process takes place within the primary geminate pair. The rate constant of the chemical reaction within the geminate pair is thus estimated to be $< 1\%$ of k_{-et}.

An important aspect of the size effect is clearly demonstrated by the donors **5–7** which have similar molecular dimensions to dimethylnaphthalene, anthracene, and phenanthrene, respectively, but whose k_{-et} fit with the other substituted benzene derivatives. Evidently it is the size of the aromatic nucleus and not the overall size of the molecule which is important.

As described previously[2a] the data can be fitted to a theoretical relationship between k_{-et} and $-\Delta G$.[8] The fitting parameters are V, an electron coupling matrix element, λ_s and λ_v, the Marcus solvation and vibrational reorganization energies, and a single frequency, ν, which is taken to be representative of the frequencies of the rearranged vibrational modes.[8] In order to allow a meaningful comparison between the data, restrictions must be placed on the number of parameters which can be varied. Vibrational reorganization energies are expected to be small for organic molecules[9] and similar for both sets of data.[10] Good fits were obtained for both curves by using a value for λ_v of 0.3 eV. For consistency with previous work,[2a,8a,b] $\bar{\nu}$ was fixed at 1500 cm^{-1}. By using these values for λ_v and $\bar{\nu}$, larger values for V and λ_s are required to fit the data of the one-ring donors compared to those of the two-ring donors. Although the absolute values obtained for the matrix coupling elements and reorganization energies depend upon the form of the theoretical equation, the choice of the value of ν, and also the fitting procedure, the data in Figure 1 indicate that both the electronic coupling and the total reorganization energy are larger for the one-ring donors compared to those of the two-ring donors.

Qualitatively the smaller V for the two-ring donors suggests a smaller orbital overlap integral compared to the one-ring donors[11a,b] and is consistent with the prediction that more complex nodal structures for the molecular orbitals of larger aromatic systems result in smaller matrix elements.[11c]

The larger λ_s for the one-ring compounds suggests a higher degree of solvation for these geminate pairs compared to those of the two-ring compounds. Support for this suggestion was obtained from exciplex emission data. Although exciplexes are solvated less strongly than geminate pairs, these species can be considered to be the contact ion pair equivalents of the solvent-penetrated geminate pairs.[12] Accordingly, exciplex solvation, obtained from differences in the emission maxima in solvents of different polarities, can be used as a guide to the solvation of the geminate pair. A constant energy difference of 0.345 ± 0.013 eV is found in the emission of exciplexes of DCA with the two-ring compounds **1–3** in acetonitrile and cyclohexane. For the corresponding exciplexes of the one-ring donors in these two solvents, a constant and higher value of 0.49 ± 0.02 eV is found, which is consistent with higher solvation in these cases.

The return electron transfer rates, k_{-et}, in these systems are evidently very sensitive to small structural changes. Differences in the matrix coupling elements and the degree of solvation between the ion pairs appear to result from differences in charge

distribution and the degree of delocalization.

Supplementary Material Available: NMR data and structures for adducts **8** and **9** and derivatives of **8** (2 pages). Ordering information is given on any current masthead page.

Generation of Simple Enols by Photooxidation. Keto–Enol Equilibrium Constants of Some Aliphatic Systems in Aqueous Solution

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There has been a revival of interest in the chemistry of simple enols recently, sparked by the development of techniques for generating them in greater than equilibrium amounts under conditions where rates of their reactions may be measured accurately.[1–4] We wish to report that we have produced yet another method of doing this and have used it to provide keto–enol equilibrium constants for a series of simple ketones in aqueous solution. These are the first reliable, wholly experimentally determined values of this quantity for these substances.

Our method involves the photooxidation of alcohols by carbonyl compounds to produce ketyl radicals, eq 1. This is a well-known

$$\text{(1)}$$
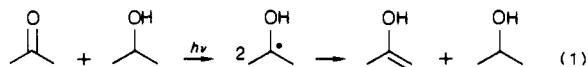
process,[5] and there is CINDP evidence that the ketyl radicals so formed may undergo disproportionation to give enols.[6] We have found that flash photolysis of solutions of acetone (0.05 M) in dilute aqueous perchloric acid containing 0.01–0.10 M isopropyl alcohol produces a short-lived transient species with strong absorbance at $\lambda = 215$ nm whose intensity depends upon the amount of isopropyl alcohol supplied. Decay of this transient adheres to the first-order rate law closely, and observed first-order rate constants measured over the range $[\text{HClO}_4] = 0.004–0.1$ M are accurately proportional to acid concentration; least-squares analysis of the data gives $k_{H^+} = (5.47 \pm 0.06) \times 10^3$ M^{-1} s^{-1}, which agrees well with $k_{H^+} = (5.38 \pm 0.08) \times 10^3$ M^{-1} s^{-1} measured before[3d] for the ketonization of acetone enol, eq 2. This evidence identifies the transient species as the enol of acetone.

$$\text{(2)}$$
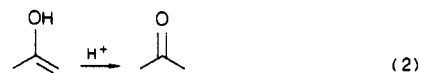
Use of other alcohols in place of isopropyl alcohol gives corresponding behavor. In such cases, however, two different ketyl

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(10) (a) Parameters can be found to fit the two-ring data which include values for λ_v as high as 0.6 eV (ref 2a). However, λ_v must be less than 0.4 eV in order to fit the one-ring data. Furthermore, molecular orbital calculations similar to those described in ref 9b suggest that λ_v is ca 0.3 eV for both (Gould, I. R.; Farid, S., unpublished results). The use of a smaller λ_v requires that V be smaller and λ_s larger than the corresponding values used to fit the data reported in ref 2a. (b) Nelson, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677.

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Table I. Rate and Equilibrium Data for Some Simple Aliphatic Keto–Enol Systems in Aqueous Solution at 25 °C[a]

no	system	$k_{H^+}^{K}/10^2$ M^{-1} s^{-1} [b]	pK_E
1	*(structure)*	0.33[c]	6.23[c]
2	*(structure)*	0.0059[d]	3.86[d]
3	*(structure)*	54	8.33
4	*(structure)*	63	8.76
5	*(structure)*	59	8.61
6	*(structure)*	75	8.76
7	*(structure)*	8.4	7.51
8	*(structure)*	2.3	7.33
9	*(structure)*	7.9	7.43
10	*(structure)*	0.98	7.52
11	*(structure)*	53	7.94
12	*(structure)*	5.8	6.39
13	*(structure)*	40	8.00

[a] Ionic strength = 0.10 M. [b] Determined by least-squares analysis of the relationship between observed first-order constants and dilute perchloric acid concentration using a 5–10-fold variation in [HClO$_4$]. [c] Reference 3d. [d] Reference 2a.

radicals are formed which can disproportionate in different ways to give two different enols. We have found, for example, that flash photolysis of a solution of acetone and cyclohexanol produces two transients, one which decays rapidly at a rate that identifies it as the enol of acetone and another which decays more slowly at a rate consistent with expectation[7] for the enol of cyclohexanone, eq 3. The two rates of decay are sufficiently different to allow

(3)
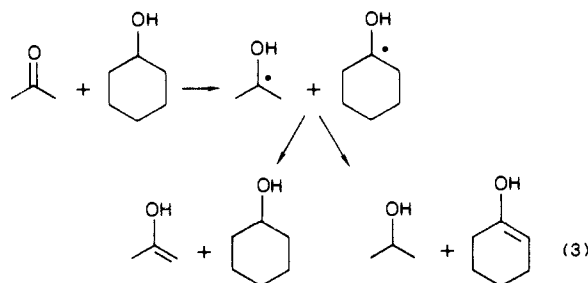
each to be determined accurately by least-squares fitting to a double exponential expression. We have used this technique with either acetone or acetaldehyde as the carbonyl compounds to determine hydronium ion catalytic coefficients for a series of simple aliphatic enols; these are listed in Table I.[8]

We have also measured rates of acid-catalyzed enolization of the corresponding ketones by bromine scavenging of the enol as it forms, and we have used these to calculate keto–enol equilibrium

constants according to the relationship $K_E = k_{H^+}^E/k_{H^+}^K$.[9] These results are listed in Table I as well.

Keto–enol equilibrium constants for some of the systems investigated here have been determined before, by halogen titration[10] and, more recently, by a variety of new methods each of which relies upon some approximation or assumption.[7,11] Values of K_E obtained by these new methods are in reasonably good agreement with the present results, showing that the assumptions made are generally well-founded, but values obtained by halogen titration are consistently too high, sometimes by many orders of magnitude. The relative stabilities of keto–enol pairs have also been investigated by ab initio calculation,[12] and, although energy differences so obtained are uniformly greater than values of ΔG derived from the presently determined keto–enol equilibrium constants, the calculations do reproduce experimentally determined effects of structure on K_E fairly well.

The data of Table I show that alkyl substitution on a carbonyl group lowers enol content: K_E is smaller for ketones than for corresponding aldehydes. This can be attributed to the electron-releasing property of alkyl groups, which, by interacting with the positive end of the carbonyl group dipole, stabilize the keto form. This effect appears to be fairly independent of the structure of the alkyl group; for example, in the series of methyl ketones, CH$_3$COR, provided by entries 3–6 of Table I, the change in K_E as R is varied from methyl to *tert*-butyl is small[13] compared to the big jump caused by replacing H with alkyl. This contrasts with the behavior of the sterically crowded "Fuson" enol systems with mesityl groups at the β-position, eq 4, where there is a marked

(4)
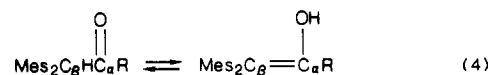
decrease in K_E with increasing size of R.[14] This difference in sensitivity to the nature of R damages a correlation of pK_E values for the two systems made recently on the basis of somewhat limited data then available;[15] for example, the correlation predicts pK_E = 10.95 for methyl *tert*-butyl ketone, whereas the measured value is 8.76.

The nature of the alkyl group, however, does influence K_E in the present series when it affects the extent of alkyl substitution at the β-position of the enol double bond. This manifestation of the well known stabilizing effect of alkyl groups on carbon–carbon double bonds makes K_E for isobutyraldehyde two orders of magnitude greater than that for acetaldehyde. The effect may be seen again in going from acetone to methyl ethyl ketone, to methyl isopropyl ketone, and from acetone to any of the cyclic ketones.

The cyclic ketones themselves show an interesting ring-size effect which makes K_E for cyclohexanone nearly two orders of magnitude greater than the closely similar values for cyclopentanone and cycloheptanone. Similar alternating changes in equilibrium constant with ring size are seen in the exo–endo double bond isomerization of the isopropylidenecycloalkane–isopropylcycloalkene system,[16] but the closely related methylenecyclo-

(7) Dubois, J. E.; El-Alaoui, M.; Toullec, J. *J. Am. Chem. Soc.* **1981**, *103*, 5393–5401.

(8) In several of the systems studied, cis and trans enol isomers are possible, and CINDP studies indicate that these will be formed in comparable amounts.[6] We could not, however, resolve the decays we observed in such cases into separate rate constants for the two isomers, which suggests that the two rate constants are, as expected, not very different.

(9) In cases where enolization could take place in two different directions to give regioisomeric enols, ratios of the isomeric bromination products were determined and these were then used to divide observed overall enolization rate constants into separate specific rates for the two different enolization reactions.

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alkane–methylcycloalkene system shows a monotonic sequence of equilibrium constants.[17]

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Detection of the Fe–O–O–Fe Intermediate in the Oxidation Reaction of Ferrous Porphyrins by Resonance Raman Spectroscopy

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In general, the oxidation reaction of ferrous porphyrins proceeds through the following intermediates:[2]

$$\underset{A}{PFe} \xrightarrow{O_2} \underset{B}{PFeO_2} \xrightarrow{PFe} \underset{C}{PFeOOFeP} \rightarrow \underset{D}{PFeO} \xrightarrow{PFe} \underset{E}{PFeOFeP}$$

Previously, we observed the IR spectra of oxyiron porphyrins (B) in O_2/Ar matrices[3] and resonance Raman (RR) spectra of ferrylporphyrins (D) in O_2 matrices,[4,5] and Balch et al. observed the ^{1}H NMR signals (pyrrole and phenyl protons of tetraphenylporphyrin (TPP) derivatives) of the Fe–O–O–Fe bridged species (C) and ferrylporphyrins (D) in toluene.[2,6-8]

In this communication, we report the RR spectra of C for the first time. Direct observation of the Fe–O–O–Fe bridge vibration described below provides definitive evidence for the existence of this elusive intermediate in the oxidation process of ferrous porphyrins.

Figure 1 (parts A and B) shows the RR spectra (406-nm excitation) of tetramesitylporphyrinatoiron(II), Fe(TMP), in toluene which were saturated with [16]O_2 and measured at $\sim$ –78 °C and $\sim$ –46 °C, respectively. The experimental techniques used for these and other measurements are basically the same as that reported previously.[9] The most significant features of these spectra are the marked strengthening of the 845-cm^{-1} band and the complete disappearance of the 574-cm^{-1} band when the temperature is raised from $\sim$ –78 °C to $\sim$ –46 °C. Figure 1 (parts C and D) shows the RR spectra of Fe(TMP) in toluene which
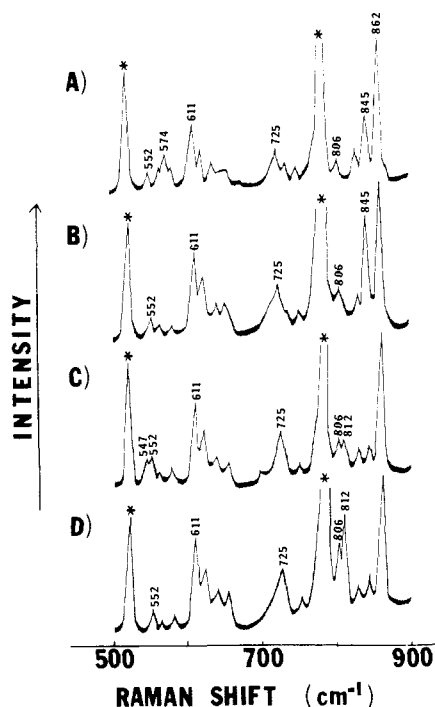
(1) (a) Marquette University. (b) Department of Chemistry, Shimane University, Matsue 690, Japan.
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Figure 1. RR spectra (406-nm excitation) of Fe(TMP) in toluene which were saturated with O_2: (A) [16]O_2, $\sim$ –78 °C; (B) [16]O_2, $\sim$ –46 °C; (C) [18]O_2, $\sim$ –78 °C; (D) [18]O_2, $\sim$ –46 °C. The asterisks denote the solvent bands.

were saturated with [18]O_2 and measured at $\sim$ –78 °C and $\sim$ –46 °C, respectively. In this case, the band at 812 cm^{-1} becomes stronger, and the band at 547 cm^{-1} disappears completely when the temperature is raised from $\sim$ –78 °C to $\sim$ –46 °C. The nature of the bands at 845 and 812 cm^{-1} is well established; these vibrations are due to the ν(FeO) of Fe(TMP)[16]O and its [18]O analogue, respectively, which are characteristic of five-coordinate ferrylporphyrins.[4,5,10]

The nature of newly discovered bands at 574 and 547 cm^{-1} is of particular interest. Since these bands are relatively weak and partially overlapped by porphyrin bands, we repeated careful measurements to confirm the reproducibility of the spectra. We assign these bands to the symmetric Fe–O stretch, ν_s(Fe–O), of (TMP)Fe–O–O–Fe(TMP), which is presumably centrosymmetric. The reasons for these assignments are listed below.

(1) These bands cannot be attributed to the ν(Fe–O$_2$) of Fe(TMP)O$_2$ since such a "base-free" O$_2$ adduct is rapidly oxidized to form (TMP)Fe–O–O–Fe(TMP) in toluene solution at $\sim$ –78 °C.[2,8] Furthermore, the observed frequency of 574 cm^{-1} is too high to assign it to the ν(Fe–O$_2$) of a five-coordinate species. For example, Fe(Pc)O$_2$ (Pc: phthalocyanato anion) in O$_2$ matrices exhibits the ν(Fe–O$_2$) at 488 cm^{-1},[11] whereas the ν(Fe–O$_2$) of Fe(TMP)(piperidine)O$_2$ in toluene ($\sim$ –78 °C) is observed at 568 cm^{-1}.[12] In the case of cobalt porphyrins, the ν(Co–O$_2$) of Co(TPP)O$_2$ in O$_2$ matrices is at $\sim$345 cm^{-1},[13] while that of Co(TPP)(piperidine)O$_2$ in toluene ($\sim$ –78 °C) is at 509 cm^{-1}.[14] However, the ν_s(Co–O) of the peroxo-bridged complex, [(NH$_3$)$_5$Co(O$_2$)Co(NH$_3$)$_5$](NO$_3$)$_4$ (642 cm^{-1}),[15] is much higher than the ν(Co–O$_2$) mentioned above.

(2) According to the NMR studies,[8] (TMP)Fe–O–O–Fe(TMP) is stable near –70 °C in toluene and, upon warming, decomposes

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