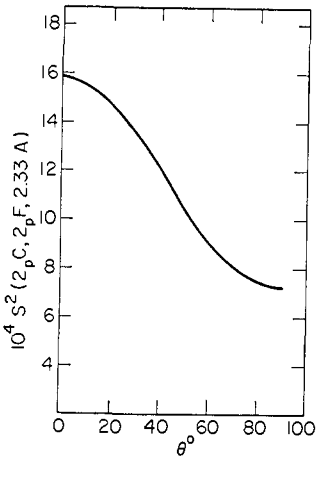

Figure 1. The relationship between S^2 for 2p orbitals centered on carbon and fluorine atoms separated by 2.33 Å and the dihedral angle θ shown in I. The S^2 value is sensitive to the selected structural parameters.

distance, over 2.5 Å, in the semiquinone and semifuraquinone.

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Received October 4, 1969

Delayed Fluorescence and Phosphorescence of Aromatic Ketones in Solution

Sir:

The observation of emission from benzophenone[1,2] and acetophenone[2] in fluorocarbon[1] and hydrocarbon[2] solvents represents a substantial breakthrough in the study of photochemical processes in solution. In the following we show that the emission from several aromatic ketones is composed of delayed fluorescence and phosphorescence components.

Sources of materials and purification methods will be described in the full paper. Solutions of the ketones in carbon tetrachloride or benzene were outgassed to $<10^{-5}$ mm using 5–7 freeze–pump–thaw cycles. Emission spectra were recorded using a Hitachi Model MPF-2A spectrophotometer (Phototube, Hitachi R-106). Corrected spectra and emission quantum yields were determined using quinine bisulfate as standard, $\phi_F = 0.56$.[3–5]

The emission spectrum of benzophenone in carbon tetrachloride at 23° is typical (Figure 1). It agrees well with the spectra obtained in benzene, perfluoromethylcyclohexane,[1] and isooctane.[2] The positions of phosphorescence 0–0 bands and the corresponding triplet excitation energies are given in Table I. These energies are 1–2 kcal/mol lower than those obtained from measurements in hydrocarbon glass at 77°K.[6] For the benzophenones a plot of E_T against Hammett's σ is fairly linear and gives $\rho = 1.03$, linear correlation coefficient $r = 0.916$.[7] The positive value of ρ may reflect the increase in electron density at the carbonyl carbon upon n–π* excitation.[8]

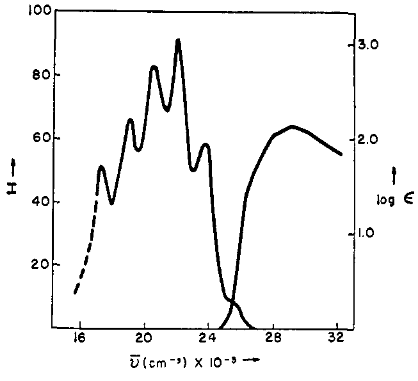

Figure 1. Corrected benzophenone emission spectrum in carbon tetrachloride: 23° on the left; n–π* absorption on the right.

Table I. Triplet Energies and Emission Bands of Aromatic Ketones in CCl_4 at 23°

Ketones X-PhCOPh-Y	E_T, kcal/mol	$S_0^0 \leftarrow T_0^1$, µm^{-1}	$S_0^0 \rightarrow S_0^1$, µm^{-1}
4,4′-diOMe	68.4	2.39	2.58
4-OMe	67.8	2.37	2.53
3,4′-diMe	67.5	2.36	2.54
H	67.6	2.36	2.52
3-CO$_2$Me	67.4	2.36	2.52
3-Cl	67.2	2.35	2.51
3,4′-diCl	66.8	2.34	2.49
4,5′-diCO$_2$Me	67.1	2.35	2.51
3,4′-diCO$_2$Me	66.0	2.31	2.46
X-PhCOMe			
H	72.0	2.52	2.65[a]
4-Cl	71.5	2.50	2.62[a]

[a] The delayed fluorescence band was much weaker in the two acetophenones studied and these values should be regarded as very approximate.

Delayed Fluorescence. A general feature of the emission spectra is the presence of a low-intensity band on the high-energy side. In the case of benzophenone the excitation spectrum for emission at 2.52 µm^{-1} is identical with excitation spectra obtained by monitoring the emission at lower frequencies. The relative intensity of the high-energy band increases with temperature. A plot of the logarithm of the ratio of the emission intensity at 2.56 µm^{-1} to that at 2.06 µm^{-1} against T^{-1} is linear, $r = 0.995$, and gives $\Delta H = 4.4$ kcal/mol for the two emitting states. The S^0–S^1 n–π* absorption of benzophenone shows good overlap with the emission band at 2.52 µm^{-1}, Figure 1, and it can be seen that the enthalpy difference corresponds closely to the spectroscopic S_0^1–T_0^1 splitting. It follows, then, that the high-energy band is activation-controlled delayed

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(1) C. A. Parker, *Chem. Commun.*, 749 (1968).

(2) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).

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(4) J. W. Eastman, *ibid.*, **6**, 55 (1967).

(5) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(6) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(7) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 172–192.

(8) The ρ value may be compared with $\rho = 0.54$ from a similar plot for E_T's measured at 77°K,[9] and $\rho = 0.58$ obtained for the rates of hydrogen abstraction by benzophenones.[10] Change in reactivity has been attributed to variation in the extent of mixing between the low-lying n–π* and π–π* triplet states.[10]

(9) M. B. Burleigh, Ph.D. Thesis, University of California, Riverside, 1966, p 72.

(10) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

fluorescence.[11,12] The entropy difference between the singlet and triplet n–π* states can be estimated from eq 1, where I_F and I_P are the relative intensities of fluorescence and phosphorescence and k_F and k_P are the rates of radiative decay from the singlet and triplet state, respectively.

$$\log\frac{I_F}{I_P} = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.203R} - \log\frac{k_P}{k_F} \qquad (1)$$

Using $k_F = 1.4 \times 10^5\ \text{sec}^{-1}$ [13] and $k_P = 1.6 \times 10^2\ \text{sec}^{-1}$,[14] $\Delta S = -3.5$ eu is obtained which gives $\Delta F = 5.4$ kcal/mol at 23°. The calculated equilibrium constant at 23° is 1×10^{-4} and checks well with the observation that at this temperature fluorescence comprises ~10% of the total emission (Figure 1). The absence of prompt fluorescence in the spectra is demonstrated by the disappearance of the fluorescence band at low temperatures and the fact that in the presence of sufficient concentration of a triplet excitation acceptor to intercept more than 90% of benzophenone triplets, the relative intensity of fluorescence to phosphorescence remains unaltered. Approximated positions of delayed fluorescence bands for several aromatic ketones are given in Table I.

The presence of significant concentrations of S^1 molecules in equilibrium with T^1 molecules can be of great photochemical significance. T^1 states may serve as reservoirs of excited molecules whose photoreactions proceed from S^1 states. Effective reaction rates will then depend on the Boltzmann population of S^1 and should be strongly temperature dependent. For molecules with small S^1–T^1 energy gaps, quenching of a photoreaction by triplet excitation acceptors need not, as has been generally assumed, signify that the reactive state is the triplet of the donor. Clearly, the mechanisms of many photoreactions require reexamination.

The Lifetime of Benzophenone Triplets in Solution. Much of the chemistry of benzophenone triplets has been studied in benzene[15] or carbon tetrachloride[16] solutions. The lifetime of benzophenone triplets in these solvents is therefore of considerable interest, and, in the case of benzene, has been the subject of several investigations.[2,15] Stern–Volmer quenching constants of the emission at 23° were obtained with naphthalene as quencher in benzene and benzil as quencher in carbon tetrachloride (benzophenone, 5×10^{-3} *M*). Lifetimes of 8.4×10^{-6} and 1.1×10^{-4} sec for benzophenone triplets in benzene and carbon tetrachloride, respectively, were calculated using the value of k_q reported in ref 2.

The quantum yield of benzophenone phosphorescence in benzene at room temperature has been estimated at 2×10^{-4}.[17] An experimental value of 1.1×10^{-3} can be inferred from the results in ref 2.[18] Our measurements give emission quantum yields of 1.6×10^{-3} in benzene and 1.5×10^{-2} in carbon tetrachloride (benzophenone, $\sim 5 \times 10^{-3}$ *M*). The radiative lifetime of benzophenone triplets at 77°K in alcohol–ether glass is 6.4×10^{-3} sec.[14] Since ~10% of the emission at 23° is delayed fluorescence, the effective radiative lifetime should be $\sim 5.7 \times 10^{-3}$ sec. Using the actual lifetimes obtained from this work, the expected quantum yields are 1.5×10^{-3} and 1.9×10^{-2} for benzene and carbon tetrachloride, respectively,[19] in excellent agreement with our observations.

Reversible hydrogen abstraction from the solvent has been suggested as the path for rapid decay of benzophenone triplets in benzene.[1,20] Although benzophenone is photoreduced in pure benzene, the hydrogen abstraction rate is too slow to contribute significantly to the decay rate.[21] We propose that a major decay process may involve formation of an adduct diradical as has been suggested for the interaction of acetophenone triplets with alkenes.[22,23] The lifetime of benzophenone triplets in carbon tetrachloride is smaller than that in perfluorocarbon solvent.[1] The contributions of impurity quenching and/or external heavy atom effect in determining the decay rate in carbon tetrachloride remain to be assessed.

Acknowledgment. This research was supported by the National Science Foundation, Grant No. GP-7941, and by the Petroleum Research Fund, administered by the American Chemical Society. J. W. M. was also supported by the National Science Foundation, Grant No. GP-8015.

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[14] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1967, p 297.

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[20] *Cf.*, however, J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

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[24] National Institutes of Health Predoctoral Fellow, 1966–1969.

[25] Petroleum Research Fund Fellow.

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Received September 25, 1969

High Resolution Nuclear Magnetic Resonance of Solid Perfluorohexane

Sir:

Temperature dependence in the structure of high resolution nmr spectra provides a well-known source of information about thermally activated molecular rate processes in solution.[1] Similarly, the temperature dependence of wide-line nmr spectra provides useful, if less detailed, information about the motions of molecules in crystals and polymers. We wish to point out that a new class of multiple-pulse nmr experiments[2] is capable of being employed in a similar spirit, with re-

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[1] C. S. Johnson, Jr., "Advances in Magnetic Resonance," Vol. I, Academic Press, New York, N. Y., 1965, p 33.

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