

## Kinetics of proton transfer reactions involving carbon

Jakob Wirz

*Institut für Physikalische Chemie, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*

**Abstract:** Enol protomers of ketones and aldehydes, carboxylic acids and esters, ketenes, as well as keto protomers of phenols are generated by flash photolysis to investigate their reaction kinetics in aqueous solution. pH-Rate profiles and buffer dilution plots provide absolute rate constants for acid and base catalysis of keto-enol protomeric reactions. Equilibrium constants of enolization spanning a range of 30 orders of magnitude are determined as the ratio of the rate constants of forward and backward reaction. Structure-reactivity and free energy relationships exhibit the systematic and predictable reactivity of transient protomers. The intrinsic barrier for proton transfer from oxygen to carbon,  $\Delta G_0^\ddagger$ , as defined by Marcus theory, amounts to  $57 \pm 2 \text{ kJ mol}^{-1}$ ; thus, the rates for thermoneutral reactions are nearly ten orders of magnitude less than those expected for proton transfer reactions of "normal" acids. The high intrinsic barrier is held responsible for the lack of excited-state adiabatic proton transfer reactions involving carbon. Such reactions generally proceed directly to ground state products through avoided crossings or conical intersections. Evidence for protonation of  $n,\pi^*$ -excited triplet ketones at the carbonyl carbon is presented.

### Keto-Enol Equilibria

Reactions of carbonyl compounds with electrophilic reagents proceed via enol intermediates. Formation of enols requires proton transfer from carbon acids, which is intrinsically slow. For this reason, carbon acids have been called pseudo-acids. Flash photolysis is an excellent tool to study the kinetics of these ground-state reactions: the labile protomers are generated in excess of their equilibrium concentrations and absolute rate constants for the recovery of these equilibria in the ground state are obtained. Combination with rate constants for the reverse reactions then determines the equilibrium constants of enolization,  $K_E$ , for a broad range of prototropic reactions.

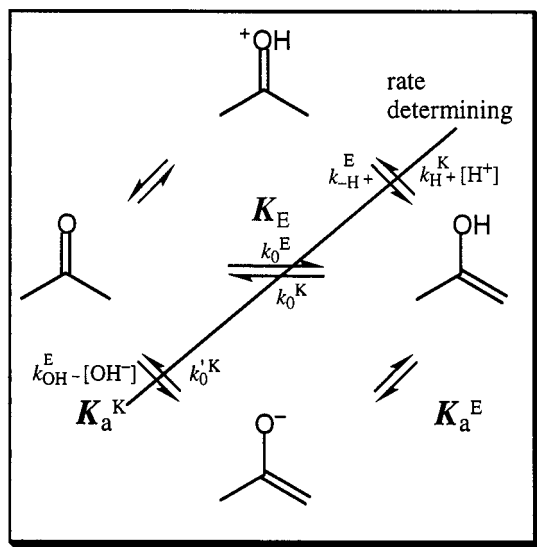
The re-establishment of protomeric equilibria in aqueous solution always obeys first-order kinetics. The observed rate constants depend on pH (specific acid and base catalysis), and on the concentration of added buffers (general acid and base catalysis). Three reaction paths need to be considered (Scheme 1), acid and base catalysis, and an "uncatalyzed" (i.e., pH-independent) reaction, the mechanism of which will be discussed below. The rate-determining steps in all three reaction paths involve proton transfer to or from carbon. Protonation equilibria are established more rapidly on oxygen, and the corresponding dissociation constants appear as downward bends in the

---

\*Lecture presented at the 17th IUPAC Symposium on Photochemistry, Sitges, Barcelona, Spain, 19–24 July 1998. Other presentations are published in this issue, pp. 2147–2232.

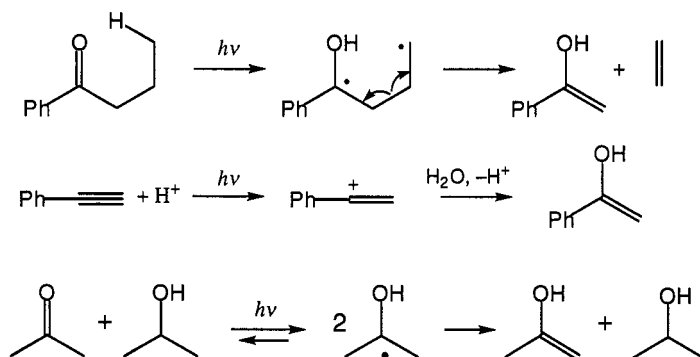
pH-rate profiles. Finally, carbon acid dissociation constants, often well outside the range normally accessible in aqueous solution, are defined by a thermodynamic cycle:  $pK_a^K = pK_a^E + pK_E$ .

Scheme 1



### Enols of Ketones and Aldehydes

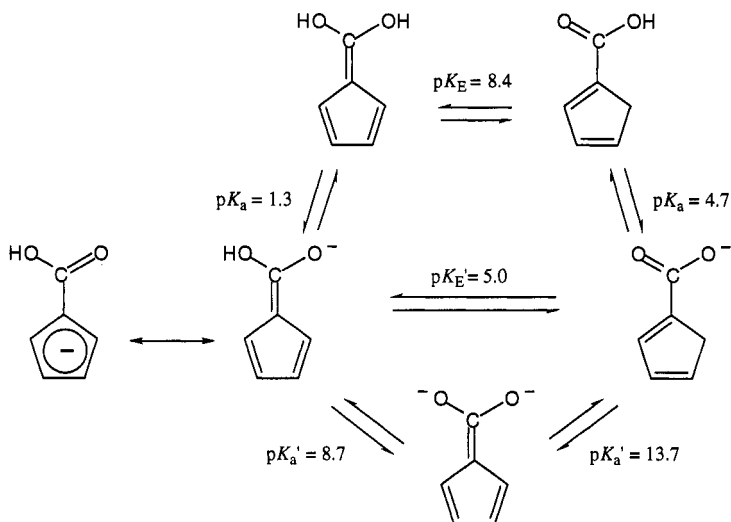
Photoreactions which generate enols as primary products are well known.



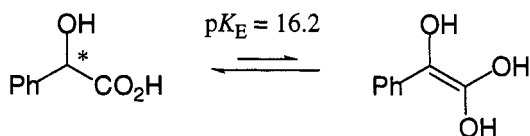
Twenty years ago, flash photolysis was first applied to measure the pH profile of a simple enol, acetophenone enol [1]. A representative selection of ketones and aldehydes has subsequently been studied [2]. The resulting thermochemical data on enol contents and acidity constants of simple ketones have led to substantial revisions of earlier data obtained by bromine titration or by NMR, and some puzzling inconsistencies of structure-reactivity relationships have, thereby, been removed. For example, the enol content of acetone in aqueous solution is about 5 ppb, rather than the 2.5 ppm quoted in many textbooks of organic chemistry. The acidity constants of simple enols are comparable to those of phenols,  $pK_a^E = 10 \pm 1$ .

### Enols of Carboxylic Acids and Esters.

The enol content of carboxylic acids is even lower than that of ketones. Photo-Wolff rearrangement of  $\alpha$ -diazoketones is a convenient method to form ketenes in aqueous solution by flash photolysis, and hydration of the ketenes is sometimes sufficiently fast ( $\approx 1 \mu\text{s}$ ) to allow detection of the resulting ene-1,1-diol intermediates. This method was used to generate fulvene-1,1-diol [3] and the enol of indene-3-carboxylic acid [4]. The high acidity of fulvenediol ( $\text{p}K_{\text{a},1} = 1.3$ ,  $\text{p}K_{\text{a},2} = 8.7$ ) is attributed to charge delocalization into the cyclopentadienyl ring (see the  $6\pi$ -cyclopentadienyl anion resonance structure shown below for the monoanion), which appears to be a stronger electron acceptor than the carbonyl oxygen atom of carbonic acid ( $\text{O}=\text{C}(\text{OH})_2$ ,  $\text{p}K_{\text{a},1} = 3.9$ ,  $\text{p}K_{\text{a},2} = 10.3$ ).



Efforts to measure the enol content of acetic acid, estimated at  $\text{p}K_{\text{E}} = 20$  [5], have so far failed. The enolization constant of mandelic acid was determined as  $\text{p}K_{\text{E}} = 16.2$  [6]. Mandelate racemase catalyzes the racemization of mandelic acid by an enolization pathway. The enzyme has a turnover rate of ca.  $1000 \text{ s}^{-1}$ , which represents an acceleration of about 14 orders of magnitude over the reaction rate in water at physiological pH!

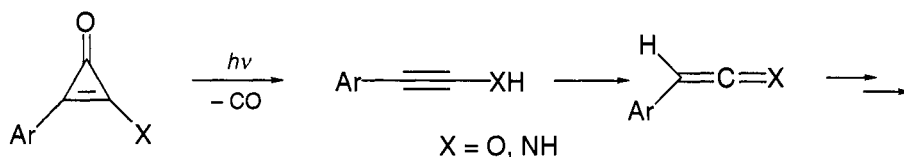


### Ynols and Ynamines

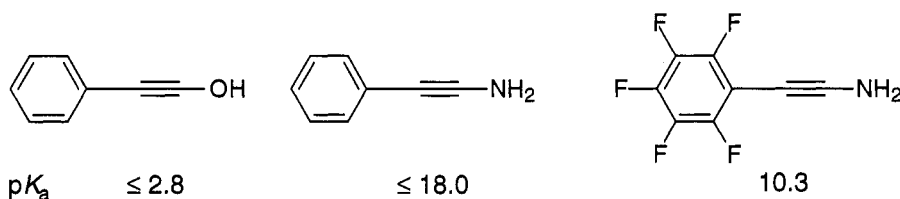
Ynols are protomers of ketenes. *Ab initio* calculations predict a very high enthalpy for the ketonization of parent ethynol ( $\Delta_r H_{\text{M}}^{\ominus}(0 \text{ K}) = -155 \text{ kJ mol}^{-1}$ ). Unimolecular rearrangement to ketene is, nevertheless, impeded by a very high energy barrier [7], and the isolated molecule is stable. Ethynol was first identified in interstellar clouds and planetary atmospheres [8] and subsequently in a tandem mass spectrometer [9]. It is formed by irradiation of hydroxycyclopropenone in

an argon matrix [10], and the matrix-isolated compound photoisomerizes reversibly to ketene [11].

Photodecarbonylation of cyclopropenones was applied to generate phenylethyne [12] and phenylethynyl amine [13] by flash photolysis, and to study their reactivity in aqueous solution.

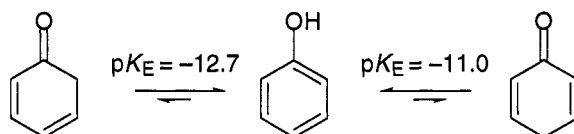


Phenylethyne is a remarkably strong acid: it dissociates fully to the anion even in dilute aqueous acid. In more concentrated acid, carbon protonation to form phenylketene becomes too fast to be measured by nanosecond flash photolysis. Phenylethyne is, therefore, more acidic than carboxylic acids. For comparison, the  $pK_a$  of 2-phenylethenol is about 9.6 and that of 2-phenylethanol 15.5. The enormous increase in acidity with increasing unsaturation might, in a simplistic way, be attributed to the higher electronegativity of  $sp$ -hybridized carbon and to charge delocalization in the enolate. The same effect is seen in ynamines: amines are extremely weak acids (the dissociation constant of ammonia is estimated as  $pK_a(NH_3) \approx 35$ ), but the  $pK_a$  of phenylethyneamine is below 18 and pentafluorophenylethyneamine dissociates to the ynamide in aqueous base,  $pK_a = 10.3$  [14].



### Keto Tautomers of Phenols

Phenol is at the other end of the scale: ketonization of phenol disrupts the cyclic conjugation, such that the aromatic enol is thermodynamically much more stable than its keto protomers 2,4- and 2,5-cyclohexadienone.



Both cyclohexadienone isomers were generated by photochemical retrocyclization of suitable adducts [15]. The pH-profile for the enolization of cyclohexa-2,4-dienone is shown in Fig. 1. The reverse rate of ketonization was determined by isotopic exchange in aqueous acid. The enolization constant,  $pK_E = -12.7$ , is obtained from the ratio of these rate constants. The enolization reaction of the ketone and the dissociation of phenol form two legs of a thermodynamic cycle, which is completed by protonation of phenolate at carbon 2:  $pK_a^K = pK_E + pK_a^E = -2.9$ . Thus, cyclohexa-

2,4-dienone is a very strong carbon acid, similar to HCl. Nevertheless, it survives for 260  $\mu\text{s}$  before it decays by protonation of water. Ketonization reactions of enols are generally catalyzed by base. The pH-profile calculated for the ketonization of phenol (lower curve in Fig. 1) shows that base *reduces* the ketonization rate by about two orders of magnitude, because the reaction of phenolate with protons accelerates ketonization at  $\text{pH} < 12$ . Proton catalysis saturates at  $\text{pH} \approx \text{p}K_a^E = 9.84$ , when the dissociation equilibrium shifts from phenolate to phenol.

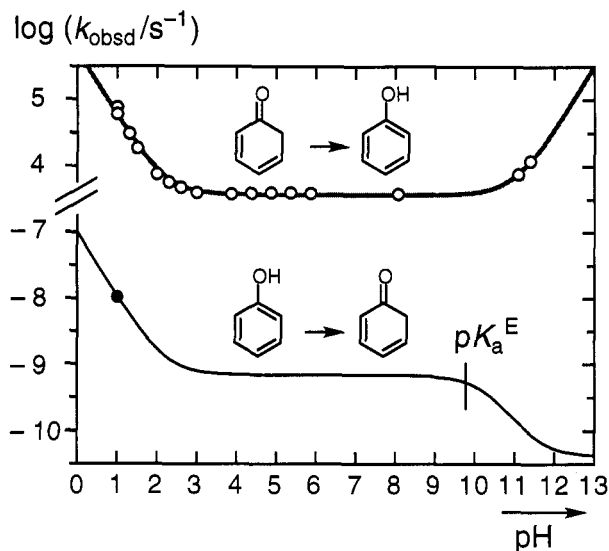
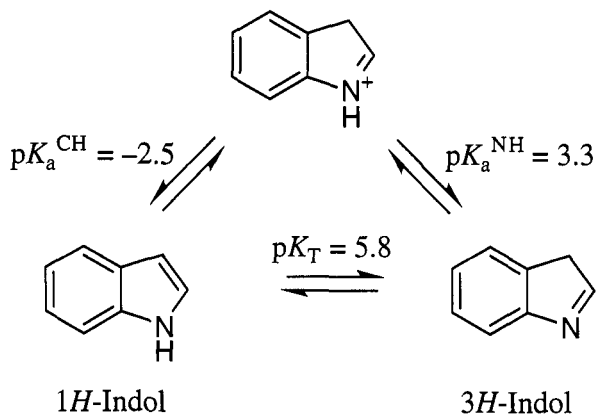


Fig. 1: pH-Rate profiles for the protomeric reaction cyclohexa-2,4-dienone  $\rightleftharpoons$  phenol.

### 3H-Indole: The Imine Protomer of Indole

3H-Indole is formed by Norrish-Type II photoelimination of *N*-indolylacetophenone [16]. Its lifetime is about 100 s in slightly basic aqueous solution. The rearrangement to 1H-indole ( $\Delta_r G^\ominus = 33 \text{ kJ mol}^{-1}$ ) is catalyzed by acid,  $k_{\text{H}^+} = 4.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , and by base,  $k_{\text{OH}^-} = 1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ .



## FREE ENERGY RELATIONSHIPS

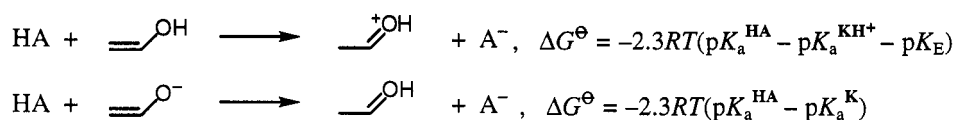
### The Brønsted Relation

Keto-enol protomeric reactions exhibit general acid and general base catalysis: the reaction rate increases linearly with increasing buffer concentrations. Buffer catalysis was applied for chiral induction by enantioselective protonation; remarkable enantiomeric excess was achieved in the photodeconjugation of  $\alpha,\beta$ -unsaturated ketones and esters by using chiral catalysts or homochiral acids to catalyze the ketonization of chiral photoenols [17].

The relative catalytic activity of different general acids and bases can be estimated from their acidity constants using the well-known Brønsted relation, eq. 1.

$$\log(k_{\text{HA}}/k_{\text{HA}'}) = \alpha \{ \text{p}K_{\text{a}}(\text{HA}') - \text{p}K_{\text{a}}(\text{HA}) \} \quad (1)$$

Equation 1 is a linear free-energy relationship. Slight deviation from linearity becomes perceptible when a wide range of general acids is used [18]. Much larger variation of the slope  $\alpha$  is seen when general acid and base catalysis is compared for substrates with widely different free energies of reaction. A plot of Brønsted slopes  $\alpha$ , determined in each case with a series of general acids, vs. the free energies  $\Delta G^\ominus$  for protonation of enols or enolates is shown in Fig. 2 ( $\text{p}K_{\text{a}}^{\text{HA}}$  is the average acidity of the general acids used for each Brønsted plot,  $\text{p}K_{\text{a}}^{\text{KH}^+} \approx -4$  was taken as the acidity constant of the protonated ketones [19], and  $\text{p}K_{\text{a}}^{\text{K}}$  is the CH acidity constant of the ketones).



The Brønsted exponent  $\alpha$  increases from  $\approx 0.2$  for strongly exergonic reactions (C-protonation of phenylethyolate) to  $\alpha \approx 0.8$  for strongly endergonic reactions (protonation of 1-naphthol at carbon atom 4 [20]).

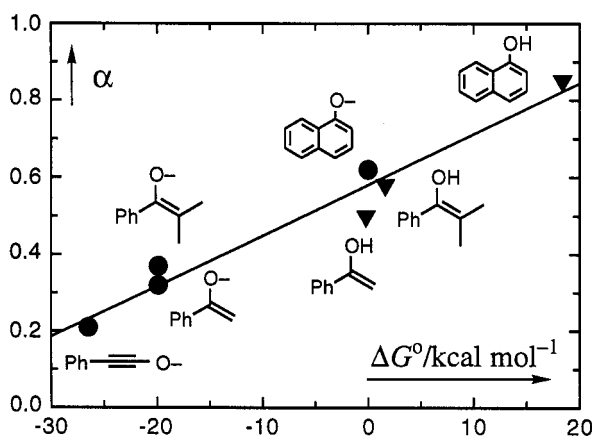
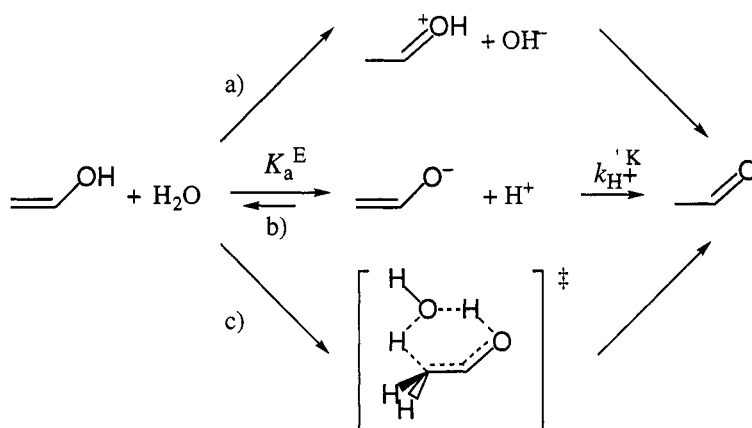


Fig. 2: Variation of the Brønsted parameter  $\alpha$  for general acid catalysis with the free energy change  $\Delta G^\ominus$  for carbon protonation of enols (▼) and enolates (●).

The observed increase of the Brønsted slope with increasing free energy of reaction is a nice exemplification of the Hammond postulate, inasmuch as the Brønsted parameter  $\alpha$  measures the extent of proton transfer in the transition state: highly exergonic reactions have an early transition state ( $\alpha \rightarrow 0$ ), endergonic reactions have a late transition state ( $\alpha \rightarrow 1$ ).

### Mechanism of the "Uncatalyzed" Reaction

We now turn to the pH-independent pathway of protomerization. Several kinetically indistinguishable mechanisms may be considered. Facile intramolecular 1,5-*H* shifts are observed in the ketonization of 1,3-dienols. Intramolecular 1,3-*H* shifts, on the other hand, are ruled out on the basis of the extremely high activation energies unanimously predicted by calculations, and because enols are kinetically stable in dry solvents or in the gas phase. Undoubtedly, the solvent participates in the reaction. Amphoteric water might intervene (a) as a general acid, (b) as a general base, or (c) in a "concerted" transfer of two protons through a bridge of one or more water molecules.



Rate constants of ketonization along paths (a) and (b) can be estimated from the Brønsted eq. (1). Predicted rate constants for path (a) are orders of magnitude below the observed rate constants  $k_0^{\text{K}}$ , but those for path (b) are in reasonable agreement with experiment [18]. The concerted mechanism (c) does not satisfactorily account for structure-reactivity relationships observed in aqueous solution. It may, however, well be the dominant mechanism in aprotic solvents containing small amounts of water. Also, third-order terms for ketone enolization appear at high concentrations of general acid *and* base catalysts, and these *are* attributed to a concerted mechanism involving both the general acid *and* base in the transition state [21]. Strong support for assignment of the pH-independent reaction in wholly aqueous solution to water reacting as a general base, path (b), comes from the Marcus treatment discussed next. For path (b), the rate coefficient of the "uncatalyzed" ketonization translates to  $k_0^{\text{K}} = k_{\text{H}^+}^{\text{K}} K_a^E$ .

### The Marcus Model of Proton Transfer.

In Fig. 3, the experimental ketonization rate constants of the various enolic species discussed above are plotted vs. the reaction free energy,  $\Delta G^\ominus = -2.3RTpK_a^{\text{K}}$  for ketonization of enolates through

carbon protonation by  $H^+$ , and  $\Delta G^\ominus = -2.3RT(pK_a^K - pK_w)$  for reaction with water. The points clearly follow a systematic, but nonlinear relationship. The upper curve represents the behavior expected for "normal" acids ("Eigen"-curve [22]), for which exergonic reactions are diffusion-controlled ( $k_{diff} \approx 10^{11} M^{-1} s^{-1}$ ), and rates of endergonic reactions decrease with a slope of  $-1$  vs.  $\Delta G^\ominus/(2.3RT)$ . The rate constants of the "pseudo"-acids studied here are much lower, particularly in the region around  $\Delta G^\ominus = 0$ , where the difference amounts to nearly ten orders of magnitude.

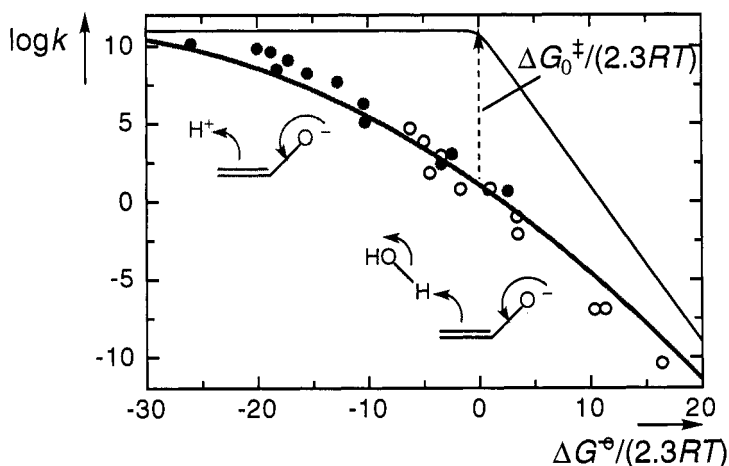


Fig. 3: Empirical relationship between reaction free energies and rate constants of ketonization of enolates. Rate constants  $k_{H^+}^K/(M^{-1} s^{-1})$ : full points (●),  $k_0^K/s^{-1}$ : empty circles (○).

The Marcus expression for proton transfer, eq. (2) [23], represents the observed data accurately:

$$k = k_{diff} \exp(-\Delta G^\ddagger/RT), \text{ where } \Delta G^\ddagger = \Delta G_0^\ddagger [1 + \Delta G^\ominus/(4\Delta G_0^\ddagger)]^2 \quad (2)$$

The parameter  $\Delta G_0^\ddagger$  is the "intrinsic" barrier, the barrier of a thermoneutral reaction ( $\Delta G^\ominus = 0$ ). It was determined as  $\Delta G_0^\ddagger = 57 \pm 2 \text{ kJ mol}^{-1}$  by nonlinear least-squares fitting to the experimental data. The rate of diffusion was assumed as  $k_{diff} = 1 \times 10^{11} M^{-1} s^{-1}$  and no corrections (statistical factors, work terms) were applied to the data.

The slope of the Marcus curve corresponds to the Brønsted-Parameter  $\alpha$ , eq. (3).

$$-2.3RT[\partial \log(k)/\partial \Delta G^\ominus]_{p,T} = (\partial \Delta G^\ddagger/\partial \Delta G^\ominus)_{p,T} = \alpha \quad (3)$$

The parameter  $\alpha$  varies substantially over the large range of  $\Delta G^\ominus$  covered by the experimental data collected in Fig. 3; it ranges from 0.2 for the most reactive enolates (phenylethynol anion) to about 0.8 for the least reactive compound (phenol). The  $\alpha$ -values resulting from the Marcus treatment are in good agreement with those determined from the Brønsted plots. Having adjusted the parameter  $\Delta G_0^\ddagger$  to fit the available data, the rate coefficients of specific and general acid catalysis for any keto-enol protomeric reaction can now be predicted. The required thermochemical data can be estimated using incremental methods or quantum mechanical calculations. Equation (3) also rationalizes the fact that the pH-independent reaction is relatively inefficient for ketones with low enol content ( $\alpha \rightarrow 0$ ), but dominates the pH-profiles of phenols ( $\alpha \rightarrow 1$ , e.g., Fig. 1).



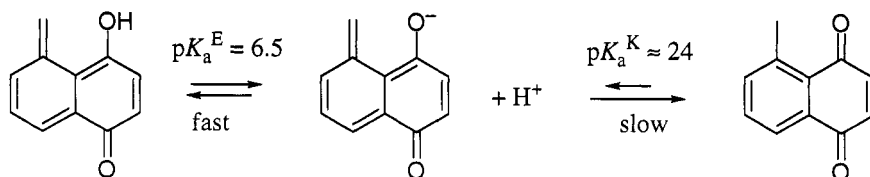
## EXCITED STATE PROTON TRANSFER REACTIONS

Now that a guideline for predicting rates of ground-state proton transfer reactions involving carbon is available, one wonders whether these rules apply to excited state reactions. Several such reactions are known, but a coherent picture is not in sight. The situation is complicated by the fact that we have to consider adiabatic reactions in the excited state, and reactions that lead to ground state products directly. Any generalization will, therefore, rest on thin ice, but let us, nevertheless, be bold.

Considering the notions underlying Marcus theory of proton transfer, it seems reasonable to assume that the same rules should apply, with a grain of salt, to adiabatic, excited-state proton transfer reactions. Numerous examples are documented for excited-state adiabatic proton transfer between heteroatoms, to mention only the classical example of 2-naphthol which was discovered by Förster. However, I am not aware of singlet-state adiabatic proton transfer reactions involving carbon. It appears that the intrinsic barrier of proton transfer to carbon is prohibitive on the time scale of singlet excited state lifetimes. This suggests that *excited-state proton transfer reactions involving carbon generally proceed directly to ground state products through avoided crossings or conical intersections*. The empirical rule of Wan and coworkers [24], who found that excited state dissociation of carbon acids is efficient only in systems leading to an "antiaromatic" ( $4n$  cyclic  $\pi$ -electron) product, supports this view. Evidence for proton transfer quenching of excited singlet states through conical intersections was recently put forth by Nau et al. [25]. In order to predict whether proton transfer to carbon will be efficient in the excited state, we need to predict the availability of funnels to the excited reactant.

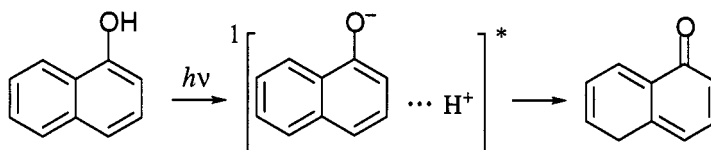
### Photoenolization of Methylnaphthoquinone

Consider for example 5-methyl-1,4-naphthoquinone which yields a photoenol by intramolecular proton transfer [26] from the methyl group to the adjacent carbonyl oxygen [27]. Formation of the enol in the ground state is complete within a few picoseconds of excitation. Enolization from the excited singlet state is too fast for intersystem crossing to the triplet state to compete ( $k_{isc} = 1 \times 10^{11} \text{ s}^{-1}$  in naphthoquinone). A symmetry-imposed crossing of the lowest singlet hypersurfaces  $S_0$  and  $S_1(n, \pi^*)$  is predicted when the proton transfer is constrained to occur in-plane. Back in the ground state, our well-established rules apply: the enol dissociates to the anion at  $\text{pH} > 6.5$ . Re-protonation at the exocyclic carbon to regenerate the starting material would be highly exergonic,  $\Delta G^\ominus / (2.3RT) \approx -24$ , favored by  $100 \text{ kJ mol}^{-1}$  over oxygen protonation. Nevertheless, the rate of carbon protonation predicted by the Marcus equation (Fig. 3) is about 2 orders of magnitude below the diffusion controlled limit, and in fact carbon protonation does not compete with oxygen protonation.



### Protonation of 1-Naphthol

Irradiation of 1-naphthol in aqueous solutions induces adiabatic dissociation to the anion. The resulting, electronically excited ion pair recombines in part by protonation of the aromatic nucleus to form the keto protomer 1,5*H*-dihydro-1-oxonaphthalene, which must be one of the strongest carbon acids known,  $pK_a^K \approx -16$ . Ion pair recombination was postulated on the basis of fluorescence lifetime measurements [28], and direct evidence is obtained by determination of isotopic exchange quantum yields as a function of pH [29]. In strongly acidic aqueous solutions, protonation at C5 yields the O-protonated ketone that was detected by pump-probe spectroscopy. It is formed in the ground state with a rate of  $5 \times 10^{10} \text{ s}^{-1}$  in 4 M  $\text{HClO}_4$ , and decays with a rate of  $1.5 \times 10^9 \text{ s}^{-1}$  by protonation of water.



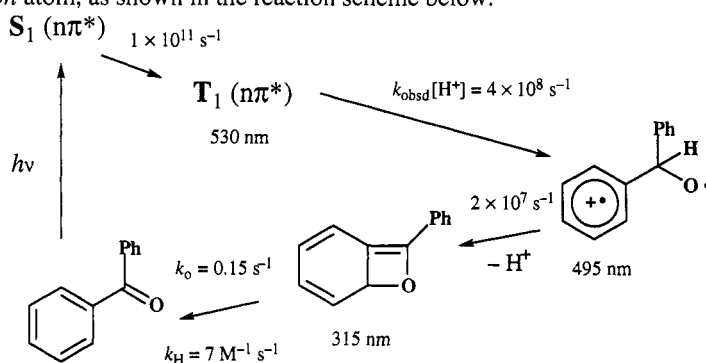
### Protonation of Singlet Phenylnitrene

Let us make a small digression to mention that any rule is established by its exception: exergonic proton transfer between heteroatoms is not always diffusion controlled. According to recent *ab initio* calculations, the lowest singlet state of phenylnitrene is open-shell [30], whereas the singlet ground state of phenylnitrenium ion is of closed-shell character [31]. Therefore, protonation of singlet phenylnitrenes to phenylnitrenium ions [32] is a symmetry-forbidden reaction. Recent measurements by picosecond pump-probe spectroscopy [33] indicate that protonation of singlet phenylnitrenes by water and even by protons is substantially slower than expected for "normal" acids. This may explain why protonation equilibria of singlet nitrenes are rarely established on the short time scales of their existence.

### Proton Transfer Quenching of Aromatic Triplet Ketones

As a final example, let me briefly present an unsolved mystery plot that has been with us for years [34]. In the course of our studies of ketones in aqueous acid, we noted that the quantum yields of their reactions, say Norrish Type II elimination of butyrophenone yielding acetophenone enol, begin to fall off at acid concentrations exceeding  $10^{-3} \text{ M}$ . Further investigation showed that  $n,\pi^*$  triplet states of aromatic ketones are generally quenched by acid with rate constants on the order of  $1-4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . This quenching does not lead to destruction of the ketones, and prolonged irradiation in acidic  $\text{D}_2\text{O}$  does not lead to deuterium incorporation ( $\phi < 10^{-3}$ ). However, the quenching does produce transient intermediates: in the case of benzophenone, proton quenching is accompanied by the formation of a short-lived transient,  $\tau = 50 \text{ ns}$ ,  $\lambda_{\text{max}} = 495 \text{ nm}$ , which decays to a second intermediate,  $\lambda_{\text{max}} = 315 \text{ nm}$ , with a lifetime of 7 s. The latter is a neutral compound which can be extracted to hexane at reduced temperature, and decays in either solvent to regenerate benzophenone. The decay rate of the second transient is not sensitive to solvent polarity, but

increases in strong acid. The only rationale I can offer is that triplet ketones are protonated at the carbonyl carbon atom, as shown in the reaction scheme below.



## CONCLUSION

Proton transfer reactions involving carbon are intrinsically slow and follow a systematic structure-reactivity relationship. The rates of keto-enol protomerization are well described by the Marcus equation for proton transfer with an intrinsic barrier of  $\Delta G_0^\ddagger = 57 \pm 2 \text{ kJ mol}^{-1}$ . This barrier largely inhibits adiabatic proton transfer reactions involving carbon in singlet excited states, and such reactions generally proceed directly to ground state products through avoided crossings or conical intersections.

Acknowledgment: This contribution is entirely due to the dedicated and talented work of Ji-In K. Almstead, Reto Born, Marco Capponi, Beat Freiermuth, Ivo G. Gut, Pavel Haspra, Bruno Hellrung, Remo Hochstrasser, Aldo Hörmann, Gaby Persy, Stefan Peterli, Norman P. Schepp, Patrick Schnider, Marie-France Schultz, Patrick Schünemann, Paul Senn, Beat Urwyler, David Wintgens, and to a continued, most fruitful co-operation with Prof. A. Jerry Kresge, Toronto.

1. P. Haspra, A. Sutter, J. Wirz, *Angew. Chem., Int. Ed. Engl.* 18, 617 - 619 (1979).
2. Z. Rappoport, Ed., *The Chemistry of Enols*, Wiley, Chichester, 1990.
3. B. Urwyler und J. Wirz, *Angew. Chem., Int. Ed. Engl.* 29, 790 (1990) and unpublished results.
4. J.-I. K. Almstead, B. Urwyler, J. Wirz, *J. Am. Chem. Soc.* 116, 954 (1994).
5. J. P. Guthrie, Z. Liu, *Can. J. Chem.* 73, 1395 (1995).
6. Y. Chiang, A. J. Kresge, P. Pruszyński, N. P. Schepp, J. Wirz, *Angew. Chem., Int. Ed. Engl.* 29, 792 (1990). Y. Chiang, A. J. Kresge, V. V. Popik, N. P. Schepp, *J. Am. Chem. Soc.* 119, 10203 (1997).
7. W. J. Bouma, R. H. Nobes, L. Radom, C. E. Woodward, *J. Org. Chem.* 47, 1869 (1982). B. J. Smith, L. Radom, A. J. Kresge, *J. Am. Chem. Soc.* 111, 8297 (1989).
8. D. J. DeFrees, A. D. McLean, *J. Phys. Chem.* 86, 2835 (1982).
9. B. van Baar, T. Weiske, J. K. Terlow, H. Schwarz, *Angew. Chem., Int. Ed. Engl.* 25, 282 (1986).

10. R. Hochstrasser, J. Wirz, *Angew. Chem., Int. Ed. Engl.* 28, 181 (1989).
11. R. Hochstrasser, J. Wirz, *Angew. Chem., Int. Ed. Engl.* 29, 411 (1990).
12. Y. Chiang, A. J. Kresge, R. Hochstrasser, J. Wirz, *J. Am. Chem. Soc.* 111, 2355 (1989).
13. Y. Chiang, A. S. Grant, A. J. Kresge, P. Pruszynski, N. P. Schepp, J. Wirz, *Angew. Chem., Int. Ed. Engl.* 29, 792 (1990).
14. J. Andraos, Y. Chiang, A. S. Grant, H.-X. Guo, A. J. Kresge, *J. Am. Chem. Soc.* 116, 7411 (1994). Y. Chiang, A. J. Kresge, S. W. Paine, V. V. Popik, *J. Phys. Org. Chem.* 9, 361 (1996).
15. M. Capponi, I. Gut, J. Wirz, *Angew. Chem., Int. Ed. Engl.* 25, 344 (1986) and unpublished results.
16. I. G. Gut, J. Wirz, *Angew. Chem., Int. Ed. Engl.*, 33, 1153 (1994).
17. O. Piva, R. Mortezaei, F. Hénin, J. Muzart, J.-P. Pète, *J. Am. Chem. Soc.* 112, 9263 (1990).
18. Y. Chiang, A. J. Kresge, J. A. Santabella, J. Wirz, *J. Am. Chem. Soc.* 110, 5506 (1988).
19. A. Bagno, V. Lucchini, G. Scorrano, *J. Phys. Chem.* 95, 345 (1991).
20. B. Hellrung, A. Hörmann, M.-F. Schultz, D. Wintgens, J. Wirz, unpublished.
21. A. F. Hegarty, J. P. Dowling, S. J. Eustace, M. McGarraghy, *J. Am. Chem. Soc.* 120, 2290 (1998).
22. M. Eigen, *Angew. Chem.* 75, 489 (1963).
23. A. O. Cohen, R. A. Marcus, *J. Phys. Chem.* 72, 4249 (1968).
24. D. Shukla, P. Wan, *J. Photochem. Photobiol. A*, 113, 53 (1998).
25. W. M. Nau, G. Greiner, H. Rau, M. Olivucci, M. A. Robb, *Ber. Bunsenges. Phys. Chem.* 102, 486 (1998).
26. In intramolecular H-transfer, proton, hydrogen atom, and hydride transfer cannot be distinguished, except in the context of a calculated wave function. Ketonization of the photoenol methyl-naphthoquinone behaves as expected for proton transfer.
27. Y. Chiang, A. J. Kresge, B. Hellrung, P. Schünemann, J. Wirz, *Helv. Chim. Acta* 80, 1106 (1997).
28. E. Pines, G. R. Fleming, *Chem. Phys.* 183, 393 (1994).
29. A. Hörmann, P. Schünemann, J. Wirz, unpublished results.
30. W. L. Karney, W. T. Borden, *J. Am. Chem. Soc.* 119, 1378 (1997).
31. C. J. Cramer, F. J. Dulles, D. E. Falvey, *J. Am. Chem. Soc.* 116, 9787 (1994).
32. R. A. McClelland, M. J. Kahley, P. A. Davidse, G. Hadzialik, *J. Am. Chem. Soc.* 118, 4794 (1996).
33. R. Born, C. Burda, P. Senn, J. Wirz, *J. Am. Chem. Soc.* 119, 5061 (1997) and unpublished work.
34. P. Senn, J. Wirz, unpublished work.