energy transfer to O_2 from a donor triplet, is unlikely to be involved in photosensitivity associated with pheomelanin.

As previously discussed, subsequent reactions of $O_2^{-}\cdot$ may lead to severe skin damage. Furthermore, pulse radiolysis showed that PM and BTH react at the diffusion-controlled rate with the solvated electron, a conclusion confirmed by the laser flash photolysis experiments where the apparent yield of e_{aq}^- increased with decreasing PM and BTH concentrations. Although we were unable to detect them, degradation products resulting from such reactions may also play a role in photosensitivity.

In conclusion, our results indicate that BTH is a good model compound for PM in that both compounds photoionize and do not readily form triplets. Nevertheles, more complete photophysical data on PM could be obtained by working with the protein-free chromophore. Further work is also required to characterize the PM and BT radicals produced after photoionization.

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Preequilibrium Carbon Protonation in the Acid-Catalyzed Hydrolysis of a Phenylketene Dithioacetal

Sir:

Carbon protonation is usually a slow, rate-determining step in the acid-catalyzed hydrolysis of vinyl ethers,[1] vinyl sulfides,[2] and ketene acetals.[3] However, the protonation step could well be a rapid equilibrium, depending on the electronic structure of unsaturated substrates. To our knowledge, such cases have never been encountered[4-6] except for one unusual case.[7]

This communication presents direct evidence that in the acid-catalyzed hydrolysis of 1,1-bis(methylthio)-2-phenylethene (**1**)[8] the initial carbon protonation is rather a rapid reversible process which precedes a rate-determining collapsing of the carbonium

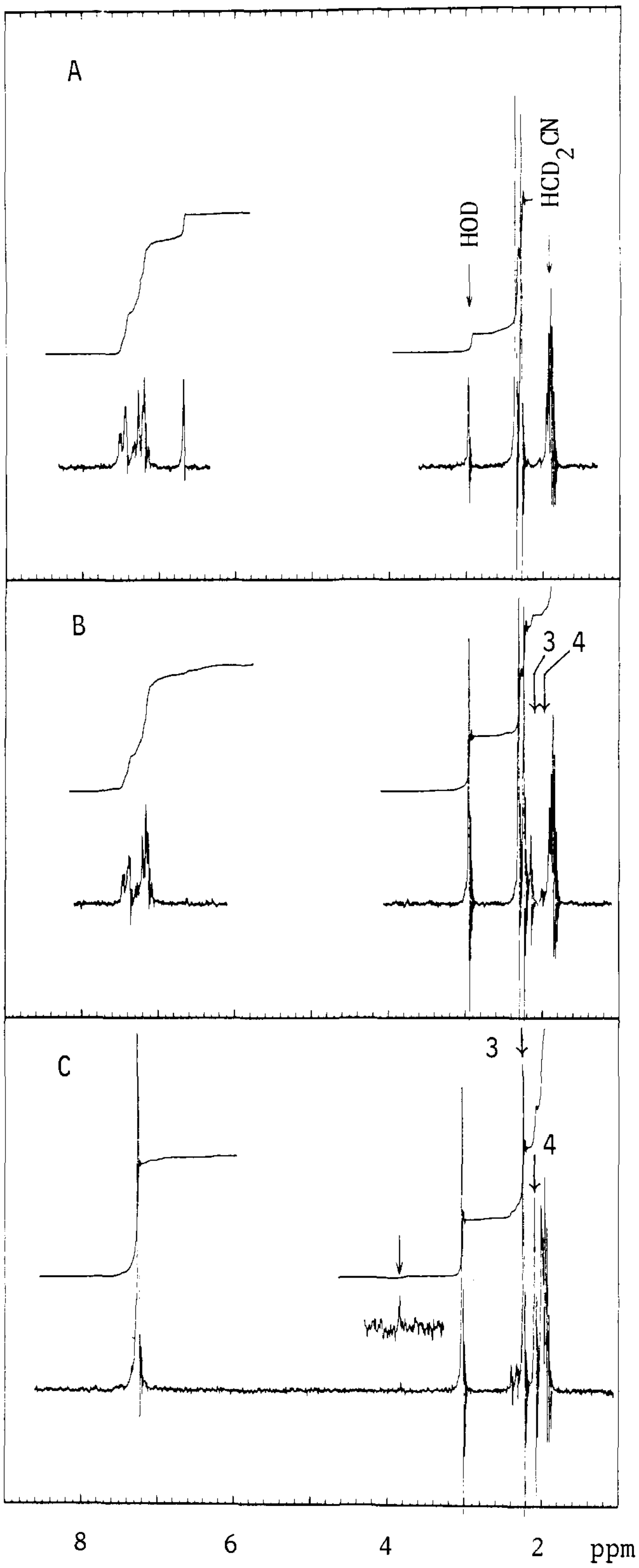

Figure 1. ^{1}H NMR spectra for the hydrolysis of **1** in 90% CD_3CN/D_2O at 35 °C. [DCl] $\simeq$ 0.002 M. $[\mathbf{1}]_0 \simeq$ 0.1 M. Reaction times are 0, 100 min, and 20 h for spectra A, B, and C, respectively. Signals at ca. 3.0 and 1.9 ppm correspond to those of solvent HOD and HCD_2CN, respectively.

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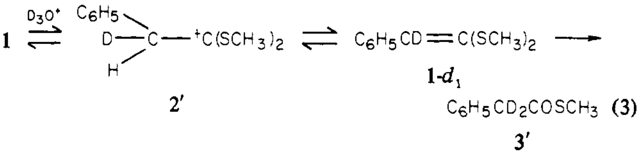
ion intermediate thus formed (eq 1 and 2).

$$\underset{\mathbf{1}}{C_6H_5CH{=}C(SCH_3)_2} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{2}}{C_6H_5CH_2\overset{+}{C}(SCH_3)_2} + H_2O \qquad (1)$$

$$\mathbf{2} + 2H_2O \xrightarrow{k_2} \underset{\mathbf{3}}{C_6H_5CH_2COSCH_3} + CH_3SH + H_3O^+ \qquad (2)$$

Figure 1 shows ^1H NMR spectral changes during the reaction of **1** in 90% CD_3CN/D_2O containing about 2 mM DCl at 35 °C.[10] Spectrum A was recorded before the addition of enough acid, the olefinic hydrogen resonance of **1** appearing at 6.69 ppm in the integral intensity of 1 H. In 100 min (spectrum B), the signal at 6.69 ppm disappeared almost completely, while the CH_3S signals at 2.32 and 2.39 ppm remained in about 80% of the original intensity. The signals for the products (arrows) showed up correspondingly in intensity equivalent to ca. 20% conversion. Spectrum C (20 h) shows the formation of methyl phenylthioacetate (**3**) (CH_3S resonance at 2.23 ppm) and methyl orthophenylthioacetate (**4**) (CH_3S resonance at 2.08 ppm) in the ratio of 5:1. The methylene resonances of these products cannot be perceived; the one for **3** is only barely discernible at 3.84 ppm (arrow). The CH_3S resonances of **1** are still observable (eq 3).



(3)

These observations evidently indicate that the carbon protonation (eq 1) is reversible and that the decay of the intermediate **2** (eq 2) is rate determining ($k_{-1} > k_2$). The rate of the H–D exchange estimated from the disappearance of the olefinic hydrogen was about 10 times greater than that of the hydrolysis. The product **4** must have arisen from the nucleophilic trapping of **2** by CH_3SH liberated on the formation of **3** (eq 4).

$$\mathbf{2} + CH_3SH \rightarrow \underset{\mathbf{4}}{C_6H_5CH_2C(SCH_3)_3} + H_2O \qquad (4)$$

Kinetic measurements for the hydrolysis were made spectrophotometrically at 295 nm with a Shimadzu UV 200 spectrophotometer. The reactions were carried out at 30 °C in aqueous acetonitrile (10 vol %), the ionic strength being maintained at 0.45 with added KCl. The reaction was found to be catalyzed by general acids ($ClCH_2CO_2H$, HCO_2H) as well as H_3O^+ ($k_{H_3O^+} = 0.126\ M^{-1}\ s^{-1}$). The hydration of **2** (eq 2) must be catalyzed by a general base.

The reaction was greatly accelerated by the addition of a thiol, 2-hydroxyethanethiol. In 0.05 M aqueous HCl containing a constant 10 vol % of organic components (CH_3CN + $HOCH_2CH_2SH$), the rate was linearly increased with thiol concentrations, $k_{obsd}\ (s^{-1}) = 4.68 \times 10^{-3} + 3.84 \times 10^{-3} \cdot [HOCH_2CH_2SH]$. The control experiments with *p*-methoxyphenyl vinyl ether, which is hydrolyzed through the rate-determining protonation,[11] showed that the rate of its hydrolysis was not affected by the addition of up to 0.5 M thiol. The acceleration observed further substantiates that the nucleophilic trapping of the intermediate **2** is rate determining. The relative nucleophilicity ($HOCH_2CH_2SH/H_2O$) of about 40 deduced here is reasonable as compared with that estimated from the reaction with a stable carbonium ion.[12]

Pseudo-first-order plots for the reaction of **1** in 10% CH_3CN/D_2O (0.05 M DCl) curved markedly from an initial slope (within 1 min) of $2.26 \times 10^{-3}\ s^{-1}$ to an ultimate slope of $3.15 \times 10^{-3}\ s^{-1}$. This is undoubtedly due to the initial H–D exchange at the 2 position of **1** and to the greater hydrolysis rate of the deuterated substrate **1**-d_1 as compared to the undeuterated **1**. In fact, the reaction of the isolated 2-deuterio substrate **1**-d_1[13] under the same conditions gave excellent linear plots with a slope ($3.16 \times 10^{-3}\ s^{-1}$) close to the approximate ultimate slope. The hydrolysis of **1**-d_1 in 10% CH_3CN/H_2O (0.05 M HCl) was slightly decelerated at a later stage of reaction. The linear plots obtained within a first half-life gave $k_{obsd} = 6.46 \times 10^{-3}\ s^{-1}$, which is 1.38 times greater than that for **1** obtained in 10% CH_3CN/H_2O and 2.04 times that for **1**-d_1 in 10% CH_3CN/D_2O.

That is, the rate constants obtained above give the secondary isotope effect $k_D/k_H = 1.38$ and the solvent isotope effect $k_{H_2O}/k_{D_2O} = 2.04$. The former is close to the typical value estimated for the hybridization change (sp^2 to sp^3) of the carbon carrying the isotope.[14] Thus, it is compatible with the mechanism involving equilibrium formation of the intermediate **2**. The normal solvent isotope effects observed agree with the apparent general acid catalysis. The rate-determining step must involve proton transfer from a nucleophilic water molecule to a general base.

All the evidence presented above points to the mechanism involving the preequilibrium carbon protonation (eq 1 and 2). Further studies on the details of the kinetics are in progress.

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Structure Elucidation with Lanthanide-Induced Shifts. 8. Geometry of Europium-Ketone Complexes[1]

Sir:

Since the initial discovery that tris(β-diketonate) complexes of europium(III) can cause substantial chemical shift changes in the NMR spectra of organic compounds,[2] considerable effort has been expended in attempts to understand and utilize these lanthanide-induced shifts (LIS).[3] We have previously demonstrated that lanthanide-induced shifts can be used for rigorous structure evaluation of nitriles.[1,4,5] For that class of compounds, interpretation of experimental data is greatly simplified by the expectation that the resulting lanthanide complex will have a nearly linear carbon–nitrogen–lanthanide array.[4-7] We next turned our attention to functional groups for which this simplifying assumption could not be made. In the case of the carbonyl group, the LIS were expected to result from the time-average shifts of two discrete complexes corresponding to coordination at each of the lone pairs of electrons on oxygen (i.e., C–O–Eu bond angle

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