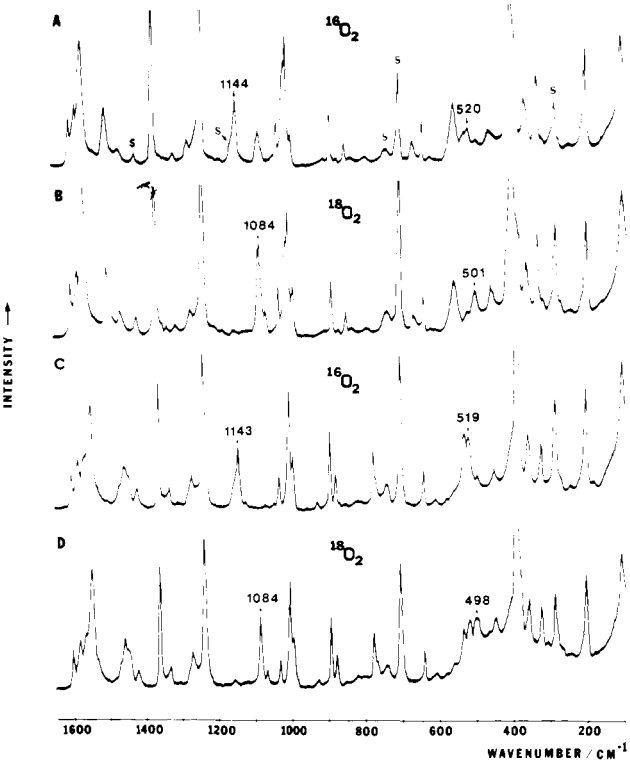

Figure 1. Resonance Raman spectra (457.9-nm excitation) of dioxygen adducts of Co(TPP) and Co(TPP-d_8) in CH_2Cl_2 containing 3% pyridine at ~−70 °C under ~4 atm of O_2 pressure: (A) Co(TPP) + $^{16}O_2$; (B) Co(TPP) + $^{18}O_2$; (C) Co(TPP-d_8) + $^{16}O_2$; (D) Co(TPP-d_8) + $^{18}O_2$. S denotes the solvent band.

as the O_2 pressure is increased. The "minibulb" method that we reported previously enables us to measure the resonance Raman (RR) spectra of dioxygen adducts of Co(II) Schiff base complexes in solution equilibria at ~−80 °C under ~3 atm of O_2 pressure. Thus, this method is ideal for RR studies of $\nu(O_2)$ of Co(II) porphyrins under "preresonance conditions". All the spectra shown below were obtained by using this method in conjunction with a Spectra-Physics Model 164 Ar ion laser (457.9-nm excitation, ~30 mW) and a Spex Model 1401 double monochromator.

Figure 1A shows the RR spectrum of Co(TPP) dissolved in CH_2Cl_2 (~10^{-2} mol/L) containing 3% pyridine and saturated with $^{16}O_2$ gas at ~4 atm of O_2 pressure. The temperature of the minibulb was kept at ~−70 °C by using a CTI Model 21 closed-cycle helium refrigerator. As expected, this spectrum is very similar to that of Co(TPP) (457.9-nm excitation) reported previously[7] except that an additional band of medium intensity appears at 1144 cm^{-1}. As is shown in Figure 1B, this new band disappears completely, and the Co(TPP) band at 1084 cm^{-1} becomes much stronger when the solution is saturated with $^{18}O_2$. These results clearly indicate that the $\nu(^{16}O_2)$ of Co(TPP)(py)O_2 is at 1144 cm^{-1} and that this band has shifted and accidentally overlaps the 1082-cm^{-1} band of Co(TPP) upon $^{16}O_2$-$^{18}O_2$ substitution. In fact, the $\nu(^{16}O_2)$ of Co(TPP)(py)O_2 obtained here is very close to that of Co(TPP)(1-MeIm)O_2 at 1142 cm^{-1} reported previously by using IR difference spectroscopy.[10] To further confirm our interpretation, we have carried out similar experiments with Co(TPP-d_8) in which the eight β-pyrrole hydrogens are substituted by deuterium. As is seen in Figure 1C, the $\nu(^{16}O_2)$ of Co(TPP-d_8)(py)O_2 is at 1143 cm^{-1}. However, the band at 1082 cm^{-1} of Co(TPP) is now shifted under the strong band near 1000 cm^{-1}. As a result, the $\nu(^{18}O_2)$ of Co(TPP-d_8)(py)O_2 is observed at 1084 cm^{-1} without any interference from other bands. The observed $\nu(O_2)$ shift from 1144 to 1084 cm^{-1} (60 cm^{-1}) is close to that of a perturbed diatomic molecule (65 cm^{-1}). As discussed previously,[7] the large shift of the $\nu(O_2)$ in going from "base-free" Co(TPP)O_2 (1278 cm^{-1}) to "base-bound" Co(TPP)(py)O_2 (1144 cm^{-1}) is attributed to the effect of the pyridine ligand, which donates the electrons to the O_2 via σ and/or π bonding to the Co atom.

Careful inspection of these spectra also reveals the presence of the $\nu(Co-O_2)$ in the low-frequency region. The band at 520 cm^{-1} in Figure 1A has shifted to 501 cm^{-1} (Figure 1B) by $^{16}O_2$-$^{18}O_2$ substitution. In the case of Co(TPP-d_8), this band shifts from 519 to 498 cm^{-1} by oxygenation (Figure 1C and D). The RR spectrum of Co(TPP)(py) obtained under similar conditions shows no appreciable bands in the 600–500- and 1200–1100-cm^{-1} regions.

Previously, Nozawa et al.[11] observed the anomalous broadening of the MCD Soret band upon oxygenation of the Co(II) complex of mesoporphyrin IX dimethyl ester and suggested the presence of the Co(II)-O_2 CT transition in the Soret region near 400 nm. Wayland et al.[12] also suggested the possibility of assigning a similar transition of Co(TPP)O_2 in the Soret region. Our RR observation together with those of Tsubaki and Yu[9] definitely supports these suggestions.

Finally, it is interesting to note that O_2 adducts of cobalt hemoglobin exhibit two $\nu(O_2)$ at ~1153 and ~1122 cm^{-1},[9] whereas that of an "unprotected" Co(TPP) shows only one $\nu(O_2)$ at 1144 cm^{-1}. A more detailed study including the effects of in-plane and axial ligands and the solvent (environment around the bound O_2) on $\nu(O_2)$ is now in progress.

Acknowledgment. The work performed at Marquette University was supported by the National Science Foundation (Grants CHE-8205522 and PCM-8114676). The work performed at the University of Kentucky was supported by the funds from the doors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., and the University of Kentucky. We thank Dr. T. Watanabe for his technical assistance.

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Reaction of Singlet Oxygen with Enol Esters: A New Path Implicating a Dipolar Intermediate

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The reactions of singlet oxygen ($^1\Delta_g$, $^1O_2$) with unsaturated organic compounds typically fall into one of three categories: [2 + 2] cycloaddition to form a dioxetane; [4 + 2] cycloaddition giving an endoperoxide; and the "ene" reaction yielding an allylic hydroperoxide.[1] The mechanism for this last transformation has proven to be enigmatic with suggestions of a concerted reaction[2] competing with proposed stepwise paths going through a biradical,[3] perepoxide,[4] or zwitterionic[5] intermediate. Herein we report the

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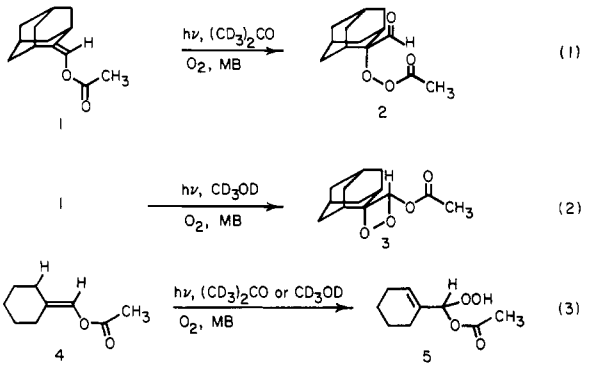
Table I. Rate Constants for Reaction of Enol Esters 1 and 4 in CD_3OD and $(CD_3)_2CO$ with $^1O_2$ at Room Temperature

enol ester	solvent	$10^{-4}k_q$, s^{-1} M^{-1}
1	$(CD_3)_2CO$	3.4
1	CD_3OD	2.1
4	$(CD_3)_2CO$	7.5
4	CD_3OD	4.8

discovery of a new reaction of singlet oxygen. Photooxidation of enol ester **1** in acetone or carbon disulfide solution gives the



acyl-shifted peroxy ester **2** in essentially quantitative yield. When the photooxidation of **1** is performed in methanol solution, the major product is dioxetane **3**. In contrast, photooxidation of enol ester **4** in methanol or acetone solution does not give a detectable amount of the acyl-shifted product or the dioxetane but gives exclusively the "ene" reaction product **5**. We measured the rate constants for quenching of $^1O_2$ by these two enol esters and find them to be essentially independent of structure and of solvent. These results indicate that the transition states for these reactions of $^1O_2$ are insensitive to the solvent and structural changes and that the selection of the eventual reaction path occurs by a common dipolar intermediate resembling a perepoxide.

Irradiation of an O_2-saturated $(CD_3)_2CO$ solution of enol ester **1**[6] containing methylene blue (MB) as sensitizer at room temperature or at −78 °C with visible light leads to its rapid consumption and the appearance of a single product in 95% yield as evidenced by changes in the ^1H NMR spectrum of the reaction solution. The photooxidation product, isolated from the reaction mixture by chromatography on silica gel at −50 °C, is identified as peroxy ester **2**.[7]

The reaction takes quite a different course when it is carried out in CD_3OD. Instead of exclusive formation of **2**, the major product, formed in 70% yield, is identified as dioxetane **3**. A related solvent-dependent reaction of $^1O_2$ with enol ethers has been reported previously by Asveld and Kellogg.[8] In the present case, the dioxetane is not sufficiently stable to permit isolation in pure form. However, low-temperature chromatography provides a solution of **3** containing, as the only impurity, 10% adamantanone. The spectral, thermal, and chemiluminescent properties of **3** permit its certain identification.[9] Under these photooxidation conditions enol ester **1** may also give a low yield (ca. 3%) of an unisolated methanol addition product detected spectroscopically after reaction in CH_3OD.

Photooxidation of enol ester **4** in acetone gives one product in 95% yield identified as hydroperoxide **5**. This ene reaction product could not be isolated, but its spectral properties[10] and reduction by $NaBH_4$ to 1-(hydroxymethyl)cyclohexene[11] confirm its structure. Similar results are obtained in CD_3OD except that the initial ene product is unstable in this solvent.

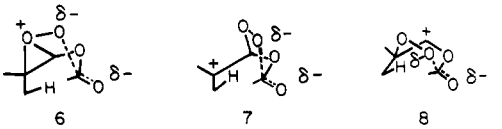
The rate constant for quenching of $^1O_2$ by these enol esters can be easily determined by monitoring the decay of the infrared phosphorescence characteristic of $^1O_2$[12] at different olefin concentrations. The results of this study are presented in Table I. We note that the measured rate constants do not reflect the dramatic change in product composition attending solvent or structure change but instead are nearly constant. To confirm that the $^1O_2$ quenching process and the product-forming reaction are the same, we photooxygenated a mixture of enol esters **1** and **4** to low conversion in $(CD_3)_2CO$ and obtained the anticipated mixture of oxygenation products **2** and **5** in appropriate yields.

The reaction of $^1O_2$ with substituted enols has been studied previously. Beuglemans and co-workers[13] report only ene and [4 + 2] cycloaddition reactions from steroidal enol and dienol acetates. Silyl enol ethers react with $^1O_2$ to give competing ene and silicon migration products.[14,15] Similarly, silylketene acetals add $^1O_2$ to give both silylperoxy esters and 1,2-dioxetanes, perhaps through a common zwitterionic intermediate.[16] Enol ethers have been intensively studied[8,17,18] and shown to give reaction-condition-dependent yields of ene, dioxetane, and solvent incorporation products with $^1O_2$.

The novel migration product obtained from singlet oxygenation of enol ester **1** in $(CD_3)_2CO$ implicates a dipolar state on this reaction surface. The observation that the rates of reaction of these enol esters are relatively insensitive to structural and solvent change but that the products formed are dramatically dependent on these parameters tends to eliminate a concerted reaction path. Instead, a sequence proceeding through a solvent-independent transition state, essentially common to enol esters **1** and **4**, to a dipolar intermediate whose fate depends on the solvent and availability of allylic hydrogens is implicated.

The structure of the transition state for these reactions may be deduced by implication from the hydrocarbon $^1O_2$ ene reaction. In that case, product isotope effects[4c] and kinetic data[12b] suggest early involvement of the allylic hydrogen. In the present case we note that adamantyl enol ester **1** does not have a suitable axially oriented allylic hydrogen; yet it reacts at a rate comparable to enol ester **4**, which does have this features. A related observation on the ene reaction of conformationally fixed cyclohexylidenecyclohexanes[19] suggests either satisfactory overlap with an equatorially disposed allylic hydrogen or, perhaps, interaction with the carbonyl carbon of the enol ester in the transition state.

These findings indicate that a product-determining dipolar intermediate is formed after the transition state in these reactions. The intermediate can be viewed as a closed perepoxide (**6**). The



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(6) The enol ester was prepared from adamantanecarboxaldehyde by reaction first with KH in DME and then inverse addition to acetic anhydride in 85% yield; ^1H NMR (CS_2) δ 1.55–2.08 (m, 12 H), 2.02 (s, 3 H), 2.31 (br s, 1 H), 2.94 (br s, 1 H), 6.76 (s, 1 H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.68; H, 8.81. Found: C, 75.95; H, 9.03.

(7) ^1H NMR ($CDCl_3$) δ 1.59–1.92 (m, 12 H), 1.98 (s, 3 H), 2.26 (br s, 2 H), 9.36 (s, 1 H); IR ($CDCl_3$) 1739, 1767 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.52; H, 7.63. Found: C, 65.68; H, 7.63. Peroxide titer 92% of theory; molecular weight (osmometry) 264 ± 26.

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(9) ^1H NMR (CD_3OD) δ 1.52–1.90 (m, 12 H), 2.14 (s, 3 H), 2.64 (br s, 2 H), 6.47 (s, 1 H). Thermal decomposition gives only admanatanone and formic acetic anhydride with chemiluminescence characteristic of adamantanone fluorescence.

(10) ^1H NMR ($(CD_3)_2CO$) δ 1.34–1.71 (br s, 4 H), 1.82–2.22 (br s, 4 H), 2.07 (s, 3 H), 5.93 (m, 1 H), 6.39 (s, 1 H).

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alternative open zwitterions **7** and **8** cannot give directly the acyl-shifted and ene products, respectively, and in our view are therefore less likely candidates. When an appropriate allylic hydrogen is available, the intermediate follows a path to the ene product regardless of solvent. Lacking an appropriate hydrogen, cyclization to the dioxetane predominates in methanol, where intermolecular hydrogen bonding satisfies part of the negative charge of the intermediate. In acetone, where external hydrogen bonds are unavailable, stronger interaction with the carbonyl group leads exclusively to the acyl-shifted product.

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o-Iodosobenzoate: Catalyst for the Micellar Cleavage of Activated Esters and Phosphates

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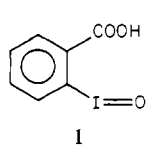
Long ago, *o*-iodosobenzoic acid (**1**) was suggested to exist in



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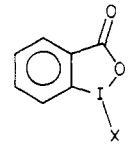

2, X = OH
3, X = O^-
4, X = $OCOCH_3$

its 1-hydroxy-1,2-benziodoxolin-3-one valence tautomeric form (**2**).[1] Cogent support for this proposal appeared in 1965.[2] From the anomalously high pK_a of **1** or **2** (variously given as 6.22[2] or 7.4[3]), we infer that its conjugate base, anion **3**, could be a potent O nucleophile near neutral pH. However, despite its well-established biochemical role as an oxidant of protein thiol groups,[4] the nucleophilic properties of *o*-iodosobenzoic acid (*o*-IBA) have not been defined.

We now report that, when solubilized in aqueous micellar solutions of cetyltrimethylammonium chloride (CTACl) at pH 8, *o*-IBA is an efficient cleavage reagent for *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl diphenyl phosphate (PNPDPP). More importantly, in the presence of excess substrate, *o*-IBA rapidly "turns over"; i.e., it is a true catalyst. Finally, the kinetic inactivity (under comparable conditions) of *m*-iodosobenzoic acid leaves little doubt that the functional group cooperativity expressed in structures **2** or **3** is essential to the catalytic activity of *o*-IBA.

Pseudo-first-order rate constants for cleavages of PNPA under various reaction conditions appear in Table I. In the absence of CTACl (run 1), nonmicellar catalysis by *o*-IBA is minimal, and the reaction is slow. Micellar cleavages are also sluggish when *o*-IBA is omitted (run 2) or when such bogus catalysts as benzoic acid (run 3) or *m*-iodosobenzoic acid[5] are added.[6] However, when 10^{-4} M *o*-IBA and 10^{-5} M PNPA are reacted in the presence of increasing concentrations of CTACl, we observe a [surfactant]/rate constant profile typical[7] of micelle-catalyzed reactions (cf. Figure 1).

Table I. Rate Constants for Cleavages of PNPA by *o*-Iodosobenzoate[a]

run	[CTACl], M	10^4[2], M	$10^4 k_\psi$, s^{-1}
1	1.0×10^{-2} [b]	1.0	2.64 ± 0.03
2	1.0×10^{-2}	0.0	4.05 ± 0.05
3	1.0×10^{-2}	1.0[c]	4.45 ± 0.16
4	1.0×10^{-2}	1.0[d]	6.20 ± 0.02
5	1.0×10^{-4}	1.0	2.66 ± 0.06
6	1.0×10^{-2}	1.0	180 ± 2.5
7	2.0×10^{-2}	1.0	185 ± 1.0
8[e]	1.0×10^{-2}	1.0	238 ± 9.0

[a] Conditions: 0.02 M phosphate buffer, 1.1 vol % DMF, pH 8.0, μ = 0.08 (NaCl), 26 ± 0.5 °C. The substrate concentration was 1×10^{-5} M, and the reactions were followed by the release of *p*-nitrophenoxide ion at 400 nm. Reproducibilities are average deviations of at least two determinations. [b] $Me_4N^+Cl^-$ instead of CTACl. [c] Benzoic acid instead of 2. [d] *m*-iodosobenzoic acid instead of 2. [e] pH 7.88 and PNPDPP instead of PNPA.

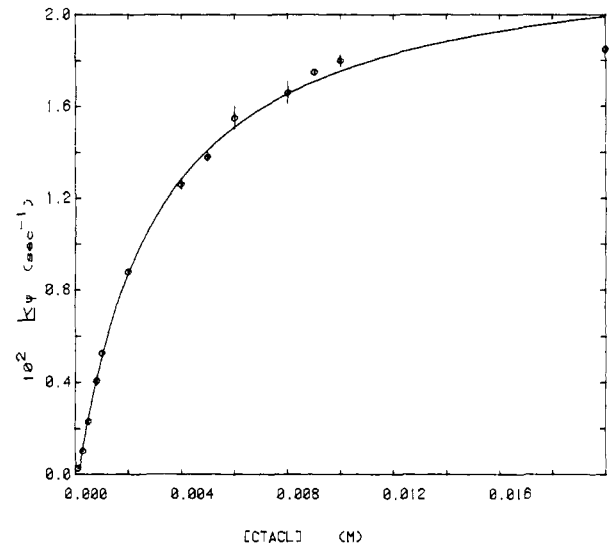

Figure 1. Pseudo-first-order rate constants, k_ψ (s^{-1}) vs. [CTACl] (M) for the micellar cleavage of 1×10^{-5} M PNPA by 1×10^{-4} M *o*-iodobenzoic acid. For other reaction conditions, see Table I and text. The solid line is generated from Lineweaver–Burke parameters described in the text.

Rate constants determined at 13 CTACl concentrations, ranging from 1.0×10^{-4} M (submicellar, run 5, Table I) to 2.0×10^{-2} M (run 7), appear in the figure; k_ψ reaches a maximum value ($\sim 1.8 \times 10^{-2}$ s^{-1}) at $\sim 1.0 \times 10^{-2}$ M CTACl (run 6) and then enters a plateau region. Lineweaver–Burke analysis[7] of these data gives $k_{micellar} = 2.18 \times 10^{-2}$ s^{-1} and $K/N = 362$ M^{-1}, where K/N is the ratio of the binding constant (for PNPA and/or **2**) to the micellar aggregation number. The solid line in Figure 1, which is generated from these parameters and a best-fit critical micelle concentration of 3×10^{-4} M, agrees very well with the experimental data up to the beginning of the plateau. From $k_{micellar}$ and $k_{buffer} = 1.8 \times 10^{-5}$ s^{-1} (for uncatalyzed cleavage of PNPA under closely comparable buffer conditions[6]), we obtain a factor of

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