

presence of C=O and SiMe but no Si-O-Si groups. UV maxima was found at 305 nm.

The present new method of preparing polysilylenes is quite versatile in designing new polymers. The work is supported in part by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, No. 63106003).

Time-Resolved Study of the Photooxygenation of 3-Hydroxyflavone

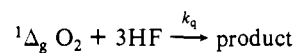
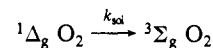
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3-Hydroxyflavones (Scheme I) are prototype molecules¹ for studying the dynamics of the proton-transfer reaction in the excited state as well as in the ground state. Their lasing action has been reported with a high efficiency of laser gain.²⁻⁴ Unfortunately, a major obstruction to the practical application of 3-hydroxyflavones as laser dyes is due to a photochemical reaction possibly involving molecular oxygen. In this communication we report a direct time-resolved study of the photooxygenation of 3-hydroxyflavone (3HF) in the normal state as well as in the tautomer state. Our results not only provide a detailed mechanism of the photooxygenation reaction but also give indirect evidence to support the role of the triplet state in the reverse proton-transfer reaction.

(i) **In the Normal State.** Studies of the 3HF (normal form) + $^1\Delta_g$ O₂ reaction have been reported by Matsuura and co-workers.^{5,6} By analyzing the photosensitization products, they proposed that 3HF undergoes the ene-ol type concerted reaction⁷ with $^1\Delta_g$ O₂ (mechanism a, Scheme I) to form the ketohydroperoxide intermediate i. In this course of study, the dynamics of the 3HF + $^1\Delta_g$ O₂ reaction was monitored by a time-resolved $^1\Delta_g$ O₂ emission (1.27 μ) detected by a near-infrared detection system.¹⁹ The sensitizer, either rose bengal, tetraphenylporphine, or tetrakis(4-sulfatophenyl)porphine, was excited at 532 nm in aerated 3HF solution. The dynamics of the quenching of $^1\Delta_g$ O₂ in the presence of 3HF can be expressed by



$$[^1\Delta_g \text{ O}_2] = [^1\Delta_g \text{ O}_2]_0 e^{-k_{\text{obs}} t}$$

$$k_{\text{obs}} = k_{\text{sol}} + k_q[3\text{HF}]$$

In the above equations, k_{sol} is the rate constant for solvent deactivation, k_q is the rate constant for the chemical quenching, and $[^1\Delta_g \text{ O}_2]_0$ is the initial concentration of $^1\Delta_g$ O₂. In a pseudo-first-order approximation, k_q is obtained by a Stern-Volmer plot of k_{obs} versus [3HF]. The results in Table I clearly demonstrate that the rate of quenching of $^1\Delta_g$ O₂ by 3HF is highly dependent on the chosen solvent. The bimolecular quenching rate constants in the nonpolar solvents, which vary from 1.6×10^4 to $1.87 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, are indicative of theoretical physical quenching rate constants of $^1\Delta_g$ O₂. This point is illustrated by observing the bimolecular quenching rate constant to be 1.5×10^4 and $1.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for 3-methoxyflavone (3MeOF) in C₆D₆ and CCl₄, respectively. 3MeOF is a compound which is chemically inert to $^1\Delta_g$ O₂ in nonpolar solvent due to the lack of the hydroxyl proton.⁹ These results are consistent with the negligible yield of products in the steady-state photolysis experiment of 3HF performed in our laboratory.¹⁰ We therefore conclude that 3HF (normal form) is chemically inert to $^1\Delta_g$ O₂ in nonpolar solvent.

Realizing that the solvents used in our experiments are different from those used by Matsuura et al., a photosensitization experiment was carried out in pyridine. The value of k_q in pyridine was observed to be $7.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is ~ 4 orders of magnitude larger than that in nonpolar hydrocarbon solvents. However, the absorption spectrum of 3HF in pyridine, unlike that in hydrocarbon solvent, has a long wavelength absorption band with a maximum at 450 nm. Upon excitation at 450 nm, an emission spectrum shows a maximum at 512 nm. These spectral features suggest that the anion species is present in pyridine. Hence, the anion form of 3HF in pyridine may be responsible for the anomalous increase of reactivity toward $^1\Delta_g$ O₂. In order to verify this proposal, the study of the 3HF + $^1\Delta_g$ O₂ reaction was performed in aqueous solution. In basic H₂O (pH = 12.0) and D₂O solution (pD = 12.0) in which the anion form of 3HF (or 3DF) predominates, k_q was observed to be 2.2×10^8 and $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. However, k_q was observed to be $2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in acidic D₂O solution (pD = 3),¹¹ which is the same order of magnitude as that in CH₃OH.

We now propose a 3HF + $^1\Delta_g$ O₂ reaction mechanism which encompasses the experimental results for a broad range of solvents. A photodynamic study of 3HF by Strandjord and Barbara^{14,15} indicates that the intramolecular hydrogen bond remains intact even in strong hydrogen bonding solvents such as MeOH. In other words, the enol proton forms a planar five-membered ring, a position in which abstraction of this proton by $^1\Delta_g$ O₂ is not facile. Hence, we suggest an alternative reaction pathway (mechanism b, Scheme I) to that proposed by Matsuura et al. (mechanism a). We propose that addition of $^1\Delta_g$ O₂ at carbons 2 and 4 of the γ -pyrone ring may take place (mechanism b) with concomitant proton transfer between the hydroxyl proton and carbonyl oxygen to form the five-membered cyclic peroxide ii. The increase of chemical reactivity of 3HF toward $^1\Delta_g$ O₂ in polar solvents can be rationalized by solvent stabilization of the transition state which presumably has a large dipole moment. It is noteworthy that there is an ~ 2.5 -fold increase of k_q in CH₃OH in comparison with

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(7) An alternative mechanism involving a four-membered cyclic peroxide was also proposed by Matsuura et al. to explain the liberation of carbon dioxide upon UV irradiation. However, irradiation at $\lambda > 455 \text{ nm}$ shows no significant CO₂ production. Thus, in this communication only the mechanism shown in Scheme I is discussed.

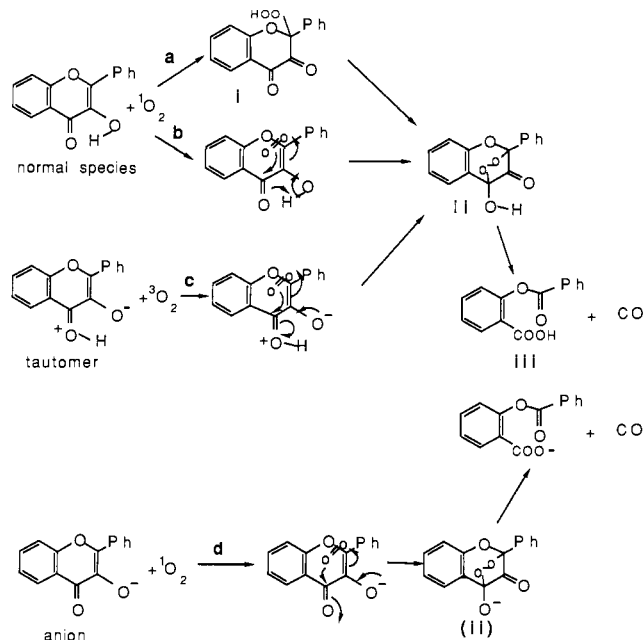
(8) In order to minimize the error in the curve fitting procedure due to a small k_q in comparison to k_{sol} , deuterium isotopes were used for some solvents.

(9) Although it is stable in nonpolar solvents, our results show that 3MeOF is extremely photosensitive in protic solvents. This type of photoreaction has been reported in ref 13 and 15.

(10) In the course of a steady-state photolysis experiment of 3HF in which $^1\Delta_g$ O₂ was sensitized by either rose bengal (RB) or tetraphenylporphyrin (TPP) dye excited at $\lambda > 455 \text{ nm}$ (150 W Xe lamp coupled with CuSO₄ 5H₂O and SG455 filters), the starting material (3HF) was quantitatively recovered after prolonged irradiation ($\sim 4 \text{ h}$) in various nonpolar solvents.

(11) Since the solubility of 3HF in acidified D₂O is low, 15% of CH₃OD was added to increase the solubility.

Scheme I



CD₃OD. This result implies that the rate-determining step for the 3HF + ¹Δ_g O₂ reaction may be due to the thermally activated proton transfer during the peroxidation reaction. The extremely high reactivity of the 3HF anion species toward ¹Δ_g O₂ is due to the strong nucleophilic C=C-O⁻ enolate ion which reacts with the electrophilic ¹Δ_g O₂ (mechanism d).¹²

(ii) **In the Tautomer State.** The photooxygenation was also performed upon direct excitation (320–360 nm) of 3HF in O₂-saturated nonpolar solvents. The reaction product is qualitatively the same as that of the sensitization experiment. According to the above results, the mechanism of the photoreaction cannot be ascribed to the 3HF (normal form) + ¹Δ_g O₂ reaction. Since the proton-transfer reaction of 3HF occurs rapidly in the excited state,¹ the tautomer is concluded to be the reactive species. On the basis of the mechanism deduced from the 3HF (normal form) + ¹Δ_g O₂ reaction, the mechanism of the tautomer + ³Σ_g O₂ reaction can be rationalized by the strong electrophilic C=OH⁺ functional group and the highly nucleophilic C=C-O⁻ functional group of the tautomer species (mechanism c).

The possible role of the tautomer S₁ state in the photooxygenation reaction is ruled out since the quenching of the steady-state tautomer emission by molecular oxygen (³Σ_g O₂ state) is negligible. Applying transient absorption and two-step laser excitation (TSLE) techniques, the existence of a long-lived tautomer ground state (lifetime of ~13 μs in nonpolar solvent) has been reported by Itoh et al.¹¹⁻¹³ We recently confirmed Itoh's results, but the assignment of the long-lived tautomer species to either the ground state or the triplet state is uncertain. By monitoring the dynamics of the transient tautomer emission from a TSLE experiment,¹⁴ our results show that ³Σ_g O₂ quenches the long-lived tautomer species with a bimolecular rate constant of 3 × 10⁹ M⁻¹ s⁻¹. However, the yield of the photoreaction monitored by the decrease of absorbance at 360 nm is <0.01, indicating that the rate of quenching by ³Σ_g O₂ is dominated by physical deactivation. The observed quenching rate constant by ³Σ_g O₂ is close to 1/9 of the diffusional controlled rate, which is the expected value for a T-T energy transfer based on theoretical calculations.¹⁴ Furthermore, the tautomer triplet state + ³Σ_g O₂ reaction is spin allowed, while the tautomer (S₀) + ³Σ_g O₂ reaction to form the five-membered cyclic peroxide (ii, Scheme I) is strictly

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Table I. Solvent Quenching Rate Constants (k_{sol}) of ¹O₂ and Bimolecular Quenching Rate Constants for the 3HF + ¹O₂ Reaction (k_q)

| solvent | k_{sol}^{-1} (μs) | | k_q (M ⁻¹ s ⁻¹) |
|---------------------------------------|----------------------------|--------------------|--|
| | this work | literature | |
| CCl ₄ | 769 | 900 (16), 700 (17) | 1.72 × 10 ⁴ |
| C ₆ H ₆ | 30 | 32 (16) | 1.87 × 10 ⁴ |
| C ₆ D ₆ (95%-d) | 250 | 700 (18) | 1.6 × 10 ⁴ |
| CH ₃ CN | 83 | 87 (19), 68 (20) | 1.05 × 10 ⁵ |
| CD ₃ CN | 1219 | 599 (19), 621 (21) | 1.14 × 10 ⁵ |
| CH ₃ OH | 10.25 | 10.4 (21) | 2.3 × 10 ⁵ |
| CD ₃ OD | 245 | 227 (21) | 9.0 × 10 ⁴ |
| C ₅ H ₅ N | 5.7 | | 7.5 × 10 ⁷ |
| D ₂ O (pD = 3) | 70 | 63 (19) | 2.5 × 10 ⁵ |
| D ₂ O (1.0 N NaOD) | 64 | | 1.9 × 10 ⁸ |
| H ₂ O (1.0 N NaOH) | 4.1 | 4.1 (19), 4.2 (21) | 2.3 × 10 ⁸ |

a spin forbidden process. Thus, the long-lived transient species is likely ascribed to the tautomer triplet state rather than the singlet ground state.¹¹⁻¹³ If this is the case, the observed 437 nm transient absorption band^{11,14} can be interpreted as the tautomer T₁ → T_n transition. In order to explain the observed tautomer emission from the TSLE experiment, we further propose that the excitation of the tautomer triplet state to a highly excited triplet state by the probe pulse (437 nm) is followed by rapid intersystem crossing to a tautomer excited singlet state (S_n), which subsequently leads to the observed tautomer fluorescence. It is noted, however, that the high efficiency of the T-S intersystem crossing is quite anomalous for nonhalogenated aromatic compounds.^{22,23} Further research focusing on the intriguing photophysics of the triplet state is currently in progress.

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Metal Oxide Bound Rhodium Dioxygen and Ozone Complexes

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The search for species capable of catalyzing oxidation of organic substrates by oxygen or by simple oxidizing reagents has been assisted by the development of catalyst species which are themselves nondegradable under oxidizing reaction conditions. In this regard, metal oxides have long been known as oxidation catalysts¹ of tremendous value. Soluble analogues² of many of these oxides have been created to help understand the reactivity of bulk materials; species with properties different from those exhibited by bulk materials may be obtained through controlled synthesis. Our approach³ involves preparing, in a controlled fashion, surface-bound organometallic species, and we now report the oxidation of two such rhodium species which can be converted under mild

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