*J. Am. Chem. Soc.* **1989**, *111*, 3542-3548

# Fluorescence Studies of Furanoxy Radicals: Intramolecular and Intermolecular Processes

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**Abstract:** Fluorescence properties of furanoxy radicals were used to investigate intramolecular relaxation and intermolecular quenching processes involving these organic doublet species. The emission spectra of several substituted furanoxy radicals are given; maxima lie in the 615–660-nm region. Excited-state lifetimes were measured and lie in the 6–13-ns range. There were solvent effects on the lifetimes as well as on the absorption and emission spectra. The temperature dependence of the fluorescence lifetimes was studied and found to be small, $E_a = 0.35$ kcal/mol, compared to that in benzyl radical. Rate constants of internal conversion (and fluorescence quantum yields) were estimated and found to follow a previously proposed correlation with Taft polar substituent constants. In addition to the intramolecular photophysics, quenching studies were carried out. In particular, the furanoxy radicals were used to quench the triplet of two polycyclic aromatics where transfer of energy was allowed and where sensitized fluorescence was observed ($k_q \sim 6 \times 10^9$ M$^{-1}$ s$^{-1}$). Details of an improved method for making measurements of $k_q$ between two transients are given. Recombination kinetics of the radicals were also measured using 5,5′-bis(furanones) as precursors of the radicals.

In organic photophysics, fluorescing radicals serve as luminescent, paramagnetic species in fluid solution.[2,3] Such probes are of interest since they can be used to elucidate the mechanisms of quenching of singlets and triplets by paramagnetic species. By use of fluorescing radicals, it has been demonstrated that energy transfer can take place in the quenching of triplet states by radicals.[4,5] Quantitative measurements with benzophenone ketyl radicals have shown that energy transfer is at least competing favorably with other processes in quenching events that have rate constants approaching the limit of diffusion control.[6,7] In these quenching experiments, the fluorescing radicals acted as the energy acceptor, and their sensitized fluorescence proved definitive in showing that energy transfer was occurring.

It has been hoped for some time that fluorescing radicals can be used to understand more fully radiationless processes.[8] They provide possibly the simplest case of a two-state system. In radicals, the lowest electronically excited state is thought to be a doublet. Thus all processes, both radiative and nonradiative, from this state to the ground doublet state are spin-allowed. This can be contrasted with the lowest excited state (triplet states) of stable organic molecules where all decay processes are spin-forbidden. Thus, in order to understand triplet–singlet processes it is usually necessary to go beyond a two-state model to consider couplings with other electronic manifolds.[9] Finally, the decay of the excited singlet states in organic molecules is complicated by lower triplet states.

In the current paper, we extend an earlier report on excited furanoxy radicals.[5] The furanoxy radicals have excited-state lifetimes that are long enough to permit easy time resolution by nanosecond flash photolysis systems. Other than characterizing the emission properties further, such as reporting emission spectra and lifetimes, we have looked at two features that were complicating the simple energy-transfer quenching model and the simple two-state decay model.

First, the excited benzophenone ketyl radical is known to be very reactive.[10] Even the excited diphenylmethyl radical is quite reactive.[11] The observed rate constants for the quenching of triplet states by ketyl radicals may not be very good examples of quenching processes dominated by energy transfer.[7] Since the furanoxy radicals have a lower doublet–doublet energy gap than either the benzophenone ketyl radical or the diphenylmethyl radical, they can quench (via energy transfer) triplet states of lower energy. Lowering the energy content of the triplet energy donors means that the possibility for complications from electron transfer is lessened. Then, depending on the redox properties of the furanoxy radicals, triplet quenching by them could provide a more confident estimate to a rate constant for triplet to doublet energy transfer. In this work such rate constants are measured, by an improved kinetic analysis, which allows for the extraction of second-order rate constants for the interaction between transients.

Second, the temperature studies on arylmethyl radicals indicated that either photochemistry or a third electronic state was complicating the simple behavior expected of a two-state model for radiationless transitions.[12] This was particularly true of the benzyl radical, where no photochemistry was seen, but the measured lifetime varied from ~1.5 μs at low temperatures (<120 K) to ~1 ns at room temperature[13] with an activation energy, $E_a$, of 3.8 kcal/mol.[12] The naphthylmethyl radical had already presented a case where a two-state model with a weak temperature dependence ($E_a = 0.3$ kcal/mol) was observed.[14] The diphenylmethyl[12] and 2-phenanthrylmethyl[15] radicals showed activation energies ($E_a = 0.8$ and 0.6 kcal/mol, respectively) more similar

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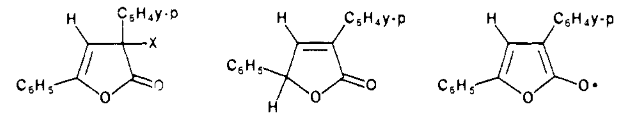
Chart I



1a, X = $CH_2C_6H_5$, y = H
1b, X = $CH_2C_6H_5$, y = $CH_3$
1c, X = $CH_2C_6H_5$, y = $OCH_3$
1d, X = $COC_6H_5$, y = H

2a, y = H
2b, y = $CH_3$
2c, y = $OCH_3$

3a, y = H
3b, y = $CH_3$
3c, y = $OCH_3$

to those of naphthylmethyl than to that of the benzyl radical. Since furanoxy radicals differ both in chemical structure and in doublet–doublet energy gap from all of these arylmethyl radicals, it was of interest to investigate the temperature dependence of their radiationless transitions.

## Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on either Perkin-Elmer Model 377 or 580 infrared spectrometers. The solvents used were all spectral grade or purified by standard procedures. Di-*tert*-butyl peroxide (DTBP) was purified by passing over an alumina column. Both benz[*a*]anthracene and chrysene were from Aldrich and were recrystallized from benzene.

**Starting Materials.** The furanones **1a**,[16] mp 148 °C, **1b**,[16] mp 164–165 °C, **1c**,[16] mp 138–139 °C, **1d**,[17] mp 186 °C, **2a**,[18] mp 107–108 °C, **2b**,[18] mp 104–105 °C, and **2c**,[18] mp 98–99 °C, and the bis(furanone) **4a**,[19] mp 287–288 °C, were prepared by reported procedures.[16-19]

**Preparation of the Bis(furanones) 4b and 4c.** To a solution of the 2(5*H*)-furanone **2b** (2.0 g, 7.6 mmol) in a mixture (1:1) of dioxane and ethanol (200 mL) was added an aqueous solution of potassium ferricyanide (2%, 50 mL). The solution was stirred at room temperature for 15 min. A methanolic solution of potassium hydroxide (10%, 10 mL) was then added, and the stirring was continued for 1 h. The precipitated solid material was filtered and washed several times with water and later with hot ethanol to give the bis(furanone) **4b**: 1.75 g, 87%; mp 258–260 °C; IR $\bar{\nu}_{max}$ (KBr) 3070, 3050, 3020, 2940 (CH), 1750 (C=O), 1620 (C=C) cm$^{-1}$. Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.93; H, 5.22. Found: C, 82.14; H, 5.18.

Treatment of **2c** (1.5 g, 5.4 mmol) with potassium ferricyanide and workup as in the earlier case gave **4c**: 1.2 g, 80%; mp 230–233 °C; IR $\bar{\nu}_{max}$ (KBr) 3080, 3050, 3000, 2950, 2830 (CH), 1750 (C=O), 1625 (C=C) cm$^{-1}$. Anal. Calcd for $C_{34}H_{26}O_6$: C, 76.98; H, 4.91. Found: C, 77.22; H, 5.18.

**Laser Flash Photolysis.** The laser flash photolysis systems have been described.[5,20,21] Various lasers were used in several combinations in the two-laser experiments, and numerous one-laser flash photolysis experiments were done. These various combinations of lasers were necessary to get sufficient concentration of transients as well as to selectively excite the appropriate substrates and/or transients.

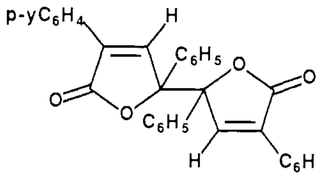
When DTBP was used as a source of *tert*-butoxy radicals, a nitrogen laser, 337 nm, was used as the photolyzing source. In these experiments, the frequency-tripled 355-nm Nd:YAG (Quanta Ray DCR-1) laser was used to excite the furanoxy radicals. This 355-nm laser was used as a single laser in the study of the temperature dependence of the fluorescence lifetimes. In the triplet–doublet quenching experiments, a 308-nm (XeCl) excimer laser was used to simultaneously excite the triplets and form the radicals. A two-laser configuration (308 nm for the first pulse and 320 nm from the Nd:YAG-pumped dye laser for the second pulse) was used for the doublet–doublet quenching experiment.

**$\gamma$ Radiolysis.** The preparation of furanoxy radicals by $\gamma$ radiolysis was carried out with a $^{60}$Co source (18 kCi), Model 109, from J. L. Shepherd & Associates, 26 000 R/min.

## Results and Discussion

**Production of Radicals.** The photogeneration of the furanoxy radicals has already been discussed in part.[5] The various radicals were produced in five different ways. First, 3-benzoyl-3,5-diphenyl-2(3*H*)-furanone (**1d**; see Chart I) was photolyzed directly resulting in cleavage of the benzoyl group from the parent molecule.[5] Second, the *tert*-butoxy radical, obtained by the photocleavage of *tert*-butyl peroxide, was used to abstract the 5-hydrogen from the 3,5-diaryl-2(5*H*)-furanones[5] (**2a–c**; see Chart I). Third, a triplet sensitization of the 3,5-diaryl-3-benzyl-2-(3*H*)-furanones (**1a–c**; see Chart I) led to the cleavage of the benzyl group in the triplet state.[5] Fourth, the oxidative 5,5′-dimers of the different 2(5*H*)-furanones [5,5′-bis(furanones), **4a–c**; see Chart II] could cleave under photoexcitation, forming two identical furanoxy radical fragments. Unfortunately all the 5,5′-bis(furanones) (**4a–c**) were very insoluble in common solvents, with the exception of pyridine. This limited their usefulness in creating high concentrations of radicals, even though two radicals could be produced from one 5,5′-bis(furanone) by one photon. A fifth method of generating the furanoxy radicals consisted of fragmentation of the radical cations of the benzylfuranones into a furanoxy radical and the benzyl carbocation.[16] The radical cations of the benzylfuranones were produced by $\gamma$ radiolysis of alkyl halide matrixes with subsequent hole transfer from the solvent radicals to the benzylfuranone.

Chart II



4a, y = H
4b, y = $CH_3$
4c, y = $OCH_3$

Table I. Solvent Effects on Fluorescence Spectra of Furanoxy Radicals

| radical | pyridine: $\lambda_{max}{}^f$/nm ($\bar{\nu}$/cm$^{-1}$) | pyridine: $\tau_M$/ns[b] | benzene/DTBP[a]: $\lambda_{max}{}^f$/nm ($\bar{\nu}$/cm$^{-1}$) | benzene/DTBP[a]: $\tau_M$/ns[b] |
|---|---|---|---|---|
| furanoxy (**3a**) | 624 (16 000) | 6.6 | 617 (16 200) | 10.7 |
| methyl (**3b**) | 651 (15 400) | 9.3 | 627 (16 000) | 12.5 |
| methoxy (**3c**) | 660 (15 200) | 10.7 | 640 (15 600) | 11.6 |

[a] Solvent (1:2) benzene to DTBP. [b] Measured (deconvoluted) fluorescence decay times.

**Fluorescence Spectra and Yields.** The fluorescence of the furanoxy radicals was initially discovered in the one-laser experiment when the benzoylfuranone **1d** was being photolyzed by 337-nm laser pulses.[5] The intrinsic nature of this emission was checked by using the two-laser technique of photolyzing the furanone

$$^1F + h\nu_1 \rightarrow {}^2R^\bullet + {}^2B^\bullet \qquad (I)$$

and then exciting any fragments at a specific delay time by a second laser

$$^2R^\bullet + h\nu_2 \rightarrow {}^2R^{\bullet *} \qquad (II)$$

The observed fluorescence comes from the $^2R^{\bullet *}$, the excited furanoxy radical. No fluorescence was observed from the benzoyl radical, $^2B^{\bullet *}$, in the time range and wavelength range under investigation. $^1F$ represents the ground state of the parent benzoylfuranone.

Additional experimentation, using a single laser pulse and studying the laser intensity dependence of the fluorescence, showed that the fluorescence was due to a two-photon mechanism,[5] namely, photolysis of the parent furanone by the first photon (process I) and excitation of the radical fragment by the second photon (process II). In the single-laser experiment both photons were of the same wavelength ($\nu_1 = \nu_2$ in the processes I and II). The standard technique of confirming a luminescence to be intrinsic involves matching the luminescence excitation spectrum of a species with its absorption spectrum. Convincing excitation spectra were difficult to run on the system because of problems

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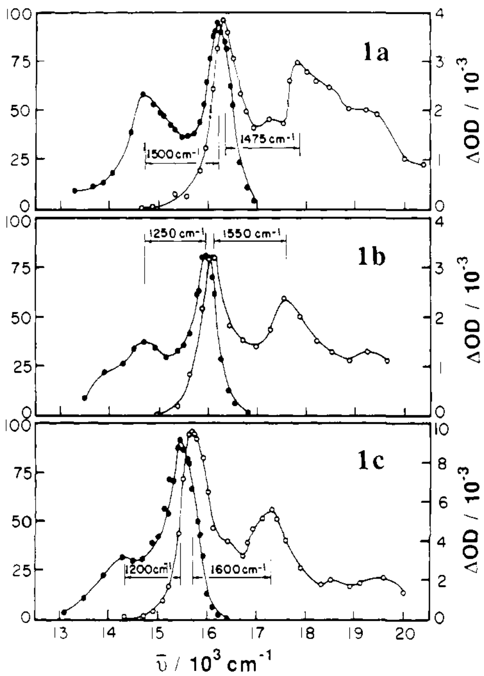

**Figure 1.** Emission and absorption spectra of furanoxy radicals in (1:2) benzene/DTBP. (a) **3a**. (b) **3b**. (c) **3c**.

**Table II.** Solvent Effects on Absorption Spectra of Furanoxy Radicals

| | $\lambda_{max}$/nm | | | |
|---|---|---|---|---|
| radical | pyridine | benzene[a] | acetonitrile[a] | benzene/ DTBP[b] |
| furanoxy (**3a**) | 380 | 370 | 365 | |
| | 455 | 445 | 445 | |
| | 560 | | | 560 |
| | 620 | 610 | 610 | 615 |
| methyl (**3b**) | 380 | 370 | 370 | |
| | 460 | 450 | 450 | |
| | 580 | | | 570 |
| | 630 | 620 | 620 | 625 |
| methoxy (**3c**) | 385 | 370 | 370 | |
| | 470 | 460 | 460 | |
| | 590 | | | 580 |
| | 650 | 640 | 635 | 640 |

[a] From ref 22. Extinction coefficients are also available from this reference. [b] Solvent (1:2) benzene to DTBP. Spectrum for $\lambda < 500$ nm not recorded.

in standardizing the dose, but a good mirror image relationship was seen between the absorption and emission spectra when plotted on an energy scale. Three such pairs of spectra are shown in Figure 1 for the mixed solvent (1:2) benzene/DTBP.

It can be seen from Table I that the fluorescence spectrum in pyridine is red-shifted relative to the spectrum in 1:2 benzene/DTBP. From Table II it can be noted that the absorption spectra of the three radicals in pyridine are also red-shifted from their corresponding absorption spectra in benzene/DTBP. This would indicate that the red-shift in fluorescence is not due simply to a solvent rearrangement in the excited state and points to a solvent effect (or complex with solvent molecules) in both the excited and ground states of the radical.

Table II contains absorption maximums of the three radicals, each in four different solvents. The three spectra in pyridine are also red-shifted relative to the corresponding spectra in acetonitrile and benzene. The results in Table II can be interpreted as indicating that red-shift in pyridine is not a polarity effect; otherwise acetonitrile, which has a large dielectric constant, should affect the spectra in a similar fashion. Also, the result in benzene[22] indicates that the aromatic ring in pyridine is not primarily responsible for the spectral shift. Even if the aromatic ring were involved, it would only explain the shifts in the excited state since $\pi$ complexes (i.e., excimers and exciplexes) are usually involved with the excited and not the ground states. By elimination, there is likely a specific pyridine–radical solvent interaction or complex.

The vibrational spacing between the two lowest energy maximums in the absorption spectra of the three radicals is consistent with the C–C stretching vibrations in aromatic hydrocarbons (see Figure 1). If the spacing between the two maximums in the fluorescence spectra of the three radicals is due to the same vibrations, then there are significant frequency shifts in **3b** and **3c**. The frequency shift of the vibration between ground and excited state in **3c** may be overestimated because of the large overlap in the emission spectrum, leading to an underestimate of the excited-state spacing. Shifts to lower vibrational frequency for species in the excited state are usual in stable aromatic molecules. However, since the shift is so large, it should be noted that the vibration might be connected with the carbon–oxygen bond. ESR studies on the unsubstituted furanoxy radical indicate that the unpaired electron is not heavily localized on the oxygen.[23] If the carbon–oxygen bond has a good deal of double-bond character when the radical is in the ground state and if the excited radical has a good deal of charge transfer to the oxygen, then the trend of the shift could also be explained. This type of behavior was observed in phenoxy radical. In phenoxyl, the totally symmetric, Wilson mode $\nu_{7a}$, which has a large contribution from the C–O stretch, was assigned to the 1505-cm$^{-1}$ vibration for the ground state by using resonance Raman spectroscopy[24] and to the 1100-cm$^{-1}$ vibration for the excited state by using the absorption spectrum.[24]

At room temperature the recombination of the furanoxy radicals could be seen to follow a second-order rate behavior with equal-concentration kinetics (i.e., linear plot of $1/\Delta$OD vs $t$), when the 5,5′-bis(furanones) were used to generate the radicals in pyridine. The estimates of these rate constants, $2k$, were $1.2 \times 10^9$, $9.2 \times 10^8$, and $3.3 \times 10^8$ M$^{-1}$ s$^{-1}$ for **3a**, **3b**, and **3c**, respectively, using $\epsilon_{max}$ from benzene.[22] The decay of the ground state of the radicals from substrates other than the 5,5′-bis(furanones) did not follow a second-order, equal-concentration kinetics. This was likely due to multiple second-order processes involving the extraneous radicals produced in the course of the other methods of preparation. Only the photolysis of the 5,5′-bis(furanones) gave a system containing a single species of radicals.

Single-laser, flash photolysis of **1d** in a methylcyclohexane glass at 77 K led to no red fluorescence. It is likely that fast radical recombination leading to the original furanone or new products, coupled with inhibited ability of geminate radicals to escape from the solvent cage in the viscous medium, was responsible for the lack of appearance of any characteristic furanoxy fluorescence. In an experiment using $\gamma$ radiolysis, furanoxy radicals were made from the benzylfuranone **1a** in a 2-chlorobutane glass at 77 K. The radical cation of **1a**, formed via charge transfer with trapped holes coming from the 2-chlorobutane glass,[25] fragmented to form the benzyl carbocation and a furanoxy radical.[16] The weak red fluorescence of the radical could be detected when the $\gamma$-irradiated cell was transferred to the laser flash photolysis system and irradiated by 355-nm laser pulses. However, the amount of radical formed was insufficient for detection of its fluorescence under steady-state irradiation in our SLM fluorometer.[26] Similar observations were made with **1a** in poly(vinyl chloride) films (thickness, ~0.1 mm)[27] at 77 K. On the other hand, in a room temperature experiment using a poly($\alpha$-methylstyrene) matrix, containing **1d**, red fluorescence due to photogenerated furanoxy radicals could be observed under 308-nm laser excitation.[28]

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**Table III.** Fluorescence Kinetics of Furanoxy Radicals in 1:2 Benzene/DTBP

| radical | $\tau_0$/ns[a] | $\tau_M$/ns[b] | $\Phi_f$[c] | $k_{ic}$/s$^{-1}$[d] |
|---|---|---|---|---|
| furanoxy (**3a**) | 217 | 10.7 | 0.05 | $8.9 \times 10^7$ |
| methyl (**3b**) | 225 | 12.5 | 0.055 | $7.6 \times 10^7$ |
| methoxy (**3c**) | 120 | 11.6 | 0.096 | $7.8 \times 10^7$ |

[a] Natural radiative lifetime from absorption spectra ($\epsilon_{max}$ in benzene[22]). [b] Measured (deconvoluted) fluorescence decay times. [c] $\Phi_f = \tau_M/\tau_0$. [d] $k_{ic} = 1/\tau_M - 1/\tau_0$.

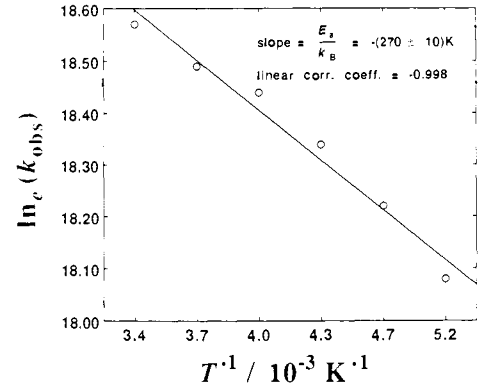

**Figure 2.** Temperature dependence of the fluorescence lifetime of the unsubstituted furanoxy radical **3a** in 2-MTHF.

The main purpose of trying to observe steady-state fluorescence was to do accurate fluorescence measurements for fluorescence quantum yields. In our previous communication we estimated the fluorescence quantum yield of **3c** to be 0.1, using the Strickler–Berg formula[29] to compute a natural radiative lifetime from the absorption spectrum.[16] This value and analogous values for radicals **3a** and **3b** are listed in Table III. A method to measure these yields using an internal actinometer in fluid solutions is being studied in this laboratory.

**Fluorescence Lifetimes and Their Temperature Dependence.** The previous measurements[5] of lifetimes were repeated with a nonlinear least-squares deconvolution routine using the Marquardt algorithm.[30] This routine was originally used for single-photon statistics[31] and was modified for the statistics of the laser system.[32] The measured lifetimes decreased from the previous results of 16 ns (without deconvolution) to 11 or 12 ns (with deconvolution); see results in Table III. The deconvolutions were even more significant when used with the temperature-dependence studies that follow and with the relatively short lifetimes of the radicals in pyridine, given in Table I.

The temperature-dependence studies were done with equipment similar to that used to study the arylmethyl radicals.[12] The furanone used in the study was **1d** in 2-methyltetrahydrofuran (2-MTHF). Using a one-laser configuration, direct photolysis at 355 nm gave the radical fluorescence, and the lifetimes were measured over the temperature range of 173–300 K. The temperature was controlled by the flow of cold nitrogen, following its passage through a coil of copper tubing placed in liquid nitrogen, and the temperature was recorded with the use of a thermocouple. The cooling rate was controlled so that the contents of the sample cell could reach equilibrium before the fluorescence lifetime was measured at a given temperature.

The results of the measurements are shown in Figure 2. The activation energy of the decay was 0.35 kcal/mol. Measurements below 173 K were hampered by the disappearance of the furanoxy radical fluorescence and the appearance of a new shorter lived emission. As stated earlier, the disappearance of furanoxy fluorescence was probably due to fast recombination of the radicals, and the new emission was primarily due to photoproduct(s) (not characterized).

The activation energy, 0.35 kcal/mol, of furanoxy radical fluorescence decay is much smaller than the activation energy of 3.8 kcal/mol[12] in the case of the benzyl radical and that of 4.6 kcal/mol in the case of the triphenylmethyl radical.[12] Note that while photochemistry[2,3,33] is implicated in the case of the triphenylmethyl radical, a third electronic state[12] plays an important role in the case of the benzyl radical. The $E_a$ value for furanoxy radical is much more in line with the activation energies that have been ascribed to a vibronic mechanism of temperature dependence.[34,35] In such a mechanism, the temperature dependence arises by the population of vibronic states (vibrational-electronic states) in the same electronic manifold. The slight increase in the rate constant as the higher vibrational levels are populated is due to differences in the Franck–Condon factors. In this case for internal conversion, the $^2D_1$ electronic state with no vibrational quanta (the vibrationless state) has smaller Franck–Condon overlaps with isoenergetic vibrational levels of the ground electronic state $^2D_0$ than do the upper vibrational levels of $^2D_1$ with these same $^2D_0$ vibrational states. The electronic mechanism of $^2D_1 \rightarrow {}^2D_2$, which is thought to be involved in the unusual temperature dependence of benzyl radical,[12] does not appear to operate in the furanoxy radical.

A rough estimate of the rate constant, $k_{ic}$, for radiationless (internal conversion) transitions can be made from the measured fluorescence lifetimes, $\tau_M$, and the natural lifetimes, $\tau_0$, calculated from the absorption spectra. Equivalently the estimated fluorescence quantum yields, $\Phi_f$, in Table III can be used along with $\tau_M$. By use of the formula

$$k_{ic} = 1/\tau_M - 1/\tau_0$$

the rate constants, $k_{ic}$, for the three radicals are listed in the last column of Table III. According to the empirical correlations of King[36] between Taft,[37] polar substituent constants ($\sigma^*$), and the rate constants for radiationless transitions,

$$\log k_{ic} = \rho^* \sum_n \sigma_n^*$$

we would expect $k_{ic}$ to decrease upon methyl and methoxy substitution ($\sigma^*$ values[37] increase in the order of $OCH_3 < CH_3 < H$).[38] Such a trend is indicated in the lifetime data (see Tables I and III) of the furanoxy radicals (particularly in pyridine).

The furanoxy radical thus becomes another convenient doublet system to study intramolecular internal conversion. Its relatively long, excited-state lifetime is easy to monitor with nanosecond laser systems. Detailed studies await a good method of measuring fluorescence quantum yields of these systems. This is currently under way in this laboratory.

**Triplet–Doublet Energy Transfer.** The most detailed study of intermolecular photophysics in this current work has been that of triplet quenching by the radicals. In our previous work,[5] we established that the observed delayed fluorescence of furanoxy radicals in the presence of triplet states was due to energy transfer from the triplet state. The delayed luminescence, seen in ex-

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**Table IV.** Sensitization of Radical[a] Fluorescence (~46 kcal mol$^{-1}$) by Triplet States

| sensitizer | $E_T$/kcal mol$^{-1}$ | successful ET |
|---|---|---|
| chrysene | 56.6[39] | yes |
| fluoranthene | 54.2[39] | yes |
| camphorquinone | 51.2[5] | yes |
| benzo[*b*]triphenylene | 50.8[39] | yes |
| fluorenone | 50.2[40] | yes |
| pyrene-1-aldehyde | 43.5–45.9[41] | no |
| anthracene | 42.0[39] | no |
| 4,4′-dimethoxythiobenzophenone | 41.1[42] | no |
| perylene | 35.1[39] | no |

[a] Radical studied was produced from **1d** whose triplet state is styrene-like (~60 kcal mol$^{-1}$). Thus $E_T$ of **1d** is greater than the $E_T$'s of all the sensitizers used.

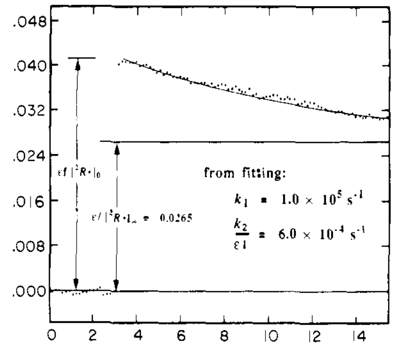

**Figure 3.** Absorption decay trace of radical **3a** in the presence of stilbene in THF. Fitting parameters refer to eq 3. *l* is the optical path length, and $\epsilon$ is the excitation coefficient of the radical at the monitoring wavelength.

periments where a triplet donor $^3D^*$ was transferring energy to the parent benzylfuranone (F) and forming the triplet furanone ($^3F^*$), could be best explained in terms of the following processes (Bz ≡ benzyl, R ≡ furanoxy radical):

$$^3D^* + {}^1F \rightarrow {}^1D + {}^3F^* \qquad \text{(III)}$$

$$^3F^* \rightarrow {}^2Bz^\bullet + {}^2R^\bullet \qquad \text{(IV)}$$

$$^3F^* + {}^2R^\bullet \rightarrow {}^1F + {}^2R^{\bullet *} \qquad \text{(V)}$$

Computer simulations showed that the growth of the experimental fluorescence trace was too gradual and its decay was too slow for an alternative triplet–triplet annihilation mechanism: $^3F^* + {}^3F^* \rightarrow {}^2R^{\bullet *} + {}^2Bz^\bullet + {}^1F$.

The other manner of verifying the energy-transfer nature of the sensitized fluorescence was to use a series of triplet states with a range of triplet energies, $E_T$, as possible energy donors. The results of these experiments are given in Table IV. It can be seen that only triplet states with $E_T$'s larger than the 0–0 fluorescence band (the $^2D_1 \rightarrow {}^2D_0$ energy gap) could sensitize the furanoxy radical fluorescence.

Once the mechanism was established as energy transfer, it became of interest to determine the rate constant for the quenching process (III). A technique for doing this was developed[7] to measure the energy transfer from naphthalene triplet to benzophenone ketyl radical. In that work, satisfactory results were obtained by using the approximation that the concentration of the quencher radical (energy acceptor) was constant over the triplet decay curves. [The triplet and the radical were coproduced by 308-nm laser flash photolysis of tetrahydrofuran (THF) solutions containing both naphthalene and benzophenone]. In the present work, the radical and the triplet were produced together by 308-nm laser flash photolysis of solutions containing both **1d** and an aromatic (benz[*a*]anthracene or chrysene). However, the approximation of the lack of radical decay proved unsatisfactory for the furanoxy radical because the furanoxy radical itself decays by 35–40% over the time range of the triplet decays under consideration. This can be seen in the decay trace in Figure 3, obtained by 308-nm laser pulse excitation of **1d** in THF. Many attempts were made to fit the decays with the mixed kinetics, using a nonlinear least-squares fit to the exact mixed decay function.[7] These attempts always led to systematically higher rate constants computed from the fluorescence decays compared to the rate constants calculated from the corresponding triplet absorption decay.

In the current work, two modifications were made to compensate for the complex kinetics of the quencher radical. First, when monitoring absorption traces of the decaying radical alone (i.e., in the absence of the triplet precursor), stilbene was used as a dummy absorber to substitute for the triplet precursor. This ensured that the concentration characteristics of the radical would be the same in the presence and absence of the triplet precursor. The absorption decay curves of the radicals, which were independent of the triplet, were needed in order to correct the triplet absorption decay traces for a very small amount of ground-state radical decay under all of the triplet curves studied. The triplet yield of stilbene was negligible in fluid solutions[43] and the triplet was short-lived (~60 ns),[44] so its photophysics was uncoupled with the rest of the system. By adjusting the stilbene concentration to match the ground-state absorbance at the excitation wavelength to that of the triplet precursor, the concentration of the radical, and thus the shape of its roughly second-order decay curve, were expected to be the same in both the presence and absence of the donor triplet.

The other modification pertained to the procedure for making the fits of the decay traces. Rather than making the simplifying assumption that the concentration of the energy acceptor (radical) is constant and then using the exact mixed kinetics and calculating the quenching rate from the extracted first-order rate,[7] the actual differential equation was solved for a varying acceptor concentration.

The reaction scheme under consideration is

$$^3M^* \rightarrow {}^1M + \text{heat} \qquad \text{(VI)}$$

$$^3M^* + {}^3M^* \rightarrow \text{products} \qquad \text{(VII)}$$

$$^3M^* + {}^2R^\bullet \rightarrow {}^1M + {}^2R^{\bullet *} \qquad \text{(VIII)}$$

$${}^iR^{\bullet *} \rightarrow {}^2R^\bullet + h\nu \qquad \text{(IX)}$$

In this reaction scheme, the donor's concentration is given by

$$\frac{d[^3M^*]}{d\tau} = -k_{VI}[^3M^*] - k_{VII}[^3M^*]^2 - k_{VIII}[^2R^\bullet][^3M^*] \qquad (1)$$

and the excited acceptor's concentration is given by

$$\frac{d[^2R^*]}{d\tau} = -k_{IX}[^2R^{\bullet *}] + k_{VIII}[^2R^\bullet][^3M^*] \qquad (2)$$

Equation 1 is a nonlinear differential equation that can be solved since it is of the Bernoulli type. Rather than solving this set of equations numerically, we chose to solve them partially by analytical methods. To do this, a functional form must be obtained for the acceptor concentration, $[^2R^\bullet]$. A modified mixed decay was chosen.

$$[^2R^\bullet] = [^2R^\bullet]_\infty + \left[\frac{\exp\{k_1 t\}}{[^2R^\bullet]_0 - [^2R^\bullet]_\infty} + \frac{k_2}{k_1}\left(\exp\{k_1 t\} - 1\right)\right]^{-1} \qquad (3)$$

Parameters for the mixed decay of the acceptor were found by using the programs previously used for the naphthalene/ketyl problem.[7] A large offset, $[^2R^\bullet]_\infty$, was needed to use this equation (see Figure 3). No chemical or physical significance is to be given to the rates, $k_1$ and $k_2$, in this offset, mixed decay function; it is only used to obtain a good analytical representation of the acceptor decay.

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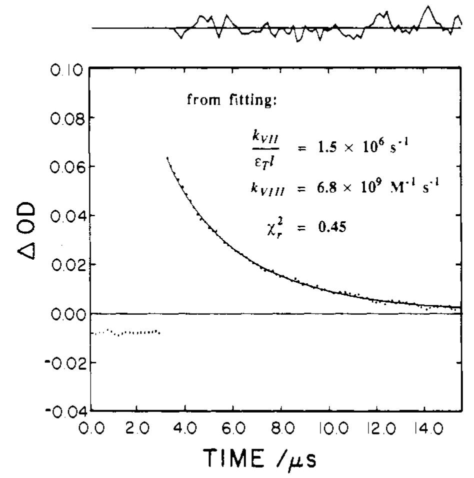

**Figure 4.** Absorption decay trace of the triplet benz[*a*]anthracene used to determine the rate constant (via eq 4) for its quenching by furanoxy radical **3a** in THF. Background absorbance due to radical absorption has been subtracted. $\chi_r^2$ and the residuals plot, at the top of the panel, are indications of the goodness-of-fit.

However, once this functional form is chosen, the differential equation can be transformed and partially integrated to give

$$\frac{1}{[^3M^*]_t} = \frac{\exp\{(k_{VI} + k_{VIII}[^2R^\bullet]_\infty)(t - t_1)\}}{[^3M^*]_{t_1}}\frac{f(t)}{f(t_1)} + k_{IX}\int_{t_1}^{t} ds\, \exp\{(k_{VI} + k_{VIII}[^2R^\bullet]_\infty)(t - s)\}\frac{f(t)}{f(s)} \quad (4)$$

where *s* is the integration variable, which has the units of time, and $f(x)$ is given by

$$f(x) = \left[1 + \frac{k_1}{k_2([^2R^\bullet]_0 - [^2R^\bullet]_\infty)} - \exp\{-k_1(x - t_0)\}\right]^{k_{VIII}/k_2} \quad (5)$$

In addition, making the steady-state approximation for eq 2 gives

$$[^2R^{\bullet *}]_{SS} = \frac{k_{VIII}}{k_{IX}}[^2R^\bullet][^3M^*] \quad (6)$$

Equations 4 and 6 are the equations used to find the rate constant, $k_{VIII}$, from triplet decay traces (Figure 4) and fluorescence decay traces (Figure 5), respectively. In these equations, $k_1$, $k_2$, $[^2R^\bullet]_\infty$, and $[^2R^\bullet]_0$ are parameters, merely describing empirically the decay of the ground state of the acceptor, $[^2R^\bullet]$. The first-order decay constant of the triplet, $k_{VI}$, is measured, and the fluorescence decay constant of the unsensitized radical, $k_{IX}$, was also measured. The adjustable parameters in the fit are $[^3M^*]_{t_1}$ (the triplet concentration at time $t_1$), $k_{VII}$ (the second-order rate constant for triplet decay), and $k_{VIII}$ (the quenching rate constant). Thus, in the final analysis there are only three adjustable parameters, in exact analogy to the mixed decay with constant acceptor concentration.[7]

The quenching experiments were carried out using a 308-nm laser flash photolysis configuration and various ratios of substrate concentrations in THF. The substrates were **1d** for the radical and either benz[*a*]anthracene or chrysene for the triplet. A series of solutions was prepared with the relative ODs at 308 nm ranging from 0.25 to 4.0 for the parent furanone and the triplet precursor.

The rate constant, $k_{VIII}$, for the quenching of benz[*a*]anthracene triplets was (6.6 ± 0.5) × 10$^9$ M$^{-1}$ s$^{-1}$ for 95% confidence interval. These values were from three different substrate ratios (ratios of the ground-state concentration of the triplet precursor to that of the radical precursor) for the fluorescence and two different ratios for the triplet absorption measurement. A value of 1.6 × 10$^9$ M$^{-1}$ s$^{-1}$ for the smallest triplet/radical ratio was neglected. This value violates the Chauvenet criterion as a justification for neglecting outliers.[45]

The five values retained for the average showed no bias for either the absorption or fluorescence traces to be larger. This is to be contrasted to the larger values obtained from the fluorescence traces when the fitting was done using the assumption of constant acceptor concentrations and mixed kinetics. The source of the bias toward faster observed decay traces for the fluorescence can be seen from eq 6. When the ground state of the acceptor, $^2R^\bullet$ in this case, decays, then the fluorescence trace, following $[^2R^{\bullet *}]_{SS}$, appears to decay faster than the triplet absorption trace, following $[^3M^*]$. (The difference in the apparent rates can be seen by comparing the decay traces in Figure 4 and 5.)

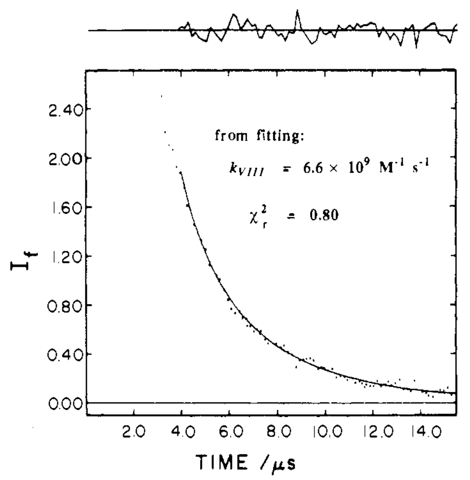

**Figure 5.** Decay trace of the sensitized fluorescence of the radical **3a** used to determine the rate constant (via eq 6) of the quenching of the triplet state of benz[*a*]anthracene by **3a** in THF.

The rate constant, $k_{VIII}$, for chrysene was (5.7 ± 1.6) × 10$^9$ M$^{-1}$ s$^{-1}$ for 95% confidence intervals. This number was based on five fluorescence decays, since the absorption measurements gave very low results. The chrysene triplet was measured at 590 nm and had interference from the radical. Even with the use of stilbene as a dummy absorber, we could not get reliable results for the absorption.

Both of these numbers are roughly one-third of diffusion controlled, using Murov's calculated value for THF.[39] This would be the spin-statistical[46] value if only the doublet was being formed in the energy-transfer process, with no quartet being formed. However preliminary results[47] of measuring the product of the fluorescence quantum yield and the triplet–doublet rate constant indicate that the value of ~6 × 10$^9$ M$^{-1}$ s$^{-1}$ may be a combined rate constant involving energy transfer and other competing processes.

One likely competing process is electron transfer, as indicated by the following calculations. Voltammetry, using a recent, modulated photolysis technique,[48] was done on radical **3c**, and its redox potentials in acetonitrile were measured as $E_{1/2}^{ox}$ = +0.70 ± 0.05 V vs SCE and $E_{1/2}^{red}$ = −0.53 ± 0.05 V vs SCE.[49] $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ for chrysene are +1.35 V vs SCE in acetonitrile[50] and −2.25 V vs SCE in *N,N*-dimethylformamide,[51] respectively. Those for benz[*a*]anthracene in acetonitrile are +1.18 V vs SCE[50] and −2.11 V vs SCE,[52] respectively. The free energy change for the electron-transfer quenching can be estimated from[53]

$$\Delta G = 23.06\left[E_{1/2}^{ox} - E_{1/2}^{red} - e^2/\epsilon r\right] - E_T \quad (7)$$

The rate constant for electron transfer within the Rehm–Weller framework[53]

$$k_q = 2 \times 10^{10}\left[1 + 0.25\left(\exp\left\{\frac{\Delta G^\ddagger}{RT}\right\} + \exp\left\{\frac{\Delta G}{RT}\right\}\right)\right]^{-1} \quad (8)$$

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can be calculated from their empirical relationship

$$\Delta G^{\ddagger} = \left[\left(\frac{\Delta G}{2}\right)^2 + (\Delta G^{\ddagger}(0))^2\right]^{1/2} + \frac{\Delta G}{2} \qquad (9)$$

and their empirical parameter $\Delta G^{\ddagger}(0) = 2.4$ kcal/mol (both from quenching data on excited aromatics in acetonitrile). Assuming no solvent effects and neglecting the Coulomb term in eq 7, $\Delta G$ is positive for either chrysene or benz[*a*]anthracene being the electron acceptor and for the radical being the donor. An analogous calculation, but with the radical **3c** as the electron acceptor, gives the electron-transfer rate constants as $1.3 \times 10^{10}$ $M^{-1}$ $s^{-1}$ for chrysene and $1.1 \times 10^{10}$ $M^{-1}$ $s^{-1}$ for benz[*a*]anthracene from eq 7–9. These rate constants are approaching the diffusion-controlled limit. However, in order to get quartet states from the initial state, excited states must be formed as intermediates; for example

$$^3M^* + {}^2R^{\bullet} \rightarrow {}^{2,4}({}^2M^{\bullet+} \cdots {}^3R^{-*}) \qquad (X)$$

$$^3M^* + {}^2R^{\bullet} \rightarrow {}^{4}({}^4M^{\bullet+*} \cdots {}^1R^{-}) \qquad (XI)$$

If the triplet anion, $^3R^{-*}$, or the quartet radical cation, $^4M^{\bullet+*}$, in the ion pairs are energetically unrealizable,[54] then the rate constant will be reduced by at least one-third (on the basis of spin statistics)[46] the limit calculated from eq 7–9. This means that energy transfer can compete effectively with electron transfer but that electron transfer is likely also occurring in the quenching of chrysene and benz[*a*]anthracene triplets by furanoxy radicals.

**Other Quenching Experiments.** An attempt was made to see a sensitized energy transfer from the diphenylmethyl radical to a furanoxy radical (doublet–doublet energy transfer). A mixture of 1:1 diphenylmethane and DTBP was photolyzed at 308 nm in the presence and absence of **1d**. At a delay of a few microseconds the diphenylmethyl radical was excited with 320-nm pulses from the Nd:YAG-pumped dye laser. Both the composite emission spectra (composed from decay curves) and the decay curves themselves showed definite quenching of the diphenylmethyl radical's fluorescence. Furthermore, the composite emission spectra of the quenched solution showed a shoulder in the region of the furanoxy radical's fluorescence. However, it was not prominent enough, given the noise level of our spectra, to assign it with confidence to the sensitized fluorescence of the furanoxy radical. The limitations on generating high concentrations of radicals, acting as the energy acceptor, make these sensitization experiments difficult for energy donors having excited lifetimes <500 ns, especially if there are competing quenching mechanisms involved.

## Concluding Remarks

Furanoxy radicals provide a good model to study radiationless transitions and energy-transfer processes. The weak temperature dependence of furanoxy radicals also show it to be a good candidate to study radiationless transitions in molecules using a two-state model. Using rough estimates of fluorescence quantum yields, the substituent effects on radiationless transitions appear to follow proposed correlations used in stable aromatic molecules. The measured rate constant of the quenching of the triplet states of chrysene and benz[*a*]anthracene at $\sim 6 \times 10^9$ $M^{-1}$ $s^{-1}$ may be only an upper bound to the rate of triplet to doublet energy transfer in THF, which as a phenomenon is confirmed by photosensitized luminescence. The certainty in these results was aided by the use of the 5,5′-bis(furanones), which produced furanoxy radicals without adding additional radical species to the system.

**Acknowledgment.** The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-3117 from the Notre Dame Radiation Laboratory. We thank Drs. D. Weir of the Radiation Laboratory and D. D. M. Wayner of the National Research Council of Canada for measuring the redox potentials of the furanoxy radicals.

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# Adsorption of Organorhodium Species on Metal Oxide Surfaces: Theoretical Aspects

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*Received June 27, 1988*

**Abstract:** Tris(allyl)rhodium reacts with hydroxylated $TiO_2$ and $Al_2O_3$ surfaces to produce oxide-bound bis(allyl)rhodium which, upon addition of $H_2$, forms oxide-bound (allyl)rhodium hydride species. The nature of the rhodium–oxygen bonding and the role of the inorganic support are analyzed via extended Hückel band calculations on two-dimensional slabs of metal oxide and organorhodium adsorbates. Side by side with this analysis we looked at discrete molecular analogues of the surface species. One- and two-oxygen-bound $Rh(allyl)_2$ and one-, two-, and three-oxygen-bound Rh(allyl)(H) models were examined. There are great similarities between the isolated molecule models and the supported interactions. Crucial to the role of the oxide support is its partial reduction, through defect structures, and resonances between support and adsorbate energy levels. The oxide support not only serves to immobilize the organometallic adsorbate but might also act as an electron reservoir or electron sink, depending upon the electronic requirements of the adsorbed complexes.

The chemistry of oxide-bound organometallic species constitutes a new and important area of heterogeneous catalysis.[1] Most of the studies have been done on polycrystalline or powder samples. Understanding the adsorption mechanism on an atomic scale requires the characterization of both the adsorbed molecule and the metal oxide surface, i.e. the composition, the atomic positions, and the eventual rearrangements of the system studied. Theoretical studies can aid in obtaining a picture of the mechanism.

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