Temperature-Programmed Desorption

C-874

University of Delaware

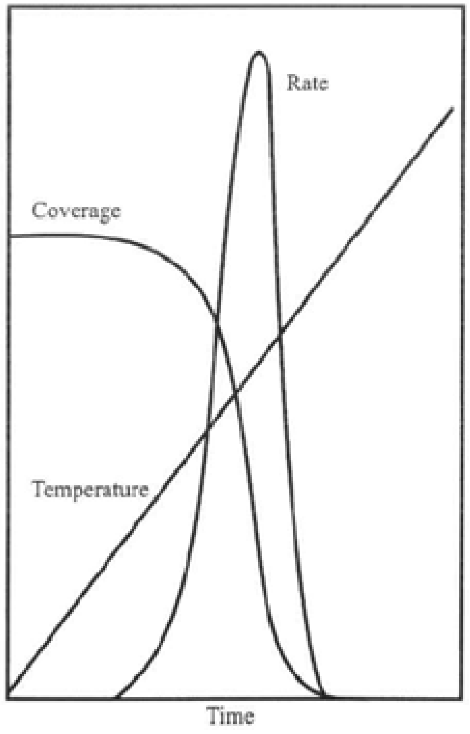
Temperature-Programmed Desorption

Alternative terms:
TPD - Temperature Programmed Desorption
TDS - Thermal Desorption Spectroscopy
TPRS - Temperature Programmed Reaction Spectroscopy
TPR/D - Temperature Programmed Reaction/Desorption

What are temperature programmed methods

- Temperature programmed methods are typically non-steady-state methods involving heating of materials according to a – usually linear – temperature program;
- The sample is placed in an inert stream of gas, or the temperature program is applied to a single crystal under vacuum;
- If a gas is previously adsorbed on the surface, gradual heating causes its desorption (TPD) with increasing temperature the desorption rate increases, reaches a maximum and then decreases as the surface is depleted of adsorbate

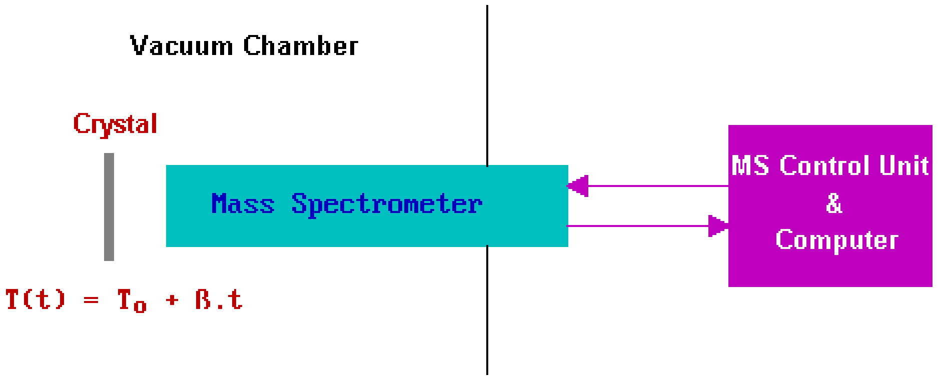
What is the measurable quantity



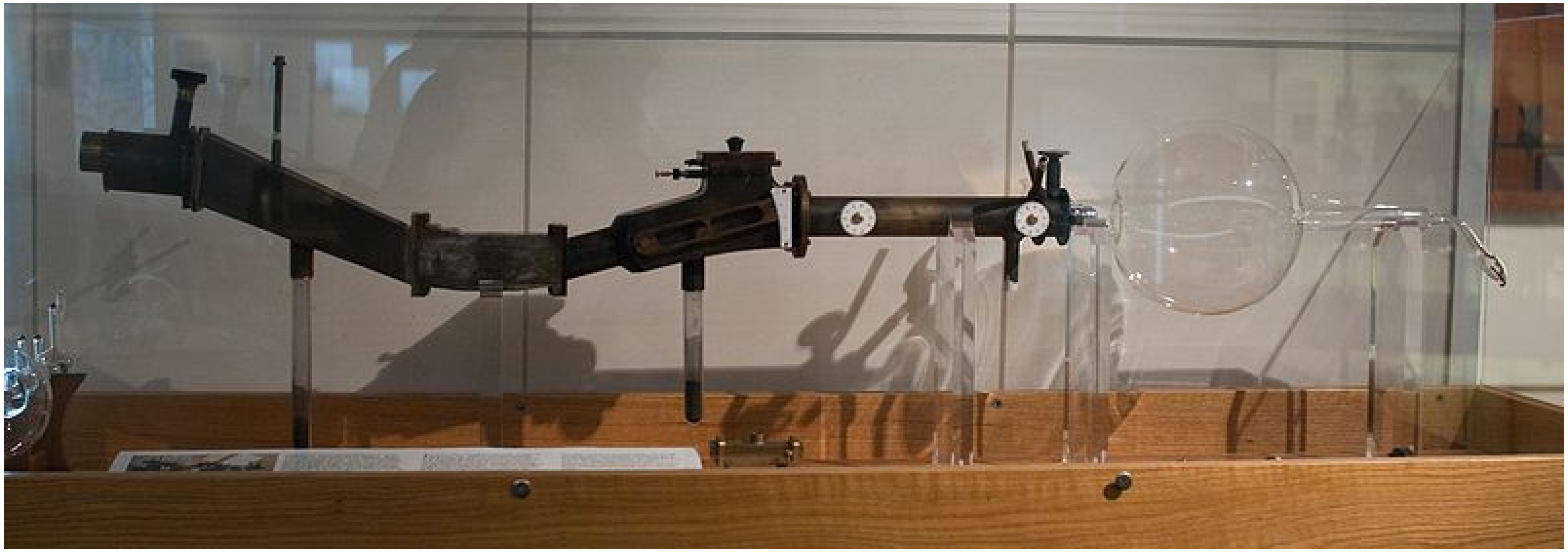
Typically, surface is heated at a linear temperature ramp and one of the following is followed:

1) Total weight of the sample (TGA);
2) Total pressure
3) Evolution of a selected mass (actually mass-to-charge ratio) by a mass spectrometer

Instrumentation Schematics

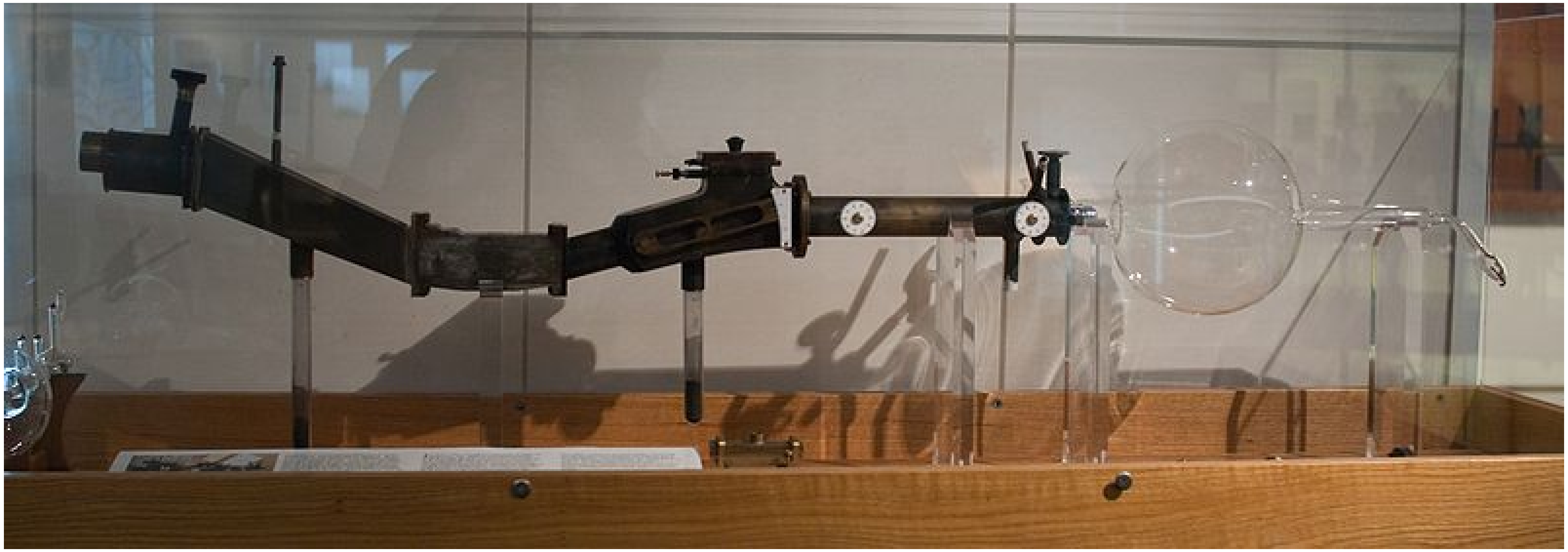


Brief review of how mass spectrometer works



In 1886, Eugen Goldstein observed rays in gas discharges under low pressure that traveled away from the anode and through channels in a perforated cathode, opposite to the direction of negatively charged cathode rays (which travel from cathode to anode). Goldstein called these positively charged anode rays "Kanalstrahlen"; the standard translation of this term into English is "canal rays". Wilhelm Wien found that strong electric or magnetic fields deflected the canal rays and, in 1899, constructed a device with parallel electric and magnetic fields that separated the positive rays according to their charge-to-mass ratio (*Q/m*). Wien found that the charge-to-mass ratio depended on the nature of the gas in the discharge tube.

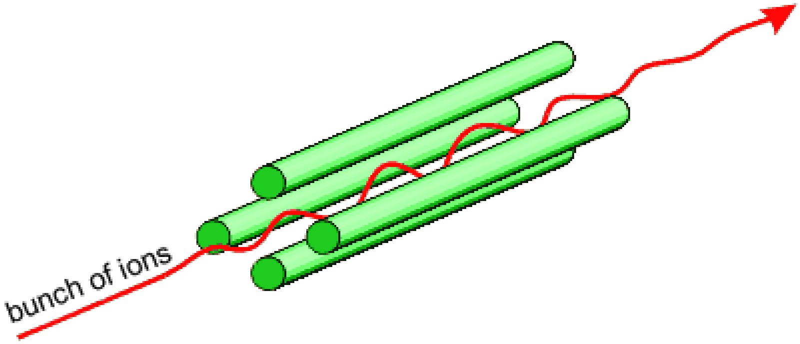
Brief review of how mass spectrometer works



English scientist J.J. Thomson later improved on the work of Wien by reducing the pressure to create a mass spectrograph. Some of the modern techniques of mass spectrometry were devised by Arthur Jeffrey Dempster and F.W. Aston in 1918 and 1919 respectively. In 1989, half of the Nobel Prize in Physics was awarded to Hans Dehmelt and Wolfgang Paul for the development of the ion trap technique in the 1950s and 1960s. In 2002, the Nobel Prize in Chemistry was awarded to John Bennett Fenn for the development of electrospray ionization (ESI) and Koichi Tanaka for the development of soft laser desorption (SLD) in 1987. However earlier, matrix-assisted laser desorption/ionization (MALDI), was developed by Franz Hillenkamp and Michael Karas; this technique has been widely used for protein analysis

Brief review of how mass spectrometer works

Quadrupole mass spectrometer (most commonly used in TPD)



The **quadrupole mass analyzer** is one type of mass analyzer used in mass spectrometry. As the name implies, it consists of 4 circular rods, set perfectly parallel to each other. In a quadrupole mass spectrometer the **quadrupole mass analyzer** is the component of the instrument responsible for filtering sample ions, based on their mass-to-charge ratio (*m/z*). Ions are separated in a quadrupole based on the stability of their trajectories in the oscillating electric fields that are applied to the rods

Brief review of how mass spectrometer works

Quadrupole mass spectrometer (most commonly used in TPD)

The sequence of events is :

Stage 1: Ionisation

The atom is ionised by knocking one or more electrons off to give a positive ion. This is true even for things which you would normally expect to form negative ions (chlorine, for example) or never form ions at all (argon, for example). Mass spectrometers always work with positive ions.

Stage 2: Acceleration

The ions are accelerated so that they all have the same kinetic energy.

Stage 3: Deflection

The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected.

The amount of deflection also depends on the number of positive charges on the ion - in other words, on how many electrons were knocked off in the first stage. The more the ion is charged, the more it gets deflected.

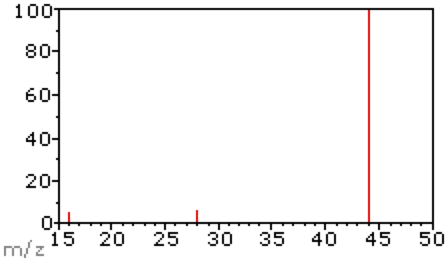
Stage 4: Detection

The beam of ions passing through the machine is detected electrically.

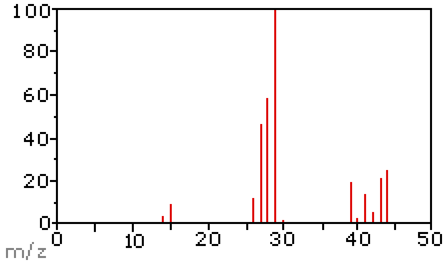
Brief review of how mass spectrometer works

Quadrupole mass spectrometer (most commonly used in TPD)

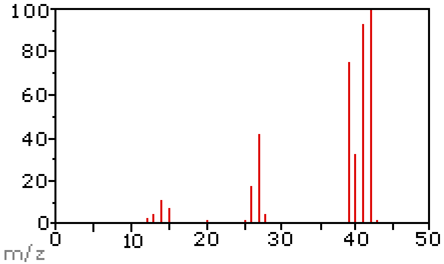
The result is a mass spectrum of a compound:



Carbon Dioxide



Propane



Cyclopropane

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/MassSpec/masspec1.htm

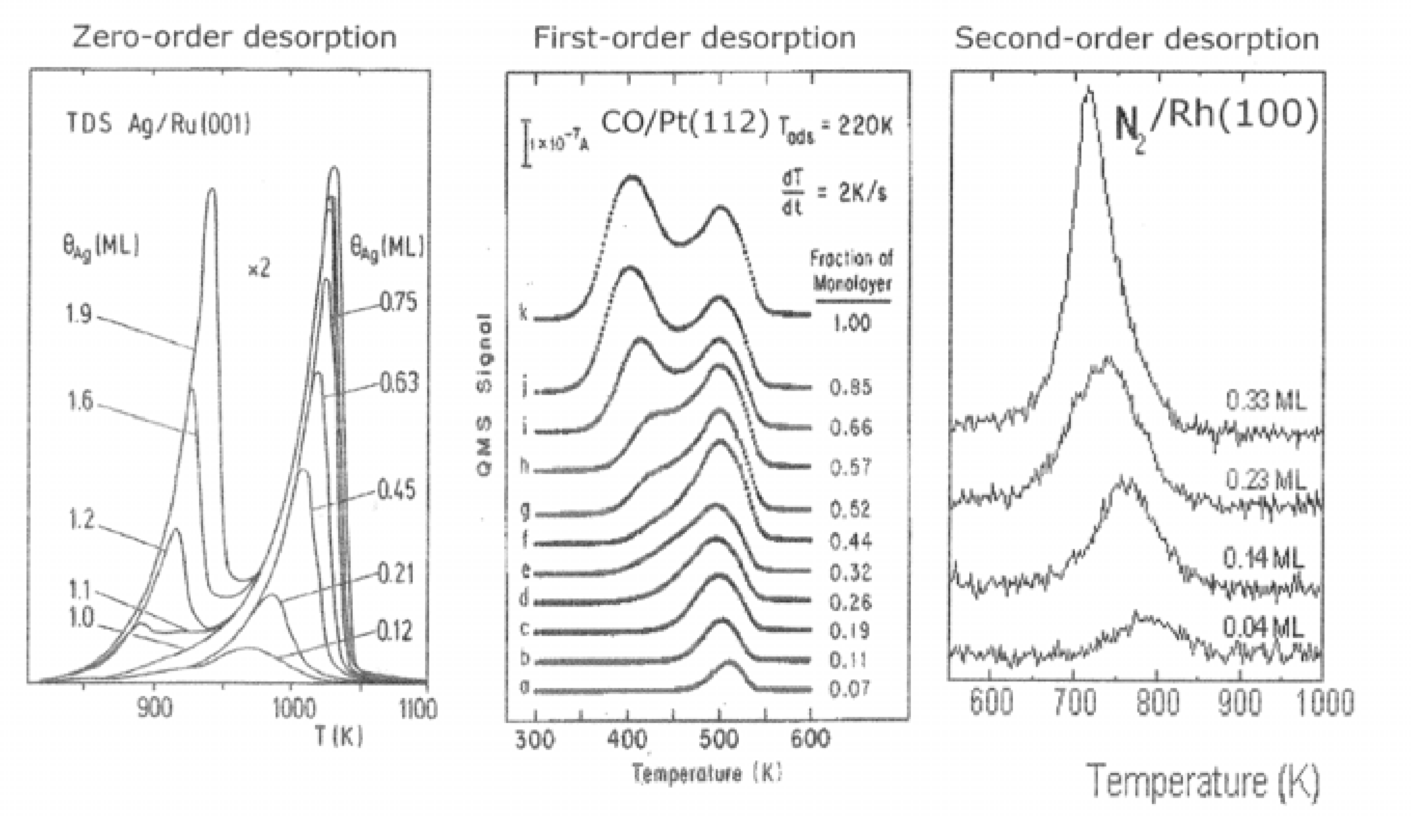
Brief review of how mass spectrometer works

Quadrupole mass spectrometer (most commonly used in TPD)

Now one can chose an m/z ration to follow as a function of time (or converted surface temperature).
Multiple m/z can be followed simultaneously.
Most common mass spectrometers can reliably follow 6-12 masses in one experiment

http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/MassSpec/masspec1.htm

Schematically:



What is the information obtained?

Obviously, the stronger the binding, the higher is the corresponding desorption temperature (need to destinguish physisorption and chemisorption, also need to compare activated and unactivated adsorption).

For unactivated adsorption.

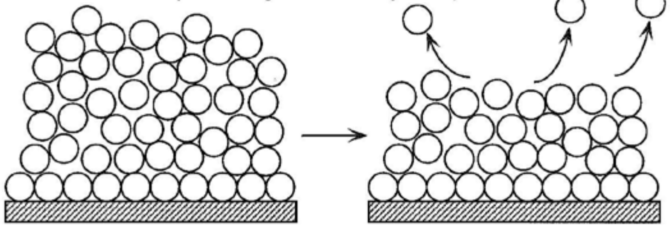
$$\boldsymbol{R}_{\mathrm{des}} = \nu\, \boldsymbol{N} \exp\left(- \boldsymbol{E}_{\mathrm{a,des}} / \boldsymbol{R}\, \boldsymbol{T} \right) \quad [1]$$

[1] **Redhead, P. A.** *Vacuum* **1962,** *12*, 203.

Zero Order

$$N(t) = -\,d\Theta/dt = \nu \exp(-E_a/RT)$$

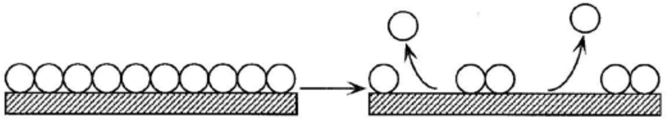
(Multilayer Desorption)



First Order

$$N(t) = -\,d\Theta/dt = \nu\, \Theta \exp(-E_a/RT)$$

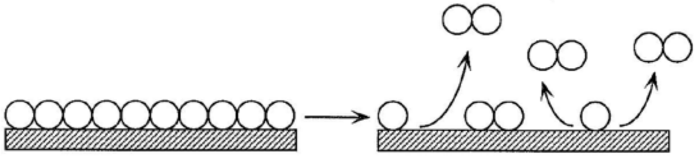
(Monolayer Desorption)



Second Order

$$N(t) = -\,d\Theta/dt = \nu\, \Theta^2 \exp(-E_a/RT)$$

(Recombinative Desorption)



Zero order desorption or reaction

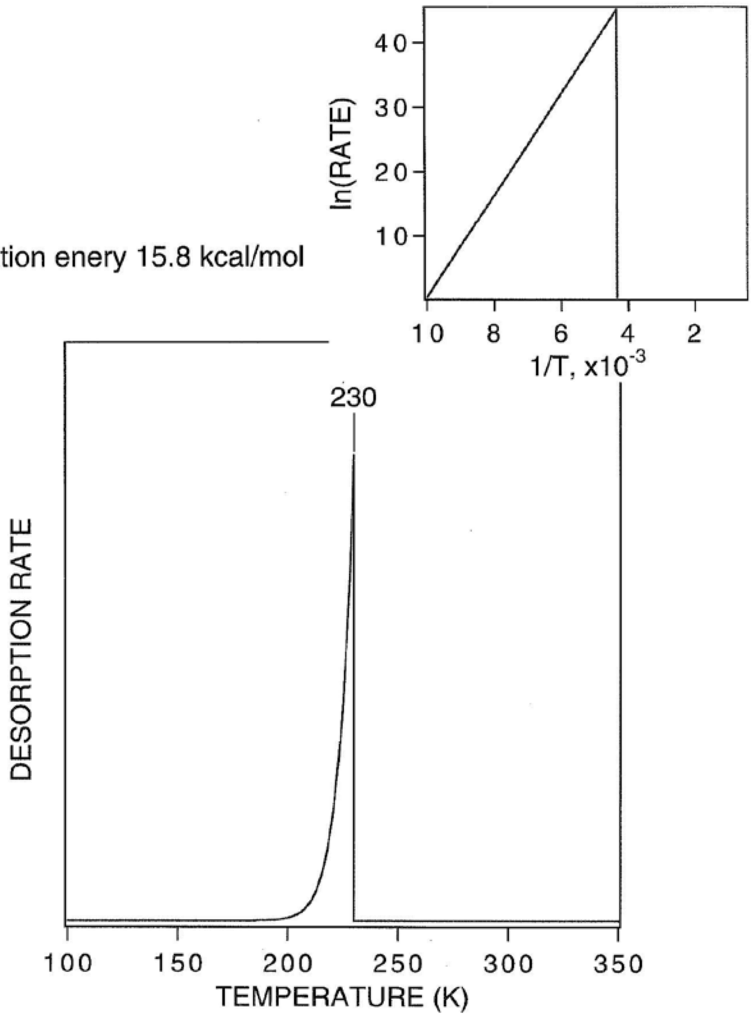
$$N(t) = -\, d\Theta/dt = \nu \exp(-E_a/RT)$$

$$\ln(N) - \ln(\nu) = -E_a/RT$$

N is the only variable in the right part of this equation, meaning that the slope of ln(N) plotted vs reciprocal temperature gives E_a/R

Zero Order Reaction/Desorption

Activation enery 15.8 kcal/mol



First order reaction or desorption

$$N(t) = -d\Theta/dt = \nu\,\Theta\,\exp(-E_a/RT) \qquad (1)$$

N - rate of desorption
Θ - coverage
t - time
ν - pre exponential factor
E_a - activation energy of desorption
R - molar gas constant
T - temperature

<u>Important assumption</u>: E_a does not depend on either temperature or coverage

For a linear heating rate, β: $T = T_0 + \beta t$

and Eq. 1 can be rewritten as

$$N(t) = -d\Theta/dt = \boxed{-\beta d\Theta/dT = \nu\Theta\exp(-E_a/RT)} \qquad (2)$$

Now differentiate eq.2:

$$-\beta d^2\Theta/dT^2 = \nu\, d\Theta/dT\exp(-E_a/RT) + \nu\Theta E_a/RT^2\exp(-E_a/RT)$$

At the peak temperature, T_p, the rate is maximum and its first derivative is zero.

$$0 = \nu\, d\Theta/dT\exp(-E_a/RT_p) + \nu\Theta E_a/RT_p^2\exp(-E_a/RT_p) =$$
$$-\nu\,\nu\Theta/\beta\exp(-E_a/RT_p)\exp(-E_a/RT_p) + \nu\Theta E_a/RT_p^2\exp(-E_a/RT_p)$$

OR

$$\boxed{E_a/RT_p^2 = \nu/\beta\exp(-E_a/RT_p)}$$

$$\boxed{E_a/RT_p^2 = \nu/\beta \exp(-E_a/RT_p)}$$

This equation does not have an analytical solution but for $10^8 < \nu < 10^{14}$ the relation between E_a and T_p is very linear and is given to within ±1.5 % by:

$$E_a/RT_p = \ln(\nu T_p/\beta) - 3.64$$

If one assumes the preexponential factor, E_a can be easily calculated.

If we don't know anything about the preexponential factor, then we need to vary the heating rate:

$$\begin{cases} E_a/RT_{p1}^2 = \nu/\beta_1 \exp(-E_a/RT_{p1}) \\ E_a/RT_{p2}^2 = \nu/\beta_2 \exp(-E_a/RT_{p2}) \end{cases}$$

$$\Delta \ln(\beta/RT^2) = \mathbf{E}_a/R\ \Delta(1/T_p)$$

Why is the pre-exponential factor for the 1st order process often close to 10^{13} s^{-1}?

Using Activated Complex Theory (or its further modifications), one can write the rate of an activated reaction as

$$v = f \times K^{AC} \frac{[AC]}{[\mathrm{Re}\,ac\tan t]}$$

, where K^{AC} is the equilibrium constant between the Activated Complex and the Reactants.
Thus, the rate constant, K, would be:

$$k = f \times K^{AC}$$

with f being the transmission factor, which according to the statistical thermodynamics is

$$f = \frac{k_b T}{h}$$

Now, since K^{AC} can be written as a ratio of the partition functions describing the transition state and the reactants, for a first-order process (such as a simple desorption) the transition state may look very similar to the reactants, setting this partition functions to be approximately the same. Thus at room temperature we have:

$$k = f \frac{q^{TS}}{q^{\mathrm{Re}\,ac\tan ts}} \approx f = \frac{k_b T}{h} = \frac{1.3806505 \times 10^{-23} \frac{J}{K} \times 298.15 K}{6.6260693 \times 10^{-34}\ J\ s} = 6.212 \times 10^{12}\, s^{-1}$$

APPLICATION OF DIFFERENT METHODS TO DETERMINE THE ACTIVATION ENERGY OF β-HYDRIDE ELIMINATION IN CYCLOHEXYL ON Cu(100)

1. The Habenschaden - Küppers or Leading Edge Method

   $E_a = 15.842 \pm .500$ kcal/mol

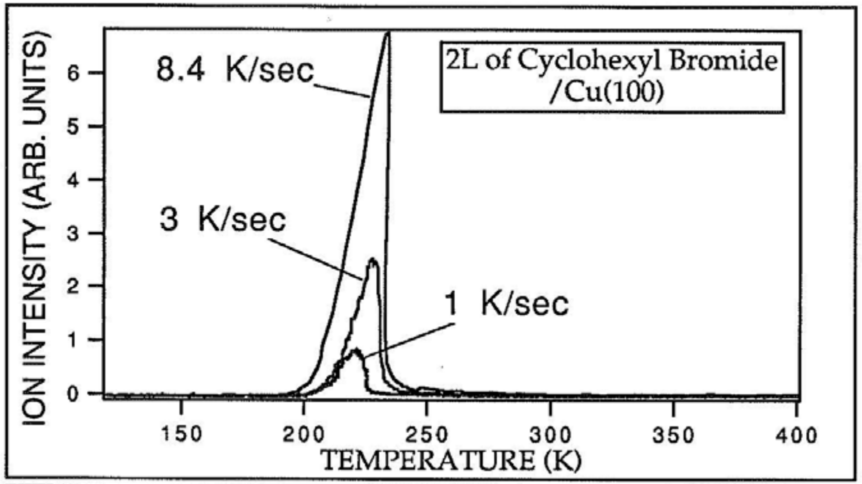
   $\nu = 5.75\mathrm{x}10^{13}$

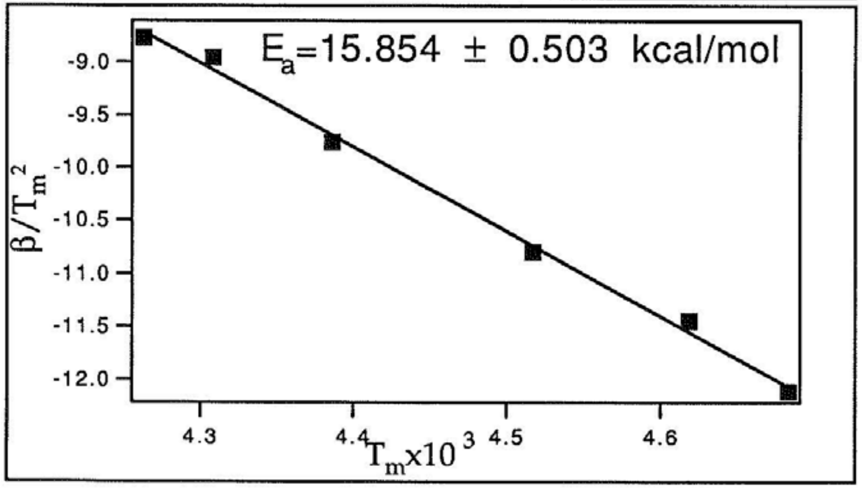
2. Heating Rate Variation Method

   $E_a = 15.854 \pm .503$ kcal/mol

3. Based on the Activation Energies calculated using first two methods, the Redhead's (peak maximum temperature) method gives the pre-exponential factor $0.5\text{-}4\mathrm{x}10^{14}$

Application of the Heating Rate Variation Method to Determine the Activation Energy of β-Hydride Eliminaion in Cyclohexyl/Cu(100)





Peak shape for the first order desorption

Let's integrate the first order kinetic equation:

$$N(t) = -d\Theta/dt = \nu\,\Theta\,\exp(-E_a/RT)$$

$$-\int_{\Theta_1}^{\Theta_2} d\Theta/\Theta = (\nu/\beta)\int_{T_1}^{T_1}\exp(-E_a/RT)\,dT = \ln(\Theta_1/\Theta_2)$$

$$\downarrow$$

use $\displaystyle\int_{-\infty}^{u}\frac{\exp(x)}{x}dx = \frac{\exp(u)}{u}\,f(u)$ for $|u| >> 1$,

where $f(u) = 1 + (1!/u) + (2!/u^2) + ...$

$$\downarrow$$

get:

$$(\nu/\beta)\int_{T_1}^{T_1}\exp(-E_a/RT)\,dT = \frac{\nu R}{\beta E_a}\Big[T_2^2\exp(-E_a/RT_2) - T_1^2\exp(-E_a/RT_1)\Big]$$

As we remember: $E/RT_p^2 = (\nu/\beta)\exp(-E_a/RT_p)$

This means that for $\Theta_1 = \Theta_0$ and $\Theta_2 = \Theta_{peak}$

$$\ln(\Theta_0/\Theta_p) = 1 - (T_0/T_p)^2\exp[-E_a/R(1/T_0 - 1/T_p)] \sim 1$$

consequently the peak is asymmetric

$$(\nu/\beta) \int_{T_1}^{T_1} \exp(-E_a/RT)\, dT = \frac{\nu R}{\beta E_a} \left[T_2{}^2 \exp(-E_a/RT_2) - T_1{}^2 \exp(-E_a/RT_1) \right]$$

$$-\int_{\Theta_1}^{\Theta_2} d\Theta/\Theta = (\nu/\beta) \int_{T_1}^{T_1} \exp(-E_a/RT)\, dT = \ln(\Theta_1/\Theta_2)$$

$$N(t) = - d\Theta/dt = \nu\, \Theta \exp(-E_a/RT)$$

$$\ln(N_p/N) = \frac{E_a}{R} \left[\frac{1}{T} - \frac{1}{T_p} \right] + \left(\frac{T}{T_p}\right)^2 \exp(E_a/R \left[\frac{1}{T} - \frac{1}{T_p} \right]) - 1$$

Something is funny!!!!! No β in the peak shape equation!!!

β - dependence is hidden in N_{peak}

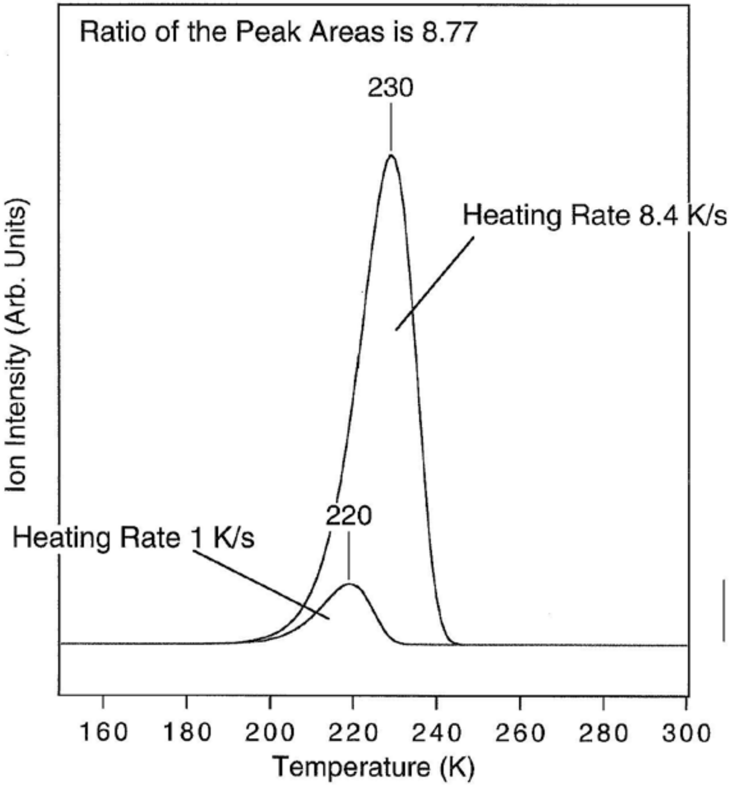
If we have made two measurements with heating rates β_1 and β_2 and found T_{peak1} and T_{peak2} at these heating rates, what would be the ratio of the measured desorption rates at peak temperatures?

$$\frac{N_{peak1}}{N_{peak2}} = \frac{\nu\,\Theta_{peak1}\exp\left(-E_a/RT_{peak1}\right)}{\nu\,\Theta_{peak2}\exp\left(-E_a/RT_{peak2}\right)}$$

We remember that $\dfrac{E}{RT_{peak}} = \ln\left(\nu T_{peak}/\beta\right)$

Then $$\frac{N_{peak1}}{N_{peak2}} = \frac{\beta_1/T_{peak1}}{\beta_2/T_{peak1}} \approx \frac{\beta_1}{\beta_2}$$

1st Order Reaction with
Activation Energy 15.8 kcal/mol
Preexponential Factor $5\times10^{13}\ s^{-1}$



THERMAL DESORPTION ANALYSIS: METHODS OF DETERMINATION OF ACTIVATION ENERGY

Polanyi-Wigner equation: $r(\Theta)=-d\Theta/dt=\nu(\Theta)\ \Theta^{n}\exp[-E(\Theta)/RT]$

r-the rate of desorption
Θ-the adsorbate coverage
t-the time
ν-the pre-exponential factor of desorption
n-the order of desorption
E-the activation energy of desorption
T-the temperature

1. The Habenschaden-Küppers or leading edge analysis.

   Select the low temeprature-high coverage side of a TPD spectrum: variations of T and Θ are insignificant.

   Arrhenius plot ($\ln(r)$ vs $1/T$) gives $-E(\Theta)/R$

2. Redhead's peak maximum method.

   For coverage-independent desorption parameters and first-order\ kinetics, differentiation of Polanyi-Wigner equation gives:

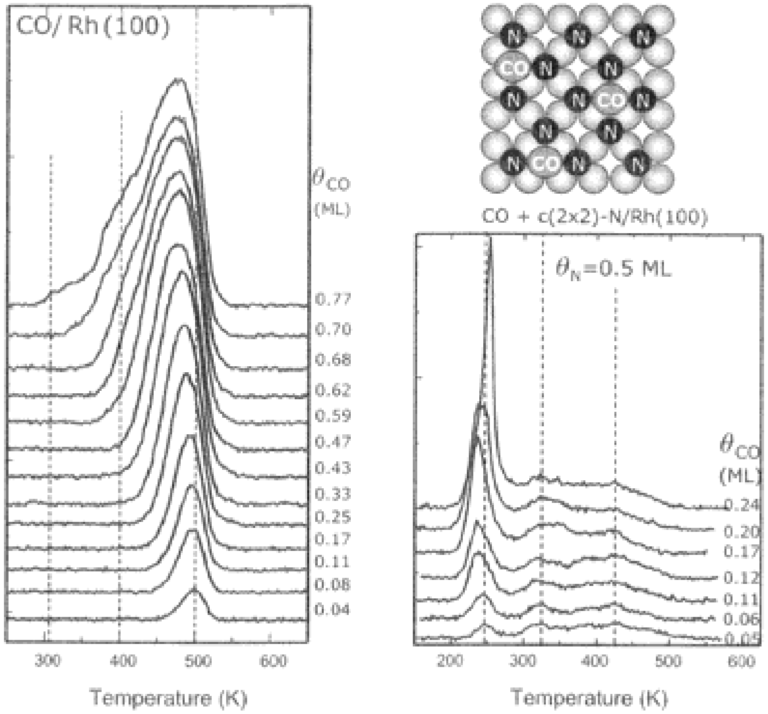
   $E/RT_m^2=(\nu/\beta)\exp(-E/RT_m)$ (where β-heating rate)

   Plots of E vs T for certain ν and β are almost linear and approximated by: $E=RT_m[\ln(\nu T_m/\beta)-3.46$

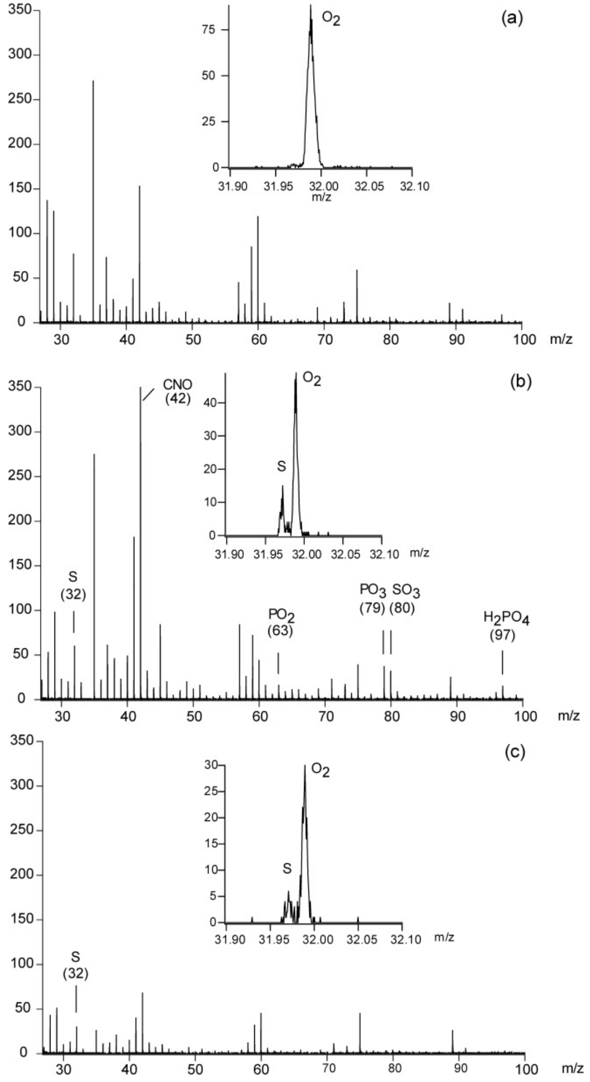
3. Heating rate variations.

   A logarithmic plot β/T_m^2 of versus $1/T_m$ gives a straight line with slope equal to $-E/R$. The method assumes that the fractional coverage left on the surface when the peak maximum is reached, is the same for all heating rates.

Lateral interactions in TPD:



Two additional remarks:
1) Modern mass spectrometry techniques can yield exceptionally high resolution

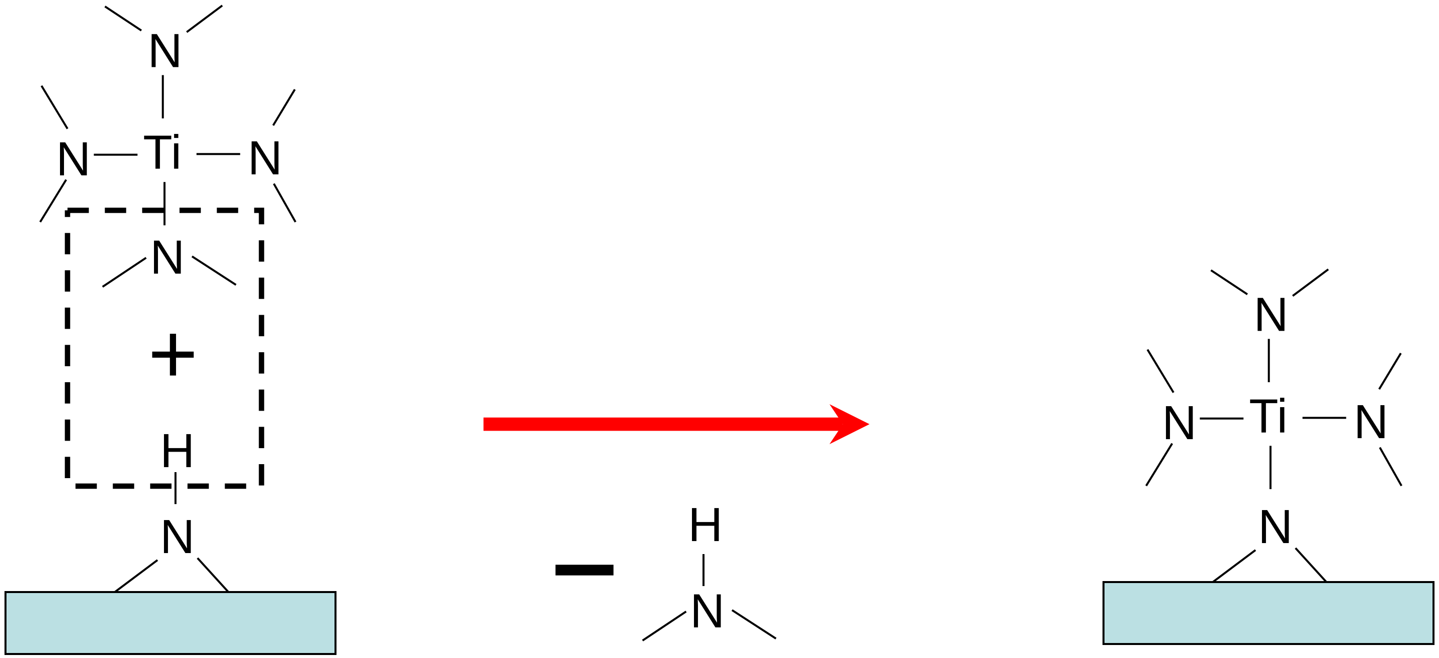


Negative ion **TOF-SIMS** spectra from the (a) Amino undecene SAM on Si(111) surface; (b) yDNA attached Si(111) surface; (c) DNA–modified Si(111) surface washed with the digestion enzyme. (m/z: 27-100)

Zhang, X., Kumar, S., Chen, J. and Teplyakov, A. V. Covalent attachment of DNA molecules on amine-functionalized Si(111) surface. *Surf. Sci.* **2009**, *603*, 2445-2475.

Two additional remarks:
2) We only considered desorption of a single product but multiple products can be deciphered

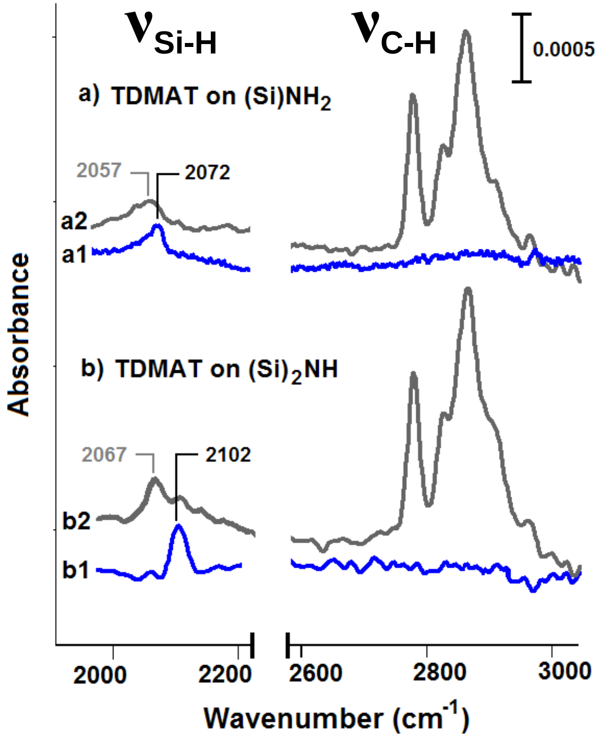
Chemistry of Transamination Process



Chemistry of Transamination Process

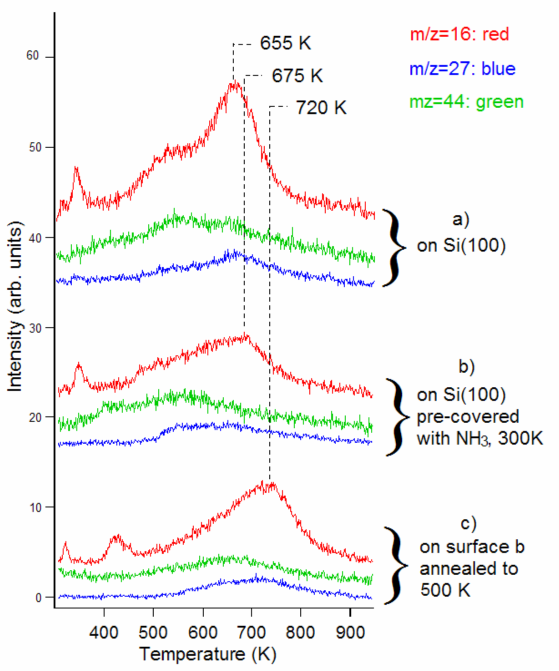
NH_X sites and the reaction with TDMAT

Chemisorption of TDMAT on $(Si)NH_X$ / (Si)H sites is confirmed by IR



TPD: TDMAT is not physisorbed. There is a reaction of TDMAT with surface sites at room temperature.

Evidence of different reactivity of NH_X sites.

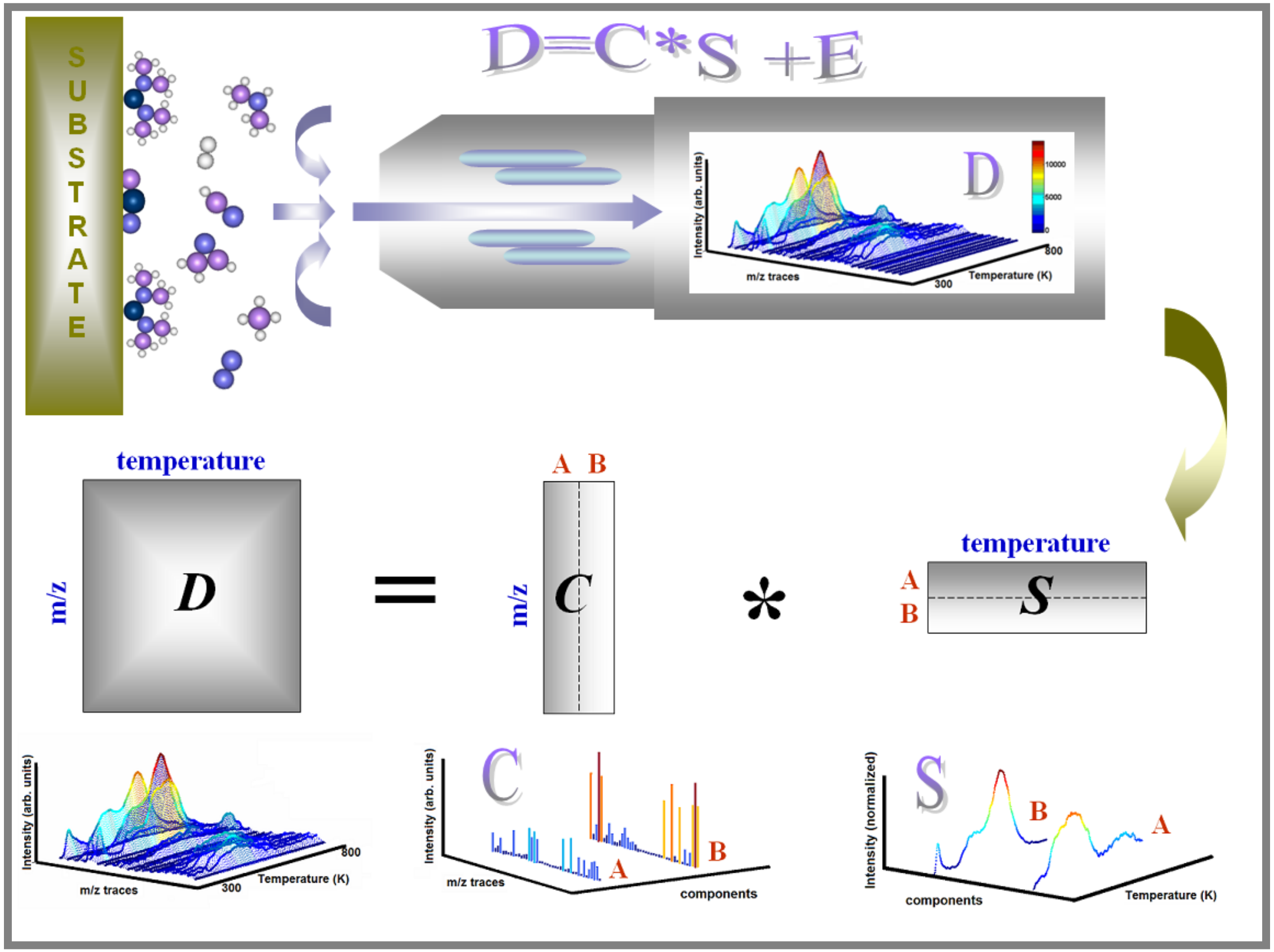


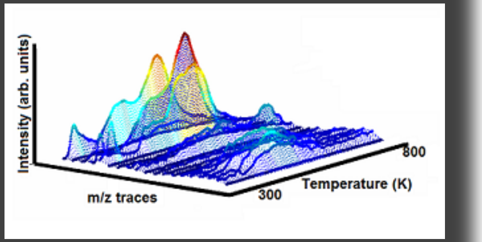
Rodríguez-Reyes, J. C. F. and Teplyakov, A. V. *J. Phys. Chem. C* **2007**, *111(44)*, 16498-16505.

Multivariate analysis:

An analytical tool for understanding TPD data

Rodriguez-Reyes, Teplyakov and Brown, *Surf. Sci.* ***2010***, *604, 2043.*





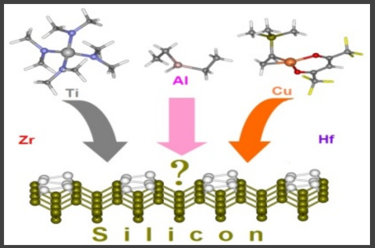
Multivariate analysis of TPD data

Details: Multivariate curve resolution (MCR) recognizes variations and correlations in m/z traces. The use of constraints (e.g. no negative intensities, N_2 have only two traces) optimize the results.

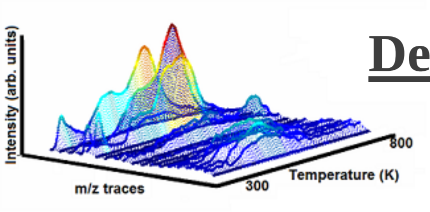
Metalorganic reactions:

Finding the source of undesired reactions

Rodriguez-Reyes, Teplyakov and Brown, *Surf. Sci.* ***2010***, *604, 2043.*

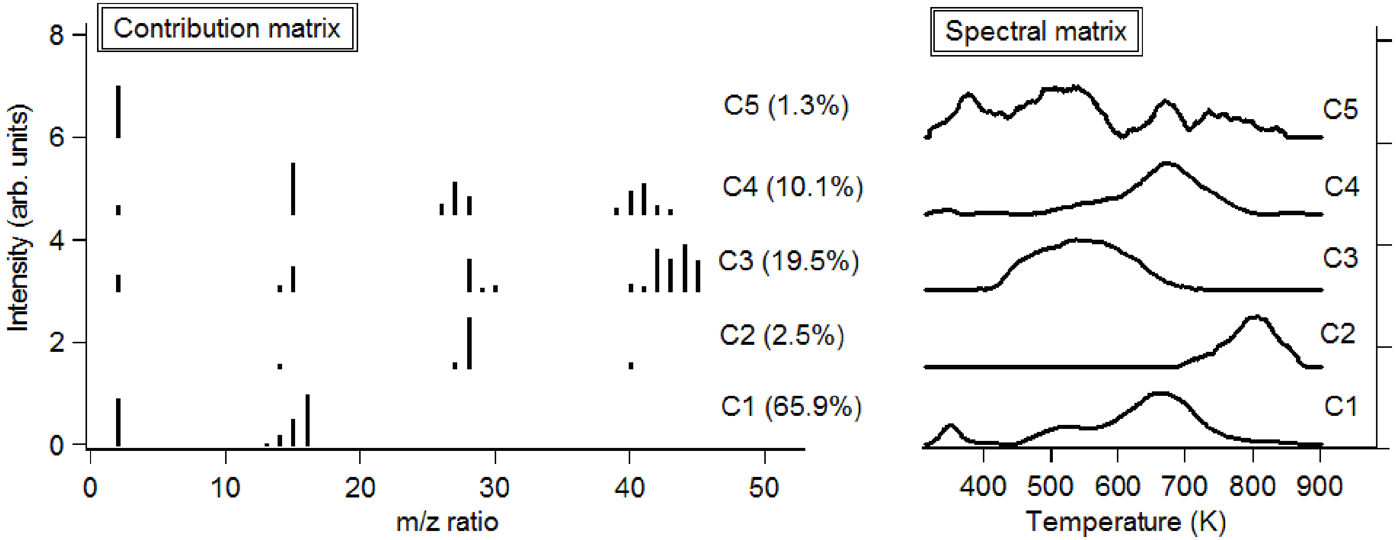


Surface reactions of metalorganics



Details: MCR-TPD data for $Ti[N(CH_3)_2]_4/Si$.

D(426x18) = C(426x5)*S(5x18)



C5: H_2

C4: $HN(CH_3)_2$

C3: C_2H_3N

C2: N_2

C1: CH_4

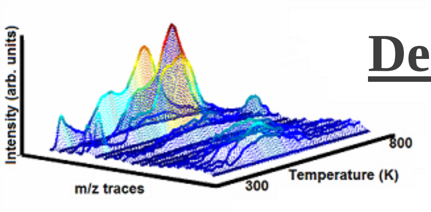
Since all significant traces are considered, the **total** evolution of gases is possible

$$Ti[N(CH_3)_2]_4 = 2.7\ CH_4 + 1.4\ HN(CH_3)_2 + 0.8\ C_2H_3N + 0.3\ N_2 + 0.5\ H_2 + TiN_{1.2}C_{0.8}$$

Metalorganic reactions:

Finding the source of undesired reactions

Rodriguez-Reyes, Teplyakov and Brown, *Surf. Sci.* ***2010**, 604, 2043.*



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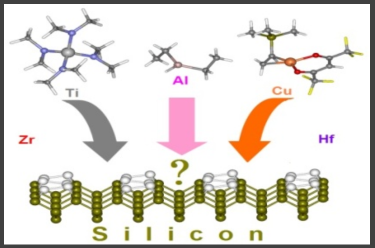
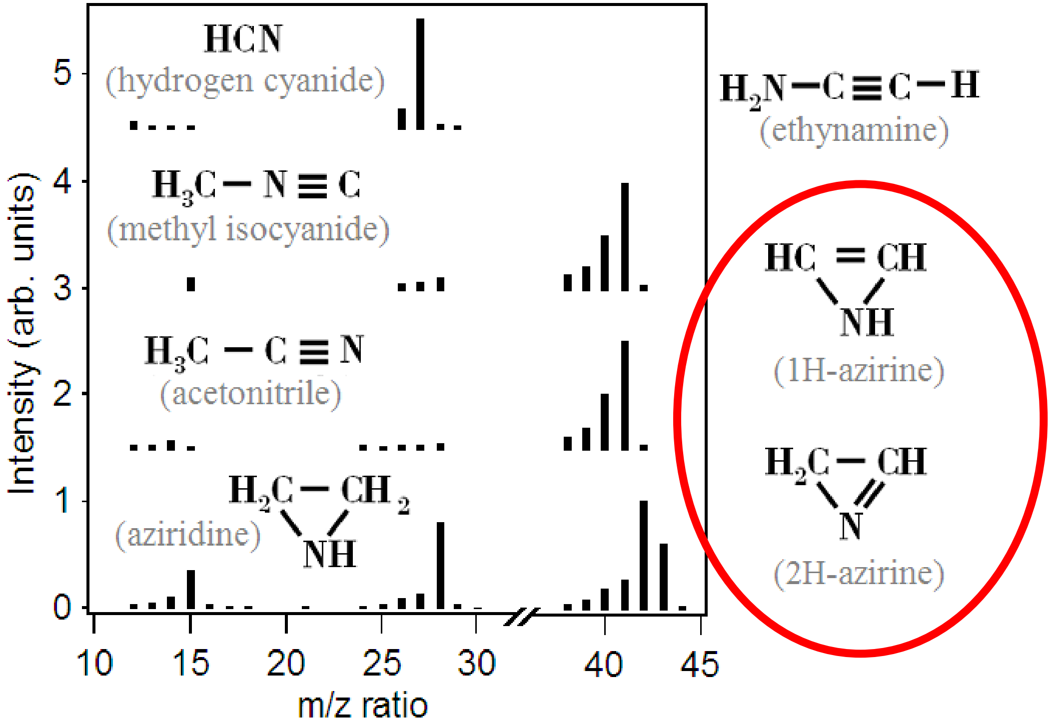


Surface reactions of metalorganics



Conclusions:

1. Temperature-programmed desorption methods give us kinetic and thermodynamic information about adsorption and reactions;
2. The most useful are thermal desorption methods based on mass spectrometry. They do require vacuum and relatively high-tech equipment but they also identify the species leaving the surface by their mass spectroscopic signature (see http://webbook.nist.gov/ for the common mass spectra);
3. Ideally, different methods and or different heating rates should be used to determine the activation energy of desorption (or reaction-limited desorption) but the Redhead method allows one to ballpark the figures quickly based on a single measurement;
4. Something should be known about the type of the reaction studied. If multiple species are involved, chemometrics or at least PCA should be used to distinguish different desorbing species. In this case, careful consideration should be given to different sensitivity factors for different compounds with respect to a masspsectrometric measurement.