Table III. CH_3-N^+-CH_3 Chemical Shifts[a]

compd[b]	^1H NMR (δ) trans	^1H NMR (δ) cis	^{13}C NMR (δ) trans	^{13}C NMR (δ) cis
1-CH_3I	3.20	2.78	51.13	46.28
2-CH_3I	3.06	2.78	51.61	46.82
3-CH_3I	3.10	2.83	51.40	46.93
4-CH_3I	3.08	2.81	51.13	46.93
5-CH_3I	3.23	2.73	54.84	49.84

[a] In acetonitrile-d_3. [b] Refers to the mixtures of 8 + 9.

phenyl)-1-pyrroline, the latter prepared as described above for the imine precursers for **1-4**. Details of these preparations will be published in a full paper delineating the synthesis of a variety of nicotine analogues.

^1H and ^{13}C NMR spectra were obtained on either a Varian XL-100 NMR spectrometer equipped with a Digilab NMR-3 FT accessory or a Bruker WP-80 spectrometer operated in the FT mode. Spectroscopic grade acetonitrile was used as received for the kinetic experiments. Hexadecane was distilled prior to use and trifluoroacetic acid-*d* was used as obtained from Aldrich.

Kinetic Experiments.[10] Typically, a solution of iodomethane in ca. 49 mL of acetonitrile which had equilibrated at 25.00 ± 0.01 °C was added all at once to an equilibrated solution of amine in acetonitrile at 25.00 ± 0.01 °C. The resultant solution was always $<1 \times 10^{-3}$ M in amine and always >0.1 M in iodomethane, thereby ensuring a greater than 100:1 iodomethane:amine ratio. The reaction was run in a specially constructed conductivity cell purchased from Beckman Instruments (Cat. No. CEL-3L01-Special) which had platinum electrodes, 250-mL volume, and a flow-through cell construction such that rapid stirring within the reaction flask caused the solution to pass through and over the cell in a continuous fashion. The cells used had cell constants of ca. 0.1. Conductivity readings were made on a Beckman Instruments RC-18A conductivity bridge. Standard curves were generated from the purified quaternary salt product in each case. The experimental data was converted to time-concentration data and analyzed by using nonlinear least-squares analysis. Extremely small deviations were obtained. The pseudo-first-order rate constant derived in this manner was transformed to the second-order rate constant by dividing by the concentration of the iodomethane. At least four runs were performed for each compound.

Kinetic Quenching Experiments.[11] Typically, a solution of amine (ca. 20 mg) in 1 mL of anhydrous hexadecane was added dropwise to a rapidly stirred mixture of 1 mL of trifluoroacetic acid-*d* and 2 mL of hexadecane under argon in a previously flame-dried pear-shaped flask. Following the addition process, the mixture was allowed to stir an additional 1-2 min and then allowed to sit unperturbed for 1 min. The bottom layer was then carefully removed by pipet and transferred to a dry NMR tube for analysis.

Product Ratio Alkylation Experiments. Typically, 10-25 mg of **1-5** were dissolved in ca. 0.2 mL of anhydrous acetonitrile-d_3 in an NMR tube. Following equilibration at 25.00 ± 0.01 °C, a solution of iodomethane-^{13}C in acetonitrile-d_3 was added *via* syringe to the equilibrated amine solution. The resultant mixture was allowed to stand at that constant temperature for >14 h before NMR analysis. Because of the potential for different relaxation rates, a delay period of >6 s was used between successive FID. Typically 100 FIDs were collected for each spectrum, and at least three alkylations were performed for each sample. The deviations were typically less than 5%. ^1H and ^{13}C NMR spectra were obtained for each alkylation reaction, and the pure products were isolated and characterized by elemental analysis.

The assignments of the trans and cis alkylation products (**8** and **9**, respectively) for **1-5** were made on the basis of nuclear Overhauser enhancement experiments reported previously[7a,9a] and on chemical shift analogies.[6] Consistancy was observed between the assignments shown in Table III, the coupling patterns and integrations in the ^1H NMR spectra and the integrations and chemical shifts in the ^{13}C NMR spectra.

1,1-Dimethyl-2-phenylpyrrolidinium iodide (**1**-CH_3I): mp 155-156 °C (lit.[36] mp 156-157 °C).

1,1-Dimethyl-2-(2-methylphenyl)pyrrolidinium iodide (**2**-CH_3I): mp 205-206°. Anal. Calcd for $C_{13}H_{20}NI$: C, 49.22; H, 6.35; N, 4.42. Found: C, 49.05; H, 6.12; N, 4.39.

1,1-Dimethyl-2-(2-ethylphenyl)pyrrolidinium iodide (**3**-CH_3I): mp 190-191 °C. Anal. Calcd for $C_{14}H_{22}NI$: C, 50.76; H, 6.69; N, 4.23. Found: C, 50.47; H, 6.78; N, 4.22.

1,1-Dimethyl-2-(2-isopropylphenyl)pyrrolidinium iodide (**4**-CH_3I): mp 237-238 °C. Anal. Calcd for $C_{15}H_{24}NI$: C, 52.18; H, 7.01; N, 4.06. Found: C, 52.12; H, 6.89; N, 4.08.

1,1-Dimethyl-2-(2-*tert*-butylphenyl)pyrrolidinium iodide (**5**-CH_3I): mp 223-224 °C. Anal. Calcd for $C_{16}H_{26}NI$: C, 53.49; H, 7.29; N, 3.90. Found: C, 53.24; H, 7.33; N, 3.80.

Acknowledgment. We thank Dr. E. B. Sanders for suggesting the procedure for synthesizing 2-(2-*tert*-butylphenyl)pyrroline and for many helpful conversations, Dr. Jerry F. Whidby and Mr. Ronald Bassfield for assistance in obtaining and interpreting the NMR spectra, Mr. Charles E. Thomas for assistance in establishing the conductometric system, Ms. Diane C. DeNagel for technical assistance, and the Philip Morris R&D Computer Group for their invaluable cooperation. We also thank the reviewers for a number of helpful criticisms and suggestions. We especially thank Dr. T. S. Osdene and Mr. Frank E. Resnik for their continued encouragement and support.

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Solvent Effects in the Photochemistry of Xanthone[1]

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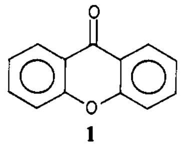
Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6. *Received March 10, 1980*

Abstract: The hydrogen-bonding properties of the media play a dominant role in the photochemistry of xanthone; for example, the bimolecular rate constant for the reaction of the triplet state with 2-propanol changes from 1.1×10^8 M^{-1} s^{-1} in carbon tetrachloride to 2.2×10^5 M^{-1} s^{-1} in neat 2-propanol. The change is attributed to an inversion of the n,π* and π,π* triplet states; while the effect is not uncommon, its magnitude is unprecedented. Self-quenching in xanthone is considerably faster than in the case of other aromatic ketones (e.g., benzophenone) and shows marked solvent dependence. The activation energy for energy transfer to γ-methylvalerophenone changes from 2.3 to 6.6 kcal/mol when the solvent is changed from carbon tetrachloride to methanol.

Introduction

Aromatic ketones have been the subject of numerous photochemical studies. Xanthone (**1**) is structurally quite similar to benzophenone, and its triplet energy is almost identical with that of acetophenone;[2] however, the few studies published on xanthone reveal striking differences between its behavior and that of other aromatic ketones. For example, studies of its phosphorescence reveal a strong dependence of the nature of the lowest lying triplet



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(1) Issued as NRCC-18712.

(2) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537.

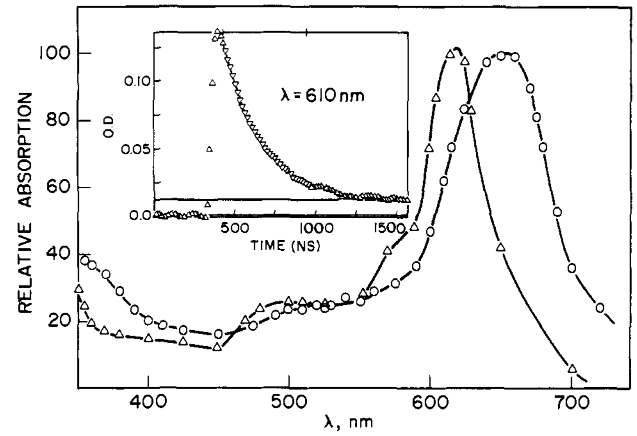

Figure 1. Normalized transient spectra of xanthone triplets in carbon tetrachloride (○) and in 2-propanol (△). Insert: Typical triplet decay trace for [xanthone] = 0.002 M in 2-propanol, fitted according to a first-order expression and using low enough excitation doses so that the T–T annihilation component accounts for less than 15% of the triplet decay.

state on the temperature and polarity of the media.[3-7] Despite an earlier controversy, it seems to be now well-established that the phosphorescence of xanthone in *n*-hexane is predominantly of π,π^* character at 4.2 K and n,π^* at 77 K.[4]

Wilkinson and Garner,[8-10] in a series of publications, have characterized the triplet state and the ketyl radical by using laser flash photolysis; they have also studied the quenching by naphthalene, oxygen, and indoles and briefly examined the solvent dependence of the triplet lifetimes. For example,[8] they report a triplet lifetime of 1.41 μs in ethanol, corresponding to a bimolecular rate constant for the interaction with the solvent of $\sim 4 \times 10^4$ M^{-1} s^{-1}. By contrast, Gramain et al.[11] report a rate constant for hydrogen abstraction from 2-propanol of 1.2×10^8 M^{-1} s^{-1} in carbon tetrachloride as solvent . Since the reactivities of ethanol and 2-propanol toward other ketone triplets usually differ by only a factor of ~2,[12] the results mentioned above would suggest a change in reactivity with the polarity of the media of roughly three orders of magnitude. Such a change is unprecedented; for comparison, in the case of the acetophenone–2-propanol system, the second-order rate constant changes from 19×10^5 M^{-1} s^{-1} in benzene to $\sim 7 \times 10^5$ M^{-1} s^{-1} in neat 2-propanol, a change of just under a factor of three.[13] In a related system, Wagner et al.[13b] have shown that the intramolecular reactivity (Norrish type II reaction) of *p*-methoxyvalerophenone decreases by a factor of nine when the solvent is changed from benzene to methanol.

Another area where literature reports seem to raise more questions than they answer refers to the process of self-quenching. This reaction has a reported rate constant of 2.1×10^9 M^{-1} s^{-1} in carbon tetrachloride;[11] by contrast, in other nonpolar solvents, like benzene and hydrocarbons, the process could not be detected.[8]

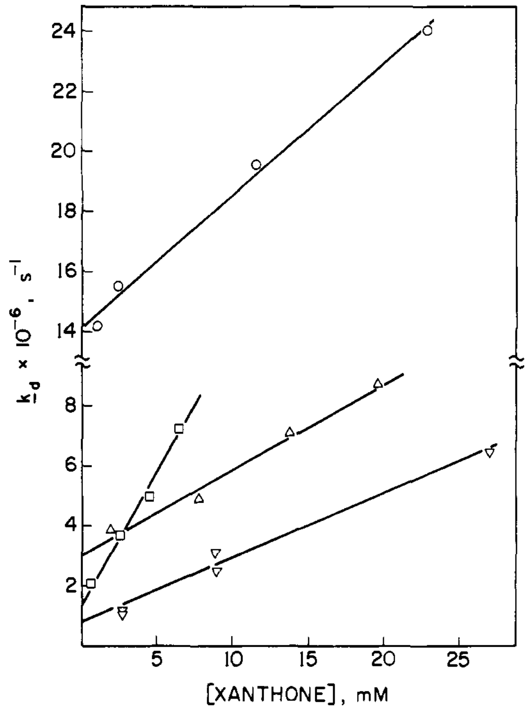

Figure 2. Representative plots of the pseudo-first-order rate constants for triplet decay vs. the concentration of xanthone in carbon tetrachloride (□), 2-propanol (△), methanol (▽), and benzene (○). All values shown correspond to zero dose extrapolations (see text).

In this paper, we report the results of a laser flash photolysis study of the reaction of xanthone triplets with 2-propanol as a function of solvent composition. We have also studied the role of self-quenching in different solvents. In addition, the reactivity toward other hydrogen donors, in particular cyclohexane and tri-*n*-butylstannane, has been investigated. Our results reveal the surprising sensitivity of the rates of quenching by hydrogen donors as well as self-quenching and kinetics of energy transfer on the hydrogen-bonding properties of the media.

Results

The samples were excited with the pulses (337.1 nm, 8 ns, 1–10 mJ) from a nitrogen laser, and the transient absorptions which resulted were monitored with a system with nanosecond response.

When a 0.0006 M solution of xanthone in carbon tetrachloride is examined, the transient spectrum observed (Figure 1) shows a broad absorption maximum at 655 nm, and is consistent with earlier reports in other solvents.[14] The signal decay can be fitted with first-order kinetics at low excitation doses, as shown in the insert in Figure 1. At higher excitation doses, the decay becomes faster and involves a second-order component. This is not unusual, and is the result of triplet–triplet annihilation; this problem is more important in polar solvents where the triplet lifetimes are longer (vide infra). The difference between the prepulse and final levels in the insert in Figure 1 is due to absorption by the xanthone ketyl radical.[8] The quantum yield of intersystem crossing was determined by comparing the yield of photosensitized formation of triplet 1-methylnaphthalene in the case of acetophenone (taken as $\Phi_{ISC} = 1.0$) and for xanthone, in matched samples and allowing for minor differences in the efficiency of energy transfer. The value obtained was $\Phi_{ISC} = 0.97 \pm 0.05$ at 25 °C in carbon tetrachloride.

The first-order rates observed at low excitation doses are concentration dependent, reflecting self-quenching of the triplet, a phenomenon that has also been observed by other groups.[11] The rate constants for self-quenching can be obtained from the slope of plots of the first-order rate constants for decay as a function of the concentration of xanthone. Figure 2 shows some representative plots. Each point in Figure 2 has been obtained by extrapolation of the kinetics of triplet decay to conditions of zero excitation dose, the latter being adjusted by using suitable neutral density filters. Figure 3 shows a set of transient absorbance vs. time traces which illustrates the effect of both concentration and

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(14) The value of λ_{max} reported in benzene is 610 nm.[8]

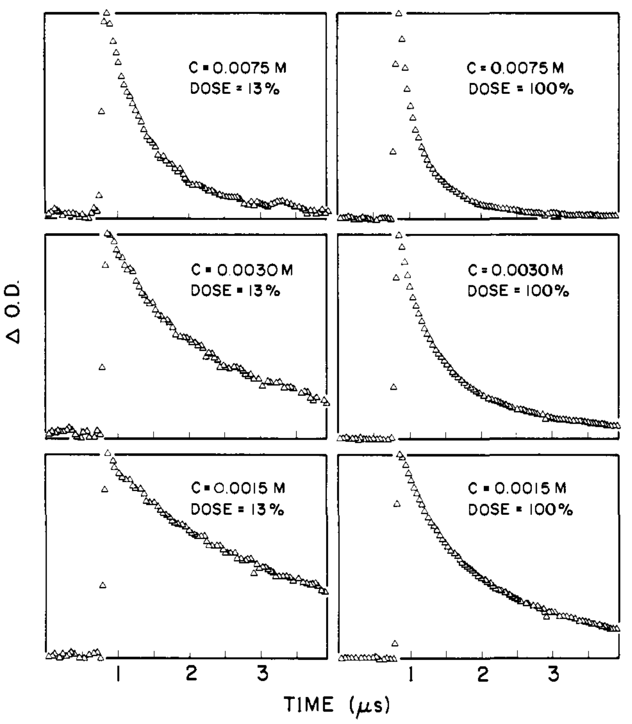


Figure 3. Effect of concentration and excitation dose on the triplet decay rates of xanthone in 50% water-acetonitrile. The monitoring wavelength was 600 nm, and typical top absorbances with full excitation dose were 0.32. The experiments with a 13% dose have been expanded accordingly.

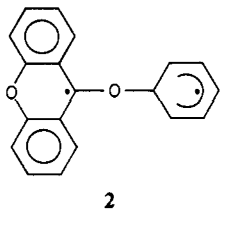
Table I. Kinetic Parameters for Triplet Decay in Several Solvents

solvent	τ_0, ns[a]	k_{SQ}, M^{-1} s^{-1} [a]
acetonitrile[b]	8300	4.5×10^8
water-acetonitrile[c]	17200	4.2×10^7
methanol	1300	2.1×10^8
benzene	71	4.3×10^8
carbon tetrachloride	700	9×10^8
cyclohexane	22	d
n-heptane	60	4×10^9 [e]
2-propanol	370	2.5×10^8
Cl_4C (0.05 M 2-propanol)	270	7.5×10^8

[a] At 22 °C; typical errors in k_{SQ} are 15%. [b] According to the manufacturer's specifications, the sample used contained 0.04% water. [c] A 1:1 mixture in volume. [d] Not measured. [e] Error could be as large as 30%.

excitation dose on the lifetimes. Table I gives a summary of kinetic results in several solvents. The triplet lifetimes given result from a double extrapolation, i.e., to zero excitation dose and to zero concentration. Lifetimes obtained in this manner should be insensitive to impurities in the xanthone, but could include a component of quenching by trace impurities in the solvents. As is usual in this type of experiment, the errors in τ_0 would be larger in the solvents leading to the longer lifetimes, while they are probably negligible in heptane, benzene, and carbon tetrachloride.

The decay of the triplet state in benzene does not lead to the formation of any other detectable transient, where in order to be identifiable a species would have to live at least as long as the triplet state and absorb at least 5–10% of the light absorbed by the triplet, anywhere in the region monitored. Our attempts to detect **2**, the transient suspected as responsible for the short lifetime, were thus unsuccessful.[15,16]



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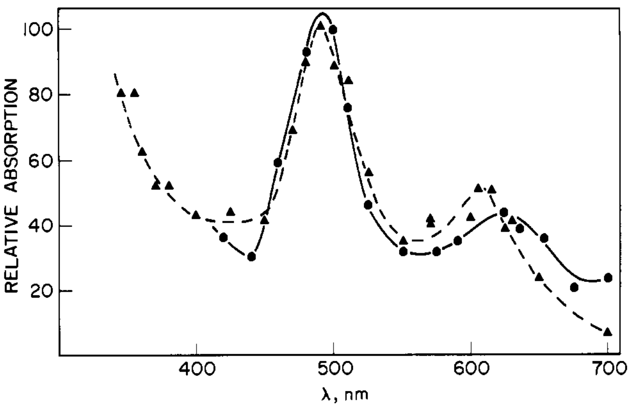

Figure 4. Spectrum of the ketyl radical from xanthone in 2-propanol (▲--) and heptane (●—).

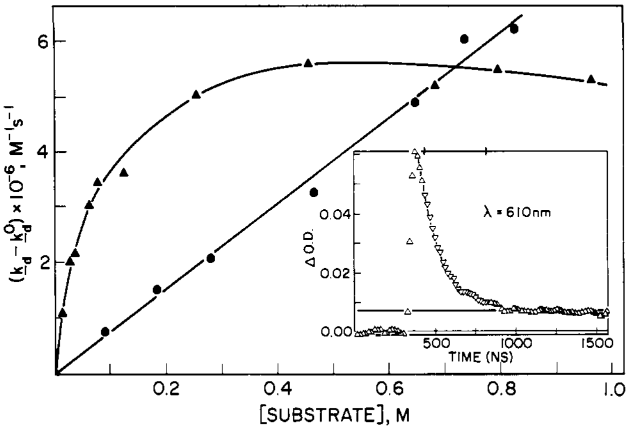

Figure 5. Quenching of xanthone triplets by cyclohexane (●) and 2-propanol (▲) in carbon tetrachloride at 22 °C. Insert: Triplet decay for 0.00064 M xanthone in carbon tetrachloride containing 0.65 M cyclohexane.

We also attempted to determine the lifetime of the triplet in diphenyl ether; in this case, τ_T is so short that the transient signal (monitored at 610 nm) simply follows the shape of the laser pulse. Quenching of the triplet by low concentrations of diphenyl ether in carbon tetrachloride leads to a rate constant of 1.3×10^8 M^{-1} s^{-1}. Extrapolation of the data to neat diphenyl ether suggests a triplet lifetime of ~1.7 ns. The decay of the triplet leads to weaker longer lived signals; significant absorptions were detected below 460 nm. These signals are presumed to result from an adduct of xanthone to the aromatic nucleus in diphenyl ether, similar to that detected in the case of benzophenone.[17]

In heptane and cyclohexane, as well as in alcohols, the decay of triplet xanthone leads to the formation of the corresponding ketyl radical. Figure 4 shows the spectra of the ketyl radical in different media; the data in heptane are in good agreement with the spectrum reported by Garner and Wilkinson in cyclohexane solvent.[8] The yields of ketyl radicals, measured at 500 nm, are about the same in cyclohexane and in 2-propanol; the same is true of the quantum yields for consumption of xanthone (determined by UV spectroscopy) which are quite similar in cyclohexane (0.80 ± 0.10) and in 2-propanol (0.70 ± 0.15). The difference, even if real, may simply reflect that different fractions of the radicals disproportionate in each system. The initial concentration of xanthone in these measurements was 0.00024 M.

We find that the triplet state of xanthone is extremely reactive in hydrogen abstraction reactions in nonpolar solvents. For example, the reaction with tri-*n*-butylstannane in carbon tetrachloride has a rate constant of 1.5×10^9 M^{-1} s^{-1}. In the case of benzo-

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(17) The detailed behavior of these adducts will be discussed elsewhere.

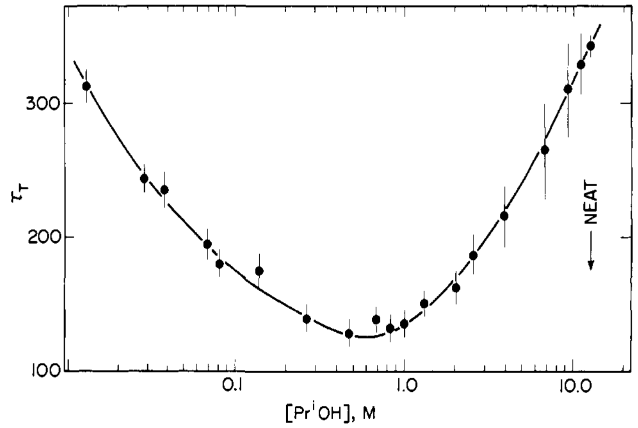

Figure 6. Effect of the composition on the lifetime of triplet xanthone in carbon tetrachloride–2-propanol mixtures, for [xanthone] = 0.0006 M.

Table II. Rate Constants for the Interaction of Xanthone Triplets with Several Hydrogen Donors

substrate	media	k_a, M^{-1} s^{-1} [a,b]
Bu_3SnH	Cl_4C	1.5×10^9
i-PrOH	Cl_4C	1.1×10^8
i-PrOH	1:1, Cl_4C-*i*-PrOH	4.1×10^5
i-PrOH	*i*-PrOH	2.2×10^5
n-heptane	*n*-heptane	2.5×10^6
cyclohexane	Cl_4C	7.7×10^6
cyclohexane	methanol	$\sim 2 \times 10^5$
cyclohexane	cyclohexane	$\sim 5.4 \times 10^6$

[a] At 22 °C. [b] Typical errors are 10–15% for most values and about 30% for those indicated as approximate figures (preceded by ~).

phenone triplets, the rate constant for the reaction is 2.9×10^8 M^{-1} s^{-1}.[18] It should be noted that for reactions as fast as these, a fivefold increase in reactivity should be regarded as a large change. The spectrum immediately following triplet decay was consistent with a 1:1 mixture of $Bu_3Sn\cdot$ and the xanthone ketyl radical.[8,18]

Good linear plots of the rate of triplet decay as a function of substrate concentration, leading (from the slope) to the second-order rate constant, are common for nonpolar substrates. Figure 5 shows the corresponding plot for cyclohexane; also included in Figure 5 is a similar plot for 2-propanol, where the nonlinearity of the plot is quite evident. We find efficient quenching by the alcohol in the low concentration region; in terms of the triplet lifetime, we find that it reaches a minimum for [*i*-PrOH] ~ 0.6 M and then starts to increase. The effect is illustrated in Figure 6. We found that the triplet lifetimes were somewhat less reproducible in mixtures containing ~10 M 2-propanol; this is reflected in the error bars shown.[19] The bimolecular rate constant can be evaluated by using eq 1, where k_a is the bimolecular rate

$$k_a = [k_d - (k_d^0 f)]/[i\text{-PrOH}] \qquad (1)$$

of interaction with the substrate, k_d the pseudo-first-order rate of decay, k_d^0 the same parameter in neat carbon tetrachloride, and f the fraction of the substrate–solvent mixture represented by carbon tetrachloride. This equation assumes that the decay of the triplet in carbon tetrachloride is the result of interaction with the solvent molecules.[22] In view of the relatively short lifetimes observed, this is almost certainly the case; however, the simple proportionality used may not be entirely correct, because the rate of interaction of triplet xanthone with carbon tetrachloride could depend upon the polarity of the solvent. Calculations with rather extreme assumptions make us confident that the errors introduced by the assumptions in eq 1 cannot exceed 20%. The values of k_a range from an extrapolated value of 1.1×10^8 M^{-1} s^{-1} at $c \rightarrow 0$ to 2.2×10^5 M^{-1} s^{-1} in neat 2-propanol, a change of a factor of 500. Table II gives a summary of rates of quenching by potential hydrogen donors.

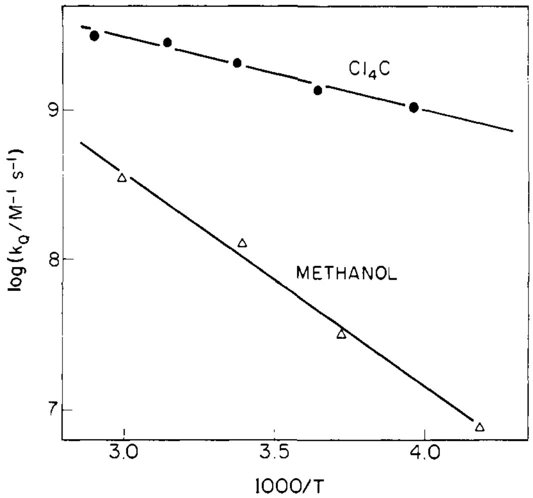

Figure 7. Arrhenius plot for the quenching of xanthone triplets by γ-methylvalerophenone in carbon tetrachloride (●) and in methanol (△).

In the cases of *n*-heptane and cyclohexane, we were somewhat worried about a characterization of the triplet state, in particular because in cyclohexane our lifetime (22 ns) was quite short, even if it did agree with earlier reports.[8] In order to confirm our assignment, we carried out several quenching experiments with 1-methylnaphthalene as a triplet-energy acceptor.[23] In addition to observing the formation of triplet 1-methylnaphthalene, we also carried out Stern–Volmer studies on the triplet yield. That is, the yields of triplet 1-methylnaphthalene (Φ_N) are expected to obey eq 2, or, if expressed in terms of transient absorbance (A_N),

$$\frac{1}{\Phi_N} = 1 + \frac{1}{k_q\tau_T[N]} \qquad (2)$$

eq 3,[24] where [N] is the concentration of 1-methylnaphthalene and α is a constant that does not need to be evaluated explicitly.

$$\frac{1}{A_N} = \alpha + \frac{\alpha}{k_q\tau_T[N]} \qquad (3)$$

The $k_q\tau_T$ values obtained were 145 M^{-1} for cyclohexane and 330 M^{-1} for *n*-heptane, which are consistent with the direct detection data if the rate of triplet quenching is taken as $\sim 6 \times 10^9$ M^{-1} s^{-1}, a very reasonable value for exothermic transfer in solvents of this type.[25]

The triplet energy of xanthone is almost identical with that of phenyl alkyl ketones.[26] We thought that the kinetics of energy transfer from xanthone to a representative phenyl alkyl ketone

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(18) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399–5400.

(19) The reasons for the difficulties in reproducing lifetimes are not clear. Fresh samples were used for all measurements, the lifetimes being somewhat shorter for partially irradiated samples in the 10 M concentration region. The sensitized decomposition of carbon tetrachloride[20] or an electron transfer from $(CH_3)_2\dot{C}OH$ to carbon tetrachloride[21] would be possible processes leading to the formation of secondary products.

(20) Pavlik, J. O.; Plooard, P. I.; Somersalt, A. C.; Guillet, J. E. *Can. J. Chem.* **1973**, *51*, 1435–1440. Encina, M. V.; Lissi, E. A. *J. Photochem.* **1974**, *3*, 237–239.

(21) Paul, H. *Int. J. Chem. Kinet.* **1979**, *11*, 495–509.

(22) It is worthwhile to point out that in the 370-nm region we observe that the decay of the triplet in neat carbon tetrachloride leads to the generation of weak longer lived transient absorptions. While these signals were too weak to study them in detail, or to assign them much importance in the interpretation of transient phenomena, it is an indication that some chemical change is taking place. From quantum yield measurements for [xanthone] = 0.00024 M, we find for the consumption of ketone $\Phi \leq 0.003$, based on an experiment with approximately 15% conversion.

(23) Triplet naphthalenes are very easy to monitor: Porter, G.; Windsor, M. W. *Proc. R. Soc. London, Ser. A.* **1958**, *245*, 238.

(24) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1980**, *13*, 815–820.

(25) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 1245–1251.

(26) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; Section 2.

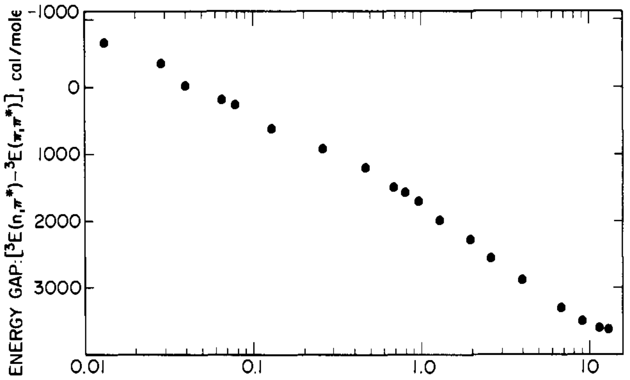

Figure 8. Energy gap between n,π* and π,π* triplet states estimated according to eq 4, as a function of 2-propanol concentration.

and its temperature dependence could shed some light on the effect of solvent on the energy levels of xanthone. We selected γ-methylvalerophenone as acceptor because its short triplet lifetime[27] makes the transfer irreversible. The approach used is the same as in earlier work.[28] Figure 7 shows an Arrhenius plot of the data obtained in carbon tetrachloride and in methanol, from which the following dependencies of the rate constants for energy transfer were derived: in carbon tetrachloride, $\log (k_{ET}/M^{-1}\ s^{-1}) = 11.0 - 2330/2.3RT$; in methanol, $\log (k_{ET}/M^{-1}\ s^{-1}) = 12.9 - 6620/2.3RT$, where RT has been expressed in cal mol^{-1}. Quantum yield studies of the direct and sensitized cleavage of γ-methylvalerophenone to yield acetophenone[28] confirm that the quenching is indeed the result of energy transfer.

Discussion

Perhaps the most striking outcome of this study is the large change in the reactivity of xanthone triplets toward 2-propanol observed in 2-propanol–carbon tetrachloride mixtures. The n,π* triplet, which can be expected to predominate in nonpolar media,[4] is more reactive than the triplet state of benzophenone (also n,π*),[11,12] probably reflecting a more favorable enthalpy change in the case of xanthone.[2,29] If we make the critical assumption that our rate constant for [i-PrOH] $\to$ 0 corresponds to the reactivity of a pure ^{3}n,π* state, and that the changes in reactivity simply reflect the Boltzmann distribution between the n,π* and π,π* levels,[13b,31] then the gap between states can be readily estimated from eq 4, where k_a^0 is the triplet reactivity when $c \to$

$$\Delta E = -RT \ln \left(\frac{k_a^0}{k_a} - 1 \right) \qquad (4)$$

0 and ΔE corresponds to $^3E(n,\pi^*) - {}^3E(\pi,\pi^*)$. Figure 8 shows a plot of ΔE as a function of the 2-propanol concentration; according to this plot, the energy gap approaches zero when [i-PrOH] ~ 0.05 M. The semilog representation has been used simply for convenience. It is important to emphasize the assumptions involved in the calculation of ΔE with eq 4. First, we have assumed that the reactivity extrapolated to zero alcohol concentration can be identified with that of the n,π* triplet and that the reactivity of the π,π* triplet can be ignored. Considering a nonzero reactivity for the π,π* triplet would lead to somewhat bigger energy gaps for high 2-propanol concentrations. While there are examples where some reactivity of the $^3\pi$,π* state is almost certain,[32,13b] in the case discussed herein it must be extremely different from that of the ^{3}n,π* state, otherwise the rate constant would not change by a factor of 500.[33] Second, in using eq 4, one is neglecting any entropy differences between the two triplets; this is unlikely to be a source of important errors. Third, we have regarded the reactivity of the n,π* triplet as solvent independent. This has been shown to be correct in the case of benzophenone triplets,[13a] where the inversion of states does not take place. In the case of xanthone, the ^{3}n,π* reactivity could decrease to some extent either as a consequence of increased state mixing when the $^3\pi$,π* state becomes low lying or as a result of hydrogen bonding at the oxygen bridge in xanthone; unfortunately, this assumption seems to be unavoidable.

Regarding the process of self-quenching, we also observe a decrease in the rate constant with increasing hydrogen-bonding character of the solvent. It should be noted that self-quenching is considerably faster for xanthone than for other typical aromatic carbonyls, i.e., it is ca. 2000 times faster than in acetophenone and 300 000 times faster than in benzophenone.[11] We believe that self-quenching must involve interaction at the oxygen bridge. In the case of diphenyl ether, we observe very efficient quenching of the xanthone triplet in a process that, as in the case of benzophenone,[15,34] must involve addition to the aromatic rings. If we generalize, we can expect molecules with the diphenyl ether type of moiety to be excellent quenchers; one such molecule is xanthone itself. While we do not have any direct evidence for charge transfer in the self-quenching process, or in the quenching by diphenyl ether, the fact that quenching by the latter has been found to correlate with its ionization potential[35] suggests that charge-transfer interactions may play a role in the transition-state configuration.

We believe that the solvent dependence of the rate constants for self-quenching must also reflect interactions with the oxygen bridge. It is important to note that the decrease in k_{SQ} is not simply a polarity effect (the rate constant is virtually the same in benzene as in acetonitrile), but is rather controlled by the hydrogen-bonding ability of the solvent. The change in the rate of self-quenching reflects other interactions in addition to the inversion of states that occurs in hydroxylic solvents. For example, in the case of 2-propanol–carbon tetrachloride mixtures, we have observed that the inversion of states occurs for a 2-propanol concentration of 0.05 M (see Figure 8). At this concentration, the rate of self-quenching has decreased by only 17% when compared with the value in pure carbon tetrachloride; this represents only 23% of the total change between the two neat solvents. If the inversion of states was the only parameter determining the change in reactivity, then the change in k_{SQ} would be 'half-way' between the values in carbon tetrachloride and in 2-propanol. In summary, the rate of self-quenching is slower for the π,π* triplet, whose reactivity also decreases as the hydrogen-bonding ability of the solvent increases.

It is interesting to view three observations made in this work as being mainly the result of the effects of the media on the n,π*–π,π* triplet gap. These observations are (i) solvent effect on the rates of reaction (see Figure 6), (ii) shift of T–T absorptions with the solvent (see Figure 1), and (iii) solvent effect on the activation energy for energy transfer to γ-methylvalerophenone. For example, the spectral shift in Figure 1 corresponds to ca. 3.4 kcal/mol; this is in fact quite close to the effect observed in terms

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[27] Grotewold, J.; Soria, D.; Previtali, C. M.; Scaiano, J. C. *J. Photochem.* **1972/73**, *1*, 471–479.

[28] Encinas, M. V.; Scaiano, J. C. *Chem. Phys. Lett.* **1979**, *63*, 305–308.

[29] Steel et al.[30] have suggested that enthalpy changes frequently do not reflect the changes in triplet energy because of a compensating effect due to resonance stabilization, e.g., acetone → acetophenone → benzophenone, which accounts for their similar reactivity in spite of the decreasing trend in triplet energy. It seems unlikely, however, that resonance stabilization would be substantially different in benzophenone and xanthone.

[30] Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953–958.

[31] (a)Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168–177. (b) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1970**, *92*, 5280–5281. (c) Previtali, C. M.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1672–1677. (d) Wagner, P. J.; Thomas, M. J.; Harris, E. *J. Am. Chem. Soc.* **1976**, *98*, 7675–7679. (e) Berger, M.; McAlpine, E.; Steel, C. *Ibid.* **1978**, *100*, 5147–5151.

[32] DeBoer, C. D.; Herkstroeter, W. G.; Marchetti, A. P.; Schultz, A. G.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 3963–3969.

[33] Considering a nonzero reactivity of the π,π* state would only affect significantly the results close to the neat 2-propanol limit. Even if we take the reactivity in neat 2-propanol as entirely due to the π,π* state [that is, $k(\pi,\pi^*) \sim 2.2 \times 10^5\ M^{-1}\ s^{-1}$], the energy gap for 9.1 M 2-propanol (corresponding to 70% 2-propanol) would be −4.4 kcal/mol instead of −3.5 kcal/mol.

[34] Nowada, K.; Hisaoka, M.; Sakuragi, H.; Tokumaru, K.; Yoshida, M. *Tetrahedron Lett.* **1978**, 137–138.

[35] Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040–4042.

of reactivity (Figures 6 and 8), and, therefore, one can suggest that T–T excitation leads to the same upper triplet in both cases, the position of this triplet being substantially less solvent sensitive than in the case of the two low-lying states. Further, the band is wider in nonpolar media; quite probably, this results from the fact that T–T excitation in carbon tetrachloride may, to some extent, take place from both triplet levels, while in polar media the gap is large enough that only π,π^* triplet is sufficiently populated to contribute significantly to the absorption band.

The increase in the activation energy for transfer to γ-methylvalerophenone when the solvent is changed from carbon tetrachloride to methanol (E_a changes from 2.3 to 6.6 kcal/mol) must also reflect the lowering of $^3\pi,\pi^*$ energy in xanthone. We note that the value in carbon tetrachloride can be regarded as "normal" for a quasi-isoenergetic transfer.[36] It is interesting that in a transfer of this type it would not be enough for the n,π^* triplet to move up in energy in polar solvents, since this could not produce such a large change in E_a; the π,π^* triplet moving down in energy must be largely responsible for the changes in the energy gap.[38]

The exceptionally high rates of self-quenching in xanthone must be due to reactivity at the ether bridge, as the extremely short lifetime in diphenyl ether suggests. The higher reactivity of xanthone relative to benzophenone, toward the aromatic nucleus, as well as in hydrogen-transfer processes in nonpolar media, must be due to a combination of increased electrophilic character of the triplet state, as well as a more favorable enthalpy change.[29]

Finally, our results show that the seemingly contradictory reports mentioned in the Introduction simply reflect conditions under which the media leads to unprecedented changes in triplet lifetimes, rates of self-quenching, and rates of hydrogen abstraction. The unusual sensitivity of xanthone to environmental properties may make it a useful probe for organized systems such as micelles, monolayers, etc.

Experimental Section

Materials. Xanthone (Fluka, puriss.) was recrystallized one time. The solvents, methanol (Aldrich, Gold Label), benzene (Fisher, Spectro.), carbon tetrachloride (Fisher, Spectro.), heptane (Fisher, Spectro.), cyclohexane (Fisher, Spectro.), 2-propanol (Fisher, cert. ACS), and acetonitrile (Photex, Spectro.), were usually of the highest purity available and were used as received. Tri-*n*-butylstannane was an Alfa-Ventron product, and 1-methylnaphthalene was obtained from Aldrich. Valerophenone (Aldrich) and γ-methylvalerophenone (Fluka) were distilled and chromatographed on alumina.

Quantum Yields. The consumption of xanthone was monitored by UV spectroscopy in the 300–360-nm region with a Cary-219 instrument. The photocleavage of valerophenone in benzene was used as a relative actinometer, taking Φ(acetophenone) = 0.30.[40] The yields of acetophenone were determined by gas chromatography with an OV-101 column.

The same instruments and a similar procedure were used to confirm that quenching of xanthone triplet by γ-methylvalerophenone leads to the corresponding photofragmentation products.[28] All irradiations were carried out at 337.1 nm, operating the laser at either 2 or 30 Hz, and the samples were rotated in a "merry-go-round" to ensure equal irradiation dose.

Sample Preparation and Temperature Control. The samples (1 mL) were contained in Suprasil cells with a 3-mm optical path. They were deaerated by using oxygen-free nitrogen. An irradiation cell with the same optical path, but a 10-mL sample capacity, was used for some of the experiments in order to minimize changes in reagent concentration. The temperature of the cell was controlled by a constant-temperature nitrogen flow in a manner similar to that normally employed in EPR spectrometers. A Suprasil vacuum jacket provided adequate windows and thermal insulation. The temperature was measured with a copper-constantan thermocouple (reference at 0 °C); in the −150 to 100 °C range, eq 5 provides a suitable approximation, where T is the temperature

$$T = 0.00213V^5 - 0.001007V^4 + 0.0438V^3 - 0.7958V^2 + 26.06V \quad (5)$$

(°C) and V the voltage in mV; the latter was amplified (X100) and measured directly by the computer via the A/D converter (see below).

A flow system in which the stock solution is deaerated with nitrogen prior and during the experiment is also available; in this case, the reaction cell is also made of Suprasil rectangular tubing (3-mm optical path).

Apparatus. Our laser flash photolysis facility has been built following many of the ideas used before to develop a similar system at the University of Notre Dame.[41,42] The excitation source is a Molectron UV-24 nitrogen laser which produces 8–10-ns pulses of up to 10 mJ at 337.1 nm. The excitation dose was adjusted between 0.5 and 10 mJ by using suitable neutral density filters. The pulses were concentrated (but not focused) on the samples by a combination of spherical and cylindrical lenses; the latter are quite useful in order to change the shape of the beam and lead to typical improvements of factors of two or three in the output signal.

The monitoring system consists of a pulsed 200-W xenon lamp as light source, a high intensity B & L or PRA-B204 monochromator, and an RCA-4840 photomultiplier tube at the detection end; only six dynodes were used. The samples were contained in Suprasil cells made of 7 × 3 mm rectangular tubing (Vitro Dynamics). The angle between the excitation and monitoring beams was around 15°, and provision was made for either front or rear excitation. The use of the small-angle approach decreases considerably the volume irradiated and is more convenient for lower energy lasers.[43,44]

The system has been fully interphased with a PDP11/03 computer which controls the experiment, gathers the data, processes information, produces suitable files on storage devices, and provides copies of graphics and other useful information.

The laser is pulsed at a frequency of 1 Hz and has been synchronized with the line frequency. Pulsing the laser regularly, regardless of the requirements of the experiment, leads to very reproducible pulse energies. When a pulse is needed for the experiment, a Uniblitz shutter is triggered following an "enable" command from the computer; at the same time, a second shutter opens to allow the monitoring beam to reach the analyzing monochromator. Another command activates the lamp pulser. All these commands are controlled via different bits from the low-byte output from a 16-bit parallel interface (DEC-DRV11). It is important to note at this point that our synchronizer–sequencer unit generates pulses to activate all the units (shutters, pulser, detection, etc.) once every second (with suitable delays); the computer role is to enable the desired units when it is ready to gather information. This type of approach makes it very easy to correct the traces for background, fluorescence, etc., by simply enabling only some of the units. For example, in order to subtract background, one enables all units except the shutter controlling the laser pulse. The high-byte output and 16-bit input in the DRV11 interface are used to control the driver unit (PRA Model 1611) of the PRA-B204 monochromator. The computer provides the pulse to drive the stepping motor, and the wavelength is checked feeding the BCD output of the PRA-1611 unit in the 16-bit input of the DRV11 parallel unit; DEC-Fortran-IV extension routines are used to process the data. Typical slits are 0.5 mm for input and 1.0 mm for output.

A DEC-ADV11-A, A/D interface is used in order to measure the intensity of the monitoring beam and is also available to monitor other parameters during the experiment (e.g., laser high voltage and cell temperature).

The photomultiplier signals are terminated into 93 Ω and into a 7A16A plug-in used in a R7912-Tektronix transient digitizer; the latter contains a 4 K local memory in which each trace, plus all associated "knob" settings, are stored. A Tektronix 607 storage monitor displays every trace stored by the transient digitizer; the memory from the latter is read by the computer via a CP-4100/CP bus Tektronix interface.[45] The trace information from the R7912 digitizer consists of 512 "x" or timebase values; each one of the x coordinates can have one, several, or no y (vertical or voltage) values associated with it. In order to process

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[36] For example, for the energy transfer from propiophenone to γ-methylvalerophenone in isooctane solvent, we obtain[37] log (A/M^{-1} s^{-1}) = 10.47 and E_a = 1.82 kcal/mol, corresponding to k (at 20 °C) = 1.3 × 10^9 M^{-1} s^{-1} (see also ref 28).

[37] Scaiano, J. C., to be published.

[38] Solvent effects on the relative position of the n,π^* and π,π^* levels have been known for many years,[39] and, in the case of intramolecular reactions, the sensitivity of *p*-methoxy-substituted ketones is known to be larger than that of the unsubstituted analogues.[13b]

[39] Rauh, R. D.; Leermakers, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 2246–2249.

[40] Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506–7512.

[41] A partial description of the Notre Dame system can be found in earlier papers; e.g.: Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 2146–2152; see also ref 24.

[42] The original software used at Notre Dame was developed in collaboration with Dr. L. K. Patterson of the Notre Dame Radiation Laboratory.

[43] Goldschmidt, C. R.; Ottolenghi, M.; Stein, G. *Isr. J. Chem.* **1970**, *8*, 29–36.

[44] Small R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 828–832.

[45] The reader interested in doing a similar type of interfacing should be aware that the Tektronix interface requires bus signals on the C and D slots of the LSI-bus; these are not available in all PDP backplanes, and, in particular, some of the newer models, like H9273-A, have the bus available only in positions A and B.

the data, it is important to generate a trace such that each x value is associated with just one y value. In order to do this, we have preferred to generate our own software, rather than use the one available from the manufacturer. For every x value, the y values are averaged if more than one is available or interpolated if that x channel contains no y information associated with it. In processing the data in this manner, one must use very strict criteria in evaluating the quality of a given trace, since it would be very easy to generate excellent looking traces from very little information, by simply playing a game of interpolations and extrapolations. By properly tuning the instrument, we found that it was easy to work under conditions where over 99% of the data was contained in the original trace recorded (i.e., less than 1% interpolation), and values as high as 99.7% were not unusual. Traces where 3% or more of the y values were generated by software were regarded as unacceptable. The video display unit was quite valuable in optimizing the experimental conditions.

A programmable photomultiplier power supply has been recently incorporated to the system and was used for the last group of experiments. The unit has been built around a Model LR-2N, Venus PMT power supply (Subtech Ltd.). The computer has been programmed to set the high voltage so that a suitable current will be drawn from the photomultiplier, based on wavelength, signal during previous shots, etc. The computer commands are fed into the power supply via one channel (″170442) from a DEC-AAV11-A 12-bit D/A converter. This unit was extremely useful for the automatic recording of transient spectra.

In general, the time resolution (in terms of interval between points) that can be achieved with the R7912 digitizer amply exceeds that necessary for nanosecond experiments; we have generally preferred to handle 100 points, rather than 512. To do this, the 400 points in the center of the trace were "nested" in groups of four, leading to the 100 points generally displayed in our traces (see Figures 1, 3, and 5); elimination of the edges of the trace makes the tuning of the instrument simpler. As a rule, we have averaged between 5 and 30 traces to carry out the kinetic measurements and 3–8 traces at each wavelength for the spectra, even if in many cases a single shot could have sufficed.

After the data had been processed, all graphic outputs were displayed in a Tektronix 4010-1 terminal, and a 4631 Tektronix unit provided hardcopy facilities. The results were also stored in double-density flexible disks.

The risetime of the system was ca. 1 ns, but the actual 'window' in which measurements could be carried out was 10 ns to 500 μs. The rate at which data could be gathered was ca. 1 trace every 3 s, though it should be noted that this rate is at present controlled by the rate at which the capacitors used for the lamp pulser are recharged.

Acknowledgment. I am grateful to Dr. D. F. Williams for his help in setting up the laser system and for valuable discussions, to S. E. Sugamori for his technical assistance, and to G. Charette for designing and building the computer interfaces.

An Electrically Neutral σ-Sulfuranyl Radical from the Homolysis of a Perester with Neighboring Sulfenyl Sulfur: 9-S-3 Species[1]

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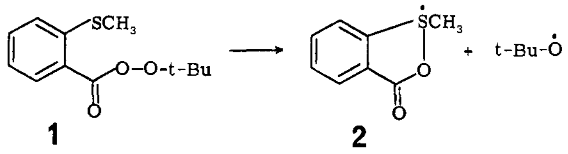
Abstract: The cyclic sulfuranyl radical **2** is generated by the low-temperature photolysis of *tert*-butylperoxy 2-(methylsulfenyl)benzoate (**1**) in methylene chloride solutions. The ESR spectrum of **2**, centered at $\langle g \rangle = 2.008_0$, shows proton hyperfine splittings by a methyl group ($a_{3H} = 9.0$ G) and H_6 ($a_H = 1.5$ G) but no resolved coupling (<0.1 G) to other protons. The pattern of coupling was unambiguously established through studies of four different regiospecifically deuterated samples of **1**. The ESR results are best interpreted in terms of a bridged radical, a 9-S-3 (nine-electron, three-coordinate sulfur) system with an S–O bond, in which the odd electron is in a σ-type orbital with large spin density on sulfur, and a σ-sulfuranyl radical. We discuss the implications of this finding in terms of earlier observations of anchimeric acceleration of thermal bond homolysis in **1** and its analogues.

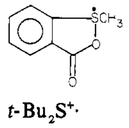
Radical-forming thermolyses of *tert*-butylperoxy benzoates which have sulfenyl sulfur substituents ortho to the carboxy function (either phenylsulfenyl or, as in the case of **1**, methylsulfenyl) have been shown[2] to proceed with anchimeric acceleration factors of as much as 10^6. Substituent effects on rate showed the decomposition of the phenylsulfenyl-substituted perbenzoate to occur via a very polar transition state with the development of positive charge on the sulfur atom.[2c,d] It has been suggested[2] that the acceleration results from S–O bonding in a transition state leading to bridged sulfuranyl radicals such as **2**. An unstable intermediate sulfurane, which would result from recombination of the *tert*-butoxy radical (formed by O–O bond homolysis) with the simultaneously formed sulfuranyl radical, has been directly observed[2d] in the thermolysis of a close analogue of **1** (eq 1).



(1)

1 **2**

Table I. ESR Parameters of Some Oxysulfuranyl Radicals

structure	⟨g⟩	proton hyperfine splittings, G		ref
		CH3S	others	
$(CH_3)_2\dot{S}OSi(CH_3)_3$	2.0076	7.7	0.2[a]	*e*
$CH_3\dot{S}(O\text{-}t\text{-}Bu)_2$	2.0096	6.5		*f*
$\dot{S}(OCH_3)_3$	2.0067		1.7[b]	*g*
	2.008_0	9.0	1.5[c]	This work
$t\text{-}Bu_2S^{+\cdot}$	2.0130		*d*	*e*

[a] From $(CH_3)_3Si$. [b] From CH_3O. [c] From H_6. [d] *t*-Bu not resolved, $a_S = 32.5$ G. [e] W. B. Gara, J. R. M. Giles, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1444 (1979). [f] W. B. Gara, B. P. Roberts, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Res., Miniprint*, 1748 (1977). [g] J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 835 (1976).

Sulfuranyl radicals (e.g., **2**) are tricoordinate species in which the valence shell of sulfur has been, at least formally, expanded

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