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Structural Effects of Olefins in the Photooxygenation with Electron-Accepting Sensitizers. Kinetic Approach to Reactive Intermediates

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Pulsed laser excitation studies on the reactive species in 9-cyanoanthracene(CNA)-sensitized oxygenation of 1,1-diphenyl-2-methylpropene (**1a**) and (*E*)-2,3-diphenyl-2-butene (**1b**) show that the reaction course is mostly governed by competitive quenching of the CNA excited singlet by **1** and oxygen to produce $1^{+\cdot}$ and $^1O_2$, respectively. The results indicate that the reaction courses of tetraphenylethylene and 2,3-dimethyl-2-butene, for example, can be explained by exclusive quenching of sensitizer singlets by the olefin and oxygen, respectively.

There remains controversy in reactive oxygen species in electron-transfer induced oxygenation of olefins.[1] The excited singlet state of cyanoaromatic sensitizers accepts an electron from olefins in acetonitrile to give the olefin radical cations and the sensitizer radical anions, and the subsequent reactions under oxygen afford various types of products depending on the structure of olefins.[2-6] Arylethylenes such as tetraphenylethylene[2,3] and (*E*)-stilbene[4] are reported to afford carbonyl compounds accompanied by oxiranes or other oxygenated products possibly through reactions of the olefin radical cations with superoxide anions ($O_2^{-\cdot}$) generated by secondary electron transfer from the acceptor radical anions to oxygen. On the other hand, alkenes exhibit completely different behavior; 2,3-dimethyl-2-butene[5] and 1,2-dimethylcyclohexene[6] give almost exclusively hydroperoxides through the ene-reaction with singlet oxygen produced by energy transfer from the sensitizer excited states.

To get deeper insight into the reaction mechanism and the factors controlling the reaction course of electron acceptor-sensitized oxygenation of olefins, we attempted a kinetic approach to determine the reaction rates for various reactive intermediates. 1,1-Diphenyl-2-methylpropene (**1a**) and (*E*)-2,3-diphenyl-2-butene (**1b**) were examined in acetonitrile in the presence of 9-cyanoanthracene (CNA) by laser excitation as well as steady irradiation (for **1a**). 9,10-Dicyanoanthracene-sensitized oxygenation of (*Z*)- and (*E*)-2,3-diphenyl-2-butene occurs exclusively via the singlet-oxygen pathway in carbon tetrachloride; however, in acetonitrile the singlet-oxygen and electron-transfer oxygenations compete with one another.[3]

Irradiation of CNA (2×10^{-4} M, M = mol dm^{-3}) with **1a** (0.01 M) in acetonitrile under oxygen with 405-nm light from a high-pressure mercury lamp yielded benzophenone (**2**), an oxirane (**3**), a hydroperoxide (**4**), and an

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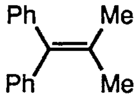
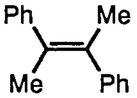
enal (**5**) (29, 13, 21, and 11%, respectively, based on **1a** consumed).7) Hydroperoxide **4** arises undoubtedly from the reaction of **1** with singlet oxygen since, in a control experiment, rose bengal-sensitized oxygenation of **1a** in acetonitrile with visible light almost exclusively afforded **4** in 90% yield. Products **2**, **3**, and **5** can arise from free radical pathways since di-*t*-butyl peroxide- (photolysis at 313 nm) or azobisisobutyronitrile-initiated (thermolysis at 80 °C) autoxidation of **1a** gave **2**, **3**, and **5** (in comparable yields of **2** and **3** with a small amount of **5**). **2** was also afforded in a considerable yield in the anodic oxidation of **1a** (platinum electrodes, 1.65 V vs. SCE) under oxygen in acetonitrile. Olefins often give carbonyl compounds and oxiranes in various pathways. However, the production of hydroperoxide **4** and enal **5** on CNA sensitization clearly indicates the generation of singlet oxygen and allylic radicals, $Ph_2C{=}CMeCH_2\cdot$, as intermediates; the latter reacts with oxygen to give peroxyl radicals, subsequently affording **5** through several steps.


1a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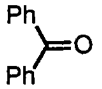
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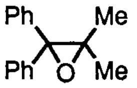
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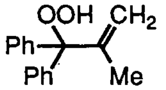
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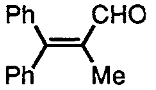
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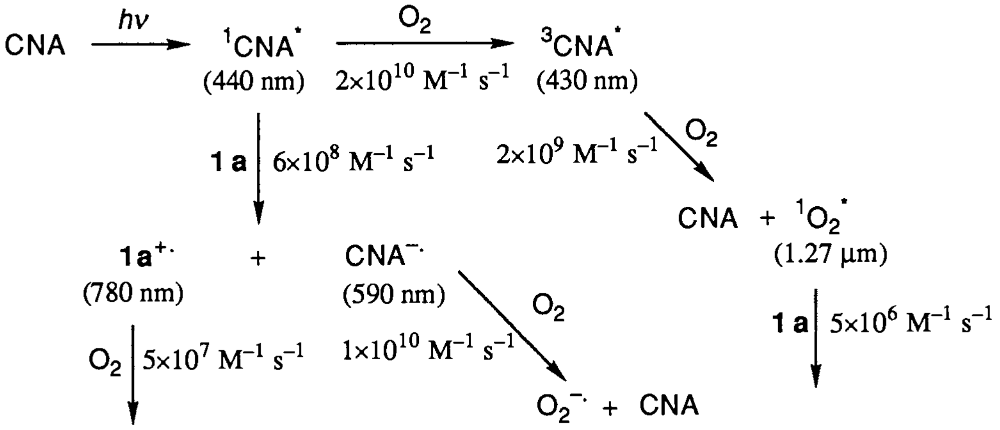
Fluorescence of CNA (lifetime τ_S = 16.8 ns) was effectively quenched by **1a** and **1b** in acetonitrile with rate constants of 6.0×10^8 and 8.0×10^8 M^{-1} s^{-1}, respectively. The estimated free energy change associated with electron transfer from ground-state **1a** or **1b** to excited singlet CNA shows that this process is exothermic.8–10) The CNA fluorescence was also quenched by oxygen with an almost diffusion-controlled rate constant, 1.6×10^{10} M^{-1} s^{-1}. Therefore, under the above oxygenation conditions ([**1a**] = 0.01 M, $[O_2] \approx 0.01$ M), the CNA singlet is quenched ≈30 times more effectively by molecular oxygen than by **1a**.

Pulsed laser excitation11) of acetonitrile solutions of CNA and **1a** afforded transient absorptions assignable to $CNA^{-\cdot}$ (λ_{max} 590 nm)12) and radical cation **1a**$^{+\cdot}$ (760–800 nm).13) These absorptions decayed with nearly the same rate constants under argon according to second-order kinetics due to their recombination. However, in the presence of oxygen, the decay curves of these absorptions consisted of first- and second-order components (**1a**$^{+\cdot}$ + $CNA^{-\cdot}$ or $O_2^{-\cdot}$); from the first-order components whose decay rates were linearly dependent on oxygen concentration, the quenching rate constants by oxygen were estimated as 1.1×10^{10} for $CNA^{-\cdot}$ and 4.8×10^7 M^{-1} s^{-1} for **1a**$^{+\cdot}$ The former value shows an efficient formation of superoxide anions under oxygen, and the latter value is ten times larger than those for stilbene derivatives reported previously;14) for example, 1.3×10^6 M^{-1} s^{-1} for (*E*)-stilbene radical cations. Similar studies on **1b** afforded a rate constant of 2.6×10^8 M^{-1} s^{-1} for **1b**$^{+\cdot}$ + O_2 reaction.15) Thus, **1a**$^{+\cdot}$ and **1b**$^{+\cdot}$ react with oxygen at much higher rates than alkene radical cations such as adamantylideneadamantane radical cations (5600 M^{-1} s^{-1}).16) These results indicate that the rate constant of reaction of olefin radical cations with oxygen varies in a wide range depending on the structure of olefins.

The quantum yield for intersystem crossing of CNA is very low (ϕ_{isc}=0.025);17) however, oxygen accelerates intersystem crossing of the CNA excited singlet.18) The efficiency of the acceleration was measured in acetonitrile by the emission-absorption method;19) a factor of k_{isc}'/k_{isc} was obtained to be 8900 M^{-1}, where k_{isc} is the rate constant for intersystem crossing of the CNA excited singlet and k_{isc}' is a second-order rate constant for oxygen-induced intersystem crossing. Use of ϕ_{isc}=0.025 and τ_S=16.8 ns affords $k_{isc} = 1.5\times10^6$ s^{-1} and $k_{isc}' = 1.3\times10^{10}$ M^{-1} s^{-1}. Under the above oxygenation conditions ([**1a**] = 0.01 M, $[O_2] \approx 0.01$ M), the quantum yield for CNA triplet formation is estimated to be nearly 0.3. The CNA triplet has a sufficient excitation energy (174 kJ mol^{-1})20) to excite $^3O_2$ to $^1O_2$ (94 kJ mol^{-1}), and is efficiently quenched by oxygen in acetonitrile (k_q=2.3×10^9 M^{-1} s^{-1}), as determined by monitoring its T-T absorption at 430 nm.17)

The production of singlet oxygen on excitation of CNA in the presence of oxygen was confirmed by observing its near-infrared emission at 1.27 μm, and the quantum yield for emission was measured to be ≈ 0.1 under air by using benzophenone as a standard (ϕ_Δ=0.29 in benzene, where ϕ_Δ is the quantum yield for $^1O_2$ formation on triplet quenching).[21] The decay of $^1O_2$ emission was accelerated by the addition of **1a** or **1b**. The rate constants for quenching of $^1O_2$ by **1a** and **1b** were determined to be 5.0×10^6 and 1.0×10^6 M^{-1} s^{-1}, respectively, by using benzophenone as a sensitizer for $^1O_2$ generation under air. These values are much lower than that reported for 2,3-dimethyl-2-butene, one of the most reactive olefins with $^1O_2$, 2.2×10^7 M^{-1} s^{-1}.[22]



Scheme 1.[23]

The direct observation of the intermediates concerned as well as the formation of various products, some of which are typical for specific pathways, clearly indicates the participation of several pathways in the present oxygenation. It is to be noted that the present olefins, **1a** and **1b**, exhibit intermediate behavior[3] between the olefins substituted only by alkyl groups and those substituted only by aromatic groups in the photooxygenation sensitized by electron acceptors. As exemplified above for CNA and **1a** (Scheme 1),[23] the sensitizer singlets interact more rapidly with molecular oxygen than with the substrates, and the intersystem crossing of the sensitizer is very much accelerated by molecular oxygen to result in efficient generation of singlet oxygen. Thus, for olefins highly reactive with singlet oxygen such as alkyl-substituted olefins, singlet oxygen plays an exclusive role in their oxygenation. However, for olefins less reactive with singlet oxygen such as aralkenes, the olefin radical cations (reactive with $O_2^{-\cdot}$ or O_2) or the species derived from them such as allylic radicals play an important role in the oxygenation. Therefore, it is reasonable to conclude that the reactivity and reaction courses of various olefins in CNA- or 9,10-dicyanoanthracene-sensitized oxygenation are strongly governed by their reactivity with singlet oxygen.

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7) Product yields were determined by GLPC. Those of **4** were determined as the corresponding alcohol after treating the reaction mixtures with triphenylphosphine.

8) The free energy change ($-\Delta G^\circ$=7.5–12 kJ mol^{-1} for CNA singlets) was estimated according to the Rehm-Weller equation[9] from the following values: $E(\mathbf{1a}^{+\cdot}/\mathbf{1a})$=1.61 V, $E(\mathbf{1b}^{+\cdot}/\mathbf{1b})$=1.57 V,[10] $E(\mathrm{CNA}/\mathrm{CNA}^{-\cdot})$ =–1.41 V,[1b] E_S(CNA)=3.04 eV.[1b]

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23) The figures in parentheses show the wavelengths of emission or absorption of the intermediates as indicated in text.

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