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Photophysics of Furanoxy Radicals. Fluorescence and Triplet–Doublet Energy Transfer[1]

K. Bhattacharyya,[2a] P. K. Das,[2a] R. W. Fessenden,[2a] M. V. George,[2] K. R. Gopidas,[2b] and G. L. Hug*[2a]

Radiation Laboratory and the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

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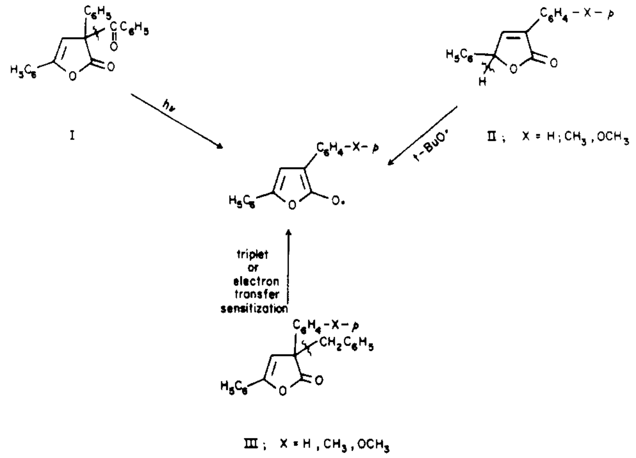
The fluorescence of furanoxy radicals in fluid solutions was characterized by measuring emission spectra and lifetimes in addition to estimating quantum yields. The fluorescence was then used to monitor the transfer of energy from various triplet states to the furanoxy radicals. It was found that triplet–doublet energy transfer occurs easily whenever the process is exothermic.

Introduction

The mechanism of quenching of triplet states by doublet states has long been of interest[3-15] as an example of paramagnetic species enhancing spin-forbidden transitions.[16,17] There has been a continuing dialogue as to whether the mechanism is charge transfer and/or energy transfer. Razi Naqvi and Wild[18] demonstrated the possibility of the energy-transfer mechanism of triplet quenching by radicals when they monitored the fluorescence of the benzophenone ketyl radical that was quenching the triplet state of benzophenone itself.[18-20] Recent studies of the fluorescence of radicals in solution[21,22] have opened up possibilities for the use of a much broader range of quenchers in the study of triplet deactivation by energy transfer to radicals.[23] However, except for the single case of benzophenone triplet being quenched by the benzophenone ketyl radical, there are no other examples of direct monitoring of the fluorescence of radicals as a means of studying the quenching of triplet states.

In this Letter we report additional examples of direct evidence for quenching of triplet states by radicals via an energy-transfer mechanism. We have found a series of furanoxy radicals that fluoresce strongly in fluid solutions and that are easily generated by a variety of flash photolysis techniques (Scheme I). The fluorescence of the furanoxy radicals has a moderate lifetime (16 ns) which opens up a range of energy-transfer experiments that are inconvenient for benzophenone ketyl radical. The excited states of these radicals also appear to be relatively inactive chemically, as opposed to the benzophenone ketyl radical[24-26] and some of the arylalkyl radicals.[22] In this Letter we report the experiments to characterize the furanoxy radical fluorescence and some experiments using this fluorescence to monitor energy-transfer quenching of triplet states by the furanoxy radicals.

SCHEME I



Results and Discussion

Fluorescence from Furanoxy Radicals. The absorption-spectral characterization of the furanoxy radicals generated from substrates I–III, in Scheme I, has already been done.[27] In the course of photolyzing 3-benzoyl-3,5-diphenyl-2(3*H*)-furanone (I) by 337-nm laser pulses (1–2 mJ/pulse) to generate the corresponding radical (Scheme I), a bright red luminescence was noticed. The question that arises immediately is whether the luminescence was due to the radical or an impurity or a photoproduct other than the radical. One way to check whether the luminescence was due to an impurity or owing to biphotonic generation of excited radicals was to do an excitation intensity dependence study. If the plot of luminescence vs. laser intensity is nonlinear, it is unlikely that an impurity is the source of the luminescence. Such an experiment was done using neutral density filters in the laser path; a solution of tris(2,2′-bipyridine)ruthenium(II) ion,

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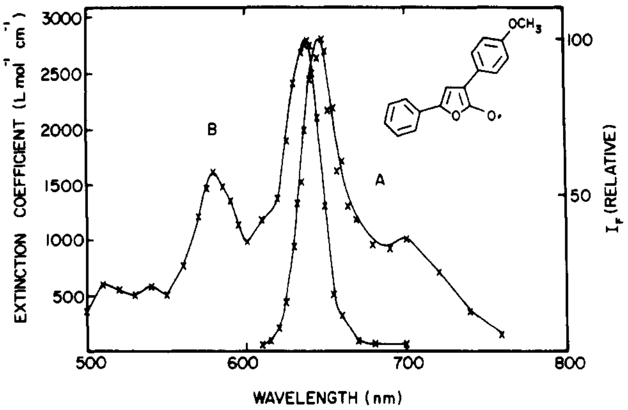

Figure 1. Fluorescence (A) and absorption (B) spectra of a furanoxy radical in 1:2 benzene:DTBP. The radical was generated by abstraction of the 5-hydrogen of II (X = OCH_3) by *tert*-butoxy radical. The fluorescence lifetime was 16 ns, and the fluorescence quantum yield was estimated to be 0.1 by using the Strickler–Berg[26] relation for the natural radiative lifetime. The fluorescence spectrum was corrected for detection system response and the absorption spectrum normalized to $\epsilon_{630} = 2400$ M^{-1} cm^{-1}.[27]

$Ru(bpy)_3^{2+}$, was the actinometer, with its luminescence at 630 nm being used as a relative measure of the laser intensity. The slope of the log–log plot of unknown luminescence vs. $Ru(bpy)_3^{2+}$ luminescence was 2.1 ± 0.2, showing that the unknown luminescence was not due to an impurity. Furthermore, it showed that the mechanism for forming the luminescence was biphotonic.

To further characterize the luminescence, another experiment was done by separating the creation of the radical from its excitation by a second laser.[24] If the radical were fluorescing, then the fluorescence could be studied without the complicating features of the radical creation. In order to perform this experiment, the *tert*-butoxy radical was produced from di-*tert*-butyl peroxide (DTBP) by photolysis with a 337-nm pulse.[28] The *tert*-butoxy radical then abstracted the 5-hydrogen from 3-(4-methoxyphenyl)-5-phenyl-2(5*H*)-furanone (II, X = OCH_3), forming a methoxy-substituted furanoxy radical (Scheme I). After about 6 μs, another laser pulse at 355 nm excited the furanoxy radical itself (355 nm does not excite the parent furanone II; X = OCH_3). The red fluorescence was seen as a result of the absorption of the delayed pulse. Fluorescence spectra were constructed from the decay curves. The fluorescence spectrum for the methoxy-substituted furanoxy radical is given in Figure 1. Also given in Figure 1 is the lowest energy absorption band of the radical. From the good overlap of the 0–0 bands of the emission and absorption spectra and from the good mirror-image relation between these two spectra when plotted on a wavenumber scale, we assign the emission to the $D_1 \rightarrow D_0$ transition of the radical. The fluorescence spectra of other furanoxy radicals formed from the abstraction of the 5-hydrogen of related furanones (II, X = H and CH_3) were similar. However, substituent effects were observed, the fluorescence from *p*-methoxy-substituted (λ_{max} = 640 nm, Figure 1) and *p*-methyl-substituted radicals (λ_{max} = 627 nm) being red-shifted relative to the unsubstituted one (λ_{max} = 617 nm).

With the intrinsic nature of the fluorescence established, the nature of the biphotonic process of producing the fluorescence from the furanoxy radical generated from I in the single laser pulse experiment, discussed above, can be understood. The first photon forms the furanoxy radical by photolysis of I, and the second photon excites the furanoxy radical itself.

It was possible to measure some of the important intramolecular photophysical parameters of the furanoxy radicals. All of the radicals studied had fluorescence lifetimes of about 16 ns in benzene, methanol, acetonitrile, and 1:2 benzene:DTBP. The lifetime measurements were all done by laser flash photolysis. An estimate of the fluorescence quantum yield can be made from the natural radiative lifetime and the measured lifetime. The former can be calculated by using the Strickler–Berg relation[29] and the absorption spectra of the lowest doublet state of the radicals. The extinction coefficient of the radical in Figure 1 is $\epsilon_{630} = 2400$ M^{-1} cm^{-1} in 1:2 benzene to DTBP solution.[27] With this ε, the Strickler–Berg formula gives a natural radiative lifetime of about 150 ns (taking the refractive index to be 1.5). When this is combined with the measured lifetime of 16 ns, the fluorescence quantum yield is estimated to be 0.1.

T-D Energy Transfer to Furanoxy Radicals. As mentioned in the Introduction, one of the most important and interesting intermolecular photophysical properties of radicals is their ability to quench triplet states. Having established the nature of the red emission, we have used the furanoxy radicals for monitoring the energy-transfer quenching of triplet states. In the first of these experiments, the radical ($^2R\cdot$) was generated in a laser flash photolysis experiment at 337 nm (Scheme I), using benzophenone in a benzene solution to photosensitize the triplet state of 3-benzyl-3,5-diphenyl-2(3*H*)-furanone (III, X = H). Bond cleavage then takes place in the triplet state of III (X = H) leaving $^2R\cdot$ and the benzyl radical, $^2B\cdot$

$$^3F^* \rightarrow {}^2R\cdot + {}^2B\cdot \qquad (1)$$

with F standing for furanone (III, X = H). The unusual observation in this experiment was that an apparently long-lived fluorescence (Figure 2) occurred. In fact, the fluorescence persisted well past the duration of the laser pulse and also well after the benzophenone triplets had decayed.

The persistence of excited radicals, $^2R\cdot^*$, for such a long time requires an extended production process. The only species left with sufficient energy to form the excited radicals are the radicals themselves and the triplet states of the parent furanone. Since the emission spectrum was that of $^2R\cdot$ itself, radical recombination processes could not account for the luminescence. This left us with the two following mechanisms. First, there was possibly a contribution of triplet–triplet annihilation to $^3F^*$ decay which was energetic enough to generate excited radicals directly from two triplet states

$$^3F^* + {}^3F^* \rightarrow {}^2R\cdot^* + {}^2B\cdot \qquad (2)$$

and second, there was the triplet–doublet energy transfer

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

To complete both mechanisms, fluorescence emission from $^2R\cdot^*$

$$^2R\cdot^* \rightarrow {}^2R\cdot + h\nu_f \qquad (4)$$

must be added. Both mechanisms (T–T, processes 1–2–4 and T–D, processes 1–3–4) lead to coupled, nonlinear kinetic equations which were solved numerically by using the Runge–Kutta–Gill technique.[30] The computer simulations of the fluorescence decay for both mechanisms are shown in Figure 2, with the constraint that the lifetime of $^2R\cdot^*$ itself was 16 ns. The *shapes* of both simulated decays were relatively independent of either the initial furanone triplet concentration or the second-order rate constants chosen. Two differences between the curves are evident. The T–T mechanism gives a very fast rise in emission intensity (Figure 2a) which follows the formation of $^3F^*$, while the T–D mechanism produces a slower growth (Figure 2b) because radicals must be formed by reaction 1 before they can participate in reaction 3. In addition, the emission intensity for the T–T mechanism drops more rapidly at longer times because it depends on the square of the concentration of triplet furanone while the intensity for the T–D mechanism falls with the first power of this concentration (since the concentration of radical $^2R\cdot$ is changing only slowly at this point). Evidently only the triplet–doublet mechanism (processes 1–3–4; curve b, Figure 2) can reproduce the slow rise and fall of emission intensity which is observed. This mechanism is consistent with the furanone triplet lifetime determined from

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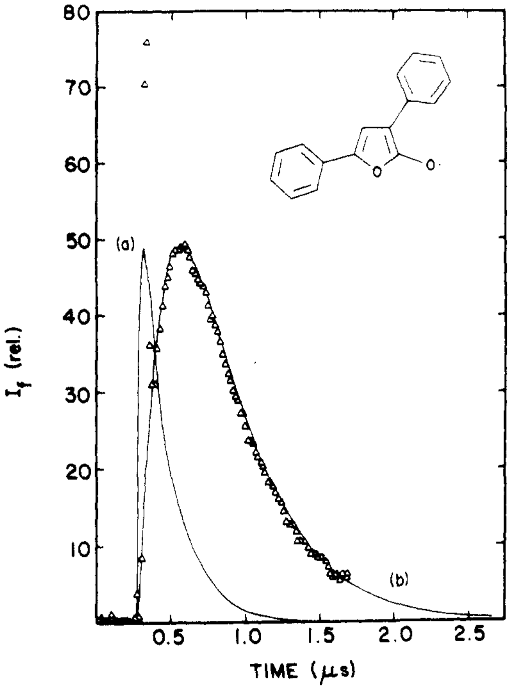

Figure 2. Fluorescence decay at 620 nm of a furanoxy radical in benzene [the radical was formed by fragmentation of the triplet of III (X = H) sensitized by benzophenone (0.1 M) under 337-nm excitation in the presence of 0.04 M III (X = H)]. Triangles are experimental points; curve a is a computer simulation of the triplet–triplet mechanism (processes 1–2–4), and curve b is a computer simulation of the triplet–doublet mechanism (processes 1–3–4) for excited radical formation. Both simulated curves were obtained by using the experimental fluorescence lifetime of 16 ns, the triplet lifetime as 400 ns (best fit in T–D mechanism), the second-order rate constants as 10^{10} M^{-1} s^{-1} ($2k$ for T–T mechanism), and 10^{-5} M for the initial furanone triplet concentration.

transient absorption measurements.

The T–D energy-transfer processes were pursued further by generating furanoxy radicals together with triplets of other molecules and monitoring any sensitized radical fluorescence. The 3-benzoyl-substituted furanone (I) was used to produce $^2R\cdot$ directly by laser flash photolysis at 355 nm in a benzene solution. Excited by the same pulse, triplet states were formed from a potential triplet sensitizer that was present in the same cell. If no triplet–doublet energy transfer occurred, one would expect to see only the short-lived fluorescence (prompt) due to $^2R\cdot$ being excited in the pulse. However, if triplet–doublet energy transfer were to occur, then one would expect to see a long-lived fluorescence component that roughly followed the triplet decay.

Experiments of this type were done using a series of triplet sensitizers (E_T = 179–240 kJ/mol). All of these triplet sensitizers have triplet energies, E_T, below 250 kJ/mol, the expected triplet energy of the parent furanone (I). This prevented excited radicals being formed by the self-sensitization, triplet mechanisms discussed above (processes 1–2 or 1–3). It was found that long-lived components of the fluorescence were observed for all the sensitizers tried that had E_T's above 197 kJ/mol (benzo[*b*]triphenylene, camphorquinone, chrysene, fluoranthene, and fluorenone), but no such fluorescence was seen when the E_T's were less than the 0–0 of the radical fluorescence at ~620 nm (192 kJ/mol) (anthracene, 4,4′-dimethoxythiobenzophenone, perylene, and pyrene-1-aldehyde). In cases where the long-lived components of fluorescence were detected, the decay of fluorescence roughly followed the decay of the triplet sensitizer. Thus, the radical fluorescence can be sensitized by triplet states under conditions where the triplet of the parent furanone is absent, yet where there is sufficient energy in a sensitizer triplet to reach the first excited doublet of $^2R\cdot$.

Using two lasers in tandem,[24] a cleaner experiment of this type was done where the creation of the radical and the triplet sensitization were separated in time. The first pulse at 337 nm generated the radical, and another pulse at 425 nm, delayed by 5 μs, generated the triplet state of camphorquinone (CQ), with E_T at 214 kJ/mol. In a first experiment of this type, the 337-nm pulse generated the radical, $^2R\cdot$, from the benzoyl furanone (I), as above. In a second experiment, the 337-nm pulse generated *tert*-butoxy radicals[28] which abstracted the 5-hydrogen from II (X = OCH_3), forming the methoxy-substituted furanoxy radical (Scheme I). Both experiments showed a long-lived fluorescence (~1 μs) which was initiated by the delayed, 425-nm pulse. The triplet state of CQ was monitored by transient absorption at both 700 and 330 nm,[31] and the fluorescence was seen to follow its decay. No luminescence was seen without the first laser pulse, showing that the long-lived fluorescence was indeed due to the radicals.

Concluding Remarks

Although the T–D energy transfer is spin-allowed and of significance in triplet quenching, there have been almost no studies, except for those of Razi Naqvi and co-workers,[18–20] of this process using fluorescence of radicals to directly monitor the process. The experiments described above demonstrate that T–D energy transfer occurs readily in all cases examined where the process is exothermic. Finally, the ease with which the furanoxy radicals can be generated by flash photolysis opens up many possibilities for investigation of other energy-transfer processes involving doublet states. These radicals have an added advantage over other fluorescing radicals studied so far in that their excited states do not seem to be as reactive or short-lived as those of benzophenone ketyl radicals[24–26] and some of the arylalkyl radicals.[22]

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Micellar Reactions of Hydrophilic Ions: A Coulombic Model

Clifford A. Bunton* and John R. Moffatt

Department of Chemistry, University of California, Santa Barbara, California 93106

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Distribution of hydrophilic ions about a spherical micelle has been estimated by using the Poisson–Boltzmann equation for finite salt and surfactant concentrations. It is consistent with rate–surfactant profiles for reactions of *p*-nitrophenyl diphenyl phosphate, 2,4-dinitrochloronaphthalene, and *N*-methyl-4-cyanopyridinium ion. Effects of sulfate ion upon reactions of nucleophilic anions in cationic micelles follow the predicted ion distribution.

Ionic micelles speed bimolecular ionic reactions by bringing reactants together at the micellar surface, and inert and reactive counterions compete for surface sites.[1–3] The extent of inhibition follows decreasing reagent ion hydrophilicity, suggesting that both

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