PHOSPHORESCENCE AND PHOTOCHEMICAL STUDIES OF SOME BENZOPHENONE DICARBOXYLIC ACID ESTERS

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Summary

Phosphorescence quantum yields and lifetimes in solution in carbon tetrachloride were measured for dimethyl esters of three benzophenone dicarboxylic acids. Curious features were noted. The triplet energies (in kilocalories per mole) varied with substitution ((3,3), 67.0; (3,4), 65.6; (4,4), 64.8), as did the phosphorescence lifetimes (14 μs, 26 μs and 45 μs respectively). The radiative rate constants $k_p = 165 \pm 10$ s^{-1} were identical. The triplets of all three ketones reacted with *n*-octane with a second-order rate constant of 1.14×10^6 M^{-1} s^{-1} at 22 °C.

1. Results and discussion

While carrying out a study of the photochemistry of benzophenone dicarboxylic acid esters [1], we noted interesting changes in their phosphorescence spectra and triplet lifetimes (in CCl$_4$) as a function of positional substitution. These changes, while not large, seemed to be unusual enough to merit further investigation. This paper reports the results of our efforts.

The molecules of interest, **1a** (3,3 substitution), **1b** (3,4 substitution) and **1c** (4,4 substitution) show similar UV absorption spectra above 300 nm. Each has a characteristic n–π^* band at about 350 nm in CCl$_4$ with a very small progressive red shift in the substitution series (3,3), (3,4) and (4,4)

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TABLE 1

Data[a] for molecules 1a - 1c and 2

Mole-cule	Substi-tution	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	$\lambda(0,0)$[b] (nm)	E_T (kcal mol^{-1})	τ (μs)	$10^3\phi_p$	$k_p{}^c$ (s^{-1})	$k_H(2)$[d]	τ^e (μs)
1a	3,3	344	120	426	67.0	14.4	2.6	180	1.18	58.8
1b	3,4	350	150	435	65.6	25.6	4.3	165	1.14	67.5
1c	4,4	354	180	443	64.8	44.6	6.8	150	1.14	52.1
2		350	160	436	65.5	32.2	5.6	175		

[a]All data for solutions 5.9×10^{-4} M in CCl_4 except where noted.
[b]Fully corrected emission spectra.
[c]From $k_p = \phi_p/\tau$.
[d]Second-order rate constant for phosphorescence quenching by n-octane.
[e]In acetonitrile solution.

(Table 1). More curious is that the molar extinction coefficients ϵ also increase in this series, from 120 M^{-1} cm^{-1} for 1a to 180 M^{-1} cm^{-1} for 1c. These small changes in ϵ at λ_{max} are suggestive of minor differences in the oscillator strength of the $S_1 \leftarrow S_0$ transition. Since this is a forbidden transition, these differences could arise from substitution effects on the degree of mixing with the $S_2 \leftarrow S_0$ transition where the intensity of the lower energy transition derives.

The phosphorescence spectra of 1a - 1c as well as of 2 in CCl_4 solution are similar in shape (Fig. 1). There are, however, pronounced shifts in these spectra. The (3,3)-substituted diester is the most blue shifted, with its (0,0)
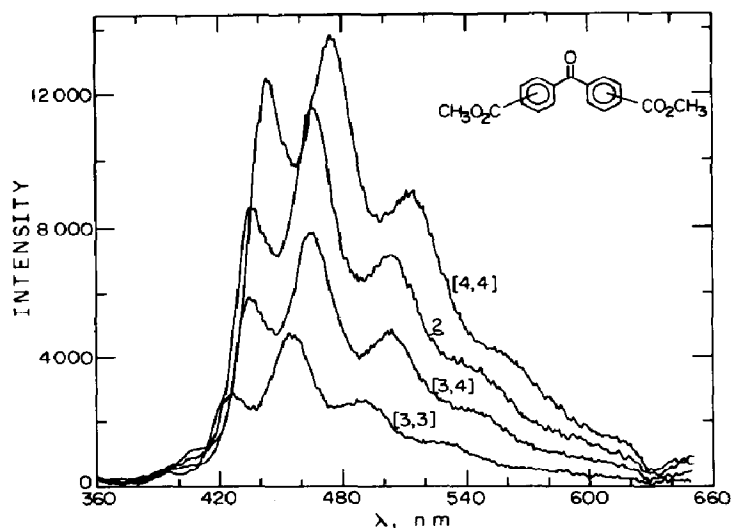
Fig. 1. Phosphorescence spectra of 1a - 1c and 2 taken at 5×10^{-4} M in CCl_4. The spectra are taken under identical conditions and are fully corrected for the wavelength dependence of the monochromator and photomultiplier response. The samples 1a, 1b and 1c are labelled according to their substitution pattern, i.e. (3,3), (3,4) and (4,4) respectively.

band occurring at 426 nm. This corresponds to a triplet energy of 67.0 kcal mol^{-1}. By comparison, the (4,4) diester has its (0,0) band at 433 nm, indicating a triplet energy of 64.8 kcal mol^{-1}. From the vibrational spacing shown in Fig. 1, these spectra are clearly due to emission from $n-\pi^*$ triplet states.

The feature of the phosphorescence which initially caught our attention was the differences in the triplet state lifetime for the three isomers of 1. These values ranged from 14 μs for 1a to 45 μs for 1b. Like all phosphorescence decay times in solution, these values are exceptionally sensitive to solvent purity and traces of residual oxygen after degassing. Consequently we took particular care always to work with the same batch of purified solvent, to test the vacuum line used for sample outgassing and to prepare simultaneously samples which were to be compared. These are routine precautions for the study of ketone reaction kinetics by phosphorescence decay measurements [1 - 3].

These differences in lifetime might be radiative or non-radiative in origin:
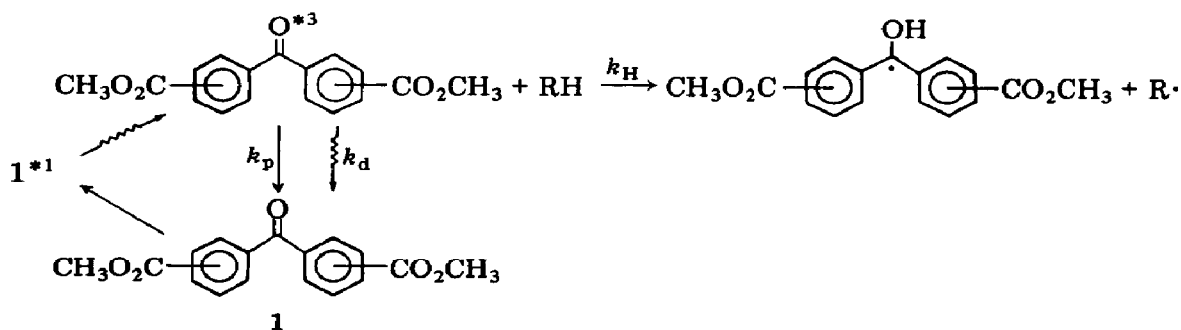
To assess the radiative contribution, we determined the radiative rate constant k_p. The phosphorescence quantum yield ϕ_p depends on k_p according to the expression

$$\phi_p = \phi_{ST} \frac{k_p}{k_p + k_{nr}} = \phi_{ST} k_p \tau \tag{1}$$

where ϕ_{ST} is the triplet formation:

$$k_p = \frac{\phi_p}{\tau} \qquad (\text{for } \phi_{ST} = 1) \tag{2}$$

It is well documented that the triplet formation occurs with essentially 100% efficiency in benzophenone (see for example ref. 4) and in 2 [5]. We assume that $\phi_{ST} = 1.0$ here as well.

From the spectra in Fig. 1 plus triplet state lifetime τ measurements, all the appropriate information could be obtained. $\phi_p(2)$ was calculated (eqn. (2)) from the known value [6] of $k_p = 180$ s^{-1} for 2. This was then used as a reference to obtain ϕ_p for 1a - 1c. In these experiments, samples were excited at $\lambda = 340$ nm, and small corrections were made for differences in sample absorbance. Quite to our surprise, essentially identical values of k_p

were obtained. There are small differences, but these are probably within experimental error. The oscillator strengths for the $T_1 \to S_0$ emission are very similar, and the lifetime differences are non-radiative in origin.

Reactivity differences among the three diesters were assessed by measuring the kinetics of hydrogen abstraction with n-octane. Samples containing 5.0×10^{-3} M **1a**, **1b** or **1c** and five concentrations of n-octane in CCl_4 were prepared and sealed in Pyrex tubes after degassing. Phosphorescence decay times were measured, and the data were plotted according to the expression

$$\frac{1}{\tau} \approx \frac{1}{\tau^0} + k_H[\text{octane}] \tag{3}$$

where τ^0 is the lifetime in the absence of octane and k_H is the quenching (hydrogen abstraction) rate constant. As indicated in Table 1, these rate constants are identical for the three isomers.

The final feature of these molecules that we wish to address is whether self-quenching (via an excimer?) might account for the short lifetime of **1a**. Self-quenching is the general term to describe the reaction

$$1^* + 1 \xrightarrow{k_{sq}} 2\ 1 \tag{4}$$

Four solutions of **1a** in CCl_4 were prepared, varying in concentration from 5×10^{-4} to 4×10^{-3} M. The data were fitted to the expression $1/\tau = 1/\tau^0 + k_{sq}[\textbf{1a}]$ and are plotted in Fig. 2. The weak dependence of τ on [**1a**] gives a value of $k_{sq} \approx 2.4 \times 10^6$ M^{-1} s^{-1}. While this value is more than 100 times larger than that for **2**, it is not sufficient to explain the lifetime differences reported in Table 1 for experiments carried out at 5×10^{-4} M. Extrapolation to zero concentration for **1a** gives $\tau^0 = 15.0$ μs, compared with 14.4 μs found at the former concentration.
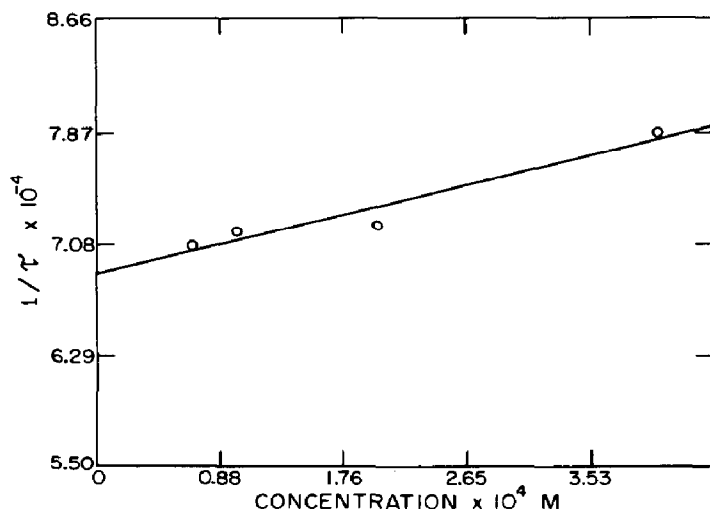

Fig. 2. Stern–Volmer plot of the reciprocal phosphorescence lifetime of **1a** in CCl_4 as a function of its concentration.

When the phosphorescence lifetimes were measured for **1** in acetonitrile solution, very similar values were found (Table 1). We conclude, therefore, that the differences in τ observed for **1a** - **1c** in CCl_4 are due to differences in non-radiative decay rates and probably arise from quenching interactions with the solvent. (Other consequences of substituents on the photochemical and spectroscopic properties of diaryl ketones are reported in ref. 7.)

2. Experimental details

The molecules **1a** - **1c** were prepared by Schäfer and Schmidt. Their synthesis and characterization will be reported elsewhere.

Samples for quantum yield measurements were placed in Pyrex cells 1 cm square. Quenching studies, which involved only lifetime measurements, were carried out on samples placed in cylindrical tubes. All the samples were rigorously degassed by five successive freeze–pump–thaw cycles on an all-glass mercury-free high vacuum line. After the fifth cycle, the pressure above each of the frozen samples was less than 1×10^{-5} Torr. The samples were sealed under vacuum and stored in the dark.

Corrected emission spectra were measured using an SLM 4800 spectro-fluorometer. Lifetime measurements were carried out using a flash photolysis device. Light flashes were provided by an NRG 0.5-5-150/B nitrogen laser which produces 500 000 W of light of wavelength 337 nm, with a time width at half-intensity of about 5 ns. This light was focused onto the samples after it had been passed through a Corning 7-60 blue filter to remove the visible component ($\lambda > 390$ nm) of the light. Emitted light from the sample was collected, passed through a 350 - 610 nm band-pass filter and a KV-418 cut-off filter and focused on a Hamamatsu R 928 photomultiplier tube. The phototube output passed through an operational amplifier and across a resistor chosen to provide optimum voltage at the expense of the RC time constant of the circuitry. RC time constants were almost always a factor of 10 less than the measured emissive decay times. The output of the circuitry was fed to a Biomation 8100 transient waveform recorder, where the signal was digitized and transferred, channel for channel, to a Tektronix 4052 computer. Repetitive signals were added to improve the signal-to-noise ratio. The intensity *versus* time data were analysed using a non-linear least-squares program. These techniques are described in more detail in earlier publications [1, 2].

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References

1 M. A. Winnik, G. C. Wang, H. J. Schäfer and W. Schmidt, *J. Photochem.*, in the press.
2 U. Maharaj and M. A. Winnik, *Macromolecules, 12* (1979) 902.
   U. Maharaj, M. A. Winnik, B. Dors and H. J. Schäfer, *Macromolecules, 12* (1979) 905.

3 A. Mar and M. A. Winnik, *Chem. Phys. Lett.*, 77 (1981) 73.
4 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings, New York, 1978, and references cited therein.
5 M. A. Winnik, *Ph.D. Thesis*, Columbia University, New York, 1969.
6 M. A. Winnik and A. Lemire, *Chem. Phys. Lett.*, 46 (1977) 283.
7 G. Favaro, *J. Photochem.*, 20 (1982) 33.
   G. Favaro and F. Maseti, *J. Photochem.*, 15 (1981) 241.
   N. C. Yang and R. L. Dusenbery, *J. Am. Chem. Soc.*, 103 (1981) 624.
   N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, 1 (1969) 159.