observed, predominantly 1:1 complexes are formed with GSSG and GSMe in agreement with Li et al.,[5] which have nearly identical ligand fields around the metal as in the 2:1 species *II* and therefore should show similar optical but different magnetic properties.

Concerning the biological relevance of the results presented here Scheme I is proposed to explain the chemical and physical properties of the EPR-nondetectable Cu pair in "Blue Oxidases" during oxidoreduction as compared to their corresponding chemical models.

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The Acidity of Water in the Transition State for Methyl Tosylate Hydrolysis

Sir:

In neutral and basic aqueous solutions, the hydrolysis of methyl tosylate obeys a two-term rate law (eq 1).[1] The observed values of k_1' and k_2 can be used to calculate the value of pK_a(‡), the acidity constant for ionization of the activated complex in the k_1' path, to give the activated complex in the k_2 path as its conjugate base (eq 2, 3).[2,3]

$$-\mathrm{d[MeOTs]}/\mathrm{d}t = (k_1'[\mathrm{H_2O}] + k_2[\mathrm{OH^-}])[\mathrm{MeOTs}] \quad (1)$$

$$[\overset{\delta+}{\mathrm{H_2O}}\cdots \underset{(\delta'-\delta)+}{\mathrm{CH_3}}\cdots \overset{\delta'-}{\mathrm{OTs}}]^{\neq} \rightleftharpoons \mathrm{H^+} + [\overset{(1-\delta)-}{\mathrm{HO}}\cdots \underset{(\delta'-\delta)+}{\mathrm{CH_3}}\cdots \overset{\delta'-}{\mathrm{OTs}}]^{\neq} \quad (2)$$

$$\mathrm{p}K_a(\ddagger) = \mathrm{p}K_a(\mathrm{H_2O}) + \log (k_1'/k_2) \quad (3)$$

We wish to report measurements of the temperature dependences of k_1' and k_2 which are sufficiently precise to allow calculation of the values of $\Delta C_p°(\ddagger)$, $\Delta S°(\ddagger)$, and $\Delta H°(\ddagger)$ for the virtual equilibrium in eq 2. Table I lists values of these parameters together with the directly measured values of $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta C_p^\ddagger$ which were used in their evaluation.

Rates were measured by following the absorbance at 235 nm of solutions in a 50-ml cell; during each run the solution was stirred and its temperature monitored. Temperature control was within ±0.003°, and the first-order rate constants were reproducible to ±0.2%. Values of $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta C_p^\ddagger$ were calculated from the rate constants as described elsewhere.[4] The agreement (Table I) between our parameters for k_1' at low ionic strengths and Robertson's[5] conductometrically determined values demonstrates the reliability of our spectrophotometric method; this method allows measurements of $\Delta C_p^\ddagger$ for reactions at ionic strengths which are too high for application of the conductometric method (e.g., for k_2 and for k_1' in solutions containing added salts).

Comparison of the values of pK_a(‡), $\Delta H°$(‡), etc., to corresponding values for model acids should yield information about the structure of the activated complex. To a first approximation, δ (eq 4, X = pK_a, $\Delta H°$, ...) should be qualitatively related to the displacement of the transition state along the reaction coordinate from reactant (H_2O) to product ($H_2OCH_3^+$).[2]

$$\delta = [X(\ddagger) - X(\mathrm{H_2O})]/[X(\mathrm{H_2OCH_3^+}) - X(\mathrm{H_2O})] \quad (4)$$

The entries in Table I lead to values for δ of 0.21, 0.13, 0.48, and 0.45 based respectively on pK_a, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$. The δ values based on $\Delta S°$ and $\Delta C_p°$ are thus qualitatively larger[9] than those based on pK_a and $\Delta H°$. Since it is well established[11] that the values of $\Delta S°$ and $\Delta C_p°$ for acid dissociation in water are primarily determined by changes in *solvent* structure and polarization which accompany the dissociation, these larger δ values which are derived from $\Delta S°$(‡) and $\Delta C_p°$(‡) suggest a hydrolysis mechanism in which solvent reorganization has proceeded to a

Table I. Thermodynamic Parameters for Processes Related to k_1' and k_2

Process	pK_a or −log k	$\Delta H^\ddagger$ or $\Delta H°$ (kcal mol^{-1})	$\Delta S^\ddagger$ or $\Delta S°$ (cal deg^{-1} mol^{-1})	$\Delta C_p^\ddagger$ or $\Delta C_p°$ (cal deg^{-1} mol^{-1})
k_1' activation	6.85^{a,c,i}	21.74 ± 0.06^{a,c,i}	−17.1 ± 0.2^{a,c,i}	−37 ± 1^{a,d,i}
	6.84^{b,c,i}	21.63 ± 0.03^{b,c,i}	−17.5 ± 0.1^{b,c,i}	−36 ± 1^{b,e,i}
	6.85^{a,c,j}	21.45 ± 0.05^{a,c,j}	−18.3 ± 0.2^{a,c,j}	−30 ± 1^{a,f,j}
k_2 activation	3.20^{a,c,k}	19.49 ± 0.02^{a,c,k}	−7.9 ± 0.1^{a,c,k}	−16 ± 1^{a,g,k}
pK_a(H_2O) equilibrium	15.74^{l,c,i}	13.34^{l,c,i}	−27.3^{l,c,i}	ca. −26^{l,h,i}
pK_a(‡) equilibrium	12.1^{m,c,o}	11^{m,c,o}	−17^{m,c,o}	ca. −12^{n,o}
pK_a($H_2OCH_3^+$) equilibrium	−2.0^{p}	ca. −4^{r}	ca. −5^{q}	ca. 5^{q}

[a] This work. [b] Reference 5. (Slightly different values are quoted in this reference; the values listed here have been recalculated from the rate constants reported there.) [c] At 25°. [d] At ca. 68° (the midpoint of the temperature range, 45–90°, over which k values were measured). [e] At ca. 48° (temperature range, 15–80°). [f] At ca. 62° (temperature range, 35–90°). [g] At ca. 50° (temperature range, 25–75°). [h] At 55°. [i] Ionic strength ≤ 10^{-3}. [j] In 0.1 F $NaClO_4$. [k] In 0.1 F NaOH. [l] Based on "best" values for water autoprotolysis from ref 6; the values for pK_a and $\Delta S°$ have been corrected to a molar standard state for the dissociating water.[1,2] [m] From parameters related to k_1' and k_2 at I = 0.1 and parameters related to pK_a(H_2O) at I = 0. [n] From $\Delta C_{p\,1}^\ddagger$ at I = 0.1 and T = 62°, $\Delta C_{p\,2}^\ddagger$ at I = 0.1 and T = 50°, and $\Delta C_p°$(H_2O) at I = 0 and T = 55°. [o] Inspection of thermodynamic data for electrolytes[7] suggests that errors arising from the combination of data from different ionic strengths (0 and 0.1) should be too small to affect any conclusion discussed here. [p] Reference 8. [q] Estimated from known values for H_3O^+, NH_4^+, and $CH_3NH_3^+$. [r] From the values for pK_a and $\Delta S°$.

greater extent at the transition state than have changes in covalent bonding. This qualitative conclusion is in agreement with proposals[2,12] that the activation process for solvolysis in water is primarily a reorganization of solvent structure. Furthermore, the value of $pK_a(\ddagger)$ itself falls in the range which has been shown for some other hydrolyses[2] to be consistent with the absence of any nucleophile–carbon covalent bonding in the transition state.

In summary, this work demonstrates the feasibility of measuring $\Delta C_p°(\ddagger)$ values and suggests that they (in combination with values of $\Delta S°(\ddagger)$) may be particularly valuable in characterizing the structure of the solvent in the transition state. However, interpretations of these values which are more quantitative than those included here should await the accumulation of a larger set of reliable $\Delta C_p°$ and $\Delta S°$ values than is presently available.[13]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

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(1) To avoid confusion concerning the standard state for water, a molar standard state is used throughout this discussion. Thus pK_a (H_2O) = 15.74 at 25° and the pH-independent part of the hydrolysis rate must be written as in eq 1.[2]

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Vibrational Circular Dichroism of 2,2,2-Trifluoro-1-phenylethanol

Sir:

We report the observation of circular dichroism (CD) in vibrational bands of liquid (*S*)-(+)- and (*R*)-(−)-trifluoro-1-phenylethanol, $C_6H_5CH(OH)CF_3$ (I). The CD of the C*–H stretching band of this same molecule was previously reported by Holzwarth et al.[1] in the first and only prior publication of vibrational CD measurements in the liquid phase. As a result of higher instrumental sensitivity we are able to improve on the earlier work and observe CD over a wider spectral region with higher signal-to-noise ratio.

The CD measurements were performed on a previously described infrared instrument.[2] Extensive modifications were made to improve the medium infrared performance;[3] the most important include the substitution of an InSb detector and a ZnSe modulator,[4] and the insertion of a second ZnSe modulator after the sample which enables artefact CD signals to be greatly reduced.[5]

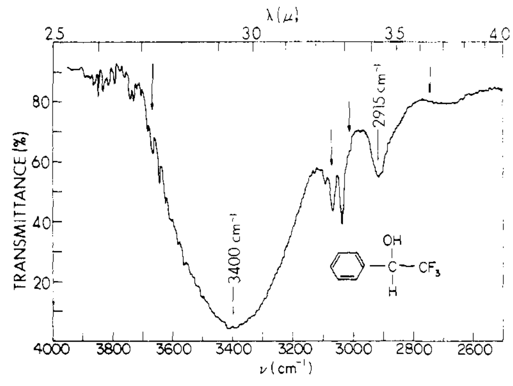

Figure 1. The transmission spectrum of liquid 2,2,2-trifluoro-1-phenylethanol with a spectral band pass of ~2 cm^{-1} and a pathlength of 20 μ. The wavelength limits of Figures 2 and 3 are indicated by arrows.

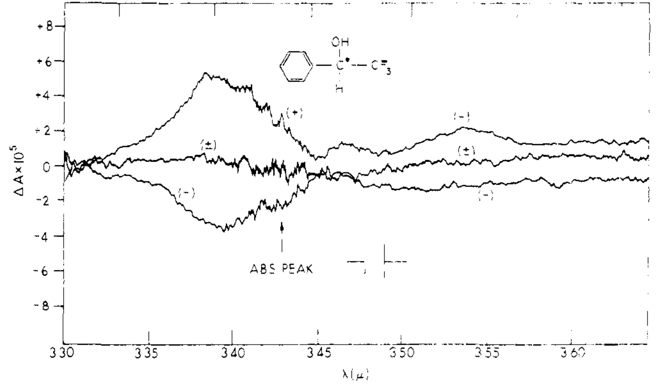

Figure 2. The CD spectrum of the C*–H stretching band of liquid 2,2,2-trifluoro-1-phenylethanol. $\Delta A = A_L - A_R$. The spectral band pass, shown in the figure, is 10 cm^{-1} and the time constant is 10 sec. The pathlength is 100 μ giving an absorbance A of 1.0 at the absorption peak, indicated by an arrow.

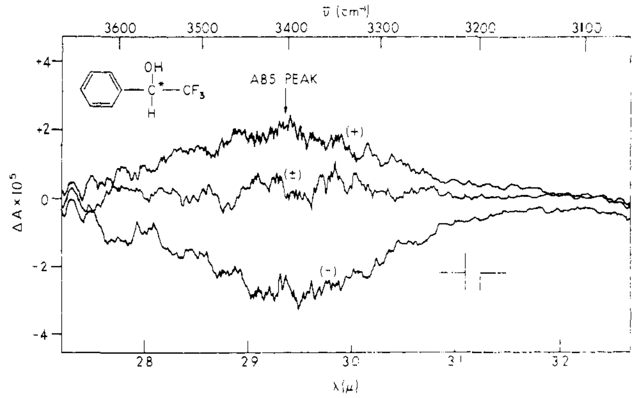

Figure 3. The CD spectrum of the O–H stretching band of liquid 2,2,2-trifluoro-1-phenylethanol. $\Delta A = A_L - A_R$. The spectral band pass, shown in the figure, is 15 cm^{-1} and the time constant is 10 sec. The pathlength is 20 μ giving an absorbance (A) of 1.0 at the absorption maximum, indicated by an arrow.

The liquid sample was held in a variable pathlength cell allowing adjustment to optimum absorbance settings. Both optical isomers and the racemic mixture of I were obtained commercially[6] and used without further purification.

Figure 1 shows the transmission spectrum of I. The O–H stretching motion is responsible for the broad 3400-cm^{-1} band; the sharp bands between 3100 and 3000 cm^{-1} are due to the phenyl C–H stretching vibrations, and the C*–H stretch is assigned to the 2915-cm^{-1} band.

Figure 2 shows the vibrational CD of the C*–H band. This consists of a principal component peaking ~30 cm^{-1}