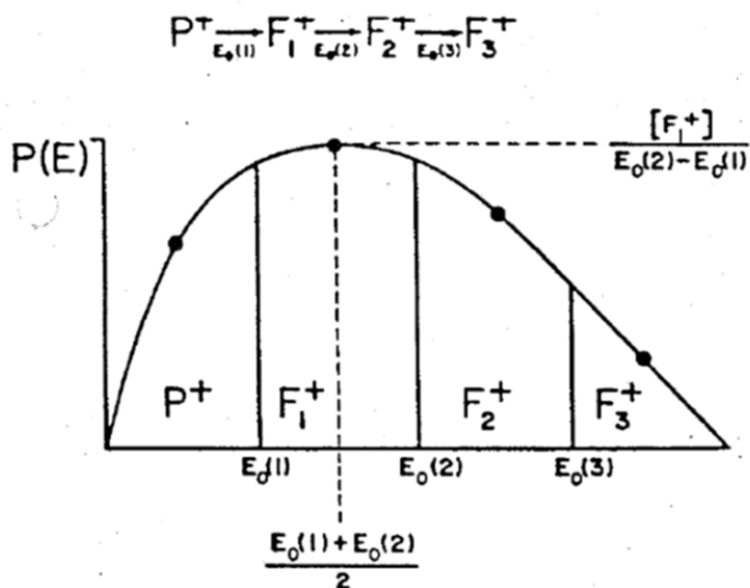


Fig. 1. Determination of internal energy distributions,  $P(E)$ , from ion abundances,  $[F_i]$ , and activation energies for fragmentation  $E_0(i)$  (see the text). The curves are normalized to the highest datum point.

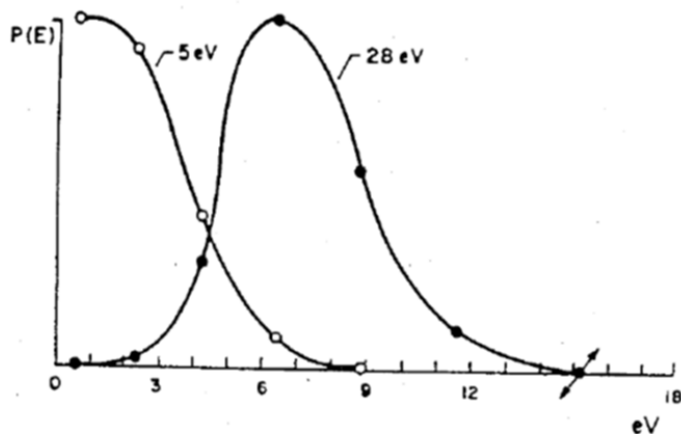
Thermochemical data

| Ion               | $m/z$ | IE/AE <sup>a</sup> | $E_0^b$ |
|-------------------|-------|--------------------|---------|
| $Fe(CO)_5^+$      | 196   | 8.0                | 0.0     |
| $Fe(CO)_4^+$      | 168   | 9.1                | 1.1     |
| $Fe(CO)_3^+$      | 140   | 10.1               | 2.1     |
| $Fe(CO)_2^+$      | 112   | 11.3               | 3.3     |
| $Fe(CO)^+$        | 84    | 13.5               | 5.5     |
| $Fe^+$            | 56    | 15.5               | 7.5     |
| $FeC^+$           | 68    | 23.6               | 15.6    |
| $W(CO)_6^+$       | 352   | 8.5                | 0.0     |
| $W(CO)_5^+$       | 324   | 9.7                | 1.2     |
| $W(CO)_4^+$       | 296   | 11.9               | 3.4     |
| $W(CO)_3^+$       | 268   | 13.7               | 5.2     |
| $W(CO)_2^+$       | 240   | 16.0               | 7.5     |
| $W(CO)^+$         | 212   | 18.6               | 10.1    |
| $W^+$             | 184   | 21.5               | 13.0    |
| $W(C_2O)^+$       | 224   | 25.9               | 17.4    |
| $(C_2H_5)_4Si^+$  | 144   | 10.5               | 0.0     |
| $(C_2H_5)_3Si^+$  | 115   | 11.0               | 0.5     |
| $(C_2H_5)_2SiH^+$ | 87    | 12.5               | 2.0     |
| $(C_2H_5)SiH_2^+$ | 59    | 14.0               | 3.5     |
| $(C_2H_5)Si^+$    | 57    | 19.4               | 8.9     |
| $SiH_3^+$         | 31    | 20.6               | 10.1    |
| $SiH^+$           | 29    | 26.8               | 16.3    |

Internal energy distributions for low energy CID

*International Journal of Mass Spectrometry and Ion Processes*, 75 (1987) 181-208

VICKI H. WYSOCKI, HILKKA I. KENTTÄMAA \*<sup>1</sup> and R. GRAHAM COOKS \*



Apparent  $P(E)$  distributions obtained for  $W(CO)_6^+$

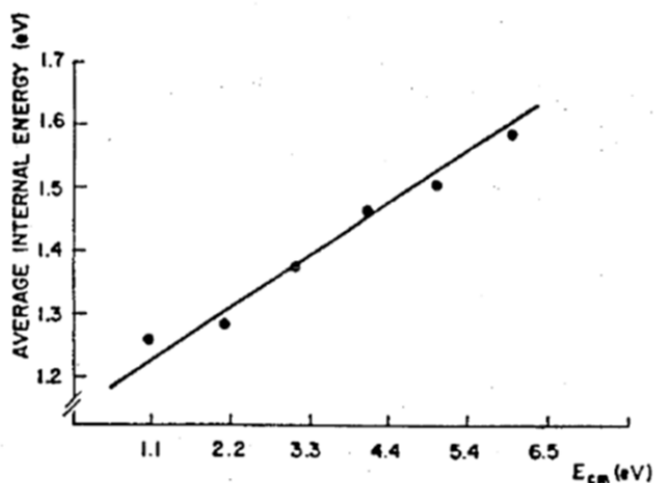
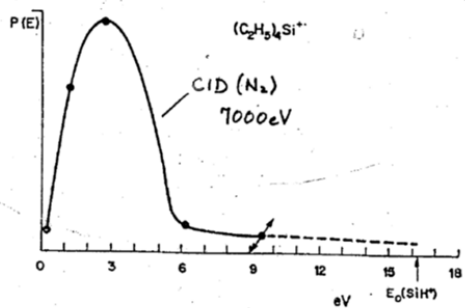
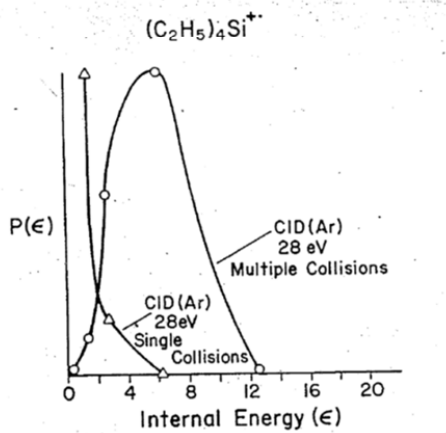
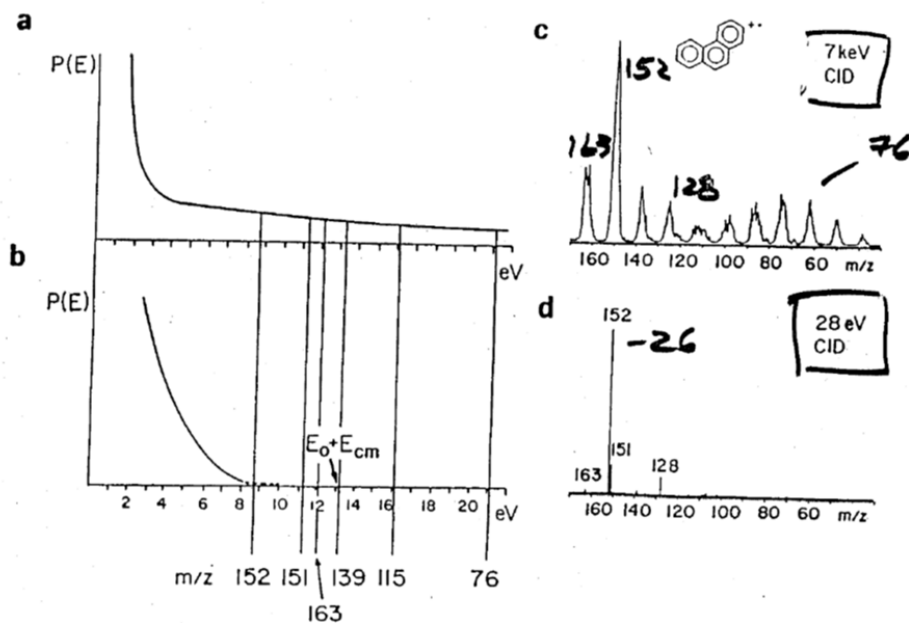


Fig. 6. The average energy of fragmenting  $(C_2H_5)_4Si^+$  ions after a single low-energy gas-phase collision with argon is apparently a linear function of the ion kinetic energy in the range of 5-28 eV (plotted as center of mass energy,  $E_{cm}$ ).

**Internal energy deposition – high and low collision energy CID**



Used for MS Short Course at Tsinghua  
by R. Graham Cooks, Hao Chen, Zheng Ouyang, Andy Tao, Yu Xia and Lingjun Li