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

Shannon L. Studer, William E. Brewer, Marty L. Martinez, and Pi-Tai Chou*

Department of Chemistry, University of South Carolina Columbia, South Carolina 29208

Received April 28, 1989

3-Hydroxyflavones (Scheme I) are prototype molecules[1] 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-hydroxy-flavones 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 tau-tomer 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) + $^1\Delta_g$ O_2 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 reaction[7] with $^1\Delta_g$ O_2 (mechanism a, Scheme I) to form the ketohydro-peroxide intermediate i. In this course of study, the dynamics of the 3HF + $^1\Delta_g$ O_2 reaction was monitored by a time-resolved $^1\Delta_g$ O_2 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 $^1\Delta_g$ O_2 in the presence of 3HF can be expressed by

$$^1\Delta_g\ O_2 \xrightarrow{k_{sol}} {}^3\Sigma_g\ O_2$$

$$^1\Delta_g\ O_2 + 3HF \xrightarrow{k_q} \text{product}$$
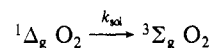
$$[^1\Delta_g\ O_2] = [^1\Delta_g\ O_2]_0 e^{-k_{obs}t}$$

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

In the above equations, k_{sol} is the rate constant for solvent deactivation, k_q is the rate constant for the chemical quenching, and $[^1\Delta_g\ O_2]_0$ is the initial concentration of $^1\Delta_g\ O_2$. In a pseu-do-first-order approximation, k_q is obtained by a Stern–Volmer plot of k_{obs} versus [3HF]. The results in Table I clearly dem-onstrate that the rate of quenching of $^1\Delta_g\ O_2$ 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 1.87×10^4 M^{-1} s^{-1}, are indicative of theoretical physical quenching rate constants of $^1\Delta_g\ O_2$. This point is illustrated by observing the bimolecular quenching rate constant to be 1.5×10^4 and 1.9×10^4 M^{-1} s^{-1} for 3-methoxyflavone (3MeOF) in C_6D_6 and CCl_4, respectively. 3MeOF is a compound which is chemically inert to $^1\Delta_g\ O_2$ 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 $^1\Delta_g\ O_2$ in nonpolar solvent.*

Realizing that the solvents used in our experiments are different from those used by Matsuura et al., a photosensitization exper-iment was carried out in pyridine. The value of k_q in pyridine was observed to be 7.5×10^7 M^{-1} 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 $^1\Delta_g\ O_2$. In order to verify this proposal, the study of the 3HF + $^1\Delta_g\ O_2$ reaction was performed in aqueous solution. In basic H_2O (pH = 12.0) and D_2O 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 1.9×10^8 M^{-1} s^{-1}, respectively. However, k_q was observed to be 2.5×10^5 M^{-1} s^{-1} in acidic D_2O solution (pD = 3),[11] which is the same order of magnitude as that in CH_3OH.

We now propose a 3HF + $^1\Delta_g\ O_2$ reaction mechanism which encompasses the experimental results for a broad range of solvents. A photodynamic study of 3HF by Standjord and Barbara[1i,j] in-dicates 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 $^1\Delta_g\ O_2$ 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 $^1\Delta_g\ O_2$ 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 $^1\Delta_g\ O_2$ 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 CH_3OH in comparison with

(1) (a) Sengupta, P.; Kasha, M. *Chem. Phys. Lett.* **1979**, *68*, 382. (b) Woolfe, G. J.; Thistlethwaite, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 6916. (c) Itoh, M.; Tokumura, K.; Tanimoto, Y.; Okada, Y.; Takeuchi, H.; Obi, K.; Tanaka, I. *J. Am. Chem. Soc.* **1982**, *104*, 4146. (d) Salman, O. A.; Drick-amer, H. G. *J. Chem. Phys.* **1981**, *75*, 572. (e) Strandjord, A. J. G.; Courtney, S. H.; Friedrich, D. M.; Barbara, P. F. *J. Phys. Chem.* **1983**, *87*, 1125. (f) Strandjord, A. J. G.; Barbara, P. F. *Chem. Phys. Lett.* **1983**, *98*, 21. (g) McMorrow, D.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 2235. (h) McMorrow, D.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.* **1984**, *81*, 3375. (i) Strandjord, A. J. G.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 2355. (j) Strandjord, A. J. G.; Smith, D. E.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 2362. (k) McMorrow, D.; Dzugan, T. P.; Aartsma, T. J. *Chem. Phys. Lett.* **1984**, *103*, 492. (l) Itoh, M.; Tanimoto, Y.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 3339. (m) Itoh, M.; Fujiwara, Y. *J. Phys. Chem.* **1983**, *87*, 4558. (n) Itoh, M.; Fujiwara, Y.; Sumitani, M.; Yoshihara, K. *J. Phys. Chem.* **1986**, *90*, 5672. (o) Itoh, M.; Fujiwara, Y. *Chem. Phys. Lett.* **1986**, *130*, 365. (p) Dick, B.; Ernsting, N. P. *J. Phys. Chem.* **1987**, *91*, 4261. (q) Brucker, G. A.; Kelley, D. F. *J. Phys. Chem.* **1987**, *91*, 2856. (r) Brucker, G. A.; Kelley, D. F. *J. Phys. Chem.* **1988**, *92*, 3805. (s) Dzugan, T.; Schmidt, J.; Aartsma, T. J. *Chem. Phys. Lett.* **1986**, *127*, 336.

(2) Chou, P. T.; McMorrow, D.; Aartsma, T. J.; Kasha, M. *J. Phys. Chem.* **1984**, *88*, 4596.

(3) Chou, P. T.; Aartsma, T. J. *J. Phys. Chem.* **1986**, *90*, 721.

(4) Parthenopoulos, D. A.; Kasha, M. *Chem. Phys. Lett.* **1988**, *146*, 77.

(5) Matsuura, T.; Matsushima, H.; Sakamoto, H. *J. Am. Chem. Soc.* **1967**, *89*, 6370.

(6) Matsuura, T.; Matsushima, H.; Nakashima, R. *Tetrahedron* **1970**, *26*, 435.

(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 λ > 455 nm shows no significant CO_2 production. Thus, in this communication only the mechanism shown in Scheme I is discussed.
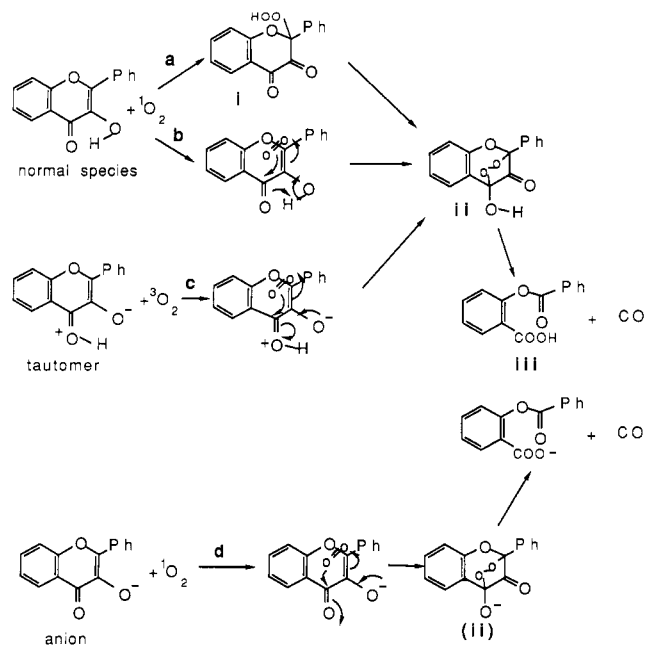
(8) In order to minimize the error in the curve fitting procedure due to a small k_q in comparison to k_{sol}, deuterium isotopes were used for some solvents.

(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 $^1\Delta_g\ O_2$ was sensitized by either rose bengal (RB) or tetraphenylporphyrin (TPP) dye excited at λ >455 nm (150 W Xe lamp coupled with $CuSO_4$ $5H_2O$ and SG455 filters), the starting material (3HF) was quantitatively recovered after prolonged irradiation (~4 h) in various nonpolar solvents.

(11) Since the solubility of 3HF in acidified D_2O is low, 15% of CH_3OD was added to increase the solubility.

Scheme I

Table I. Solvent Quenching Rate Constants (k_{sol}) of $^1O_2$ and Bimolecular Quenching Rate Constants for the 3HF + $^1O_2$ 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_6H_6	30	32 (16)	1.87×10^4
C_6D_6 (95%-d)	250	700 (18)	1.6×10^4
CH_3CN	83	87 (19), 68 (20)	1.05×10^5
CD_3CN	1219	599 (19), 621 (21)	1.14×10^5
CH_3OH	10.25	10.4 (21)	2.3×10^5
CD_3OD	245	227 (21)	9.0×10^4
C_5H_5N	5.7		7.5×10^7
D_2O (pD = 3)	70	63 (19)	2.5×10^5
D_2O (1.0 N NaOD)	64		1.9×10^8
H_2O (1.0 N NaOH)	4.1	4.1 (19), 4.2 (21)	2.3×10^8

CD_3OD. This result implies that the rate-determining step for the 3HF + $^1\Delta_g$ O_2 reaction may be due to the thermally activated proton transfer during the peroxidation reaction. The extremely high reactivity of the 3HF anion species toward $^1\Delta_g$ O_2 is due to the strong nucleophilic C=C—O⁻ enolate ion which reacts with the electrophilic $^1\Delta_g$ O_2 (mechanism d).[12]

(ii) In the Tautomer State. The photooxygenation was also performed upon direct excitation (320–360 nm) of 3HF in O_2-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) + $^1\Delta_g$ O_2 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) + $^1\Delta_g$ O_2 reaction, the mechanism of the tautomer + $^3\Sigma_g$ O_2 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 S_1 state in the photooxygenation reaction is ruled out since the quenching of the steady-state tautomer emission by molecular oxygen ($^3\Sigma_g$ O_2 state) is negligible. Applying transient absorption and two-step laser excitation (TSLE) techniques, the existence of a long-lived tautomer ground state (lifetime of $\sim$13 μs in nonpolar solvent) has been reported by Itoh et al.[11-o] 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 $^3\Sigma_g$ O_2 quenches the long-lived tautomer species with a bimolecular rate constant of 3×10^9 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 $^3\Sigma_g$ O_2 is dominated by physical deactivation. The observed quenching rate constant by $^3\Sigma_g$ O_2 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 + $^3\Sigma_g$ O_2 reaction is spin allowed, while the tautomer (S_0) + $^3\Sigma_g$ O_2 reaction to form the five-membered cyclic peroxide (ii, Scheme I) is strictly

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-o] If this is the case, the observed 437 nm transient absorption band[11,14] can be interpreted as the tautomer $T_1 \rightarrow T_n$ 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.

(15) Matsuura, T.; Takemoto, T.; Nakashima, R. *Tetrahedron* **1973**, *29*, 3337.
(16) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *104*, 2065.
(17) Salokhiddinov, K. I.; Dzhagarov, B. M.; Byteva, I. M.; Gurinovich, G. P. *Zh. Prikl. Spektrosk.* **1981**, *34*, 892.
(18) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756.
(19) Chou, P. T.; Frei, H. *J. Chem. Phys.* **1987**, *87*(7), 3843.
(20) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423.
(21) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201.
(22) Keller, R. A. *Chem. Phys. Lett.* **1969**, *3*, 27.
(23) Keller, R. A. *Molecular Luminescence*; W. A. Benjamin, Inc.: New York, 1969; p 453.

Metal Oxide Bound Rhodium Dioxygen and Ozone Complexes

H. Eric Fischer and Jeffrey Schwartz*

*Department of Chemistry, Princeton University
Princeton, New Jersey 08544-1009*

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 catalysts[1] of tremendous value. Soluble analogues[2] 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 approach[3] 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

(12) Saito, I.; Matsuura, T. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 511.
(13) Wolfbeis, O. S.; Knierzinger, A.; Schipfer R. *J. Photochem.* **1983**, 2167.
(14) Brewer, W. E.; Studer, S. L.; Standiford, M.; Chou, P. T. *J. Phys. Chem.*, in press.

(1) For example, see: Wachs, I. E.; Saleh, R. Y.; Chan, S. S.; Chersich, C. *Chemtech* **1985**, 756; *Appl. Catal.* **1985**, *15*, 339. Wachs, I. E.; Chan, S. S. *Appl. Surf. Sci.* **1984**, *20*, 181.
(2) For example, see: Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528 and references cited therein.
(3) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302.