further strong support for molecular vaporization since spallation would be expected to generate materials on the filters having band intensity distributions identical to that of the starting sample.[6] Similar results were obtained from the sequencing reaction carried out to give very long labeled DNA strands (Figure 2B). Careful analysis of this gel reveals that DNA strands in excess of 1000 nucleotides long have been vaporized.

These experiments suggest that it is now feasible to perform gas-phase analysis of long-chain nucleic acids. Moreover, nondestructive molecular vaporization of DNA is a crucial requirement for mass spectral analysis of this class of macromolecule. Coupling this vaporization with laser ionization theoretically allows mass analysis of these species with single nucleotide resolution. Such a method would have an enormous impact on DNA and RNA analysis. The potential even exists to develop this technology into a time-of-flight, mass spectral based, dideoxy DNA sequencing method that would obviate the need for a polyacrylamide gel electrophoresis step and would thus be several orders of magnitude faster than current technology.

Electrophilic Catalysis Can Explain the Unexpected Acidity of Carbon Acids in Enzyme-Catalyzed Reactions

John A. Gerlt* and John W. Kozarich

Department of Chemistry and Biochemistry
University of Maryland, College Park, Maryland 20742

George L. Kenyon

Department of Pharmaceutical Chemistry
School of Pharmacy, University of California
San Francisco, California 94143

Paul G. Gassman*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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Many enzymes catalyze the abstraction of a proton from a carbon adjacent to a carbonyl/carboxylic acid group (α-proton of a carbon acid). However, the rate of proton abstraction is much greater than that predicted from the ΔpK_a between the substrate in solution and the active-site base; turnover numbers are frequently $\approx 10^2$–10^5 s^{-1} (Table I),[1-28] implying a ΔpK_a of $\leq$2–5.[29] Entropic contributions to the observed rate accelerations could be important in increasing rates, since an active site will both approximate the base to the carbon acid and align the C–H σ-bond with the π-system of the carbon acid. However, measurements of both the effective molarities in intramolecular base-catalyzed enolization reactions[30] and the effect of conformational restriction on the pK_a values of ketones[31] indicate that these effects cannot explain the observed rates. Transiently stable intermediates are observed in many reactions, suggesting that the pK_a values of the carbon acid and the base are similar. Electrophilic catalysis is often used as a *qualitative* explanation for the ability of bases to abstract protons from weakly acidic substrates. In fact, the available X-ray structures of active sites which catalyze proton abstraction (Table I) reveal that electrophilic catalysts are *always* proximal to the carbonyl/carboxylic acid groups of the substrates. We herein demonstrate that electrophilic catalysis is *quantitatively* sufficient to explain the observed rates of the enzymatic reactions.

The pK_E (where K_E relates the concentrations of keto and enol tautomers of a carbon acid) is the difference between the pK_a values of the α-proton of the keto tautomer and the hydroxyl group of the enol tautomer.[18] We now point out that the pK_E is also the difference between the pK_a values of the α-proton and the carbonyl group bound proton of the carbonyl-protonated acid. On the basis of the available X-ray structures (Table I), we suggest that the pK_a value of the α-proton of the carbonyl group protonated acid and not the pK_a value of the substrate in solution is critical to understanding the kinetics of proton abstraction.

The pK_E of mandelic acid, 15.4,[2] relates the pK_a of the α-proton of the keto tautomer, 22.0, to the pK_a for the enol tautomer, 6,6; it also relates the pK_a value of the α-proton to that of the carbonyl group bound proton of *protonated* mandelic acid (Scheme I). Assuming that the pK_a of the carbonyl group bound proton of protonated mandelic acid is $\approx$–8,[32,33] then the pK_a of the α-proton must be $\approx$7.4. This value is similar to the pK_a values of $\approx$6.4 recently assigned to the lysine and histidine bases in the active site of mandelate racemase.[5]

pK_E values are not yet available for aliphatic carboxylic acids which are substrates for α-proton abstraction. However, we assume that the pK_E values for these will be $\approx$3 units greater than that measured for mandelic acid, i.e., the enol tautomer is relatively less stable.[34] Since the pK_a values of the carbonyl group bound protons of these protonated acids are $\approx$2 units higher than that of mandelic acid,[33,35] the pK_a values of the α-protons of the

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(3) The pK_a of mandelate anion is approximated as 30, the pK_a of phenylacetate anion: Renaud, P.; Fox, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 5705.
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(34) The pK_E of acetaldehyde is 6.23, that of 2-methylpropanal is 3.86, and that of 2,2-diphenylacetaldehyde is 0.98.[18]

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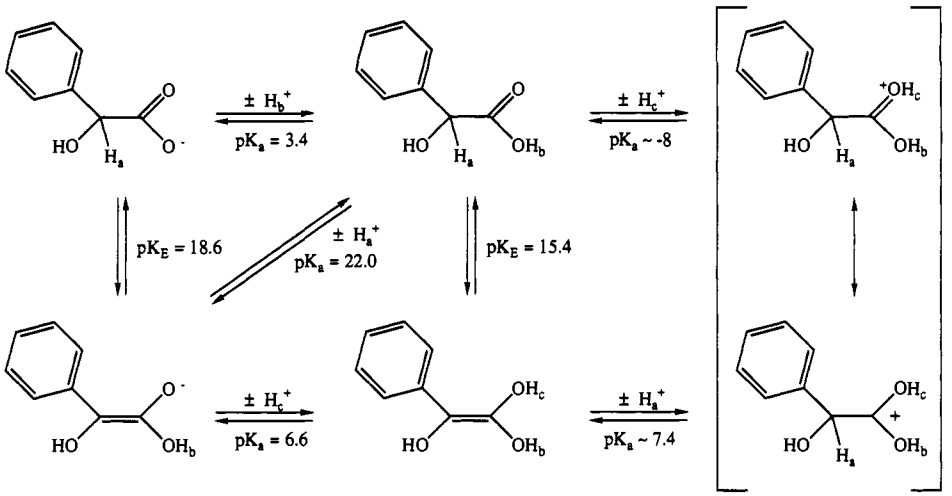
Table I. Crystallographic Characterized Enzymes Catalyzing Proton Abstraction from Carbon Acids

enzyme	k_{cat}, s^{-1}	substrate	pK_a, of substrate	base(s)	pK_a of base	acid(s)
mandelate racemase	700[a]	mandelate	22[b]–30[c]	Lys/His[a]	6.4[e]	Mg^{2+}/Lys/His[d]
enolase	1200[f]	PGA[g]	>22–30[h]	H_2O/2Glu[i]	~8[j]	Lys/His[h]
glycolate oxidase	150[k]	glycolate	>22–30[h]	His[l]	7?[m]	Tyr/Arg[l]
ferricytochrome b_2	130[n]	lactate	>22–30[h]	His[o]	5.3[p]	Tyr/Arg[o]
triose phosphate isomerase	8300[q]	G3P[r]	~17[s]	Glu[t]	6[u]	His[t]
	600[q]	DHAP[v]	~19[w]			
Δ^5-3-ketosteroid isomerase	53 000[x]	Δ^4-3-keto steroid	16.1[y]	Asp[z]	<5[aa]	Tyr[z]
		Δ^5-3-keto steroid	12.7[y]			
citrate synthase	100[bb]	acetyl CoA	~19?[cc]	Asp[dd]	6.5[ee]	His[dd]

[a] Reference 1. [b] Reference 2. [c] Reference 3. [d] Reference 4. [e] Reference 5. [f] Reference 6. [g] 3-Phosphoglyceric acid. [h] Reference 7. [i] Reference 8. [j] Reference 9. [k] Reference 10. [l] Reference 11. [m] Reference 12. [n] Reference 13. [o] Reference 14. [p] Reference 15. [q] Reference 16. [r] Glyceraldehyde 3-phosphate. [s] Reference 17. [t] Reference 19. [u] Reference 20. [v] Dihydroxyacetone phosphate. [w] Reference 21. [x] Reference 22. [y] Reference 23. [z] Reference 24. [aa] Reference 25. [bb] Reference 26. [cc] See text. [dd] Reference 27. [ee] Reference 28.

Scheme I



protonated acids are predicted to be ≈10–12. In enolase, the pK_a of the general base, a water molecule hydrogen-bonded to two carboxylate groups, is 8.[9] The pK_a of the histidine base in ferricytochrome b_2 also has been determined (5.3), but no value is available for glycolate oxidase. Thus, the pK_a values of the protonated substrates are compatible with the observed k_{cat} values.

For most ketones and aldehydes, we assume that the pK_E values reported for acetone and acetaldehyde, 8.3 and 6.2, respectively,[18] and the pK_a values for their carbonyl group bound protons, −3[33,36] and −4,[33,37] respectively, are appropriate.[38] If so, the pK_a values of the α-protons of protonated ketones and aldehydes are likely to be ≈4. Although no pK_E and pK_a values are available for thioesters, the analogy which equates thioesters with ketones[39] suggests that the pK_a values of the α-protons of protonated thioesters also may be ≈4. These values are nearly matched to the pK_a values of the bases in the active sites of triose phosphate isomerase (6), ketosteroid isomerase (<5),[38] and citrate synthase (6.5).

Stepwise mechanisms involving initial protonation of the *neutral* carbon acid as described here or initial abstraction of a proton from a neutral or anionic carbon acid to generate an *isolated* enolate (carbanion) are not in energetic accord with the observed rates of the enzymatic reactions. However, *concerted general acid–general base catalysis* provides the low-energy route consistent with the observed rates.[40] Since the energy difference between the keto and enol tautomers of a carbon acid is large, the Hammond postulate predicts that the ionization properties of the transition state in proton abstraction will resemble those of the enol tautomer.[41] Thus, that protonation of neutral carbon acids decreases the pK_a values of their α-protons to match those of active-site bases[49] clarifies not only the rates of proton abstraction but also the existence of intermediates.[42,43]

We have described the effect of electrophilic catalysis on the acidity of the α-protons of carbon acids by assuming the formation of the enol tautomer of the acid. However, similar effects can be achieved by assuming formation of either hydrogen-bonded enolates or metal-coordinated enolates. Thus, the carbanionic character frequently associated with these reactions can be rationalized.

The unexpectedly low pK_a values of carbon acids demanded by the rates of proton abstraction can be explained by known principles of physical organic chemistry.[44] We expect that our

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(38) Since the pK_E values for a Δ^5-3-keto steroid and a Δ^4-3-keto steroid are 2.7 and 6.1, respectively,[23] the pK_a values of the α-protons of protonated unsaturated ketones are less than those for other ketones. This does not invalidate our explanation since the pK_a of the base in ketosteroid isomerase is low.

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(43) In some reactions the observed rate of proton transfer is greater than that expected on the basis of the activation energy necessarily associated with the pK_E. One source of the decreased activation energy is that the energetics of the proton transfer from the general acid to general base catalyst must also be included in the free energy difference between the enzyme–substrate and the enzyme–intermediate complexes. Alternatively, the enzyme may stabilize the intermediate: Albery, W. J.; Knowles, J. R. *Biochemistry* **1976**, *15*, 5631.

reasoning will be useful in understanding the mechanisms of reactions catalyzed by structurally uncharacterized enzymes such as glyoxalase I,[45] proline racemase,[46] and both vitamin K dependent[47] and biotin-dependent[48] carboxylases.

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Gas-Phase Reactions of Iron Porphyrins with NO_2: Oxygen Atom Transfer to Anionic and Cationic Iron Porphyrins

H. L. Chen, T. E. Hagan, S. E. Groh, and D. P. Ridge*

Department of Chemistry and Biochemistry and Center for Catalytic Science and Technology University of Delaware, Newark, Delaware 19716

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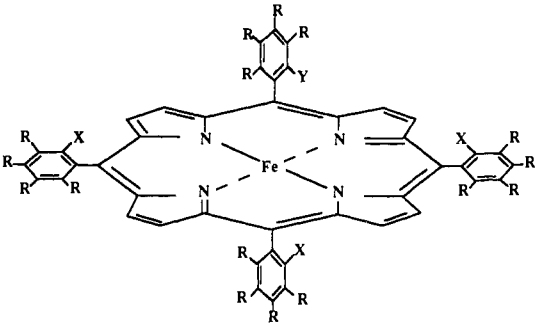
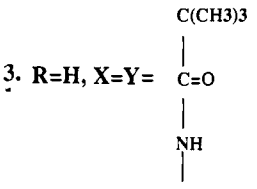
We report the observation of bimolecular O atom transfer reactions between NO_2 and ionic iron porphyrins in the gas phase. Both molecular anions (iron(I)) and cations (iron(III)) of iron(II) porphyrins accept an O atom from NO_2, forming species which are nominally iron(III) and iron(V), respectively. Species of this kind have not been previously observed in the gas phase and are thought to be important in a number of oxidative processes catalyzed by iron porphyrins and related species.[1] These processes include the oxidative processes catalyzed by cytochrome P450[2] and the selective air oxidation of alkanes.[3]

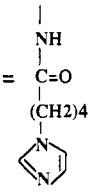
The reactant ions were introduced into the ion trap of a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer[4] (FTMS-2000 Extrel, Madison, WI) using previously described methods involving a heated sample probe and an electron beam[5,6] or laser desorption.[7] Ions were generated from iron(II) tetraphenylporphyrin (**1**), iron(II) tetrakis(pentafluorophenyl)porphyrin (**2**), iron(II) tetrakis(*o*-pivalamidophenyl)porphyrin (**3**),[8] and iron(II) (*o*-(5-imidazol-1-ylvaleramido)phenyl)triphenylporphyrin (**4**).[9] Typically NO_2 was present at a pressure of 10^{-7} Torr. Under these conditions bimolecular reactions can be unambiguously identified.



1. R=X=Y=H **2.** R=X=Y=F

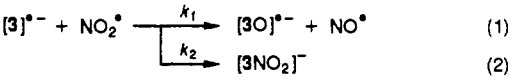


3. R=H, X=Y=



4. R=X=H, Y=

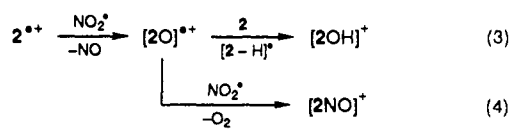
The anion of **3** reacts according to eqs 1 and 2. The primary



products react further to form $[3(NO_2)_2]^{\bullet-}$. Intermediates in the conversion of $[3O]^{\bullet-}$ to $[3(NO_2)_2]^{\bullet-}$, $[3NO_3]^-$ and $[3(NO_3)(NO_2)]^{\bullet-}$, occur at small steady-state concentrations. We note that $3(NO_2)_2^-$ also results from the condensed-phase reaction between NO_2^- and **3**.[10] The observation of reaction 1 suggests that $NO_2^{\bullet}$ is bound to $\mathbf{3}^{\bullet-}$ through an O atom.

The reactions of $\mathbf{4}^{\bullet-}$ with $NO_2^{\bullet}$ are essentially the same as those of $\mathbf{3}^{\bullet-}$, giving $[4O]^{\bullet-}$, $[4(NO_2)]^-$, and finally $[4(NO_2)_2]^{\bullet-}$. $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$, on the other hand, are *not* observed to form $[1O]^{\bullet-}$ and $[2O]^{\bullet-}$. Instead they form $NO_2^{\bullet}$ adducts and transfer an electron to $NO_2^{\bullet}$. This suggests that the oxo moieties in $[3O]^{\bullet-}$ and in $[4O]^{\bullet-}$ are stabilized by the ortho amido substituents in those species.

On exposure to $NO_2^{\bullet}$, $\mathbf{2}^{\bullet+}$ disappears exponentially with time and is eventually completely converted to products. The ratio of $[2NO]^+$ product to $[2OH]^+$ product is independent of reaction time but proportional to the ratio of $NO_2^{\bullet}$ pressure to **2** pressure. These observations are consistent with reactions 3 and 4[11] where $[\mathbf{2} - H]^{\bullet}$ is the radical formed by H atom transfer from **2**. The



rate constant for the first step of reactions 3 and 4 is much smaller than the combined rate constants for the second steps of 3 and

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(11) Reaction 4 may be viewed as a reaction between the O atom in $[2O]^{\bullet+}$ and $NO_2^{\bullet}$ to form O_2 and $NO^{\bullet}$. The details of the mechanism, which presumably leaves NO bound to the metal, are not known.

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