

Bringing light to dark reactions

Keto–enol tautomerization

derivation of the rate law of tautomerization

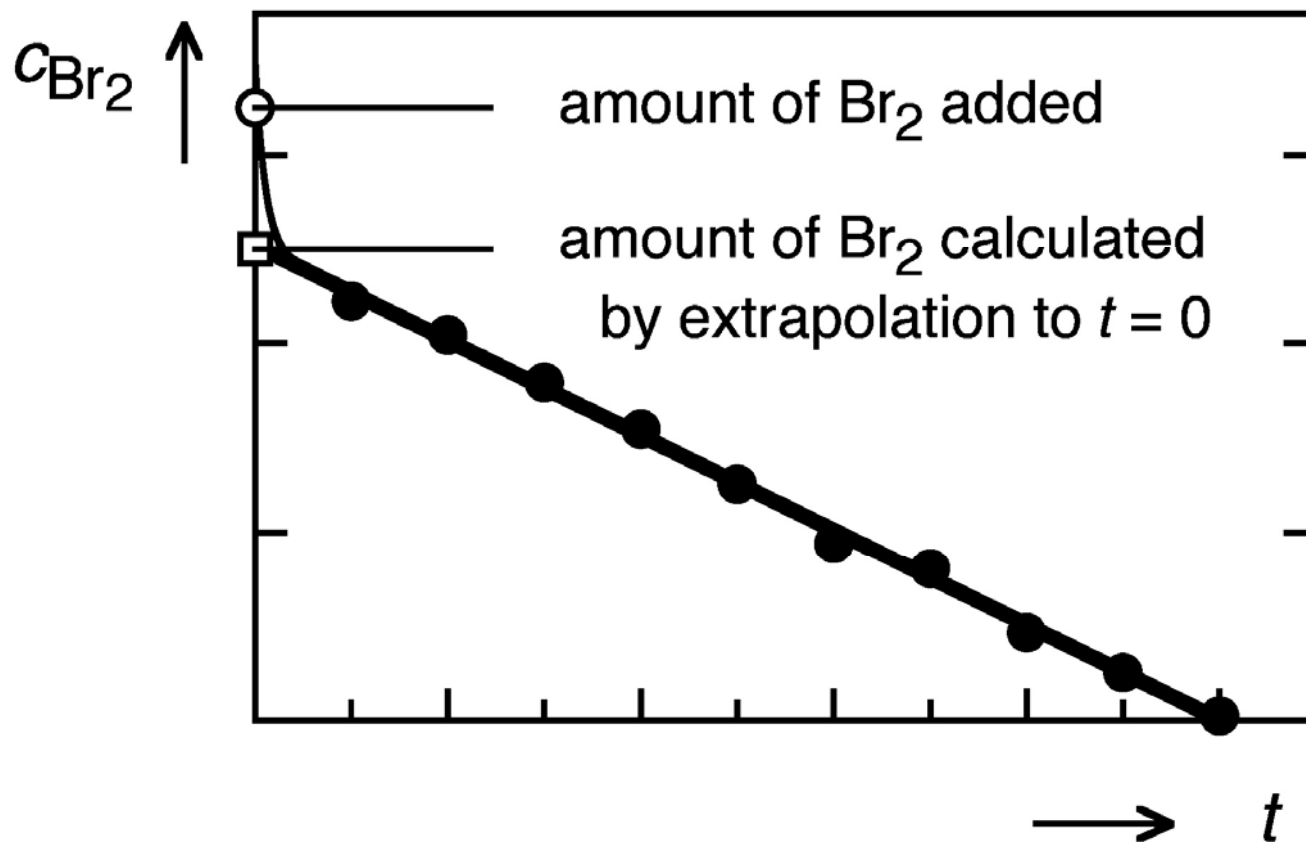
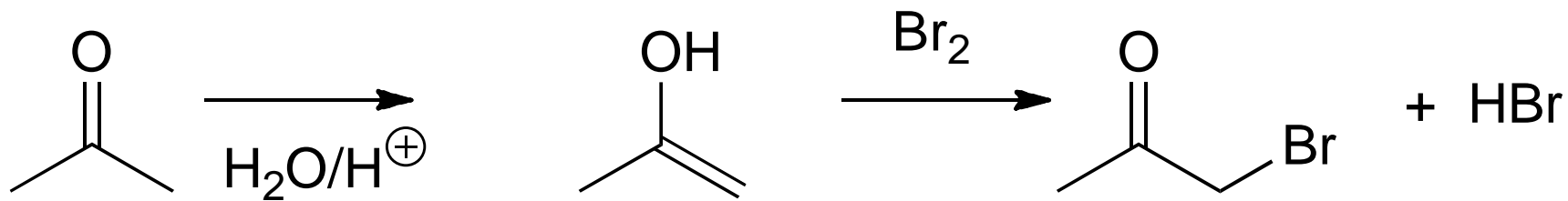
pH–rate profiles

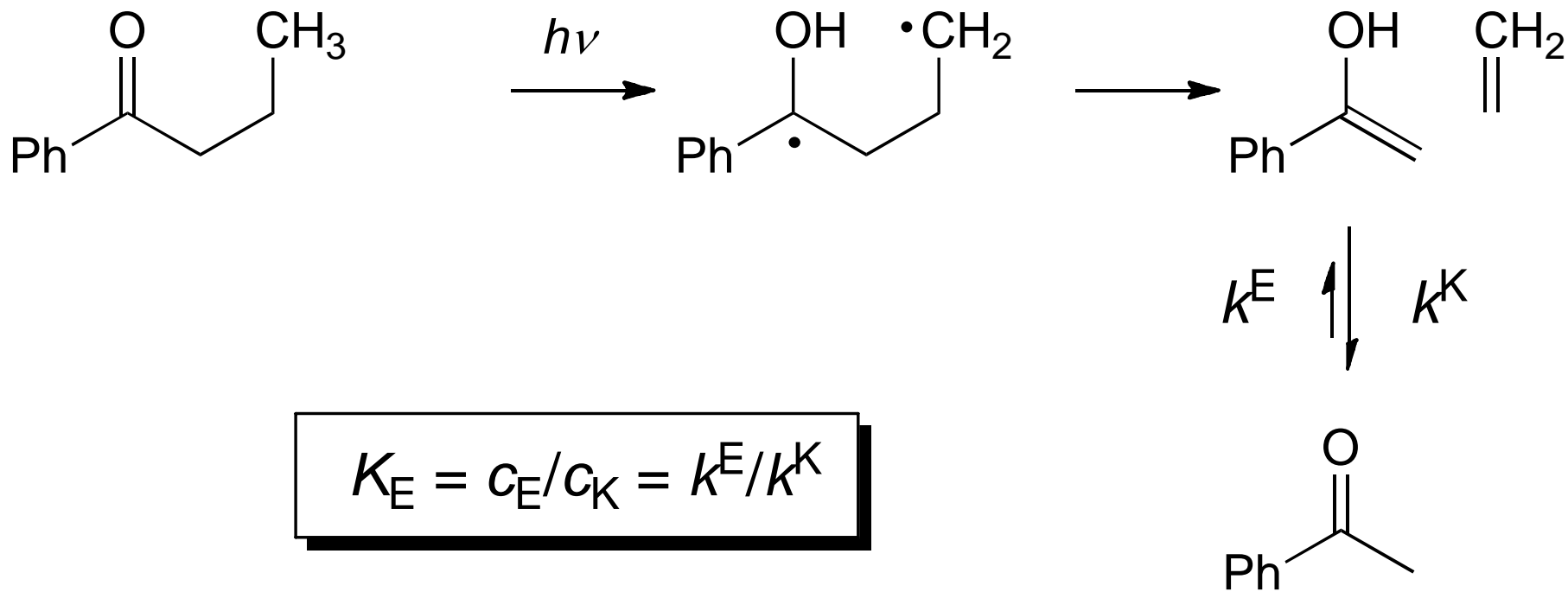
general acid and general base catalysis

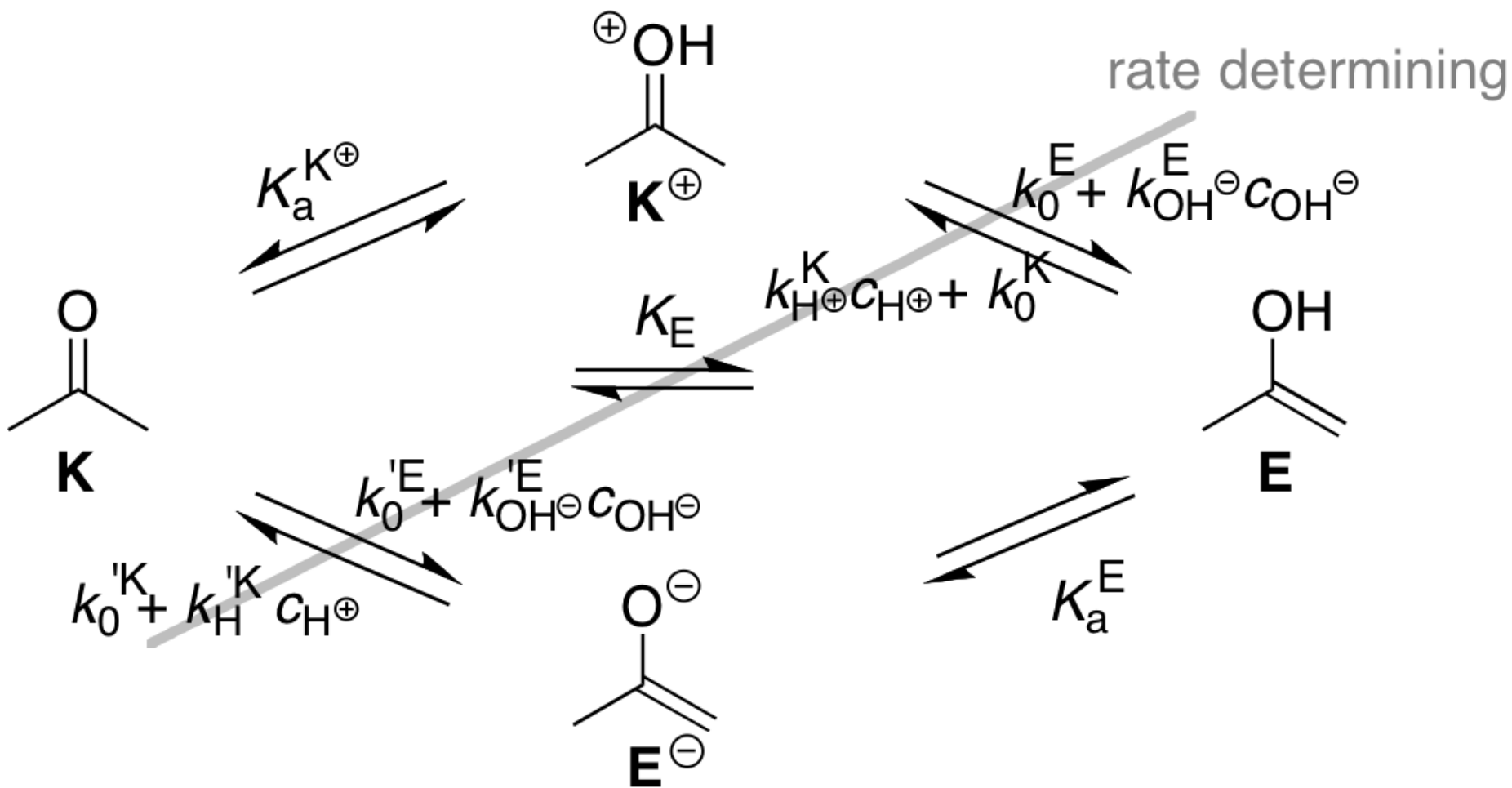
examples

rate–equilibrium relationships (Bronsted, Marcus)

mechanism of the “uncatalyzed” reaction







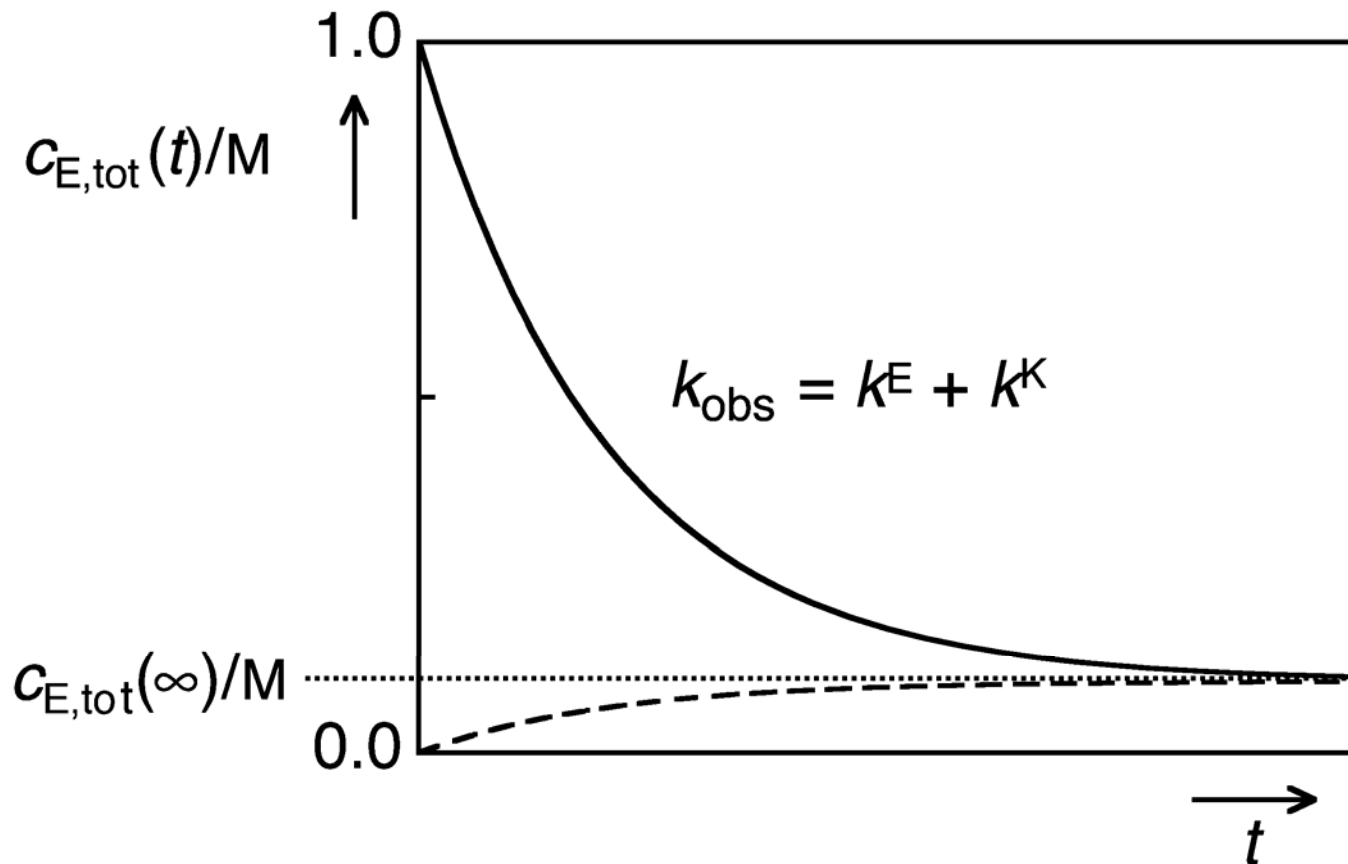
$$\Sigma \Delta_r G^{\circ} = 2.3RT \Sigma pK_r = 0$$

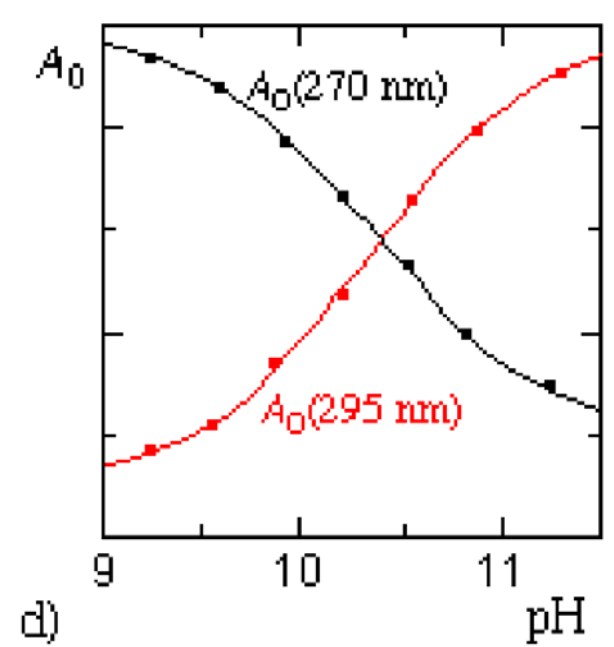
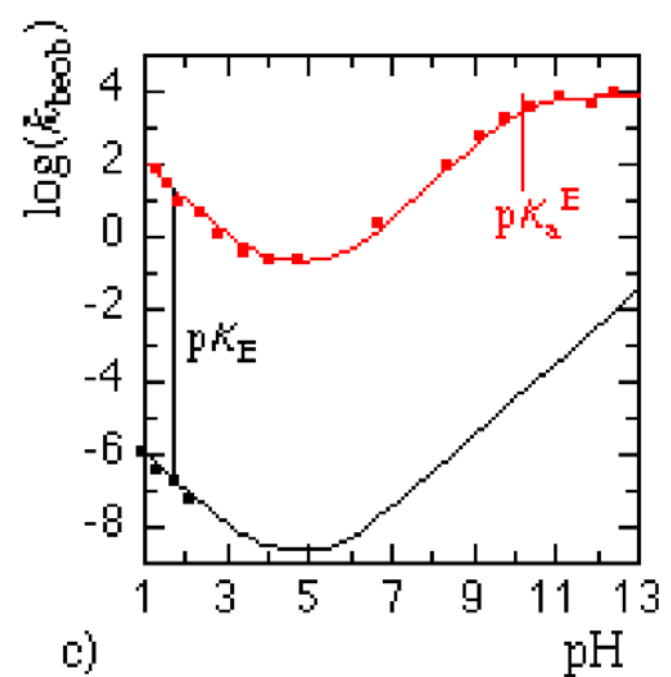
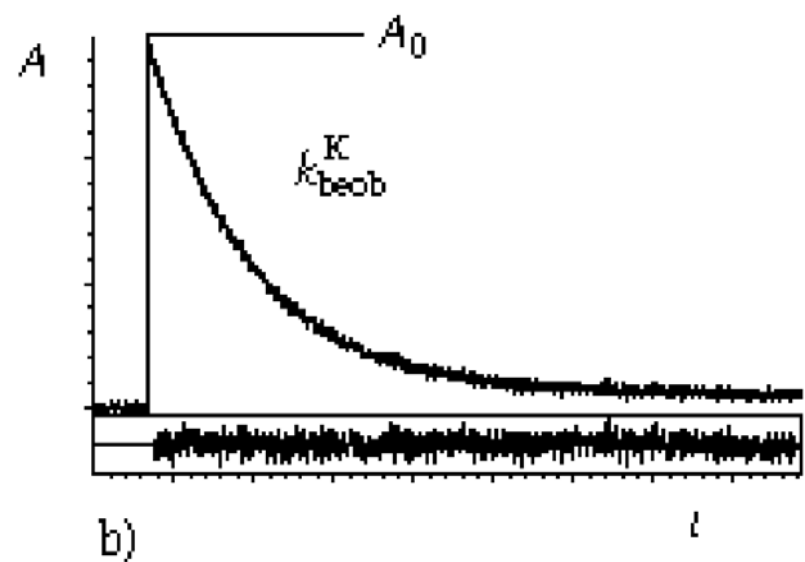
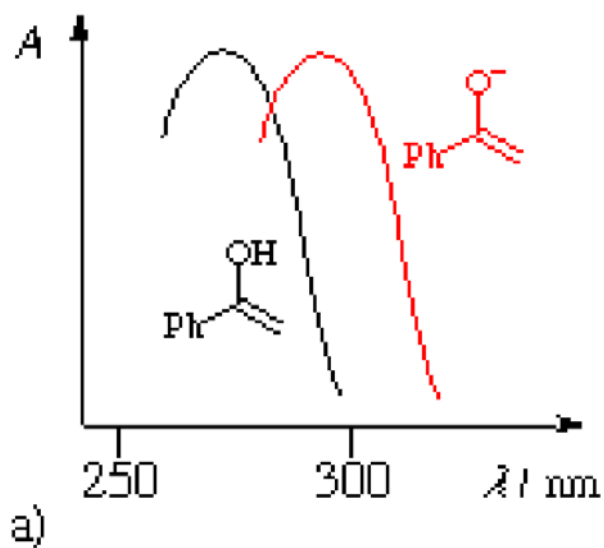
$$v^K = \left[\left(k_0^K + k_{H^\oplus}^{\prime K} K_a^E \right) + k_{H^\oplus}^K c_{H^\oplus} + k_0^K \frac{K_a^E}{c_{H^\oplus}} \right] \frac{c_{H^\oplus}}{K_a^E + c_{H^\oplus}} c_{E,\text{tot}}(t) = k^K c_{E,\text{tot}}(t)$$

$$v^E = \left[\left(k_0^K + k_{H^\oplus}^{\prime K} K_a^E \right) + k_{H^\oplus}^K c_{H^\oplus} + k_0^K \frac{K_a^E}{c_{H^\oplus}} \right] K_E \frac{K_a^{K^\oplus}}{K_a^{K^\oplus} + c_{H^\oplus}} c_{K,\text{tot}}(t) = k^E c_{K,\text{tot}}(t)$$

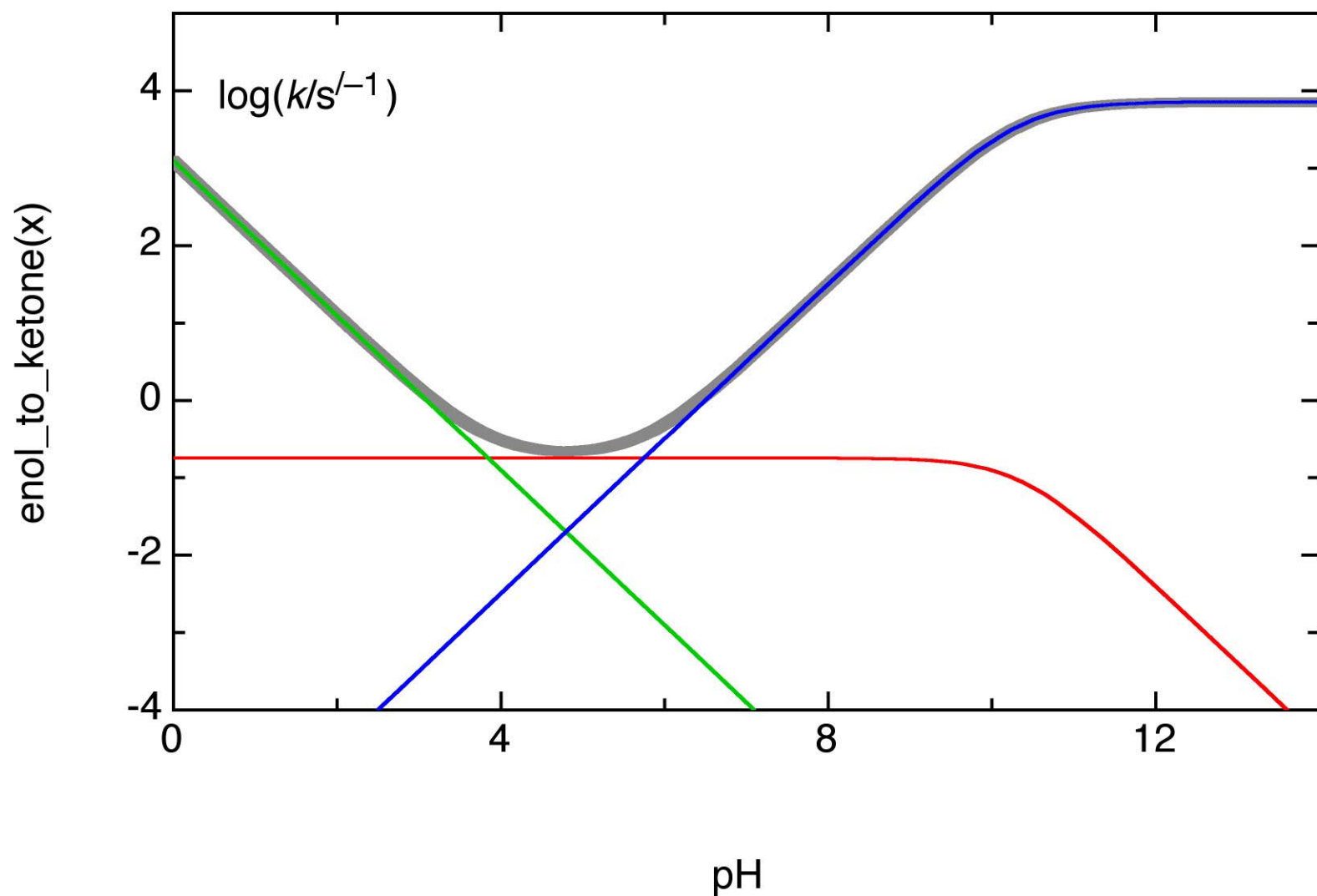
$$c_{E,\text{tot}}(t) = \left[c_{E,\text{tot}}(0) - c_{E,\text{tot}}(\infty) \right] e^{-(k^E + k^K)t} + c_{E,\text{tot}}(\infty)$$

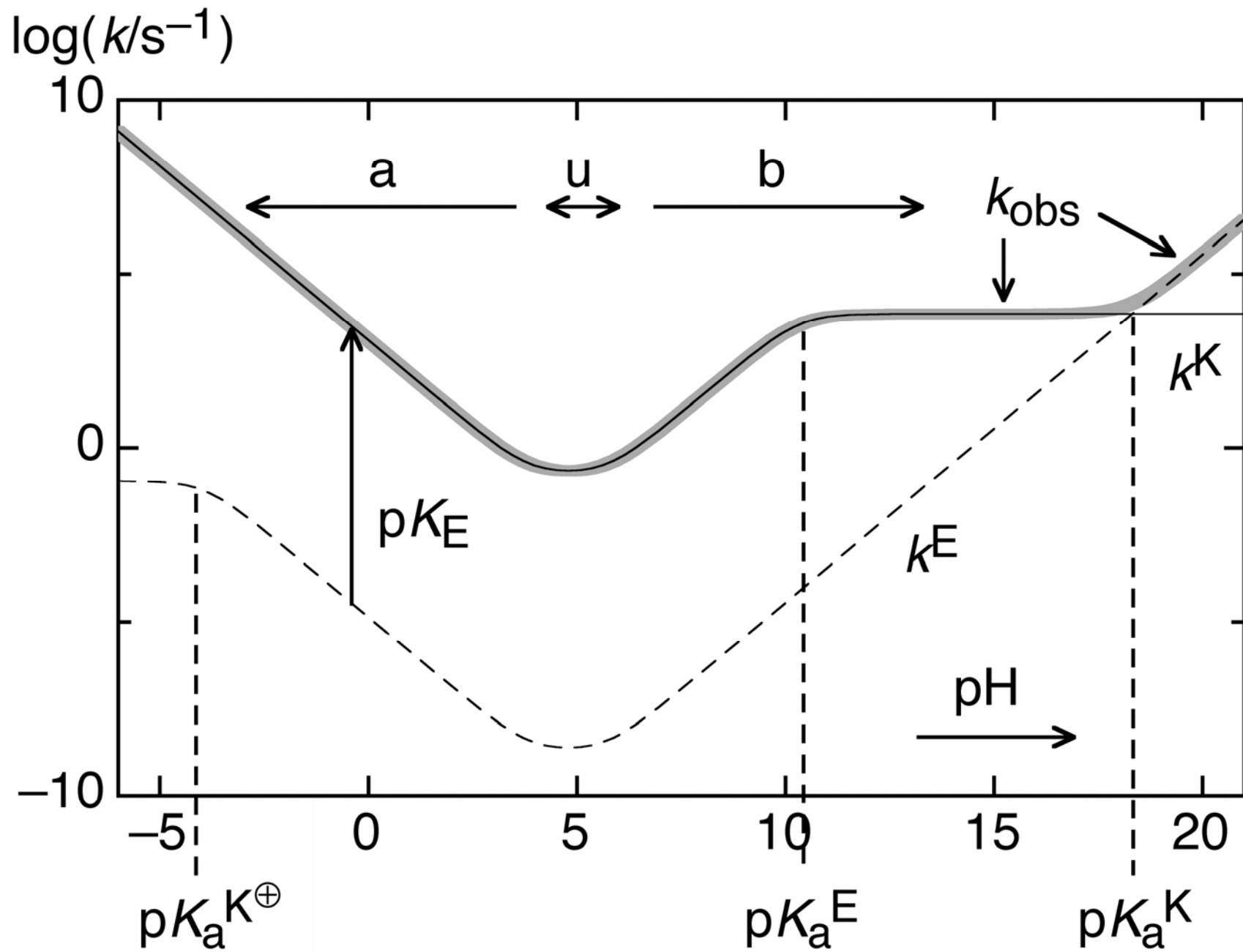
Can we measure k^E and k^K separately?





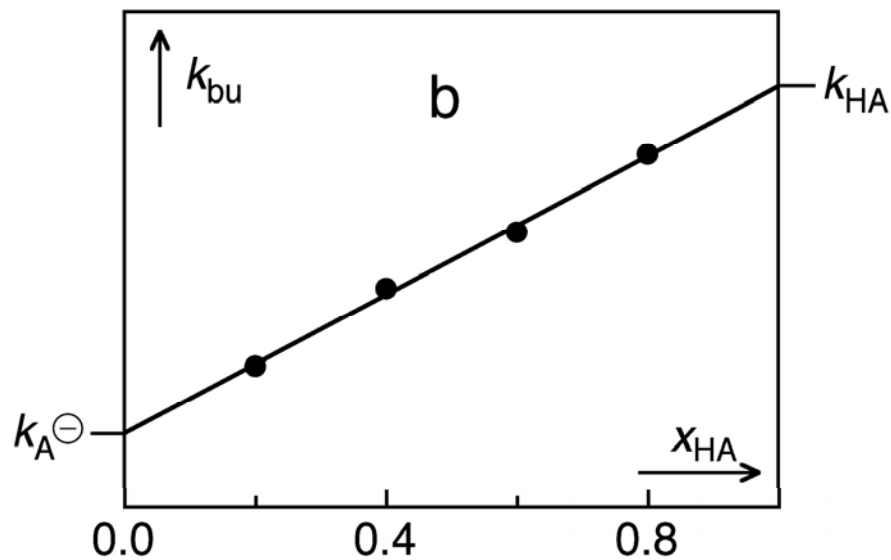
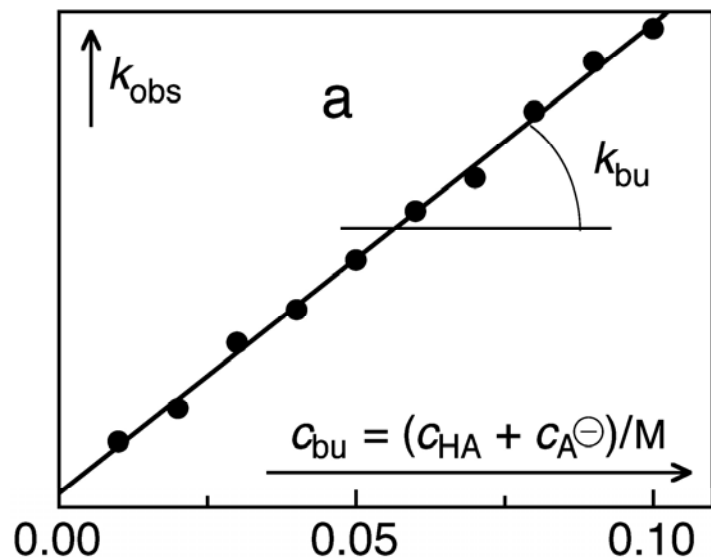
$$v^K = \left[\underbrace{\left(k_0^K + k_{H^\oplus}^{\prime K} K_a^E \right)}_{\text{red}} + \underbrace{k_{H^\oplus}^K c_{H^\oplus}}_{\text{green}} + \underbrace{k_0^K \frac{K_a^E}{c_{H^\oplus}}}_{\text{blue}} \right] \frac{c_{H^\oplus}}{K_a^E + c_{H^\oplus}} c_{E,\text{tot}}(t) = k^K c_{E,\text{tot}}(t)$$

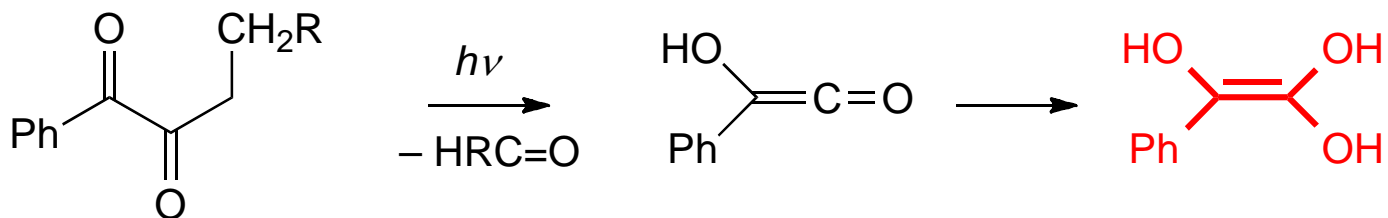
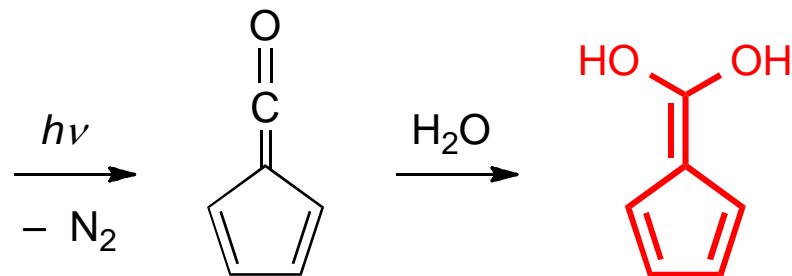
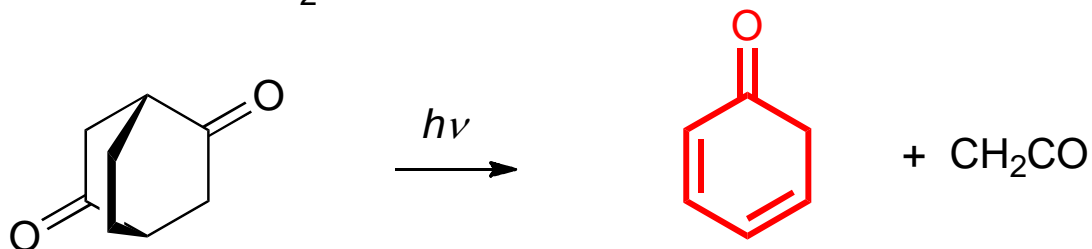
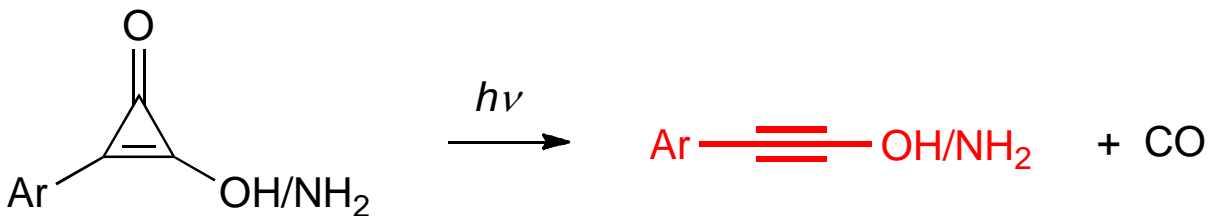
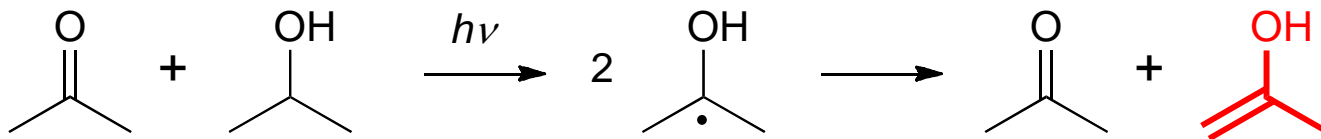
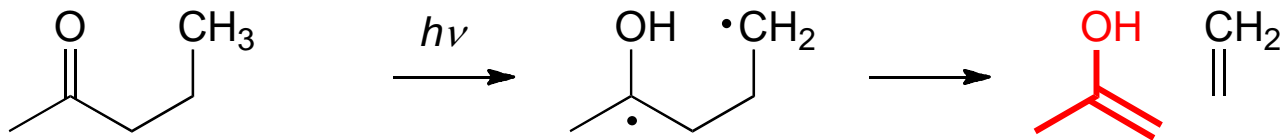






Buffer catalysis





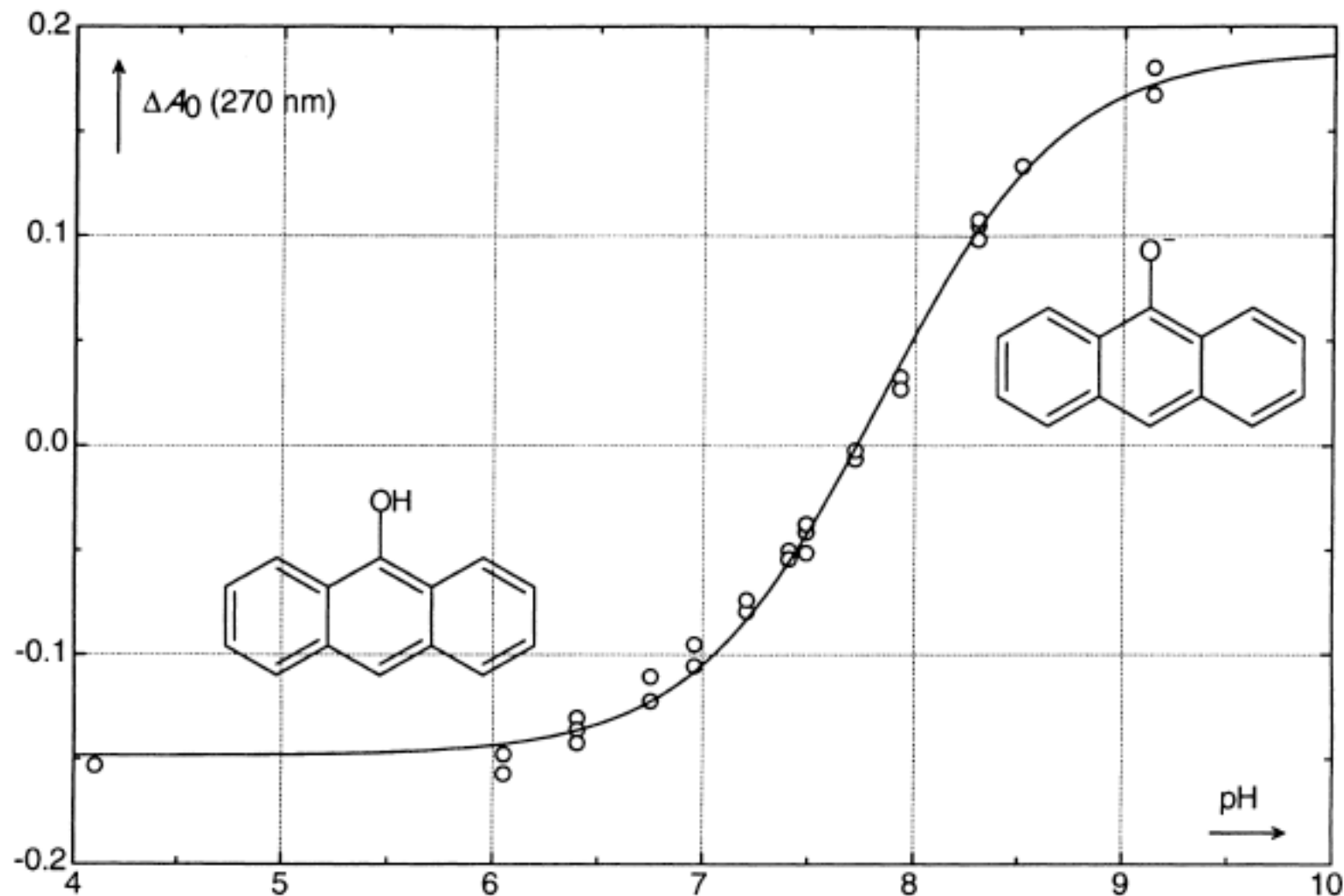
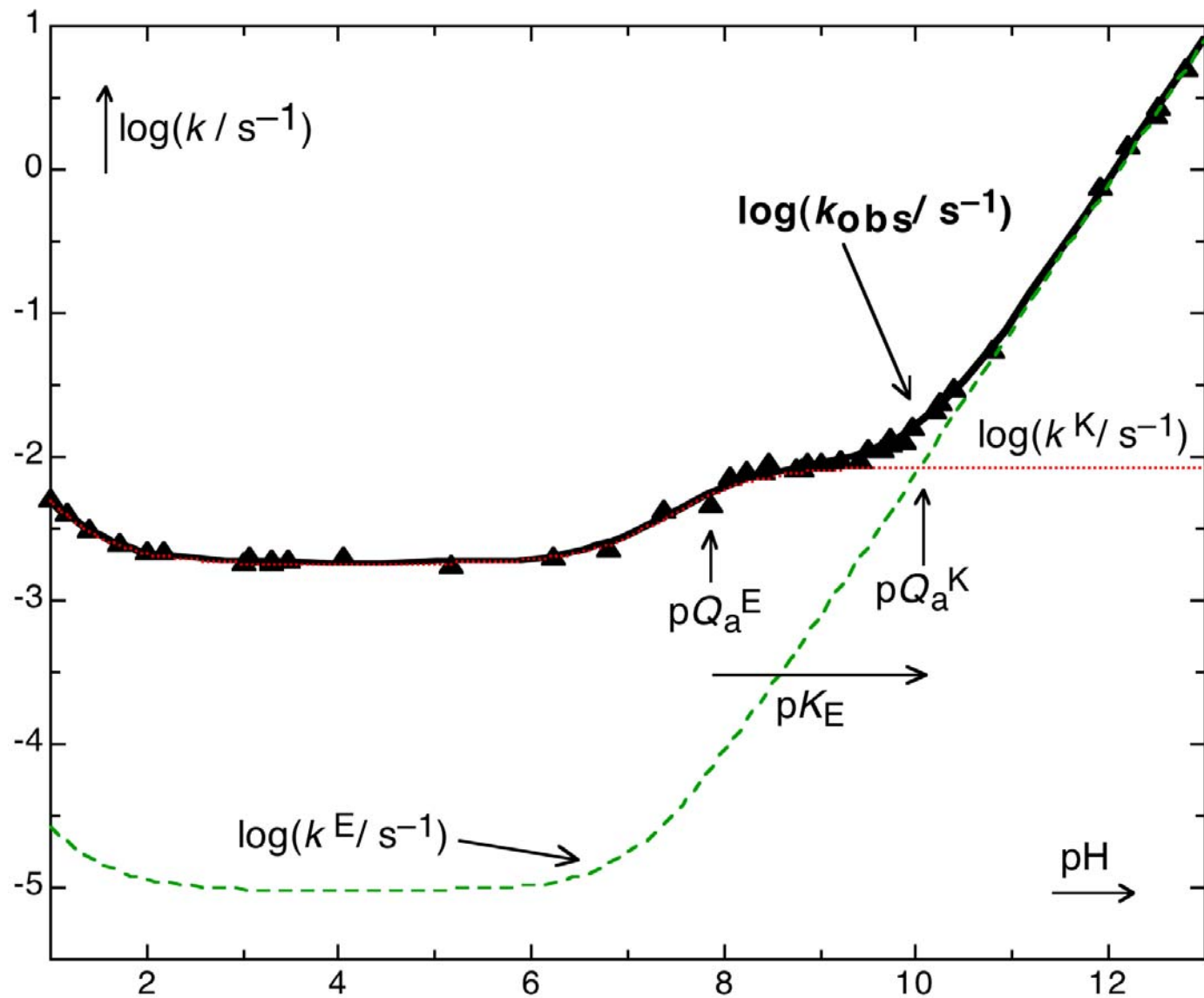
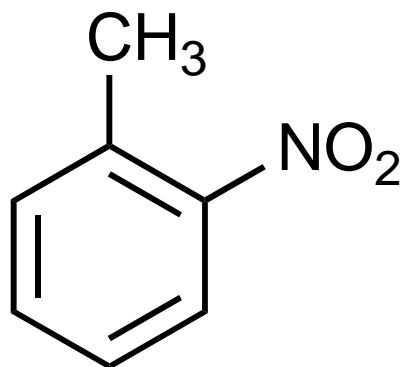
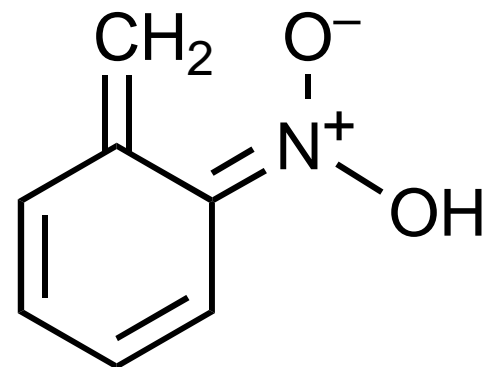
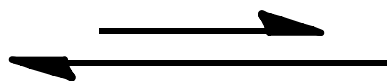


Fig. 2. Titration curve for the ionization of E determined by flash photolysis. The data points are initial absorbances A_0 at 270 nm immediately after the flash. The solid line is the best fit of Eqn. 5 to the data points.

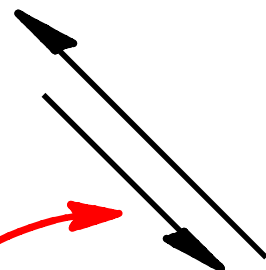




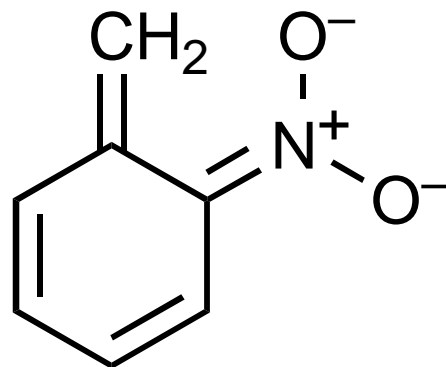
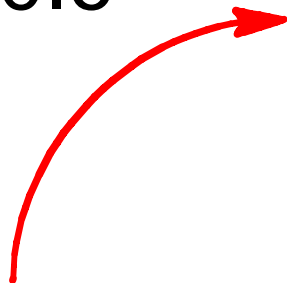
$pK = 17.0$



$pK_a \approx 20.6$

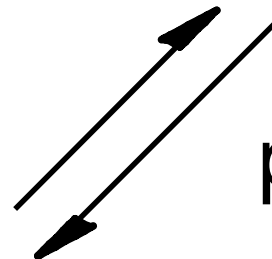


H/D-exchange

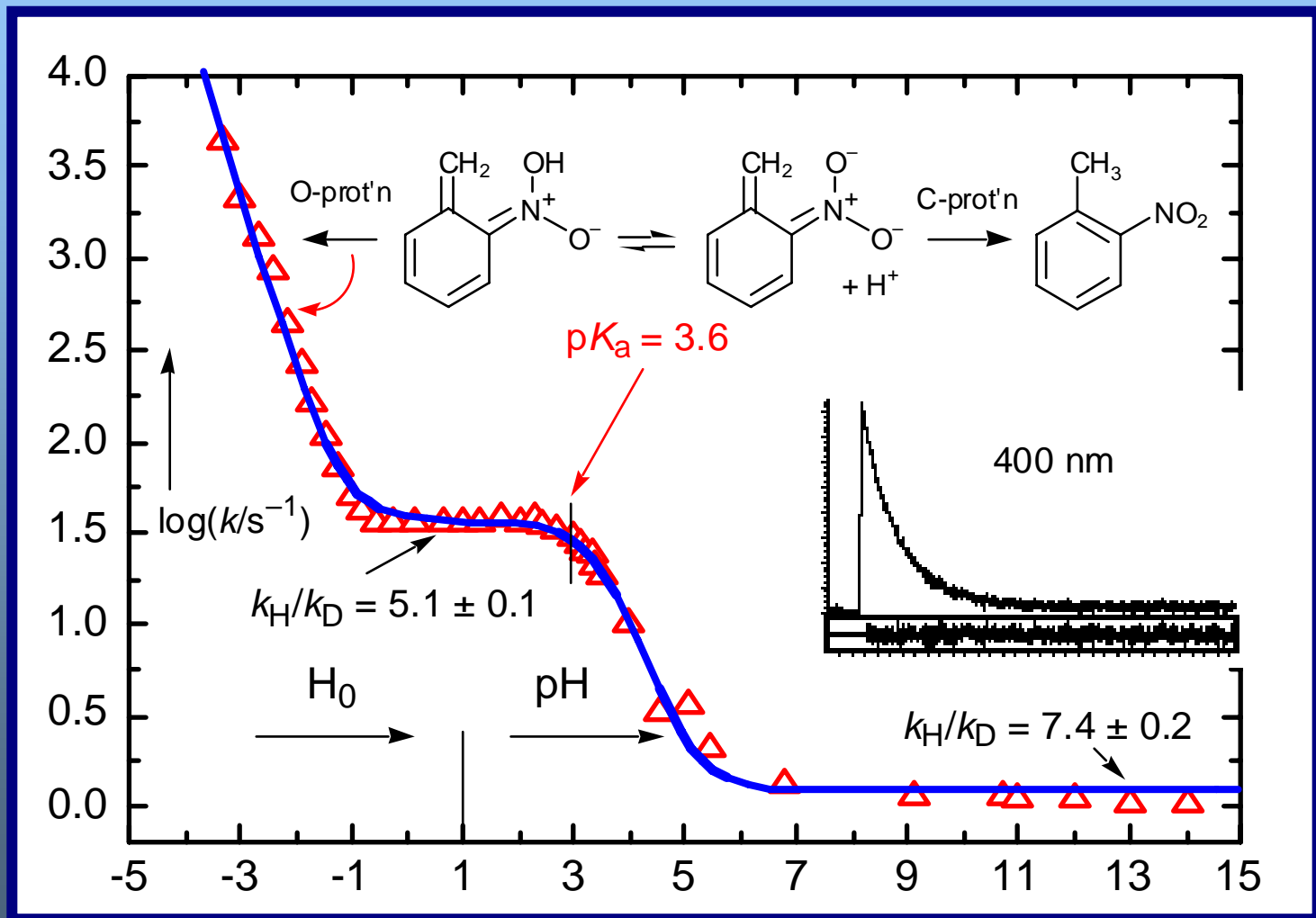


+ H⁺

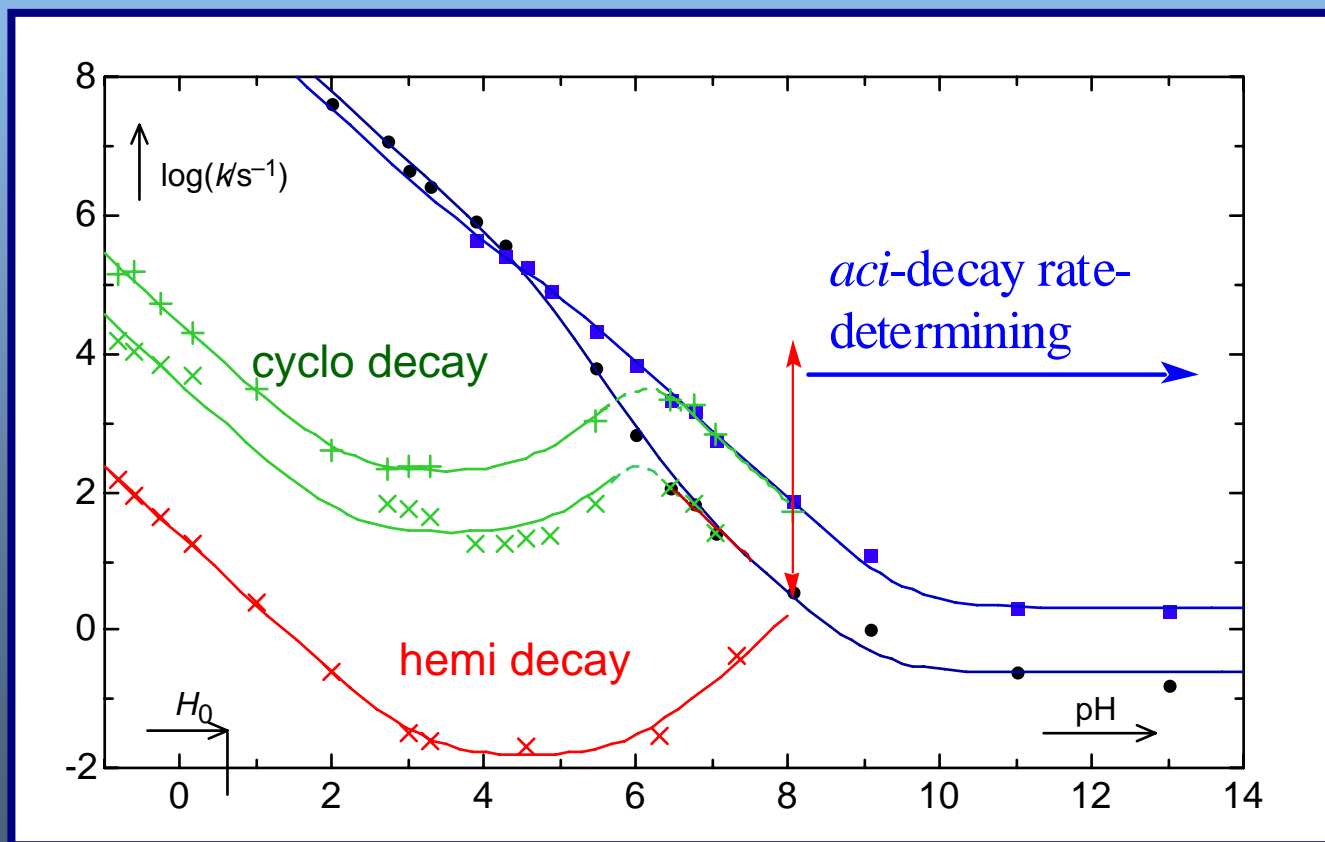
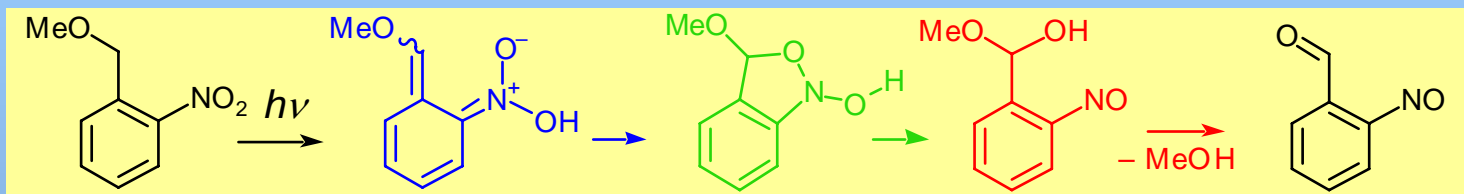
$pK_a^{aci} = 3.6$

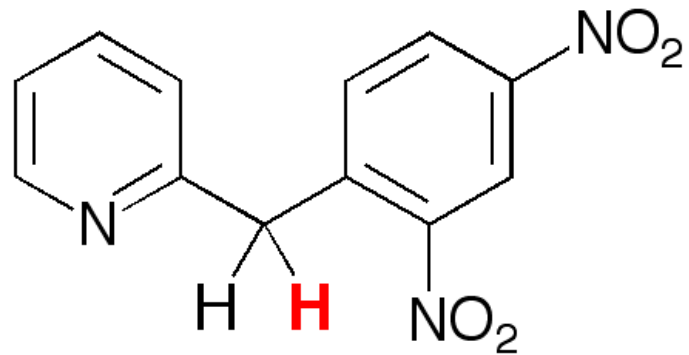


pH-rate profile: *o*-nitrotoluene



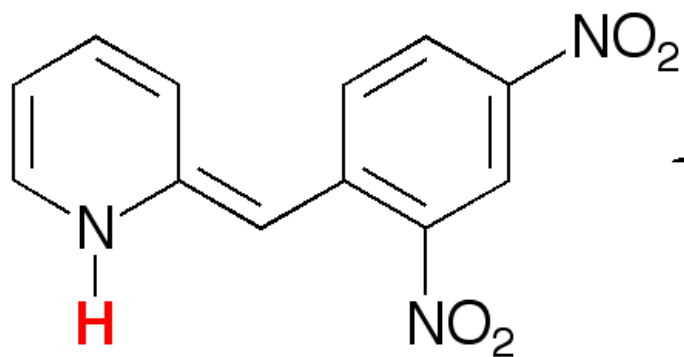
o-Nitrobenzyl methyl ether: pH-profile



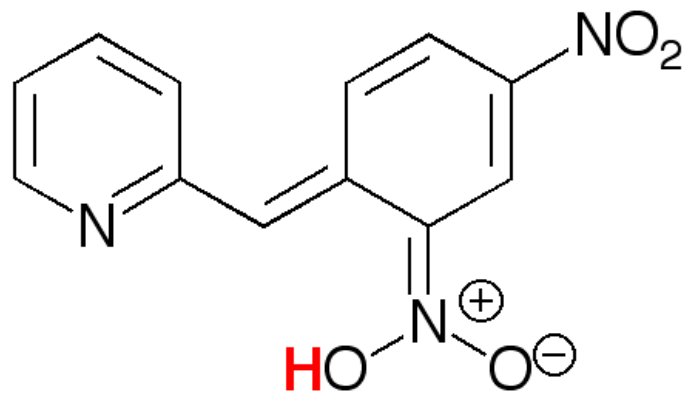


1 CH

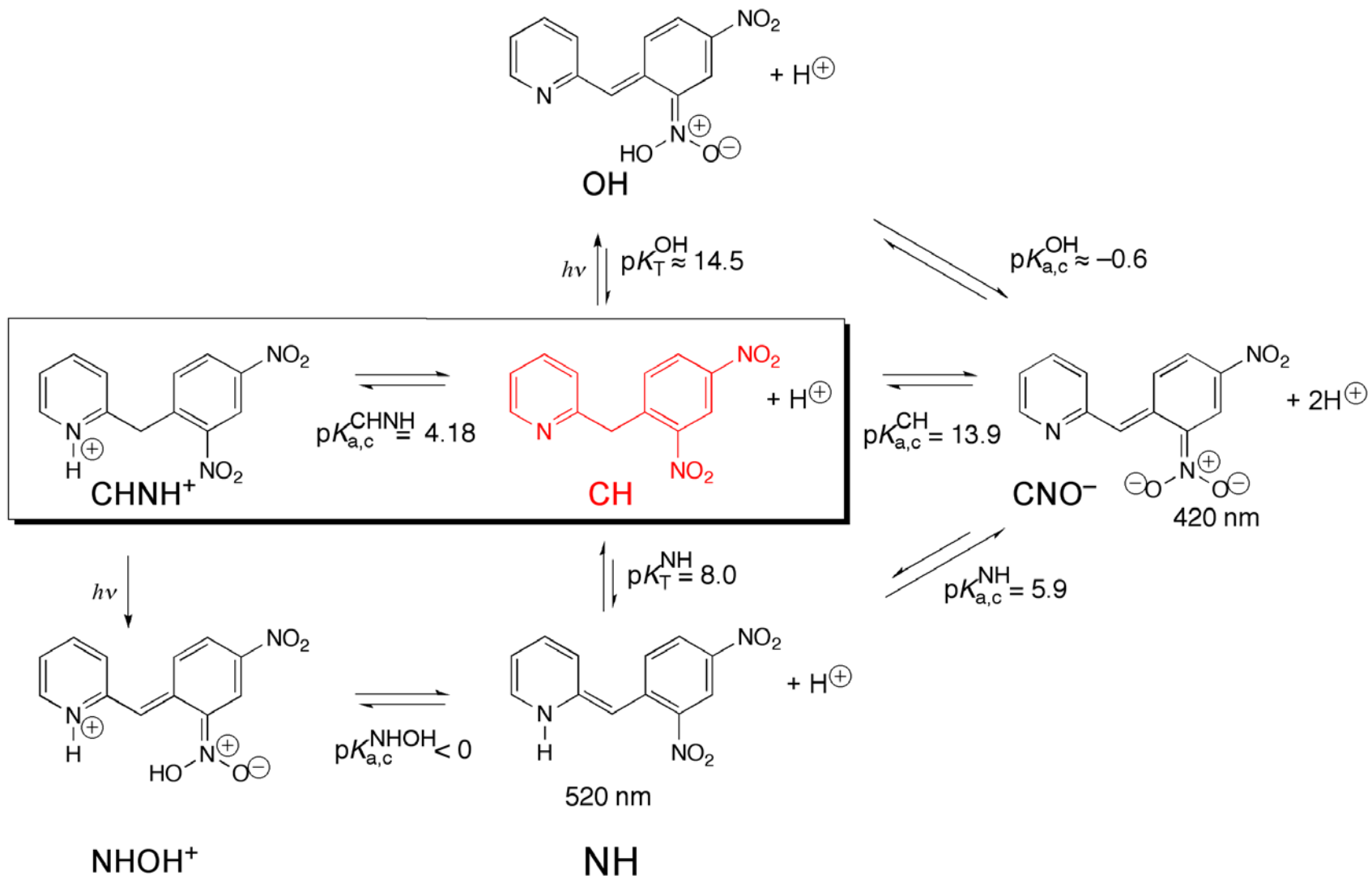
hν

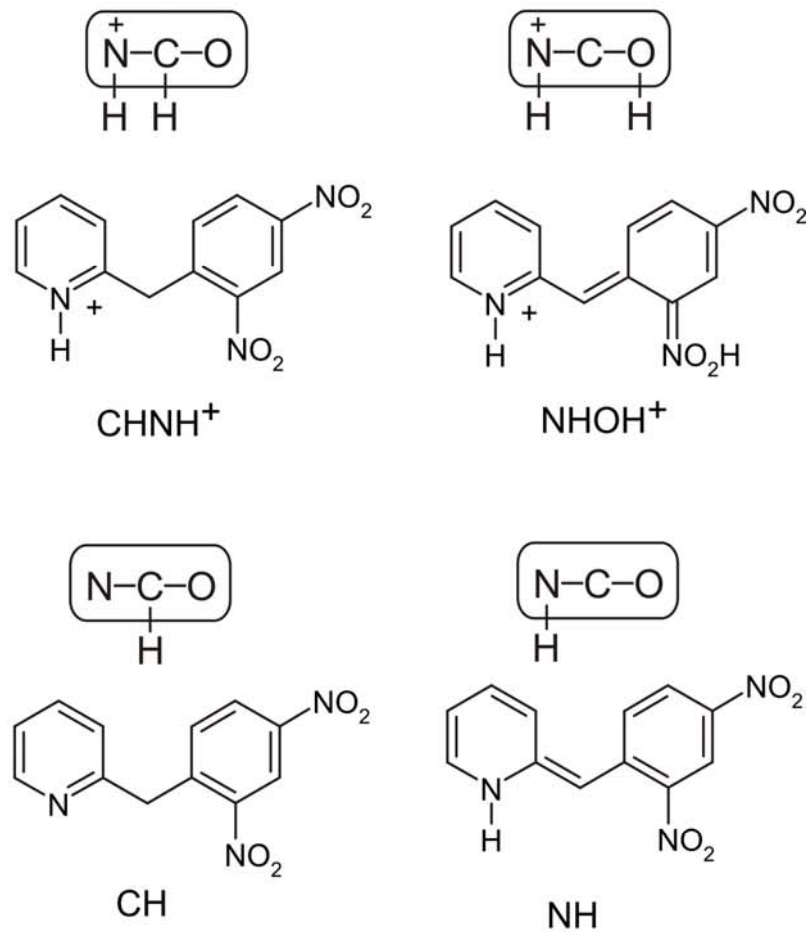
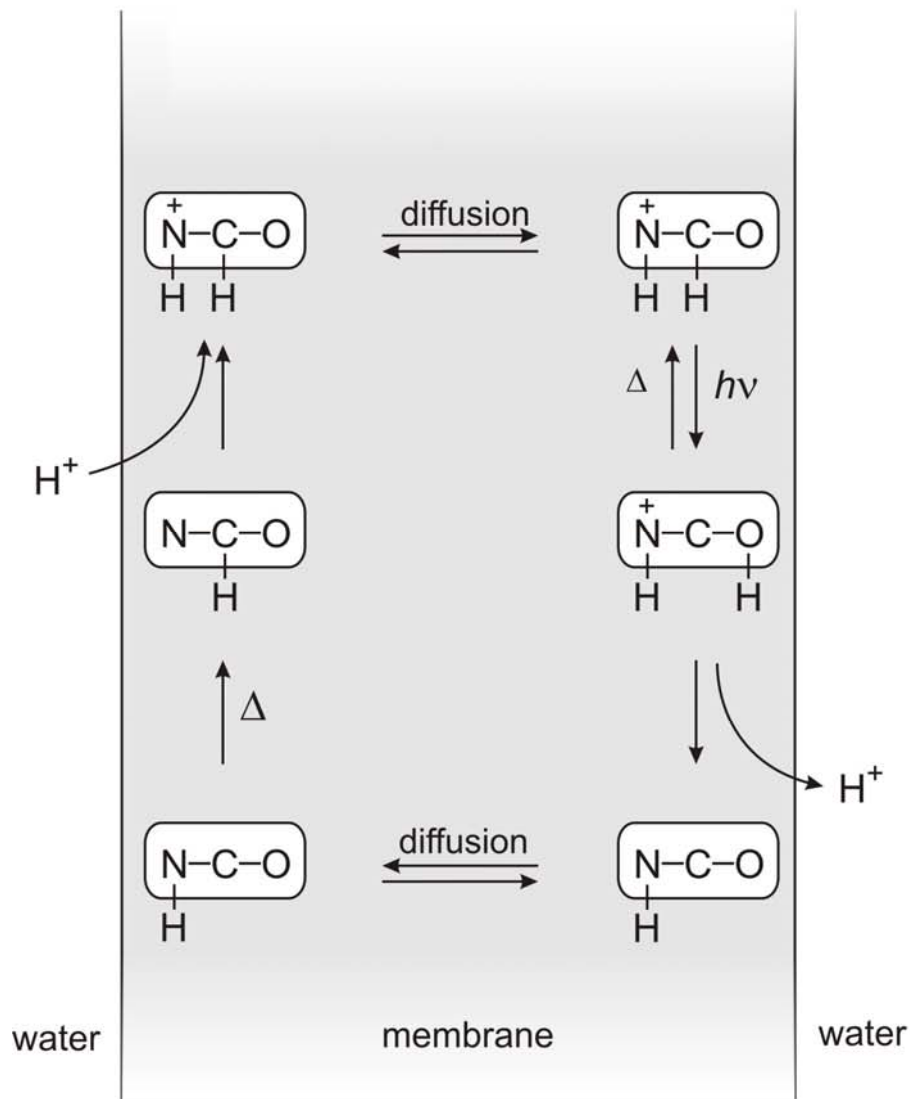


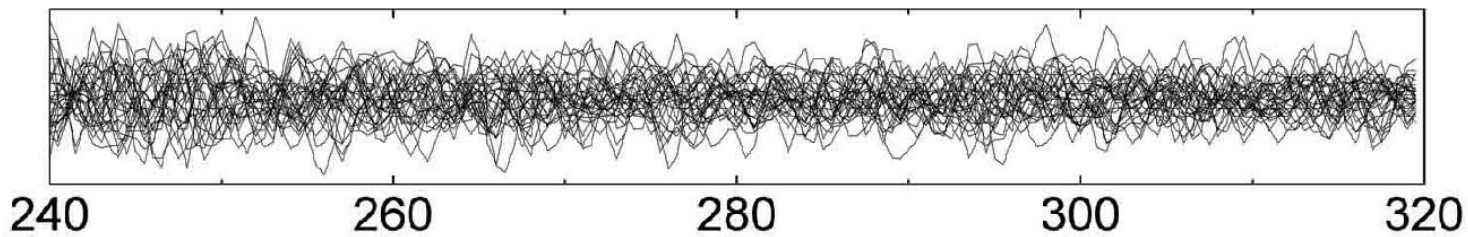
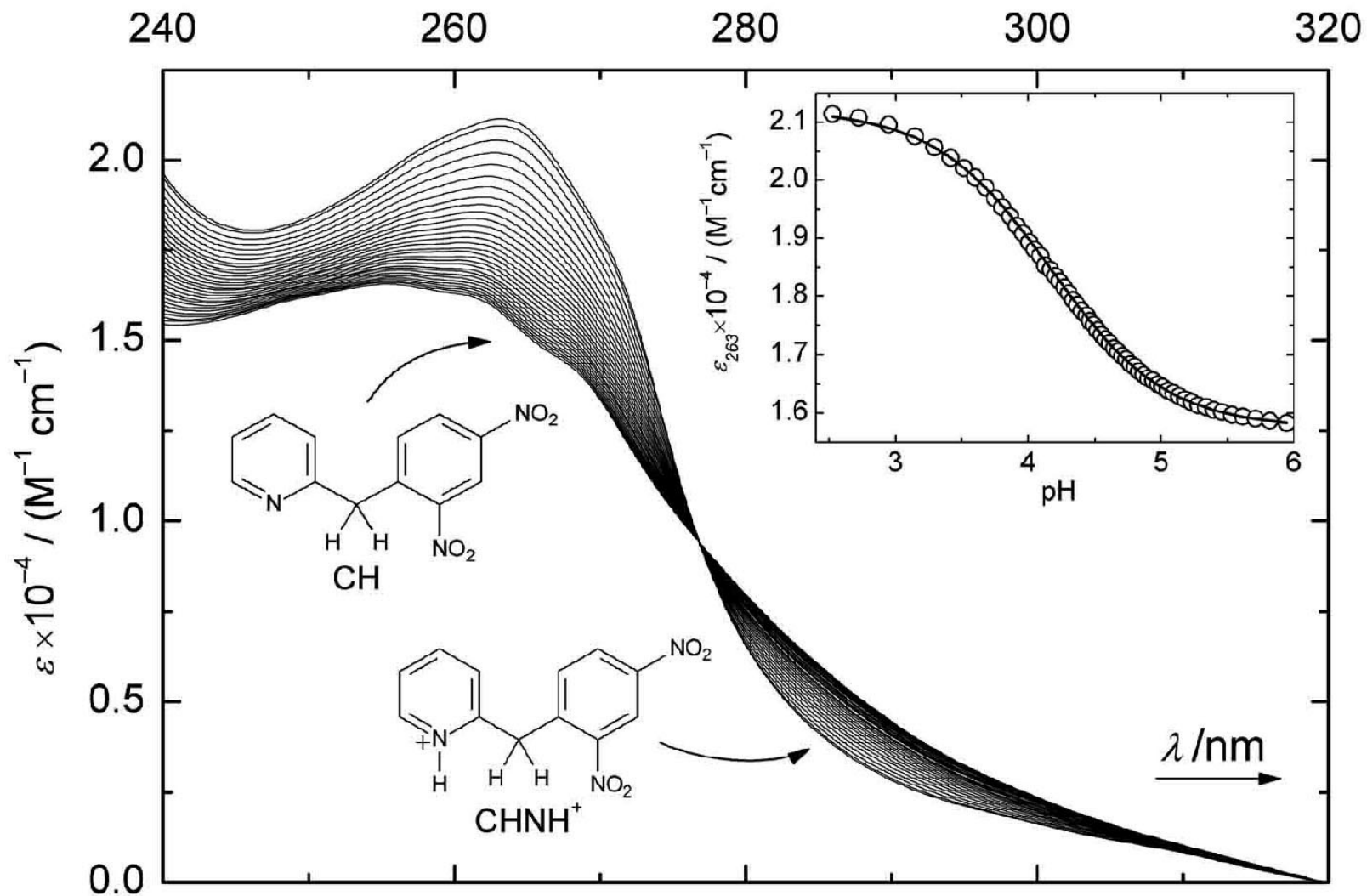
NH

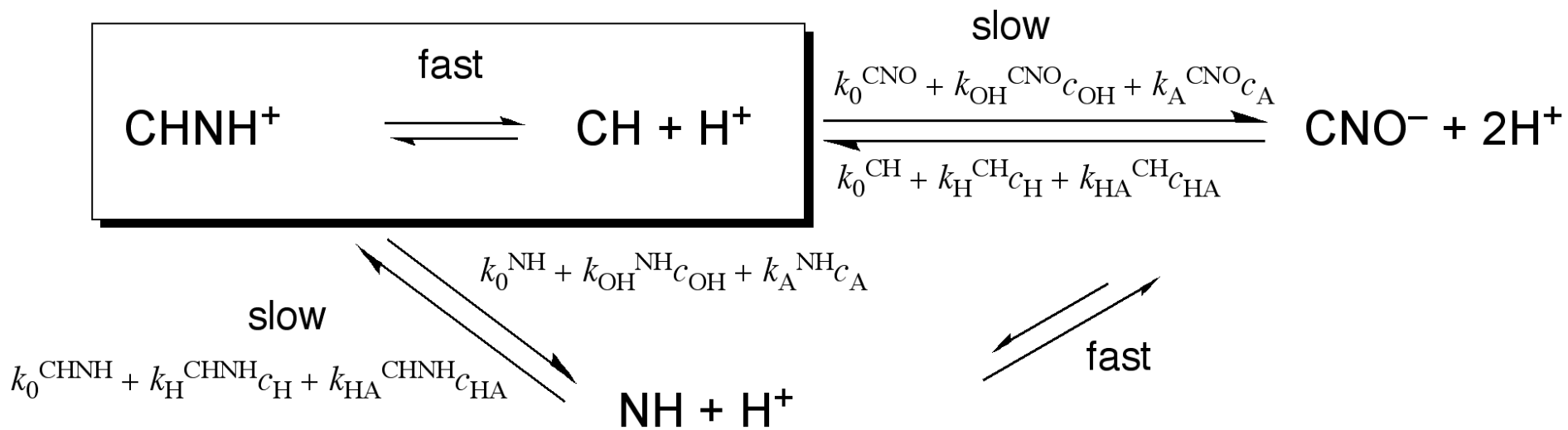


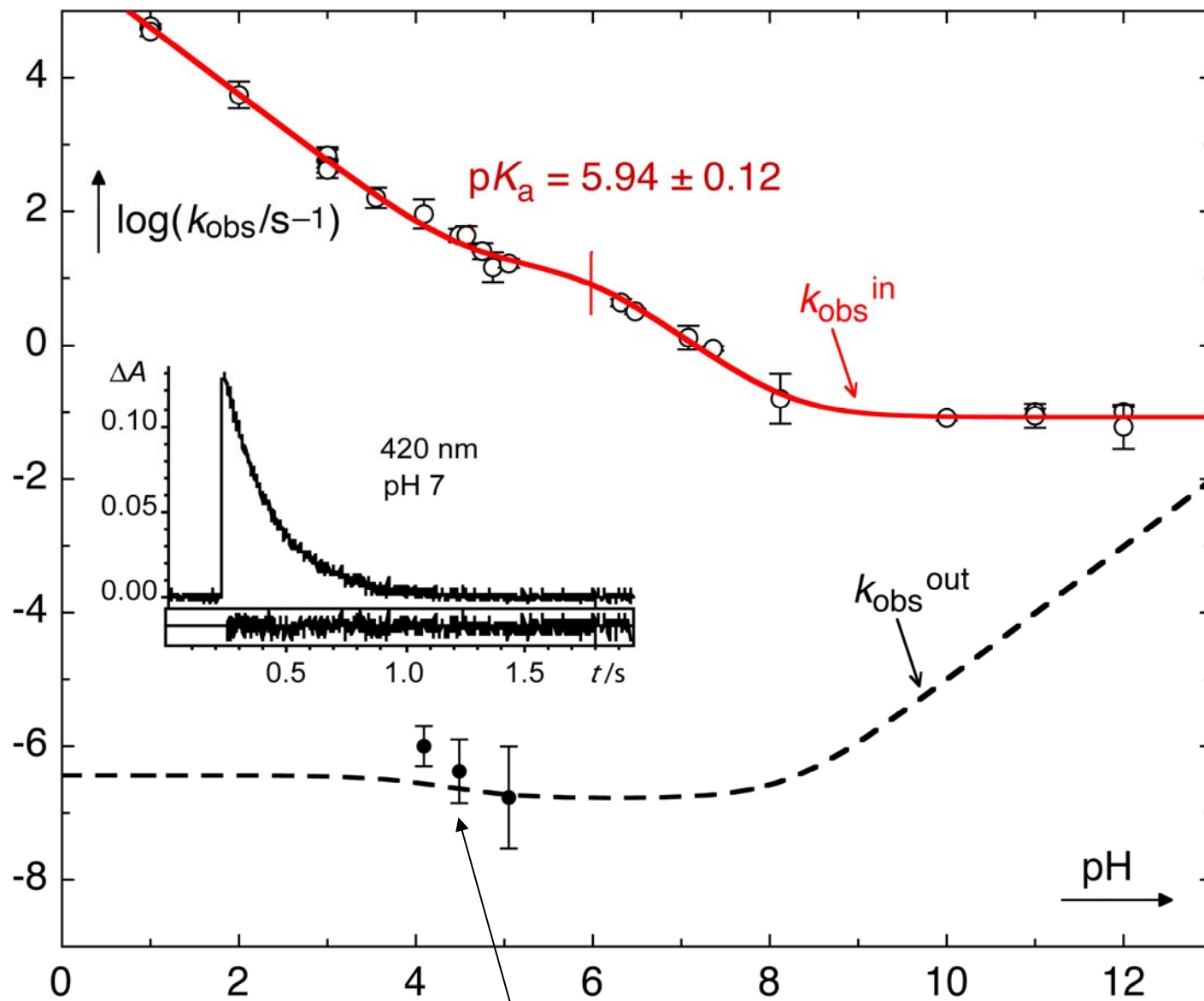
OH



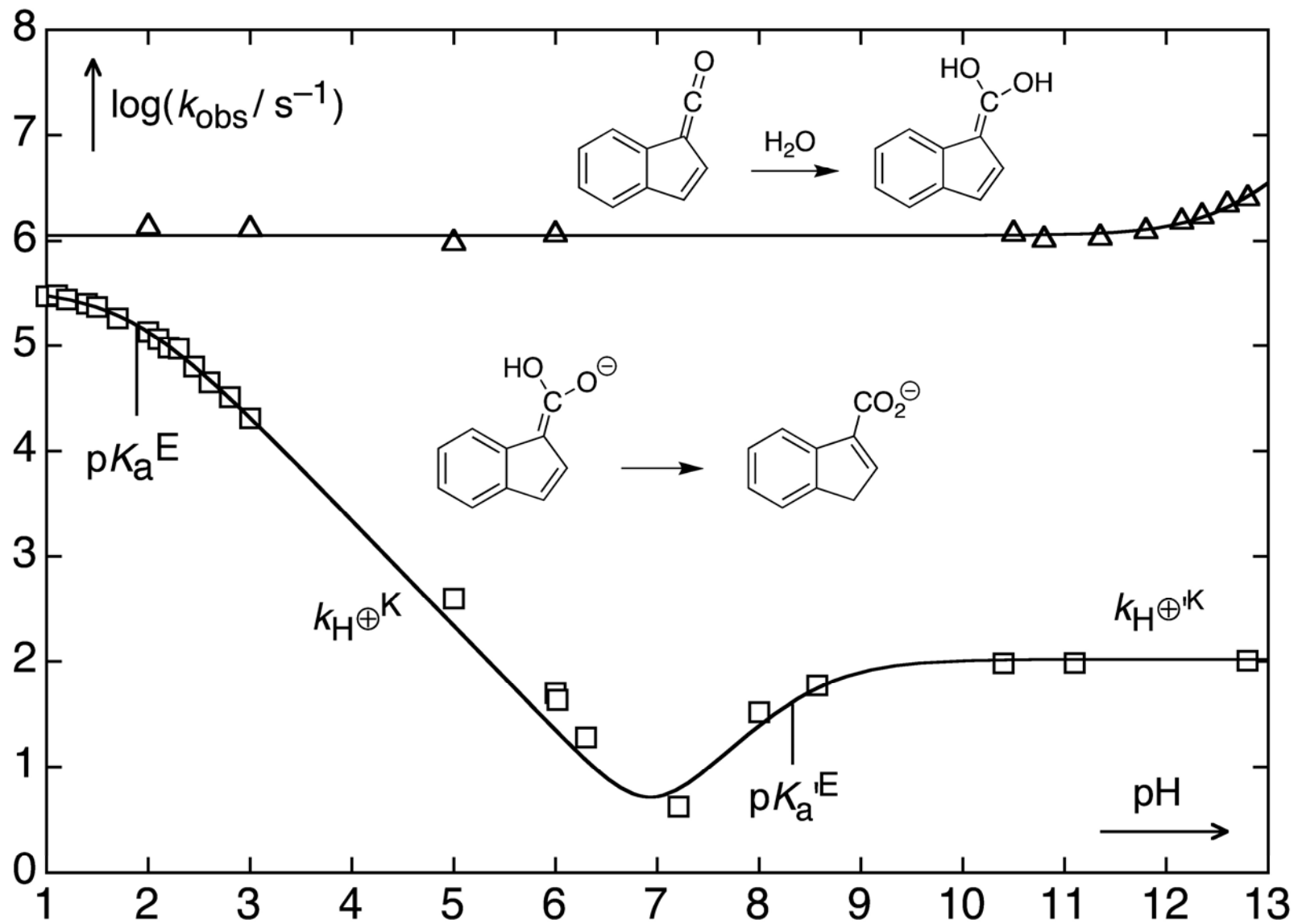


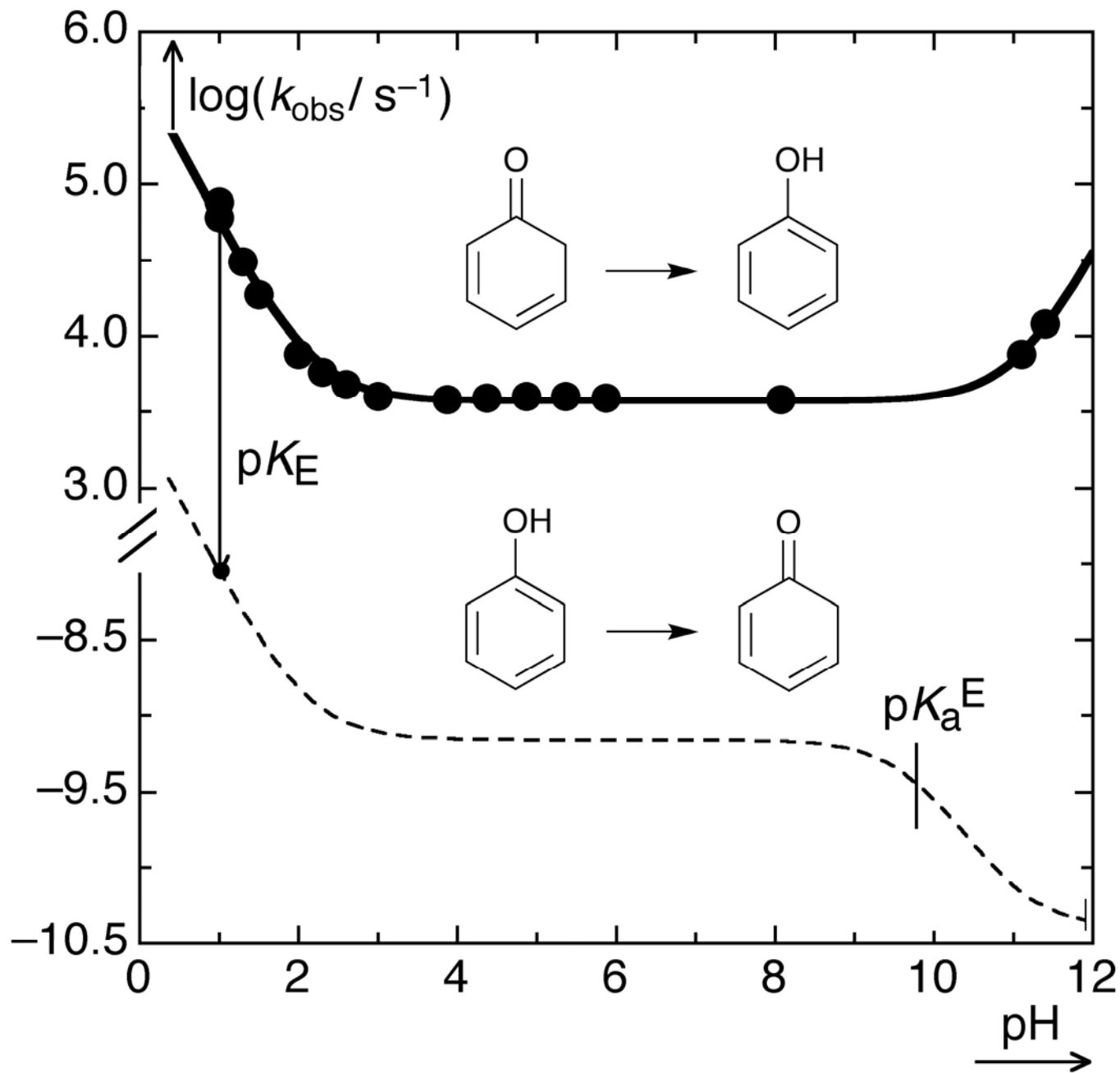


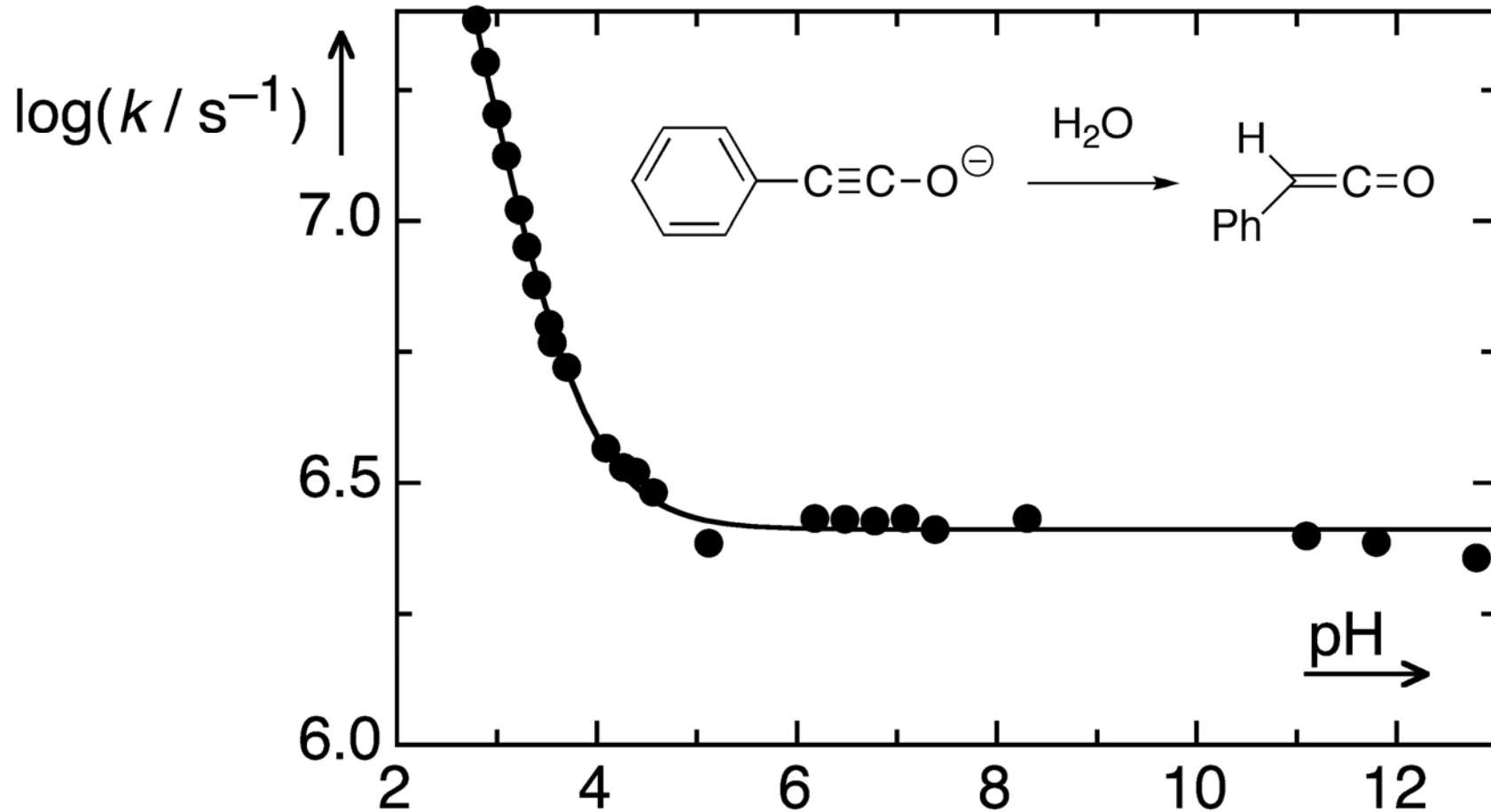


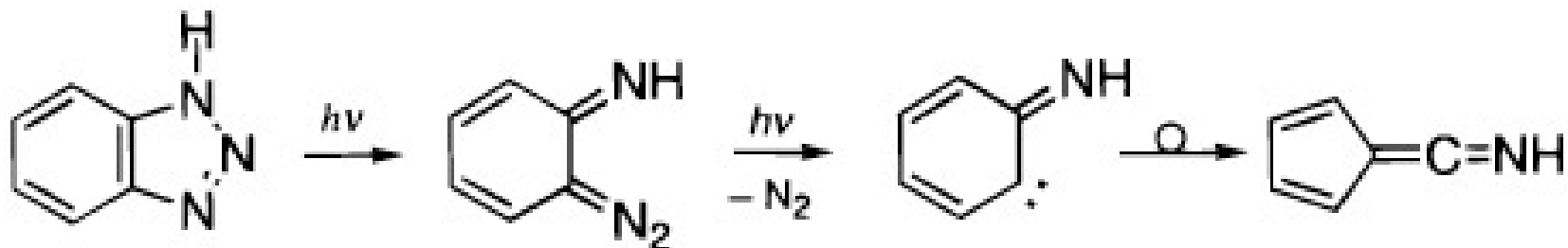
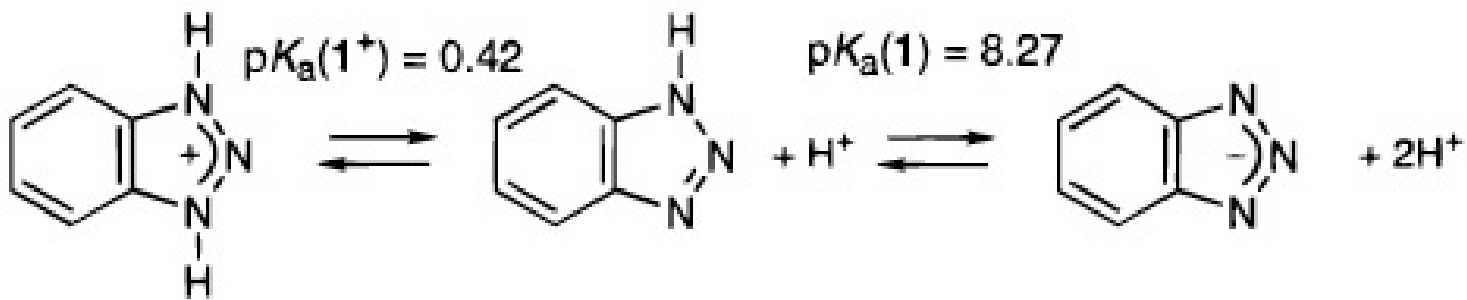


Intercepts of buffer dilution plots









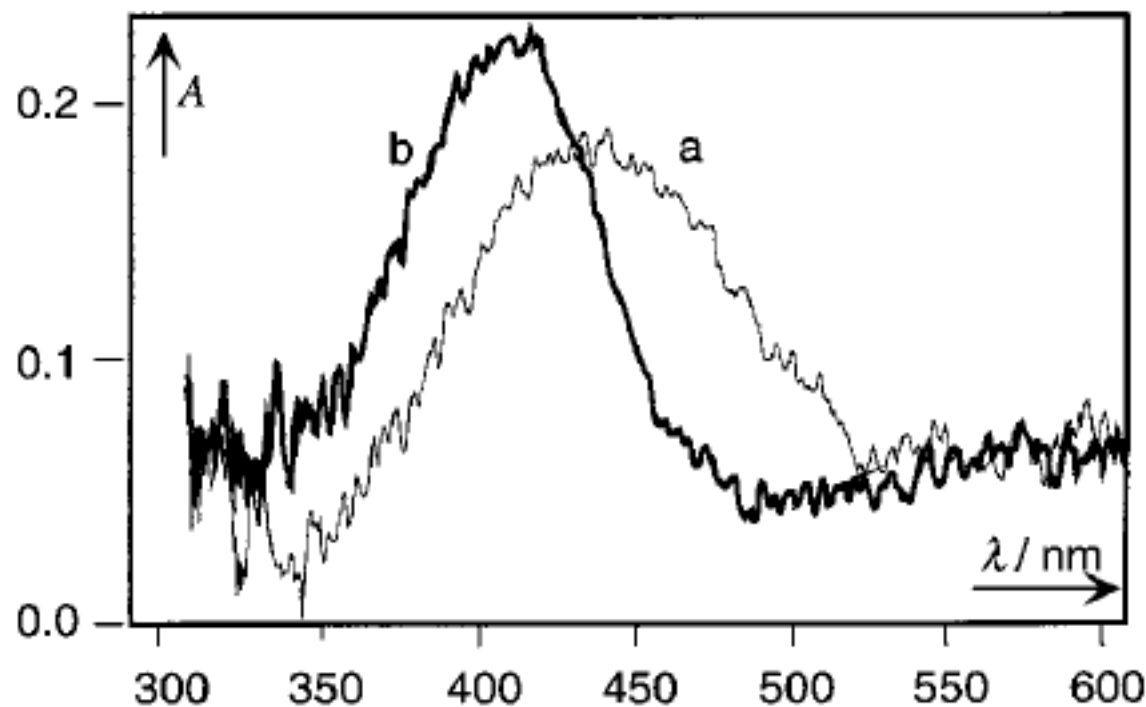
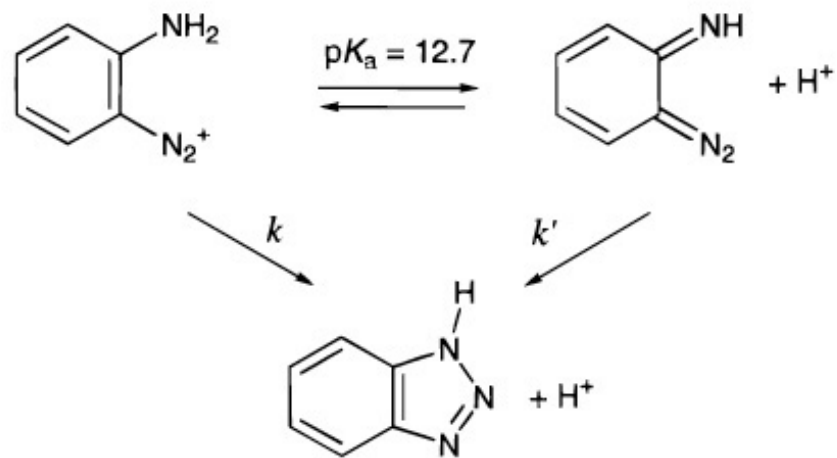
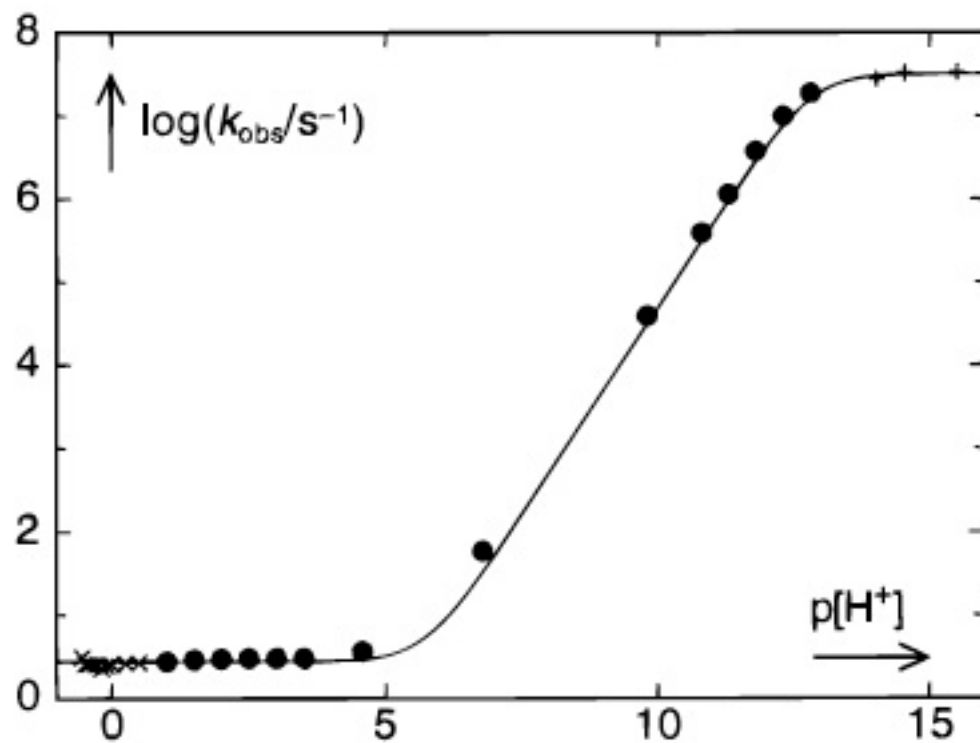


Figure 1. Absorption spectra of the transient generated by flash photolysis of **1** using an excitation pulse from a KrF-excimer-laser ($\lambda_{\text{exc}} = 248 \text{ nm}$, 100 mJ per pulse, pulse width $\sim 25 \text{ ns}$, delay after the pulse maximum $\sim 30 \text{ ns}$). Spectrum a: 1.0 N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



Bronsted equation

$$\log \left(\frac{k_{\text{HA}}}{p} \right) = \log G_{\text{A}} + \alpha \log \left(\frac{qK_{\text{a}}^{\text{HA}}}{p} \right)$$

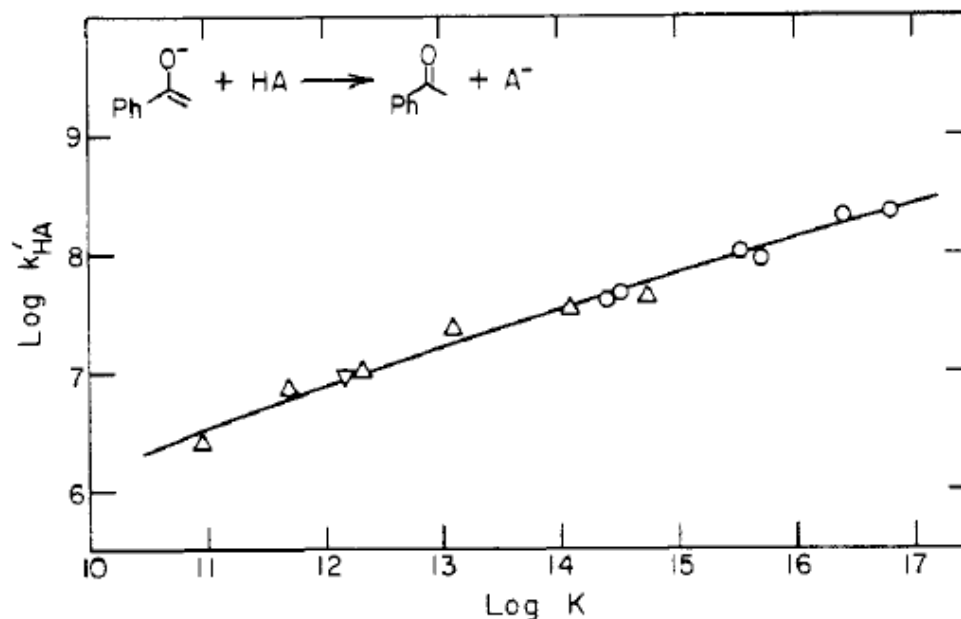
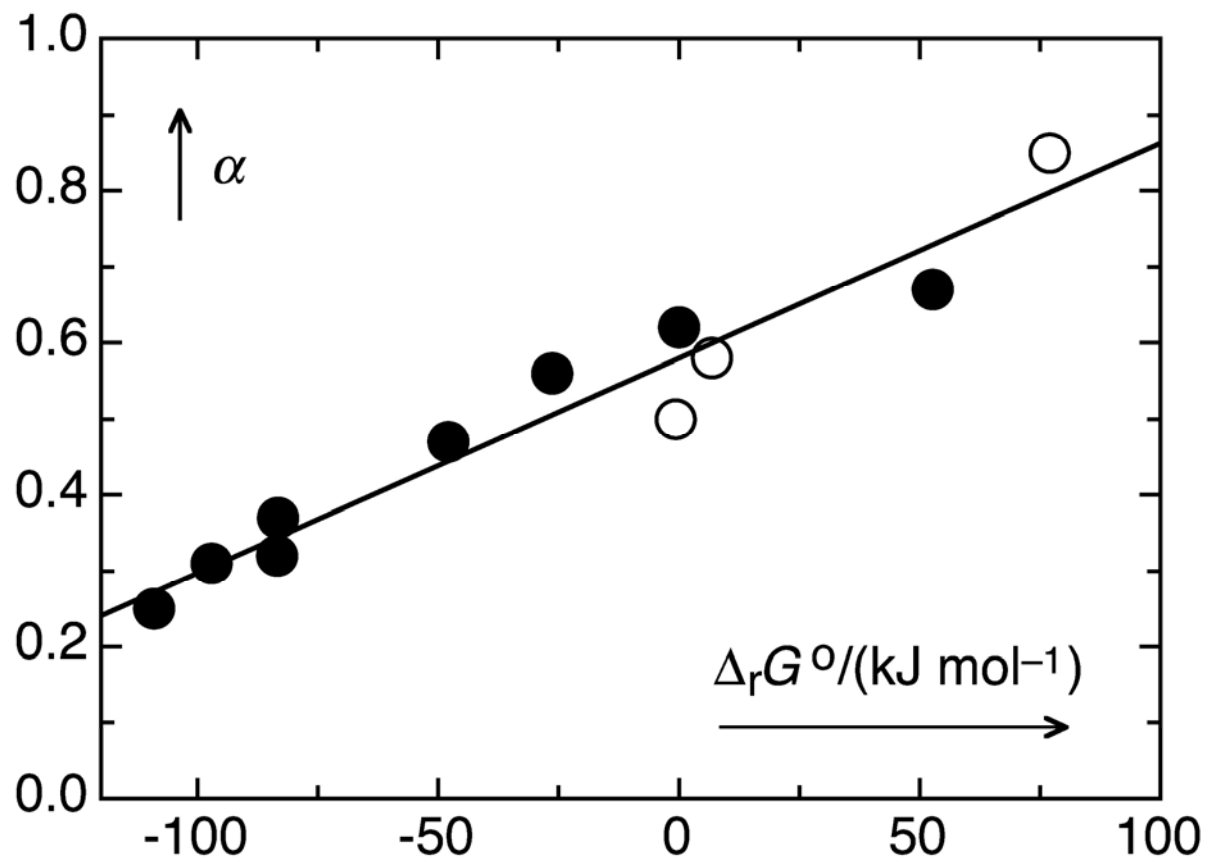
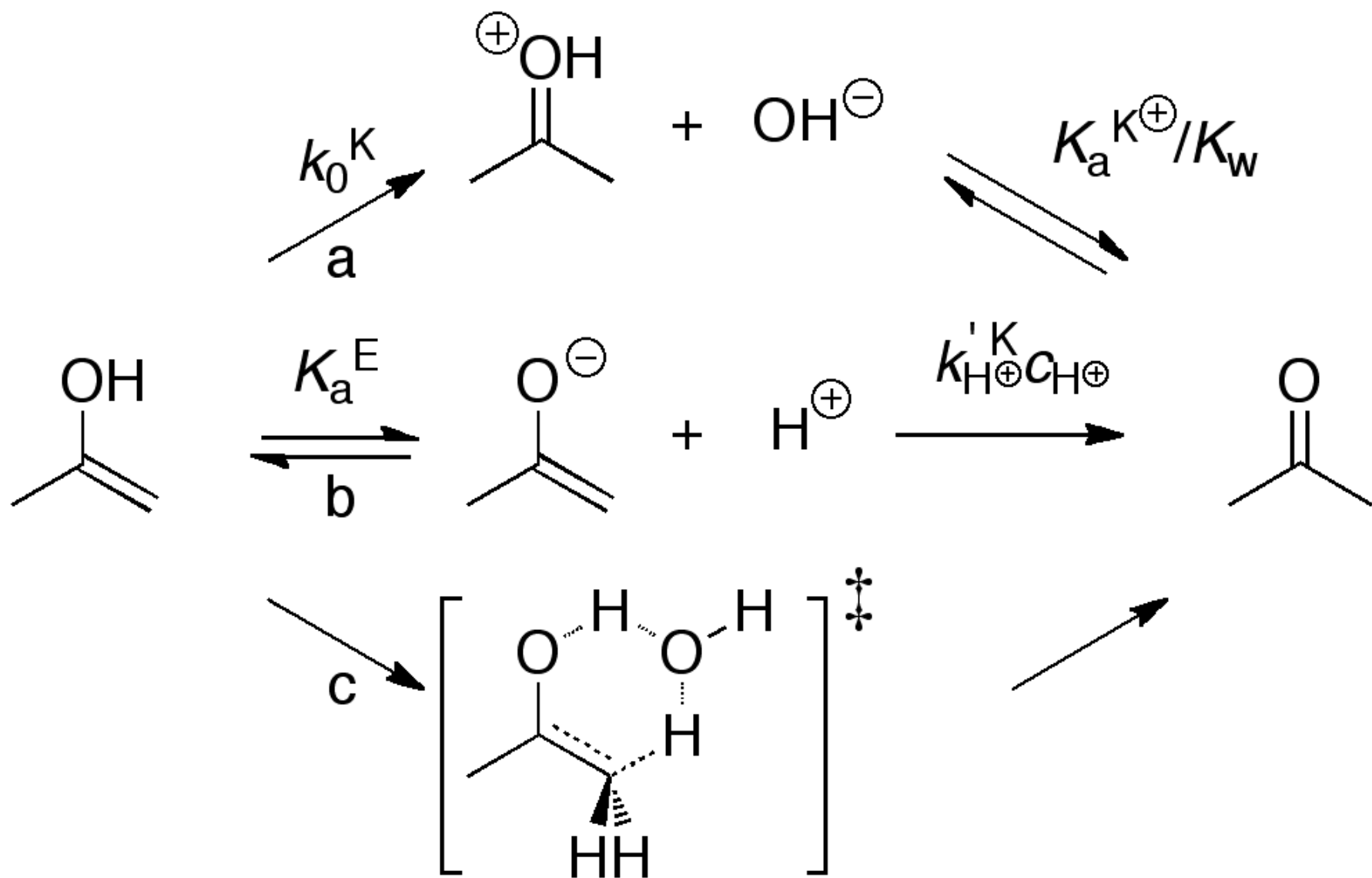


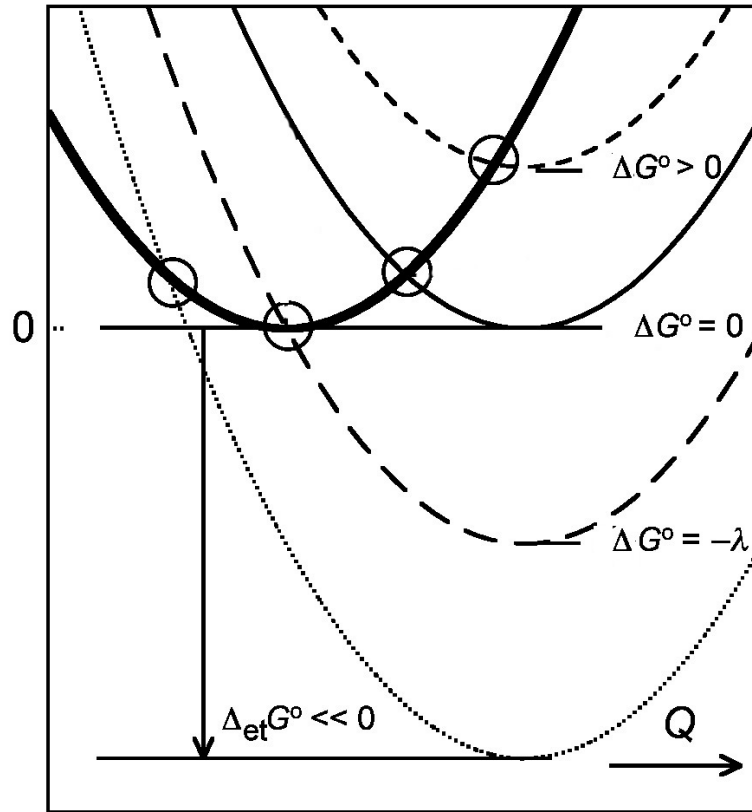
Figure 1. Rate–equilibrium relation for the ketonization of acetophenone enolate ion in aqueous solution at 25 °C catalyzed by RCO_2H (○) and RPO_3H^- (including HOPO_3H^-) (△). The points represent “chemical” rate and equilibrium constants with symmetry-induced contributions removed by using the following statistical factors: $p = 1$, $q = 2$ for RCO_2H ; $p = 1$, $q = 3$ for RPO_3H^- ; $p = 2$, $q = 3$ for H_2PO_4^- ; $p = 3$, $q = 1$ for PhCOCH_3 .

Bronsted α variation with ΔG



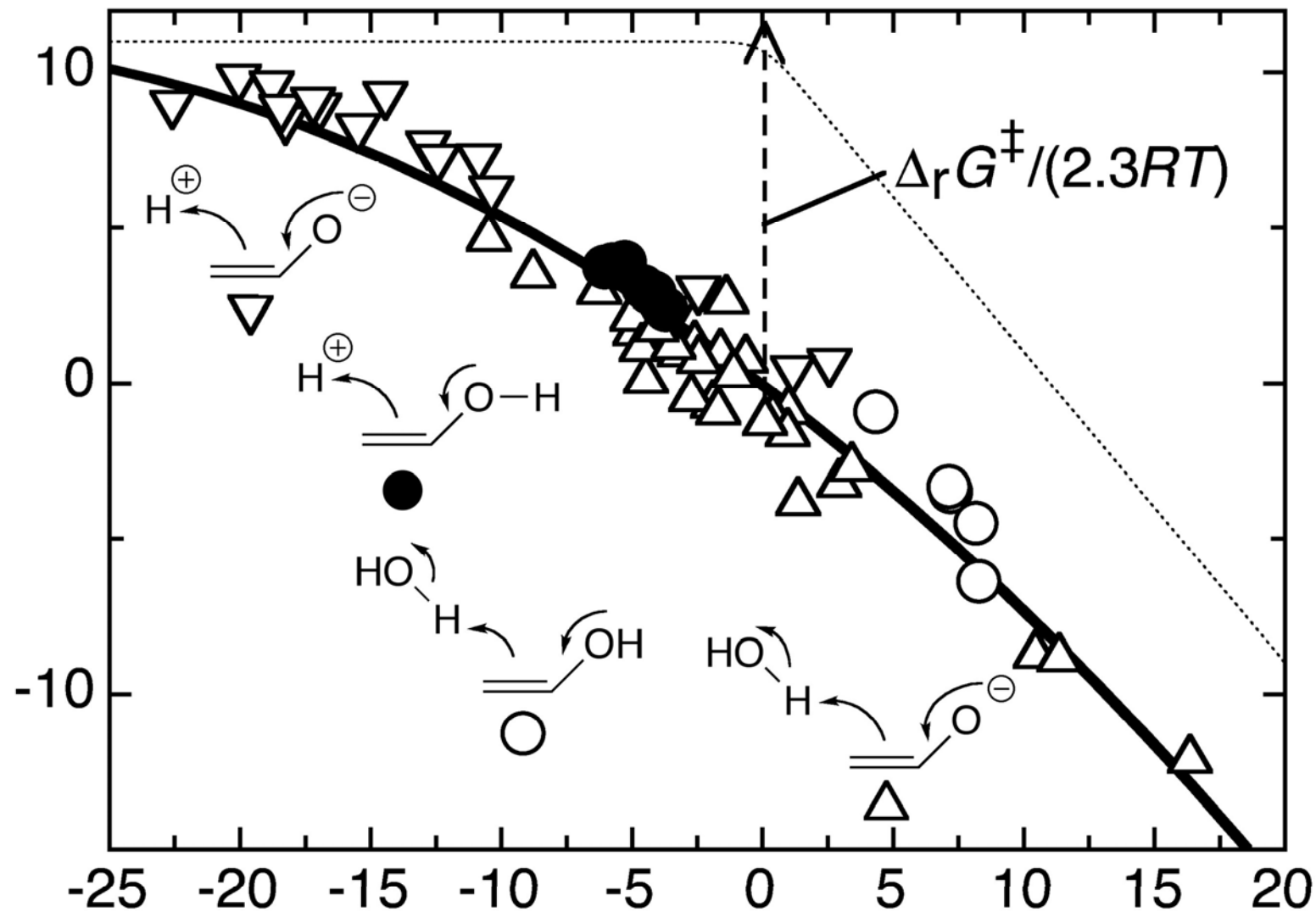


Marcus theory



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

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



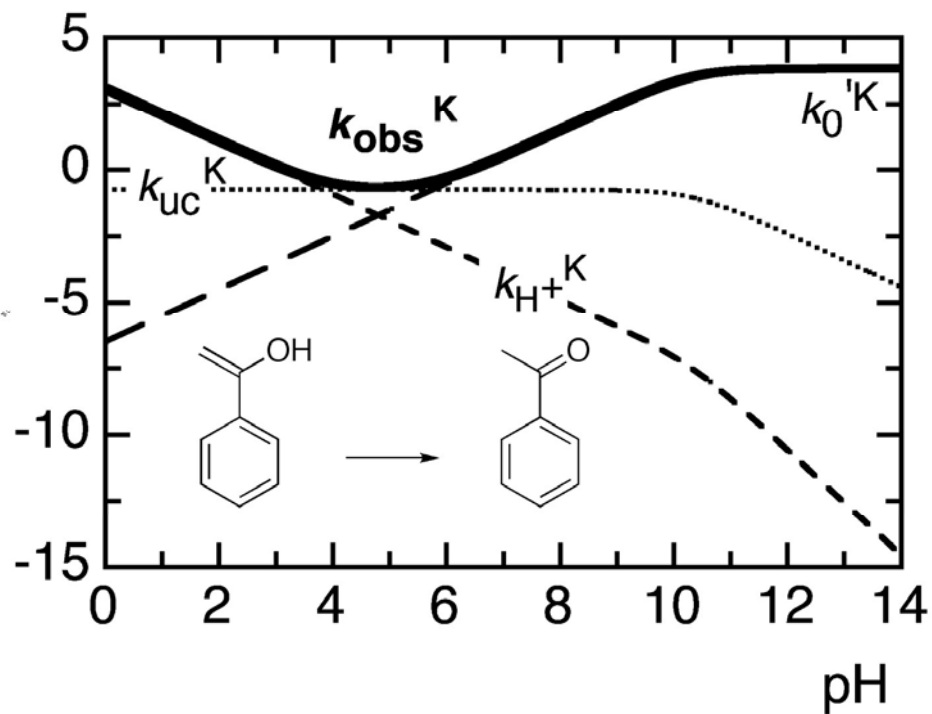
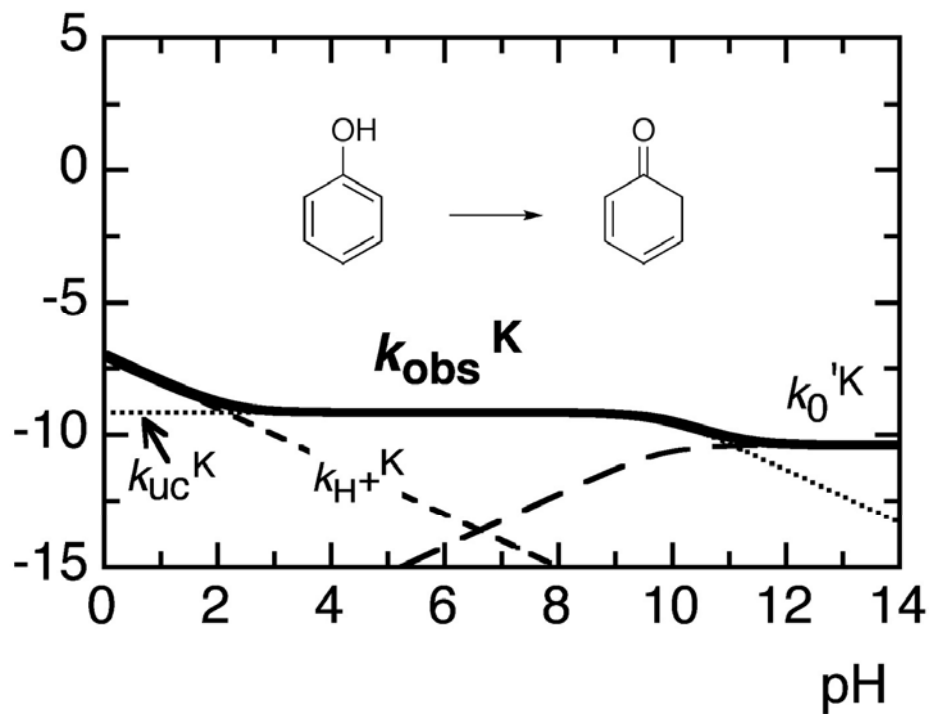
$\Delta_r G^0/(2.3RT)$

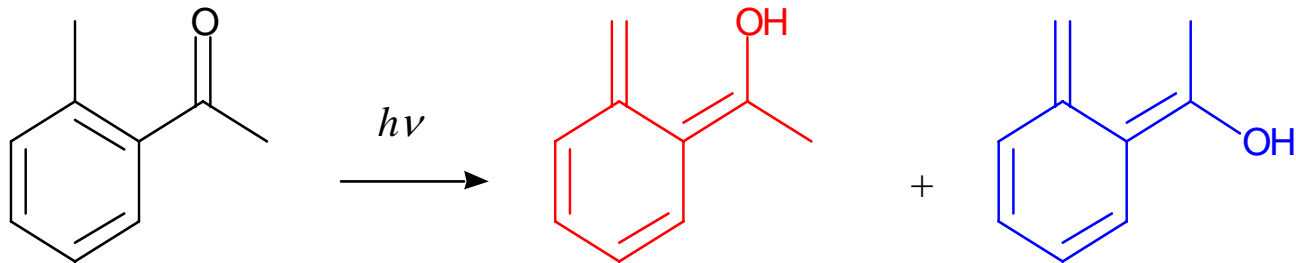


$$\alpha = \left(\frac{\partial \Delta_{\mathbf{r}} G^{\ddagger}}{\partial \Delta_{\mathbf{r}} G^{\circ}} \right)_{p,T} = \left(1 + \frac{\Delta_{\mathbf{r}} G^{\circ}}{4 \Delta_{\mathbf{r}} G_0^{\ddagger}} \right) / 2$$

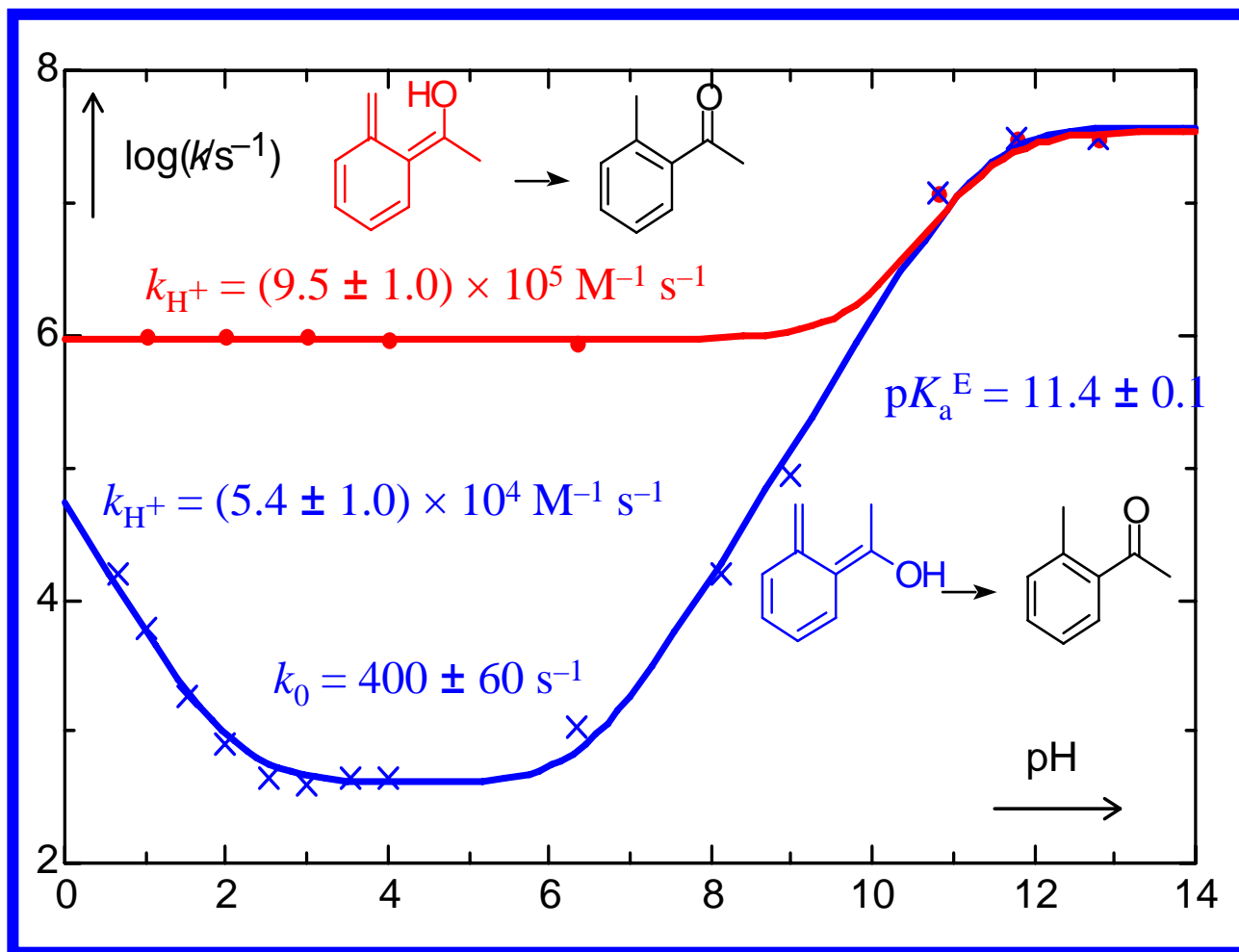
$$\left(\frac{\partial^2 \Delta_{\mathbf{r}} G^{\ddagger}}{\partial [\Delta_{\mathbf{r}} G^{\circ}]^2} \right)_{p,T} = \left(\frac{\partial \alpha}{\partial \Delta_{\mathbf{r}} G^{\circ}} \right)_{p,T} = \frac{1}{8 \Delta_{\mathbf{r}} G_0^{\ddagger}}$$

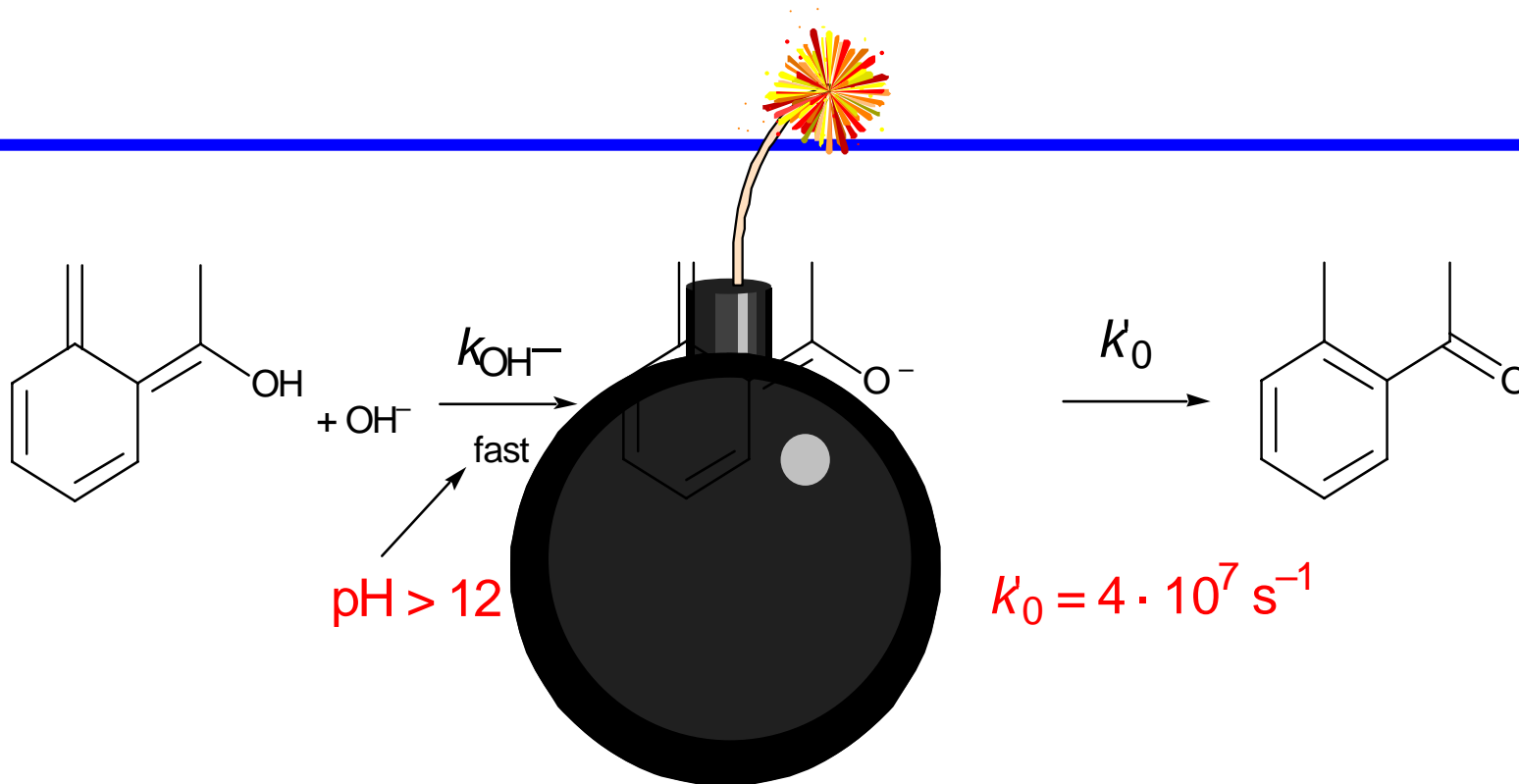
$\log(k/ \text{s}^{-1})$





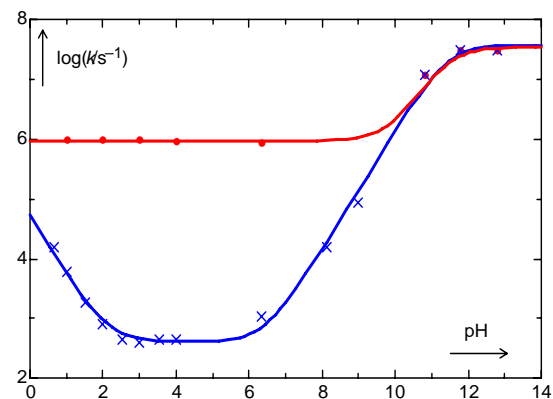
$$pK_E(\text{calc}) = 25$$





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