Slide 1:

Quantification and Analysis of
Acid- and Base-Catalysis in

Slide 2:
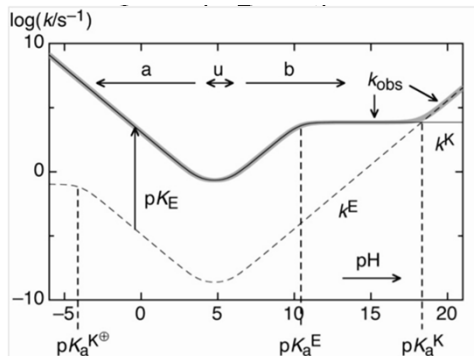
Some Preliminaries

Water as solvent (why?)

Autoionization: H_2O (aq) $\rightleftharpoons$ H^+(aq) + HO^-(aq)
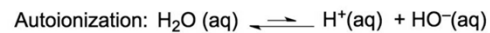
Ion product: $K_w°(298\ K) = a_{H+}a_{HO-} = \gamma_{H+}(c_{H+}/c_{H+}°)\ \gamma_{HO-}(c_{HO-}/c_{HO-}°)$

$\approx 1.008 \times 10^{-14}$, $pK_w°(298\ K) \approx 14.00$,

Activity coefficients γ depend on ionic strength: $I = \frac{1}{2}\ \Sigma z_j^2 c_j$

Pure water: $\gamma_j = 1$; brine ($I = 0.1$ M): $\gamma_{H+} \approx 0.83$, $\gamma_{HO-} \approx 0.76$,

hence $K_{w,c}(298\ K, I = 0.1\ M) = c_{H+}\ c_{HO-}$

$= K_w°(298\ K)\ c_{H+}°c_{HO-}°/(\gamma_{H+}\gamma_{HO-}) \approx 1.598 \times 10^{-14}$ M^2,

$p[K_{w,c}(298\ K, I = 0.1\ M)/M^2] \approx 13.80$

Slide 3:

Definition of pH

IUPAC
GOLD BOOK

pH

The quantity pH is defined in terms of the
activity of hydrogen(1+) ions (hydrogen ions) in
solution:

$$pH = -\lg[a(H^+)] = -\lg[m(H^+)\ \gamma_m(H^+)\ /\ m^\Theta]$$

where $a(H^+)$ is the activity of hydrogen ion
(hydrogen 1+) in aqueous solution, H^+(aq),
$\gamma_m(H^+)$ is the activity coefficient of H^+(aq)
(molality basis) at molality $m(H^+)$, and
$m^\Theta = 1\ mol\ kg^{-1}$ is the standard molality.

Slide 4:

Notes:

1. pH cannot be measured independently
   because calculation of the activity
   involves the activity coefficient of a single
   ion. Thus it can be regarded only as a
   notional definition.

Slide 5:

A concise summary of thermodynamics
(W. J. Moore in *Physical Chemistry*)

1. The First Law say you can't win;
   the best you can do is break even.

2. The Second Law says you can break
   even only at absolute zero.

3. The Third Law says you can never reach
   absolute zero.

Slide 6:

Never mind!

Acidity constants: HA (aq) $\rightleftharpoons$ H^+(aq) + A^-(aq)
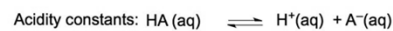
$K_a°(T) = a_{H+}a_{A-}/a_{HA}$

$K_a°(H_2O, 298\ K) = a_{H+}a_{HO-}/a_{H_2O} = a_{H+}a_{HO-} = K_w°(298\ K)$;

$pK_a°(H_2O, 298\ K) = 14.0$ (not 15.74!)

$K_a°(H^+, 298\ K) = a_{H+}/a_{H+} = 1$; $pK_a°(H^+, 298\ K) = 0$ (not −1.74!)

We measure concentrations: $A = \varepsilon cd$ (LFP, spectrophotometry);

hence, we determine concentration quotients: $K_{a,c}(T) = c_{H+}c_{A-}/c_{HA}$

and need to know the hydrogen ion concentrations: c_{H+}

Keep ionic strength I constant, if necessary by addition of, e.g., KCl

We need buffers for $3 < pH < 11$

c_{H+} is best calculated from the buffer ratio c_{HA}/c_{A-} and known $K_{a,c}(I, T)$-values

given in the literature or known $K_a°$-values using known $\gamma_j(I, T)$:

For pH ≤ 3 (.. 4): c_{H+} = nominal concentration of a strong acid ($HClO_4$);

For pH ≥ (10...) 11: $c_{H+} = K_{w,c}(298\ K, I)/(c_{HO-})_{nom}$

Cross-check

Measure pH with a glass electrode.
The glass electrode must be calibrated!
 (See provider instructions, e.g., Metrohm)
Remarkably, glass electrode readings $(pH)_{meas}$ are closer to pc_{H+} that to pa_{H+}! [1]
Your results should hold within:

$$(pH)_{meas} - (pc_{H+})_{calc} = 0.03 \pm 0.02$$

[1] H. Sigel, A. D. Zuberbühler, O. Yamauchi, *Anal. Chim. Acta*, **1991**, *255*, 63.

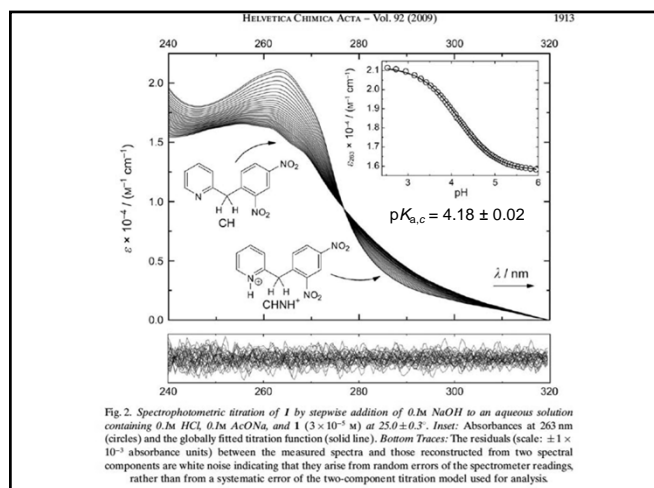## The practical approach

Choose a well-known (preferably monoacid) buffer with known pK_a near (±1 unit) to that pK_a which you want to determine.

Titrate with 0.1 M strong base starting with 0.1 M HA plus dye or with 0.1 M strong acid starting with buffer salt plus dye.

Record spectra and get pH readings between small additions of titrant.

Global analysis of the spectral series (number of components) and fit of an appropriate titration function.


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$pK_{a,c} = 4.18 \pm 0.02$

Fig. 2. *Spectrophotometric titration of* **1** *by stepwise addition of 0.1M NaOH to an aqueous solution containing 0.1M HCl, 0.1M AcONa, and* **1** *(3×10^{-5} M) at 25.0 ± 0.3°. Inset: Absorbances at 263 nm (circles) and the globally fitted titration function (solid line). Bottom Traces: The residuals (scale: ±1 × 10^{-3} absorbance units) between the measured spectra and those reconstructed from two spectral components are white noise indicating that they arise from random errors of the spectrometer readings, rather than from a systematic error of the two-component titration model used for analysis.*

The resulting concentration quotients

$$K_{a,c}(AH) = c_{H^+} \, c_{A^-}/c_{AH}$$

can be converted to thermodynamic acidity constants using activity coefficients from tables or estimated by the Debye–Hückel equation ($\gamma_{AH} \approx 1$):

$$K_a^\circ(AH) \approx K_{a,c}(AH) \, \gamma_{H^+}\gamma_{A^-}/\gamma_{AH}$$

ion	$I = 0.01$	$I = 0.05$	$I = 0.1$
H^+	0.914	0.86	0.83
Li^+, $PhCOO^-$	0.907	0.835	0.80
Na^+, HCO_3^-, $H_2PO_4^-$	0.902	0.82	0.775
HO^-, F^-, ClO_4^-, $HCOO^-$	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, NO_3^-	0.899	0.805	0.755
Mg^{2+}	0.69	0.52	0.45
Ca^{2+}, $phthalate^{2-}$	0.675	0.485	0.405
CO_3^{2-}, $oxalate^{2-}$	0.663	0.45	0.36
SO_4^{2-}, HPO_4^{2-}	0.660	0.445	0.355
PO_4^{3-}	0.395	0.16	0.095

Rate constants of keto–enol conversions

$$\Sigma\Delta_r G^\circ = 2.3 RT \Sigma pK_r = 0$$
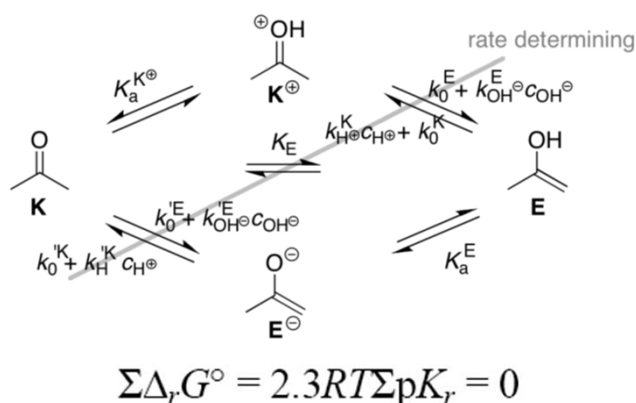
$$v^K = \left[\left(k_0^K + k_{H^\oplus}'^K K_a^E\right) + k_{H^\oplus}^K c_{H^\oplus} + k_0'^K \frac{K_a^E}{c_{H^\oplus}}\right]\frac{c_{H^\oplus}}{K_a^E + c_{H^\oplus}} c_{E,tot}(t) = k^K c_{E,tot}(t)$$

$$v^E = \left[\left(k_0^K + k_{H^\oplus}'^K K_a^E\right) + k_{H^\oplus}^K c_{H^\oplus} + k_0'^K \frac{K_a^E}{c_{H^\oplus}}\right] K_E \frac{K_a^{K\oplus}}{K_a^E + c_{H^\oplus}} c_{K,tot}(t) = k^E c_{K,tot}(t)$$

$$c_{E,tot}(t) = \left[c_{E,tot}(0) - c_{E,tot}(\infty)\right]e^{-\left(k^E + k^K\right)t} + c_{E,tot}(\infty)$$

J. Wirz, *Adv. Phys. Org. Chem.*, Vol. 44, **2010**, 325
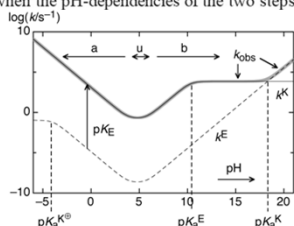
Slide 1

Can we measure k^E and k^K separately?

$c_{E,tot}(t)/M$

1.0

$k_{obs} = k^E + k^K$

$c_{E,tot}(\infty)/M$

0.0

t

Slide 2

A

250   300 $\lambda\, / \,nm$

a)

A A_0

k_{obs}^K

b) t

$\log(k_{obs})$

4
2
0
-2
-4
-6
-8

pK_a^E

pK_E

1 3 5 7 9 11 13   pH

c)

A_0 $A_0(270\ nm)$

$A_0(295\ nm)$

9   10   11   pH

d)

Slide 3

$$v^K = \left[\left(k_0^K + k'^K_{H^\oplus} K_a^E\right) + k_{H^\oplus}^K c_{H^\oplus} + k_0^{'K}\frac{K_a^E}{c_{H^\oplus}}\right]\frac{c_{H^\oplus}}{K_a^E + c_{H^\oplus}} c_{E,tot}(t) = k^K c_{E,tot}(t)$$

$\log(k/s^{-1})$

enol_to_ketone(x)

4
2
0
-2
-4

0   4   8   12

pH

Slide 4

$\log(k/s^{-1})$

10

a   u   b k_{obs}

0

pK_E k^K

k^E

pH

-10

-5   0   5   10   15   20

$pK_a^{K\oplus}$ pK_a^E pK_a^K

Slide 5
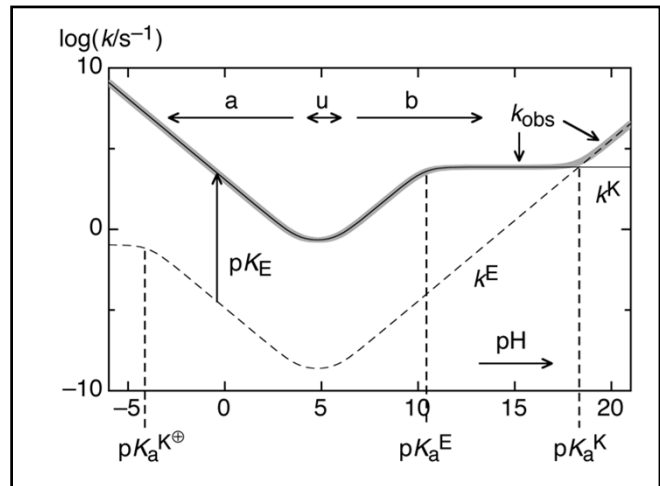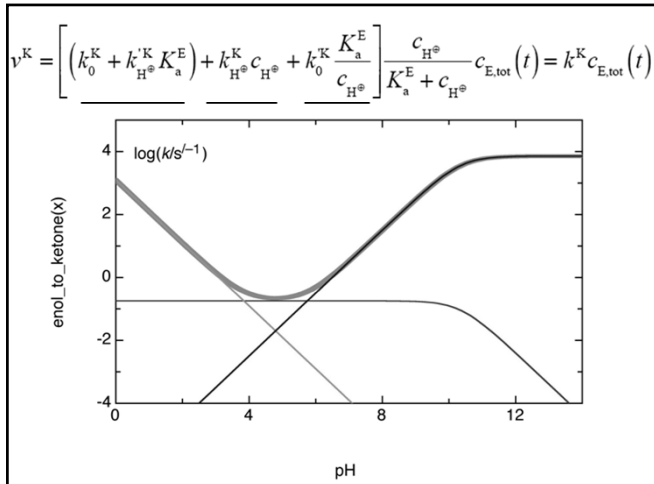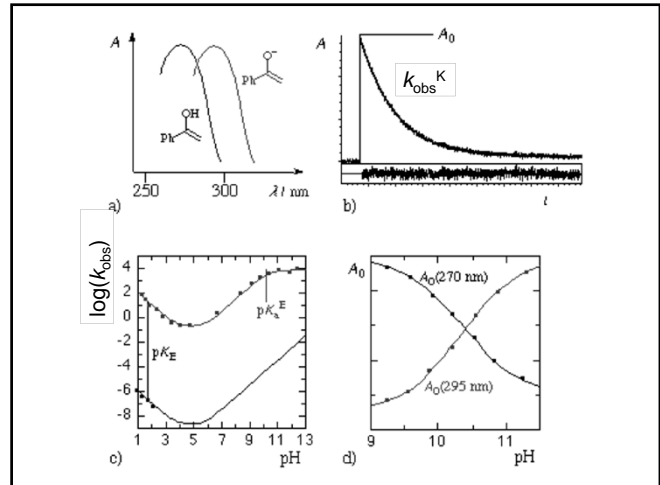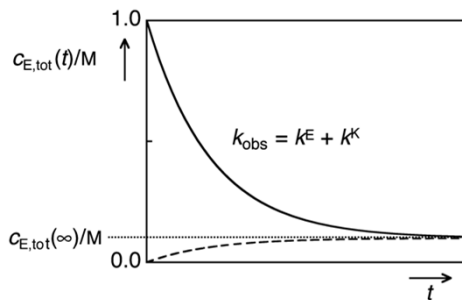
Useful Rules to Interpret pH–Rate Profiles

1. *Positive curvature indicates a change in the reaction mechanism.* In the areas of positive curvature, two reaction paths with different pH-dependence are competitive. The two regions of positive curvature near the bottom of the two curves indicate a change from the acid-catalyzed to the uncatalyzed path (around pH 4), and from the uncatalyzed to the base-catalyzed reaction (pH 6).

2. *The same reaction mechanism operates in the regions to the left and right of negative curvature.* In general, negative curvature can arise from two causes:
   (a) *Pre-equilibria:* Acid catalysis of ketone enolization saturates around pH = $pK_a^{K\bullet}$. base catalysis of enol ketonization saturates around pH = pK_a^E.
   (b) A *change in the rate-determining step* of a reaction can also give rise to negative curvature, when the pH-dependencies of the two steps differ.
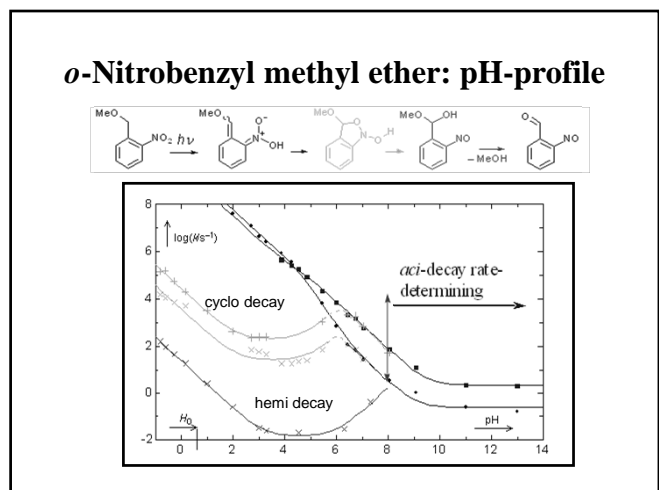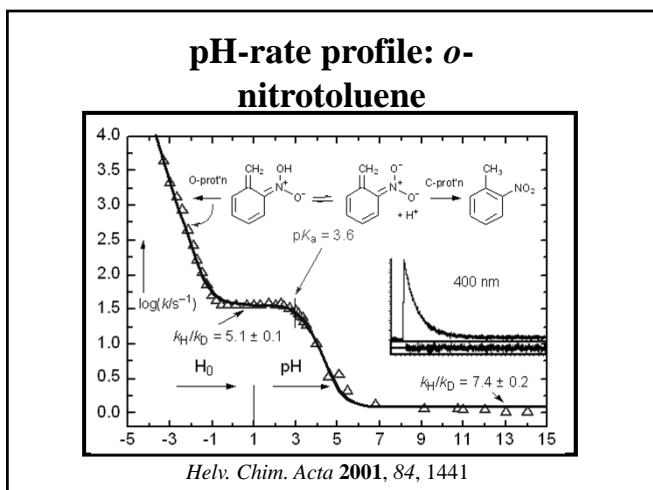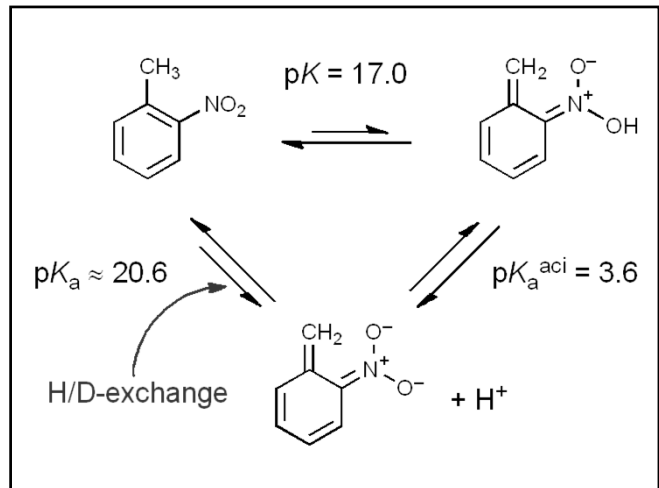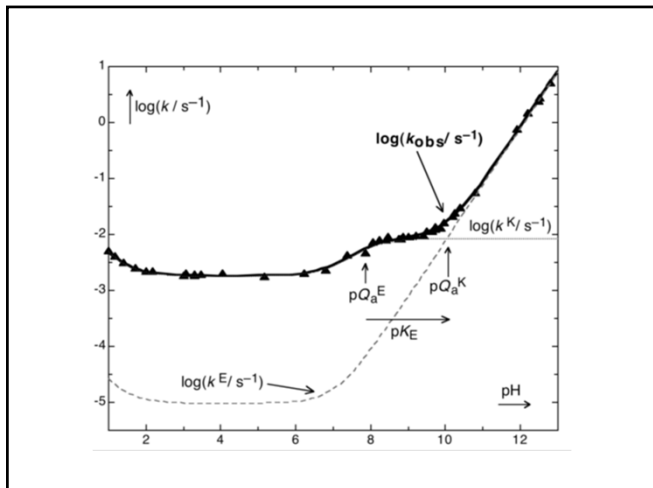

$\log(k/s^{-1})$

10

a   u   b k_{obs}

0

pK_E k^K

k^E

pH

-10

-5   0   5   10   15   20

$pK_a^{K\oplus}$ pK_a^E pK_a^K

Slide 6

Buffer catalysis

k_{obs}

a

k_{bu}

$c_{bu} = (c_{HA} + c_{A^\ominus})/M$

0.00   0.05   0.10

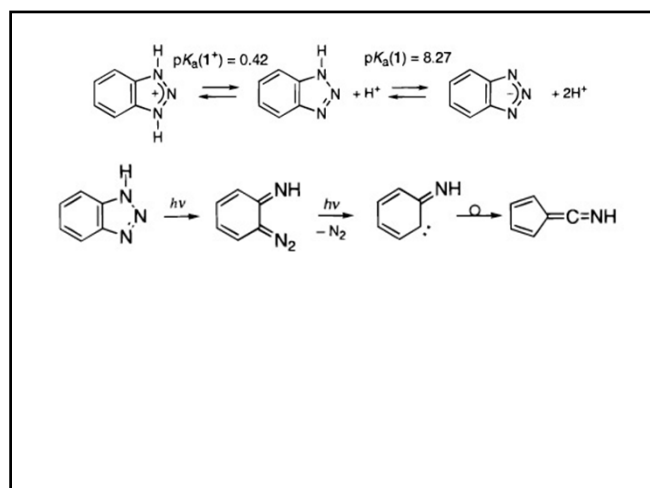k_{bu}

b

k_{HA}

$k_{A^\ominus}$
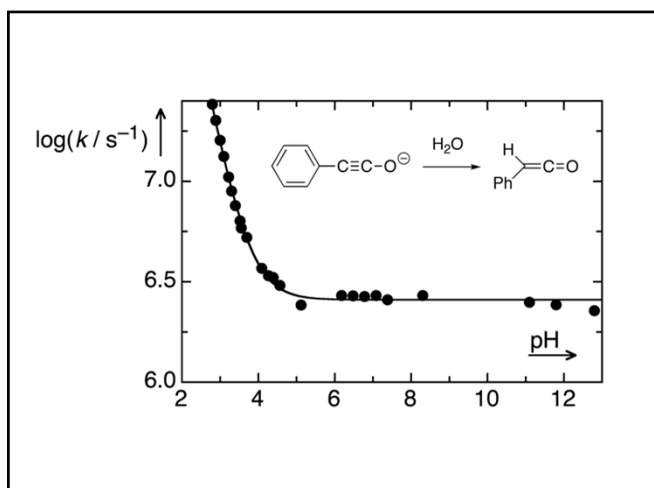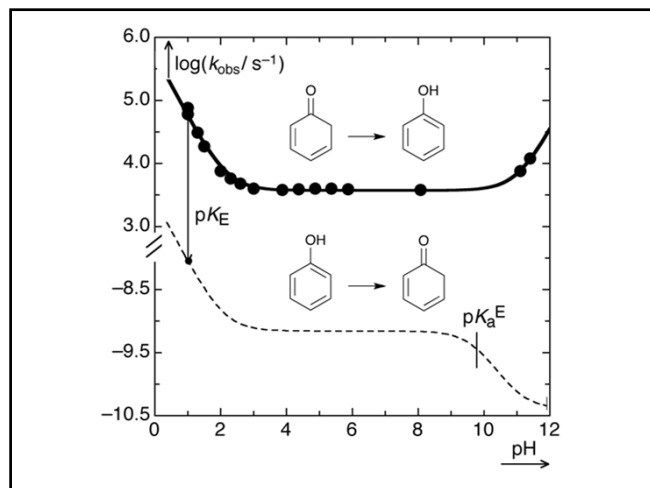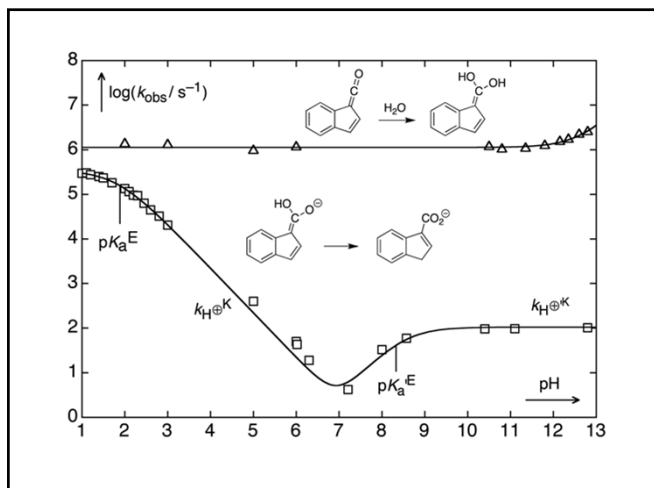
x_{HA}

0.0   0.4   0.8
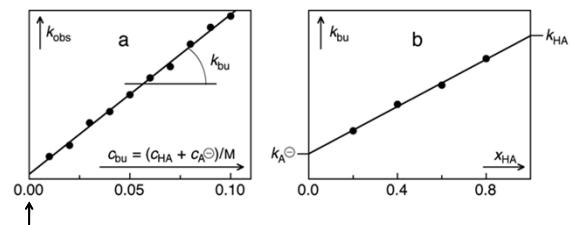
Extrapolation to zero buffer concentration is required to determine rate constants of wholly aqueous solutions for pH–rate profiles.

The individual contributions of the general acid and general base components of the buffer are obtained for a plot of k_{bu} vs. the buffer ratio $x_{HA} = c_{HA}/(c_{HA}+c_{A^-})$.

ΔA_0 (270 nm)

pH

Fig. 2. *Titration curve for the ionization of* **E** *determined by flash photolysis. The data points are initial absorbances A_0 at 270 nm immediately after the flash. The solid line is the best fit of Eqn. 5 to the data points.*

$\log(k / s^{-1})$

$\log(k_{obs}/ s^{-1})$

$\log(k^K / s^{-1})$

pQ_a^E pQ_a^K

pK_E

$\log(k^E / s^{-1})$

pH

$pK = 17.0$

$pK_a \approx 20.6$ $pK_a^{aci} = 3.6$

H/D-exchange $+ H^+$

pH-rate profile: *o*-nitrotoluene

O-prot'n   C-prot'n

$pK_a = 3.6$

$\log(k/s^{-1})$

$k_H/k_D = 5.1 \pm 0.1$

400 nm

H_0 pH

$k_H/k_D = 7.4 \pm 0.2$

Helv. Chim. Acta **2001**, *84*, 1441

o-Nitrobenzyl methyl ether: pH-profile

$\log(k/s^{-1})$

aci-decay rate-determining

cyclo decay

hemi decay

H_0 pH

Intercepts of buffer dilution plots

Figure 1. Absorption spectra of the transient generated by flash photolysis of **1** using an excitation pulse from a KrF-excimer-laser (λ_{exc} = 248 nm, 100 mJ per pulse, pulse width ~25 ns, delay after the pulse maximum ~30 ns). Spectrum a: 1.0 N aqueous NaOH. Spectrum b: 0.001 N aqueous NaOH.

Bronsted equation

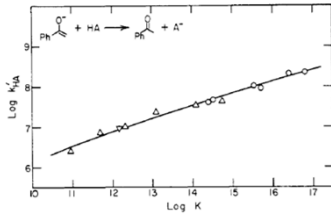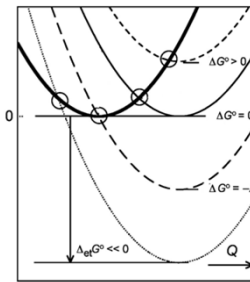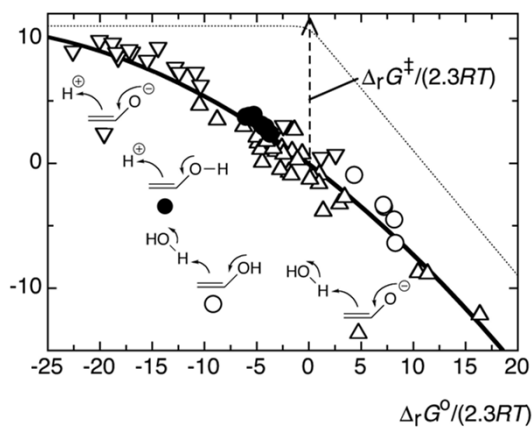$$\log\left(\frac{k_{HA}}{p}\right) = \log G_A + \alpha \log\left(\frac{qK_a^{HA}}{p}\right)$$

Figure 1. Rate–equilibrium relation for the ketonization of acetophenone enolate ion in aqueous solution at 25 °C catalyzed by RCO$_2$H (O) and RPO$_3$H$^-$ (including HOPO$_3$H$^-$) (△). The points represent "chemical" rate and equilibrium constants with symmetry-induced contributions removed by using the following statistical factors: $p = 1$, $q = 2$ for RCO$_2$H; $p = 1$, $q = 3$ for RPO$_3$H$^-$; $p = 2$, $q = 3$ for H$_2$PO$_4^-$; $p = 3$, $q = 1$ for PhCOCH$_3$.

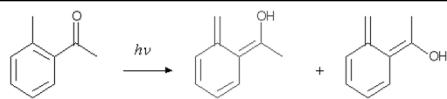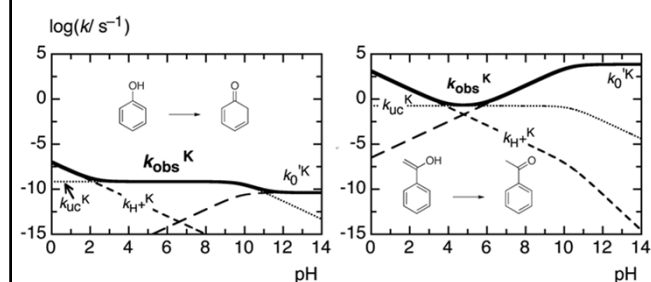## Bronsted α variation with ΔG^o
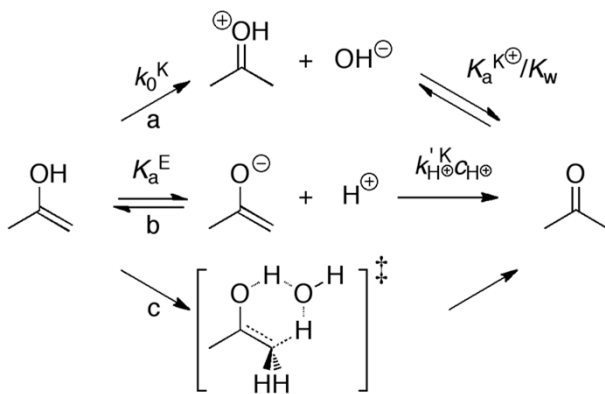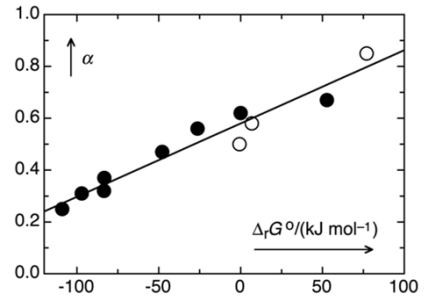
Marcus theory

$$\log\frac{k}{k_d} = \left(\frac{-\Delta_r G^\ddagger}{\ln(10)RT}\right), \text{ where } \Delta_r G^\ddagger = \Delta_r G_0^\ddagger\left(1 + \frac{\Delta_r G^o}{4\Delta_r G_0^\ddagger}\right)^2$$
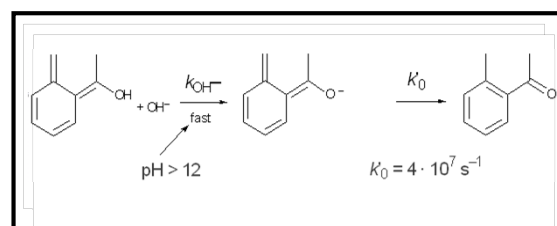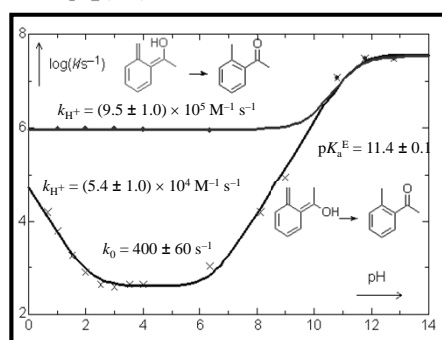
$$\alpha = \left(\frac{\partial \Delta_r G^{\ddagger}}{\partial \Delta_r G^{\circ}}\right)_{p,T} = \left(1 + \frac{\Delta_r G^{\circ}}{4\Delta_r G_0^{\ddagger}}\right)/2$$

$$\left(\frac{\partial^2 \Delta_r G^{\ddagger}}{\partial\left[\Delta_r G^{\circ}\right]^2}\right)_{p,T} = \left(\frac{\partial \alpha}{\partial \Delta_r G^{\circ}}\right)_{p,T} = \frac{1}{8\Delta_r G_0^{\ddagger}}$$
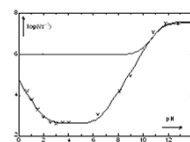

But: Why does base catalysis saturate?

Change in rate-det. step!

Conclusions

• When will YOU do flash photolysis?

• beware of artefacts
• buffer catalysis
• experts in reading pH–rate profiles

• equilibrium constants K_E spanning 30 orders magnitude
• assignments of elementary reactions
• LFER