sumption [measured polarographically[9]], ascorbate consumption [measured by HPLC/EC[10]], and allylic alcohol product formation. These quantitative experiments confirm that 2-amino-1-(1-cyclohexenyl)ethanol (CyHEA-OH) is the *only* product formed during enzymatic turnover. Similarly, trapping experiments with the epoxide trapping agent 4-(*p*-nitrobenzyl)pyridine (NBP)[9] confirmed the absence of epoxide products. Thus, DBM processing of CyHEA gives rise only to allylic hydroxylation at C-2, and neither epoxidation nor allylic rearrangement is observed.[26]

The absolute configuration of the enzymatic product was determined with the elegant method of Mosher et al.[27a,b] Upon derivatization of racemic synthetic CyHEA-OH[28] with (*S*)-*O*-methylmandelic acid, two diastereomeric derivatives were obtained which were separated by preparative TLC by using 45% ethylacetate in hexane. HPLC analyses on silica gel showed that the similarly derivatized enzymatic product yielded only material which co-eluted with the slow eluting diastereomer of synthetic CyHEA-OH. The (*S*)-*O*-methylmandelate derivatives were then examined by NMR, and the signal arising from the vinyl proton was identified by NMR decoupling experiments. The vinyl proton of the fast eluting diastereomer appeared at 5.69 δ, while that of the slow eluting diastereomer appeared at 5.32 δ with an upfield shift of 0.375 ppm. Using the Mosher model (Figure 1), the slow eluting isomer having the upfield vinyl NMR signal was assigned an absolute configuration of *R*, while the other isomer was assigned the *S* configuration. Thus, enzymatically produced CyHEA-OH is assigned an absolute configuration of *R*, and no (*S*)-CyHEA-OH is detectable by HPLC, TLC, or NMR.

There is evidence that DBM oxygenation of benzylic olefinic and heteroatom functionalities proceeds via initial electron abstraction to give a substrate radical cation.[9,10,12] Thus, the absence of epoxide products from oxygenation of CyHEA by DBM—implying an inability of the activated copper–oxygen species to effect radical cation formation from a *non*conjugated olefinic moiety—is consistent with the well-known difference in oxidation potential and reactivity between conjugated and nonconjugated olefins.[29] On the other hand, it is well known that allylic and benzylic C–H bonds exhibit strikingly similar chemical reactivities.[23] This suggests that the probable mechanism for allylic hydroxylation of CyHEA is analogous to that proposed for benzylic hydroxylation of phenethylamines, i.e., hydrogen atom abstraction to form a resonance stabilized benzylic (or allylic) radical.[19]

Groves and co-workers[30] found that cytochrome P-450 catalyzes both epoxidation and allylic hydroxylation of cyclohexene, and they propose that epoxidation by P-450 proceeds via an olefinic cation radical whereas allylic oxygenation proceeds via an allylic radical. However, they observed that allylic hydroxylation of cyclohexene is accompanied by allylic rearrangement and that methylenecyclohexane gives rise to both 2-methylenecyclohexanol and 1-cyclohexenylmethanol. In contrast, we find that allylic hydroxylation of CyHEA by DBM proceeds without rearrangement. It is possible that geometric constraints at the DBM binding site prevent interaction of the activated oxygen species with carbon centers in the cyclohexene ring. However, we have also observed that DBM catalyzes allylic hydroxylation of *cis*-2-hexenylamine with hydroxylation occurring cleanly at C-4 and without any detectable allylic rearrangement.[31] These results may be suggestive of a mechanism in which copper interacts with the olefin moiety during the catalysis, thus precluding rearrangement of the double bond. Such copper–olefin interactions have been proposed to account for the lack of allylic rearrangement in oxidation by peroxides in the presence of copper salts.[32]

The demonstration of facile, stereoselective allylic hydroxylation by DBM suggests new possibilities for the design of inhibitors and pseudo-substrates for this enzyme, a goal which is being actively pursued in a number of laboratories.[33-37]

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (HL28164).

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[26] As with many DBM substrates[9,12,14] examination of the time course of CyHEA oxygenation reveals that time-dependent enzyme inactivation occurs with apparent kinetic constants $k_{\text{inact}} = 0.33$ min^{-1} $K_I = 82.5$ mM.

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[29] The $E_{1/2}$ for the oxidation of cyclohexene is 0.33 V higher than that of α-methylstyrene. $E_{1/2}$ values were calculated from ionization potentials (IP) for cyclohexene and α-methylstyrene (*Hand Book of Physics and Chemistry*; 58th ed.; Weast, R. C., Ed.; CRC Press: E74, with $E_{1/2}$ = 0.89 (IP) − 6.04 (Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916).

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Proton-Transfer Reactions of Sulfonium Ylides: Unit Brønsted Slopes Do Not Require Diffusion-Controlled Proton Transfer[†,1]

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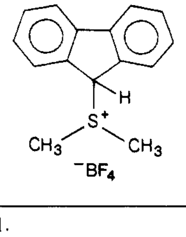
We report here evidence that the Brønsted β coefficient of 1.0 for deprotonation of a sulfonium salt overestimates the amount of bond formation to the base catalyst in the transition state; in the reverse protonation direction $\alpha = 0$ underestimates the degree of proton transfer from the acid catalyst. Proton transfers to and from carbon occur directly[2-4] so that an acid catalyst must break a hydrogen bond to water before it can protonate a carbanion. We suggest that a value of $\alpha_d \approx -0.2$ for desolvation offsets $\alpha = 0.2$ for protonation to give $\alpha_{\text{obsd}} = 0$; β_{obsd} is then 1.0. This estimate is supported by the dependence on phenol acidity of ΔG for transfer of phenols and substituted benzenes from the gas phase to water. Similar effects of hydrogen bonding on the nucleophilic reactivity of bases have been reported.[5,6]

Figure 1 shows that the Brønsted plot for ^{1}H and ^{3}H exchange of dimethyl-9-fluorenylsulfonium tetrafluoroborate (**1**) in D_2O[7]



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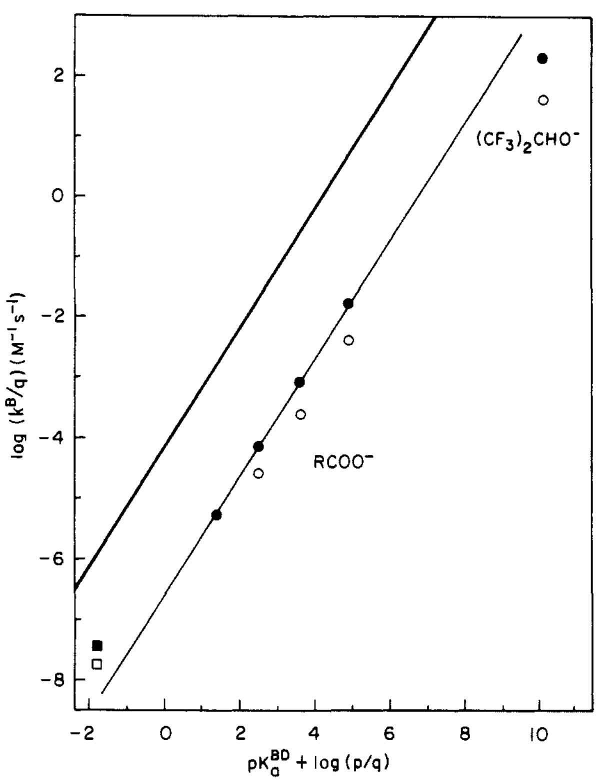
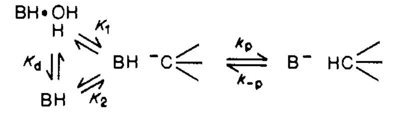


Figure 1. Brønsted plot for general base catalysis of C(9)-^{1}H (closed symbols) and ^{3}H (open symbols) exchange catalyzed by oxygen anions (●, ○) and D_2O (■, □) from dimethyl-9-fluorenylsulfonium tetrafluoroborate in 95% D_2O:5% Me_2SO (v:v) at 25 °C and ionic strength 1.0 M (KCl). The lower light line is drawn with a slope of 1.0 through the points for $RCOO^-$ catalyzed ^{1}H exchange. The upper bold line is a limiting theoretical Eigen curve[2,8] with $k_{diff} = 3 \times 10^9$ M^{-1} s^{-1}.

Scheme I



has a slope of β = 1.0 for ^{1}H exchange catalyzed by $RCOO^-$. The calculated rate constant[8] for protonation of the ylide by RCOOH, $k^{BH} = 2 \times 10^7$ M^{-1} s^{-1}, is independent of pK_a, with α = 0, but is well below the diffusion-controlled limit. The primary kinetic isotope effects for acetate-catalyzed exchange, $k^H/k^T = 4.13 \pm 0.18$ (in D_2O) and $k^D/k^T = 1.55 \pm 0.05$ (in H_2O), are related by the Swain–Schaad[9] relation: $\ln(k^H/k^T)/\ln(k^D/k^T) = 3.24 \pm 0.25$. This value agrees with the theoretical[9] value of 3.26 and is consistent with largely rate-limiting proton transfer. The primary isotope effects decrease from $k^H/k^T = 4.70$ for 1,1,1,3,3,3-hexafluoro-2-propanol anion ($\Delta pK = 4$) to $k^H/k^T = 2.3$ for D_2O ($\Delta pK = 16$). These small isotope effects are qualitatively consistent with an asymmetric transition state as proposed by Westheimer.[10] Similar observations of unit Brønsted slopes and small primary kinetic isotope effects for other carbon acids[11-14] have been interpreted as evidence for essentially complete proton transfer[15,16] or a diffusion-controlled reaction.[13,14]

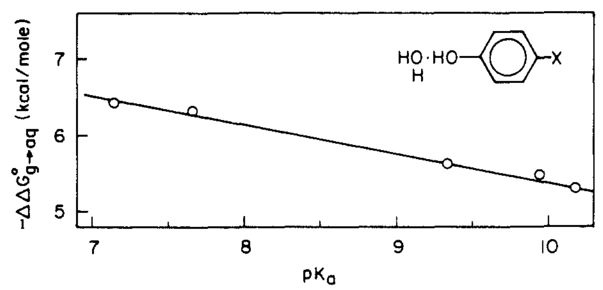


Figure 2. Dependence of the difference in free energy of transfer from the gas phase to water of substituted phenols, and the corresponding benzenes, on the pK_a of substituted phenols in water.[17]

These results can be explained in the reverse direction (Scheme I) by direct protonation of the carbanion by an acid BH that is initially hydrogen bonded to water. The Brønsted α = 0 reflects both the equilibrium constant for breaking the hydrogen bond to water, K_d, and the rate constant for direct proton transfer to carbon, k_p.

There is indirect evidence that the equilibrium constant for desolvation is smaller for stronger acids, which corresponds to a negative value for $\alpha_d = \partial \log K_d/\partial \log K_a$. Figure 2 shows that the difference in free energy of transfer from the gas phase to water for a series of substituted phenols, compared with the corresponding benzenes, is more favorable for acidic phenols.[17] This reflects an increase in the strength of the hydrogen-bonding interaction $ArOH{\cdot}OH_2$ with more acidic phenols with $\alpha_d = -0.26$.[18] Equilibrium constants for the interconversion of 1-arylethyl alcohols and ethers[19] and the data collected by Guthrie[20] for replacement of the OH group by OCH_3 at carbon, phosphorus, and sulfur centers give values of $\alpha_d = -0.25$ for breaking a hydrogen bond from ROH to water. These values suggest that an estimate of $\alpha_d \approx -0.2$ is reasonable; it is similar in magnitude to $\beta_d \approx -0.2$ estimated for desolvation of amine bases.[5]

We conclude that in order to obtain an estimate of the amount of bond formation to the base catalyst in the transition state for k_{-p} (k_p in the protonation direction), the observed value of $\beta(\alpha)$ should be corrected for the solvation (desolvation) step, $1/K_d$ (K_d). The correction will be larger when the observed Brønsted coefficient approaches 1.0 (0); a correction of −0.2 appears to be reasonable according to eq 1 and 2.[5] These results add to a

$$\beta_{corr} = 0.8\beta_{obsd} \tag{1}$$

$$\alpha_{corr} = 0.2 + 0.8\alpha_{obsd} \tag{2}$$

growing list of examples in which solvation of both neutral[5,6] and

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(7) Rate constants for C(9)-^{1}H exchange in 95% D_2O:5% Me_2SO-d_6 (v:v) at 28 °C and 1 M ionic strength (KCl) were determined by monitoring the relative areas of the C(9)-^{1}H to nonexchanging C(1–8)-^{1}H by NMR. Rate constants for C(9)-^{2}H exchange of dimethyl-9-[^{2}H]-9-fluorenylsulfonium tetrafluoroborate in 95% H_2O:5% Me_2SO (v:v) catalyzed by CH_3COO^- were determined by quenching aliquots in acid, lyophilizing, redissolving in 95% D_2O:5% Me_2SO-d_6 (v:v) (containing 0.1 M DCl), and measuring relative peak areas by NMR. Rate constants for C(9)-^{3}H exchange in H_2O and D_2O were determined by quenching aliquots in acid, absorbing them onto Whatmann 3MM filter papers, and measuring the nonvolatile radioactivity of dimethyl-9-[^{3}H]-9-fluorenylsulfonium tetrafluoroborate.

(8) Calculated from the spectrophotometrically measured $pK_a^{CH} = 13.7$ in 95% H_2O:5% Me_2SO (v:v) assuming there is no secondary solvent isotope effect on the rate constant for protonation of the ylide.

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anionic[21] species can have significant effects on observed structure-reactivity parameters in water.

Registry No. 1, 116724-74-4; H_2, 1333-74-0; D_2, 7782-39-0; T_2, 10028-17-8; H_2O, 7732-18-5.

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Direct Observational Studies of a Singlet Alkylcarbene: Methylmethoxycarbene, a Remarkably Selective Nucleophile

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Many carbenes have been spectroscopically characterized under matrix isolation conditions or by time-resolved methods in solution,[2] but very few *alkylcarbenes* have been *directly* observed. Facile 1,2-hydrogen migration[3,4] particularly limits the persistence of *singlet* alkylcarbenes, although several *triplet* alkylcarbenes, where spin barriers mitigate rearrangement, have been spectroscopically observed.[5] Electron donation from α-heteroatomic substituents stabilizes singlet carbenes; singlet methylcarbene should[3b] and does preferentially rearrange to ethylene, but methylchlorocarbene displays a rich intermolecular chemistry.[6] α-Oxygen (2p-2p overlap) stabilization is superior to that of α-chlorine (3p-2p overlap), so that methylmethoxycarbene is of special interest.[7,8]

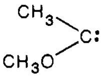
Now we report the direct spectroscopic observation of methylmethoxycarbene (**1**, MeCOMe) in *both* matrices and solution. Not only does the stabilization provided to this alkylcarbene by the methoxy substituent permit its observation but it also confers powerful, intermolecular nucleophilic selectivity.

Table I. Relative Reactivities of MeCOMe toward Alkenes at 25 °C[a]

alkene	k_{rel}
$Me_2C{=}CHMe$	2.13
$Me_2C{=}CH_2$	2.18
trans-$MeCH{=}CHMe$	1.00[b]
$CH_2{=}CHCOOMe$	362
$CH_2{=}CHCN$	686
$CH_2{=}CClCN$	22300

[a] The experimental relative reactivities, GC calibrations, and cross-check results will appear in the Ph.D. Thesis of B. K. Wilk. Error limits are ≤5%. [b] The data are normalized to *trans*-butene.

3-Methyl-3-methoxydiazirine (**2**)[9] was isolated in a nitrogen matrix (**2**:N_2 ~ 1:800) at 10 K and irradiated at 312 nm for 12 h. A photolabile intermediate was generated that had strongest IR bands at 1330, 1320, 1288, 1275, 1160, 1100, and 550 cm^{-1}. We assign these bands to MeCOMe in analogy to previous characterizations of alkoxycarbenes.[8] The carbene bands were accompanied by photoproduct bands that were augmented by additional broad band irradiation (λ > 340 nm). MeCOMe photoproducts, identified by IR, included acetone (~Me), methylvinyl ether (~H), and ketene and methane (Me-O fragmentation, followed by disproportionation) in an approximate ratio of 60:30:10 (%), respectively. A small amount of methylmethoxydiazomethane (**3**; 2020, 1260 cm^{-1}) was produced in the matrix by photoisomerization of **2**; it could be rapidly and *selectively* destroyed by irradiation at 465 nm.



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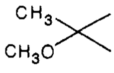
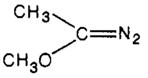


2



3

$CH_3CH(OCH_3)_2$

4

UV-vis spectra of these irradiated matrices reveal a broad band centered at ~390 nm, with growth identical with that of the IR bands attributed to **1**. Importantly, the UV "action spectrum" for photochemical destruction of the IR bands of **1** matched the UV absorption spectrum, so that we attribute the 390-nm band to MeCOMe.[11,12] *No* UV-vis absorption corresponding to diazoalkane **3** (at ~465 nm) could be observed.

The MeCOMe assignment was confirmed by methanol trapping. Irradiation of **2** at 335 nm in a 4:1 2-methylbutane/MeOH glass at 20 K afforded the IR absorptions of MeCOMe (and photoproducts). Warming the glass to 80 K caused the disappearance of the carbene bands, together with the growth of IR bands due to acetal **4**.

Irradiation of pentane, isooctane, or acetonitrile *solutions* of **2** (A_{380} ~ 1.2) with a 14 ns, 70-90 mJ, 351-nm pulse from a XeF excimer laser[13] afforded a single transient signal in the 250-500-nm region, with a broad maximum between 370 and 400 nm.[14] The transient appeared within the laser pulse, and, in pentane, it decayed with first-order kinetics (quenching by **2**) with $k \sim 5 \times 10^5$-2×10^6 s^{-1}. The signal was not very intense, so that kinetic results are less precise than desired. Nevertheless, the solution transient absorption matched that of the matrix species and is assigned to MeCOMe.

The MeCOMe absorption could be quenched by MeOH, acrylonitrile, and α-chloroacrylonitrile in pentane solution at 20

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(11) This is in agreement with the calculated spectrum; see below.

(12) We previously attributed the 390-nm absorbance of MeCOMe to **3**.[13] We revise this assignment in view of the evidence presented here.

(13) Moss, R. A.; Shen, S.; Hadel, L. M.; Kmiecik-Ławrynowicz, G.; Włostowska, J.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1987**, *109*, 4341.

(14) Close inspection reveals *two* closely spaced maxima, consistent with the presence of *trans*- and *cis*-**1**; see below.

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