Lifetimes and Rate Constants of Triplet Aromatic Ketones in Organic Solvents

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Summary Determination of the triplet lifetimes of benzophenone and acetophenone in organic solvents by measurement of the phosphorescence decay allows direct estimation of the rate constants of interaction of these triplets with a variety of substrates.

AROMATIC ketones, such as benzophenone and acetophenone, are generally considered not to phosphoresce in normal solvents at room temperature,[1] although strong benzophenone phosphorescence in a fluorocarbon solvent has been observed[2] and Bäckström and Sandros[3] saw a weak blue emission from benzophenone in benzene. The reasonably long lifetime of benzophenone triplets in benzene (*ca.* 10^{-5} sec.)[4] led us to believe that we should be able to record reasonable phosphorescence spectra at room temperature. This is indeed the case, and in Figure 1 we show the emission of benzophenone and acetophenone in iso-octane as solvent at 23°. The spectra show good agreement with those obtained in rigid media[5] and in fluorocarbons.[2] The quantum yields of emission were 4×10^{-4}([benzophenone] $= 1{\cdot}0 \times 10^{-2}$M, $\lambda_{\text{excit}} = 385$ nm.) and 4×10^{-4} ([acetophenone] $= 2{\cdot}0 \times 10^{-3}$M, $\lambda_{\text{excit}} = 330$ nm.). Benzophenone does not emit in alcohols[6] because of chemical reaction of the triplet or in ethers[7] or amines[8] due to physical quenching and reaction. It is, therefore, not surprising that emission studies in solvents like EPA (ether, isopentane, alcohol) yield negative results at room temperature.

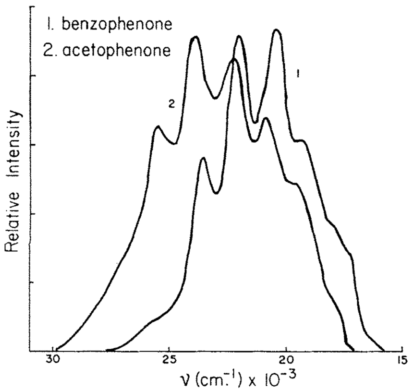

FIGURE 1. *Emission spectra of benzophenone* (1) *and acetophenone* (2) *in iso-octane at* 23°. *The intensity is in terms of quanta per unit frequency interval.*

Much of the photochemistry of benzophenone, especially rate studies, depend upon the triplet lifetime of benzophenone.[8,9] The most commonly used value for the triplet lifetime is that obtained by Bell and Linschitz[4] who observed a transient absorption in the flash photolysis of benzophenone in benzene which they associated with the benzophenone triplet–triplet absorption. As these authors emphasized, the lifetime of the triplet may depend strongly on solvent purity. The only solvent they used was benzene which is relatively unreactive. Furthermore, the interpretation of the data was complicated by the presence of another species which absorbed in the same region as the benzophenone triplet, and was thought to be the ketyl radical. Recently, there has been some question as to the correctness of the rate constants which they determined.[10] For these reasons, we measured the lifetime of triplet benzophenone directly from the decay of its triplet emission using solvents of the same purity that were employed for the rate studies. Then, using Equations (1) and (2) below, the rate constants for interaction, k_S, of a wide variety of substrates, S, with the triplet, can be obtained.

$$1/\tau_S = 1/\tau_0 + k_S\,[\mathrm{S}] \qquad (1)$$

$$I(0)/I(\mathrm{S}) = 1 + \tau_0\, k_S\,[\mathrm{S}] \qquad (2)$$

τ_S and τ_0 are the observed lifetimes of the triplet in the presence and absence of the substrate and $I(0)$ and $I(\mathrm{S})$ are the corresponding steady-state emission intensities.

The solvents were "Spectrograde," routinely distilled once through a Vigreux column, the middle cut being employed. More rigorous distillation and gas chromatographic purification did not produce solvents in which τ_0 was appreciably longer. However, τ_0 is to be regarded only as an experimentally measured quantity and not as an "intrinsic" constant of triplet benzophenone in the appropriate solvent. Even though a better method of purifying the solvents used may be found, this will not affect our values of k_S. The lifetime apparatus which is very simple, is similar to that described before[11] except that the excitation and emission light beams were passed through Corning filter combinations 7-60 and 3-72, 5-96 respectively. The first filter passes light in the 300—400 nm. region, while the latter two filters pass from 440 to 590 nm. The steady-state emission spectra were recorded on a Farrand spectrofluorimeter and appropriately corrected.[12]

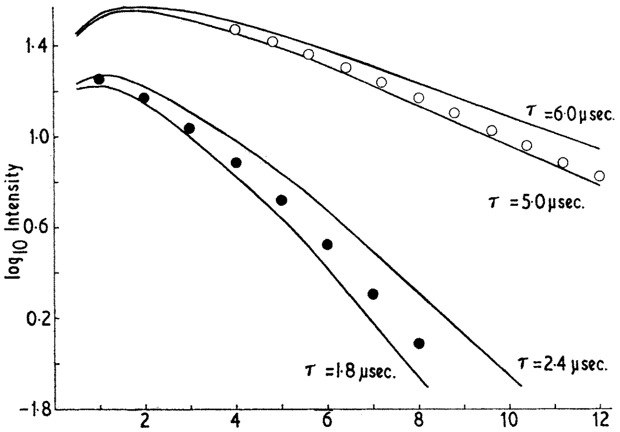

FIGURE 2. *Emission intensity as a function of time for the decay of benzophenone triplet in benzene* ○, *and iso-octane* ●. *The points are taken from the oscilloscope trace. The full line curves are the computer-calculated profiles for the appropriate* τ *values. Temperature* 31°.

Typical data for benzophenone (5×10^{-2}M) in benzene and iso-octane are shown in Figure 2. The average τ_0 values for several runs were $\tau_0 = 5{\cdot}4 \pm 0{\cdot}2$ and $2{\cdot}0 \pm 0{\cdot}1$ μsec. for benzene and iso-octane as solvents at 31°. In the case of benzophenone in benzene, the concentration was varied from 5×10^{-2}M to 5×10^{-4}M without finding a significant change in τ_0. However there is significant temperature dependence in τ_0. Plotting $\log_{10}(1/\tau_0)$ against $1/T$ yields "activation energies" of 3·4 and 4·1 kcal. mole^{-1} for benzophenone in benzene and iso-octane, respectively. Although it is possible that these activation energies originate from impurity quenching, at present we believe that they represent genuine activation energies of interaction of the triplet with the solvent. For acetophenone (2×10^{-2}M) we obtained $\tau_0 = 3{\cdot}3 \pm 0{\cdot}2$ and $2{\cdot}0 \pm 0{\cdot}1$ μsec. in benzene and iso-octane at 23°.

Even though the $1/e$ time of the flash was 0·2 μsec., the "tail" extends as far as 6 μsec. This means that the slope of the log I_{em} against t curve only approaches the "correct" value of $1/(2{\cdot}303\tau)$ for $t > 6$ μsec. For emissions with short lifetimes ($\tau < 6$ μsec.), plotting log I_{em} against t over the region of significant emission and determining τ from the average slope results in τ values considerably larger than the "correct" values. All experimental data were therefore fitted to those obtained from a computer-generated model.

The 1000-fold variations in the quantum yields of benzophenone and acetophenone in going from the glass at −196° to iso-octane at 23°, parallel the 1000-fold variations in lifetimes ($\Phi^{\mathrm{benzo}}_{-196} = 0{\cdot}74$, $\tau_0 = 4{\cdot}7$ msec., $\Phi^{\mathrm{aceto}}_{-196} = 0{\cdot}62$, $\tau_0 = 2{\cdot}3$ msec.).

The interaction rate constants for a variety of substrates

TABLE

Interaction rate constants for various substrates with triplet benzophenone and acetophenone

Ketone	Solvent	Temp. (°C)	Substrate	$k_{\mathrm{S}} \times 10^{-9}$ ($\mathrm{M}^{-1}\mathrm{sec.}^{-1}$)	Method (equation)
benzophenone	benzene	31	naphthalene	$6\cdot8 \pm 0\cdot7$	1
"	"	31	"	$6\cdot6 \pm 0\cdot4$	2
"	"	23	"	$6\cdot1 \pm 0\cdot3$	2
"	iso-octane	31	"	$9\cdot5 \pm 0\cdot6$	1
"	"	31	"	$8\cdot5 \pm 0\cdot4$	2
"	"	23	"	$6\cdot4 \pm 0\cdot4$	2
"	benzene	23	azoisopropane	$2\cdot4 \pm 0\cdot1$	2
"	"	23	DBH	$2\cdot2 \pm 0\cdot1$	2
"	iso-octane	23	azoisopropane	$2\cdot8 \pm 0\cdot1$	2
"	"	23	DBH	$2\cdot6 \pm 0\cdot1$	2
"	benzene	23	isoborneol	$0\cdot008 \pm 0\cdot001$	2
acetophenone	"	23	naphthalene	$7\cdot7 \pm 0\cdot3$	2
"	iso-octane	23	"	$13\cdot5 \pm 0\cdot5$	2

are shown in the Table. Naphthalene is a common "diffusion controlled" quencher of triplets. Our values agree well with those suggested by Wagner[10] but are significantly greater than those obtained by Bell and Linschitz.[4] Also, the variation in k_{S} with temperature closely parallels the variation in the reciprocal of the viscosity of the solvent. Benzophenone is also commonly used as a triplet sensitizer. For example the triplet sensitization of azo-compounds has been investigated; quantum yields exist, but no rate data.[14,15] The data show that the values of k_{S} for azoisopropane and 2,3-diazabicyclo[2,2,1]hept-2-ene (DBH) are close to but significantly less than the diffusion controlled limit. Benzophenone triplets may also hydrogen abstract. As an example of this we show k_{S} for isoborneol. This value of $0\cdot8 \times 10^{7}\mathrm{M}^{-1}\,\mathrm{sec.}^{-1}$ may be compared with the value of $1\cdot0 \times 10^{7}\mathrm{M}^{-1}\,\mathrm{sec.}^{-1}$ recently reported by Guttenplan and Cohen[16] using a chemical method.

Preliminary data indicate that these emission techniques can be used to study triplet reactivity for a wide range of solvents and substrates. Among the latter are alcohols, amines, ethers, and thioethers. Under the same conditions we find the emission of triplet benzaldehyde is much weaker. We have as yet not obtained good kinetic data in solution for this molecule, but results of emission studies from gaseous benzaldehyde triplets at room temperature have recently been reported.[17]

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