

CORRELATION BETWEEN PHOSPHORESCENCE LIFETIMES AND RATIOS OF STEADY STATE PHOSPHORESCENCE TO FLUORESCENCE INTENSITY FOR BIACETYL IN VARIOUS SOLVENTS

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Summary

The phosphorescence of biacetyl in fluid solutions is quenched not only by oxygen but also by impurities resulting from the distillation procedure and from the freeze-pump-thaw degassing technique. A linear correlation between the measured phosphorescence lifetimes and the ratios of the phosphorescence to the fluorescence intensities is established; the slope affords reliable calculations of the biacetyl triplet lifetimes from steady state measurements and additionally the determination of the rate constant k_p of radiative triplet deactivation. This constant is dependent on the solvent, whereas the fluorescence constant k_F is not.

1. Introduction

The quenching of biacetyl phosphorescence in solution at room temperature has been used as a standard procedure in many mechanistic investigations of energy transfer and triplet state reactivities [1 - 13]. However, the reported triplet lifetimes of biacetyl which are required to calculate kinetics data from Stern-Volmer measurements vary over a wide range (Table 1). Phosphorescence intensities different by up to a factor of 3.5 have even been reported by the same researcher using the same sample preparation technique [2, 8]. In order to yield reliable data about the influence of charge transfer on the selectivity of photoreactions of biacetyl with electron-rich olefins [14 - 16] we needed accurate triplet lifetimes to correlate the quenching rate constants of biacetyl phosphorescence with the oxidation potential of the quenchers [14, 15]. Therefore we have measured the lifetime and the phosphorescence intensity of biacetyl in the presence of oxygen as well as under "oxygen-free" conditions using different degassing techniques in benzene and acetonitrile. Whereas the fluorescence intensity is not quenched by oxygen because of its short lifetime (9.85 ns in benzene),

TABLE 1

Phosphorescence lifetime τ_P , ratio I_P/I_F of phosphorescence to fluorescence intensity and ratio ϕ_P/ϕ_F of phosphorescence to fluorescence quantum yield at room temperature

τ_P (μs)	I_P/I_F	ϕ_P/ϕ_F	<i>Solvent</i>	<i>Reference</i>
980 - 1030			Benzene	[1]
178 - 644		8.4 - 29.6	Benzene	[2]
440 - 528			Benzene	[3]
		7.5	Benzene	[4]
460			Benzene	[5]
200			Acetonitrile	[6]
145			Acetonitrile	[7]
336			<i>n</i> -Hexane	[7]
135			Benzene	[7]
135	12 ^a		Benzene	— ^b
—	12 - 20 ^a		Benzene	[8]
	28.5 ^c		Acetonitrile	[9]
634			Iso-octane	[12]

^aNo information about the correction of the spectra.

^bRef. 8, note 8.

^cSpectra corrected (spectral bandwidth, 8 nm).

the phosphorescence intensity and lifetime strongly depend on the purification of biacetyl[†] and on the technique of oxygen removal [8].

When the rate constant k_q for triplet quenching by oxygen [17] is assumed to be $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and the oxygen concentration in the nitrogen degassing technique is assumed to be 10^{-6} M [14], then $k_q \tau_P [\text{O}_2] = 1 - 10$ for $\tau_P = 100 \mu\text{s} - 1 \text{ ms}$. By means of the fluorescence intensity as an internal standard [8] it is possible to examine the phosphorescence properties of biacetyl under different experimental conditions.

2. Experimental details

Benzene and acetonitrile (Merck, Uvasol) were purged with argon for at least 1 h. Biacetyl (EGA Chemie) was distilled under reduced pressure at room temperature and was condensed using a CO_2 -acetone cooling mixture. Only freshly distilled biacetyl was used[†]. The biacetyl solutions were purged in triangular cuvettes with argon for 1 min before the cuvettes were sealed with a Teflon stopper. Two different purities of argon were used: 99.998% Ar (Linde) with $[\text{O}_2]_{\text{max}} = 2 \text{ vol.ppm}$ and 99.9999% Ar with $[\text{O}_2]_{\text{max}} = 0.5 \text{ vol.ppm}$ (Messer Griesheim).

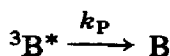
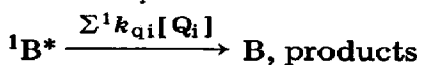
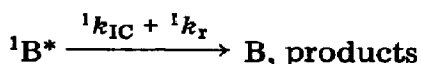
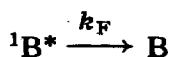
In order to obtain a small quenching effect by dissolved oxygen the stopper of the cuvette was lifted for a few seconds to allow air to dissolve in

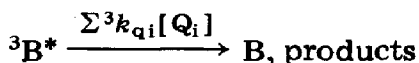
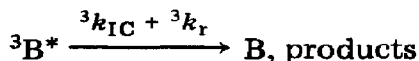
[†]Old samples of biacetyl exhibit shorter phosphorescence lifetimes owing to impurities caused by thermal and photochemical decomposition.

the biacetyl solution, which was originally prepared with argon. Emission spectra were recorded on a Perkin-Elmer MPF-3L fluorescence spectrometer at 20 °C using a triangular cuvette (excitation wavelength, 420 nm; excitation bandwidth, 40 nm; emission bandwidth, 2 nm). The ratios I_p/I_F of the phosphorescence to the fluorescence intensity maximum were taken from the emission spectra corrected for the spectral response of the phototube. The phosphorescence intensity at the emission maximum (520 nm) was calculated by subtracting the fluorescence intensity at this wavelength from the total emission intensity. The fluorescence intensity at 520 nm was measured for samples whose phosphorescence had been totally quenched (saturation with air). Relative quantum yields were calculated by integrating the areas under the peak of the corrected luminescence spectra. Fluorescence lifetimes were determined with an Edinburgh Instruments 199M fluorescence lifetime spectrometer system using the single-photon counting technique. Phosphorescence lifetimes were measured by an apparatus consisting of parts of an Aminco-Bowman spectrophotofluorometer 4-8106 (excitation and emission monochromator; sample chamber) and parts of an Applied Photophysics flash photolysis apparatus (spectroflash switching unit; 100 J xenon flash-lamp LR20; power supply; photodiode for triggering the oscilloscope; filter-bias unit; photomultiplier). An extra high tension power supply type E1 by Farnell Instruments and a Textronix oscilloscope with a dual time base 5812N complete the apparatus. The rectangular geometry was the same as that for the steady state measurements. For several measurements a conventional computer-controlled Osram BCS 44 studio flash-lamp was used [18] instead of the LR20 flash-lamp. The flash intensity was smaller and the full width at half-maximum was 21 μs (LR20 flash-lamp; 12 μs). However, equal lifetimes were obtained with the same sample using both flash-lamps. The lifetimes were calculated using phosphorescence intensities monitored at 520 nm between 100 and 1000 μs after the flash had been initiated.

3. Results and discussion

From the kinetics scheme





the expressions for the quantum yields and lifetimes are easily derived:

$$\phi_{\text{F}} = \frac{K_{\text{F}}}{k_{\text{F}} + {}^1k_{\text{IC}} + {}^1k_{\text{r}} + \sum {}^1k_{\text{qi}}[\text{Q}_i] + k_{\text{ISC}}} = k_{\text{F}}\tau_{\text{F}} \quad (1)$$

$$\phi_{\text{P}} = \frac{k_{\text{ISC}}\tau_{\text{F}}k_{\text{P}}}{k_{\text{P}} + {}^3k_{\text{IC}} + {}^3k_{\text{P}} + \sum {}^3k_{\text{qi}}[\text{Q}_i]} = k_{\text{ISC}}\tau_{\text{F}}k_{\text{P}}\tau_{\text{P}} \quad (2)$$

The fluorescence lifetimes of 0.2 M biacetyl in benzene (9.85 ± 0.08 ns) and acetonitrile (8.01 ± 0.08 ns) are similar to those reported in the literature [6, 19]. There was no difference between the air-saturated and the argon-purged samples. Together with the ratio of the relative fluorescence quantum yields in benzene and acetonitrile

$$\frac{\phi_{\text{F}}(\text{benzene})}{\phi_{\text{F}}(\text{CH}_3\text{CN})} = 1.317$$

the ratio of k_{F} in both solvents is calculated according to eqn. (1):

$$\frac{k_{\text{F}}(\text{benzene})}{k_{\text{F}}(\text{acetonitrile})} = 1.07$$

The absence of an oxygen quenching effect on the fluorescence of biacetyl justifies the use of the fluorescence intensity as an internal standard [8] for the investigations of the phosphorescence properties of biacetyl. From eqns. (1) and (2) a linear correlation is obtained between the phosphorescence lifetime and the ratio of the phosphorescence to the fluorescence quantum yields in the presence of various singlet and triplet quenchers of arbitrary concentrations:

$$\tau_{\text{P}} = \frac{k_{\text{F}}}{k_{\text{ISC}}k_{\text{P}}} \frac{\phi_{\text{P}}}{\phi_{\text{F}}} \quad (3)$$

In order to use the phosphorescence intensities I_{P} and the fluorescence intensities I_{F} at the emission maxima a constant c has to be considered according to the different shapes of the phosphorescence and the fluorescence spectrum and the inner filter effect:

$$\tau_{\text{P}} = \frac{k_{\text{F}}}{k_{\text{ISC}}k_{\text{P}}} c \frac{I_{\text{P}}}{I_{\text{F}}} \quad (4)$$

For biacetyl the magnitude of c is 0.544, calculated with the $I_{\text{P}}/I_{\text{F}}$ value for a solution of 0.2 M biacetyl in benzene and the ratio of the integrated phosphorescence spectrum to the integrated fluorescence spectrum for a solution of 0.02 M biacetyl in benzene. The correlation of eqn. (4) fits for different kinds of sample preparation (Fig. 1) in the same solvent and the slope

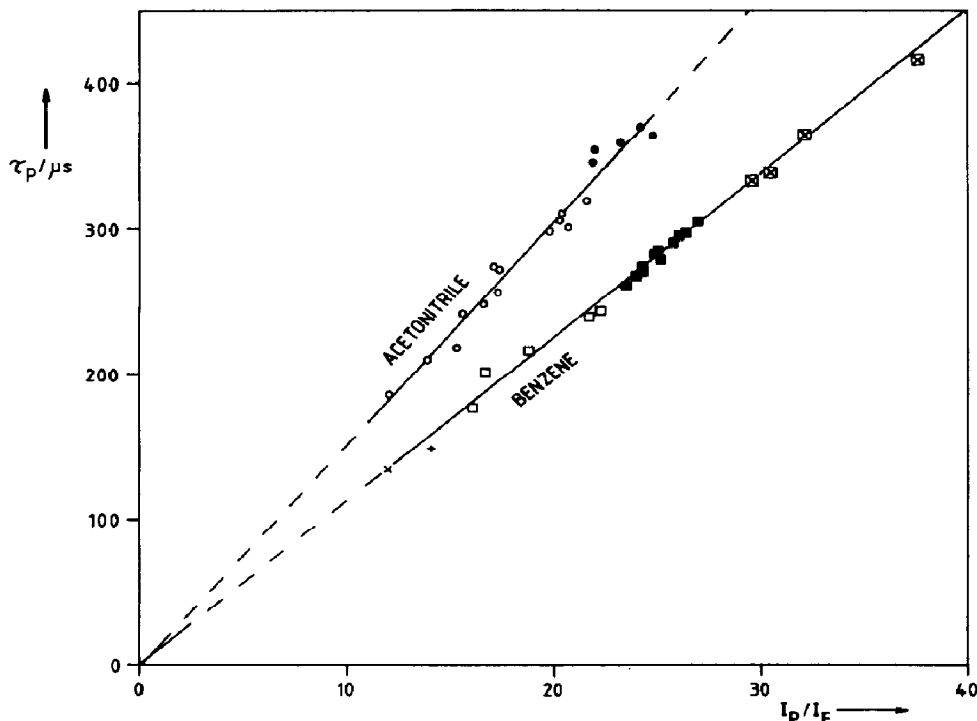


Fig. 1. Phosphorescence lifetime τ_p of biacetyl vs. the ratio I_p/I_F of phosphorescence to fluorescence in benzene and acetonitrile: \boxtimes , purged with argon ($[O_2] \leq 0.5$ vol.ppm); \bullet , \blacksquare , purged with argon ($[O_2] \leq 2.0$ vol.ppm); \circ , \square , exposed to air (see text) after argon purging; $+$, two freeze-pump-thaw cycles after argon purging (in benzene); \times , value from ref. 8 (in benzene).

$k_{FC}/k_{ISC}k_P$ of eqn. (4) is independent of the kind and the amount of quencher.

Different values of the I_p/I_F ratios and τ_p were obtained for different methods of oxygen removal (Fig. 1). The highest values were obtained only by purging with high purity argon ($[O_2]_{\max} \leq 0.5$ vol.ppm) in benzene. Shorter lifetimes and smaller I_p/I_F ratios were measured by degassing with normal argon ($[O_2]_{\max} \leq 2$ vol.ppm), mostly used for welding. In contrast, degassing by means of the freeze-pump-thaw technique results in much smaller phosphorescence intensities, as recently reported by Jones *et al.* [8]. The I_p/I_F ratios gradually decrease with the number of freeze-pump-thaw cycles, indicating decomposition of biacetyl with formation of quenching impurities. For example, the I_p/I_F value decreases from an original value of 14.9 (two freeze-pump-thaw cycles) to 6.3 after ten freeze-pump-thaw cycles with 0.2 M biacetyl in benzene.

Furthermore, higher temperatures also cause smaller phosphorescence intensities. Measuring the emission at 35 °C results in a constant decrease in the phosphorescence intensity; this is another indication of the lability of

biacetyl[†]. There was no difference in the I_P/I_F ratios and in the lifetimes of T_1 and S_1 on lowering the concentration of biacetyl from 0.2 to 0.02 M.

The linear regression equations according to eqn. (4) are

$$\tau_P = -(0.2 \pm 5.2) \mu s + (11.3 \pm 0.2) \mu s \frac{I_P}{I_F} \quad (5)$$

in benzene and

$$\tau_P = -(1.6 \pm 13.0) \mu s + (15.3 \pm 0.7) \mu s \frac{I_P}{I_F} \quad (6)$$

in acetonitrile. The magnitude of τ_P/ϕ_P in benzene is $8088 \pm 147 \mu s$, calculated with eqns. (3) - (5) and $\phi_F = 0.0025$ [2, 5], compared with $7810 \mu s$ measured by Almgren [2]. The corresponding magnitude of k_P is $124 \pm 2 s^{-1}$ ($128 s^{-1}$ [2]; $100 s^{-1}$ [5]). For the solvent acetonitrile, $k_P = 68 \pm 3 s^{-1}$, calculated with eqns. (3), (4) and (6) and

$$\phi_F(\text{acetonitrile}) = \frac{\phi_F(\text{benzene})}{1.317} = 0.0019$$

The sum of the solvent effect on k_P and k_{ISC} can be calculated with eqns. (4) - (6) and the ratio $k_P(\text{benzene})/k_P(\text{acetonitrile})$:

$$\frac{(k_P k_{ISC})(\text{benzene})}{(k_P k_{ISC})(\text{acetonitrile})} = 1.45$$

With the calculated k_P for both solvents the ratio of the intersystem crossing rate constant in benzene to that in acetonitrile is

$$\frac{k_{ISC}(\text{benzene})}{k_{ISC}(\text{acetonitrile})} = 0.80$$

This contrary influence of solvent on k_{ISC} and k_P indicates that changes in triplet lifetimes cannot be interpreted only in terms of influences on the non-radiative decay rates and that spin-orbit coupling may be different for singlet and triplet states, caused by differences in geometries and charge distributions, which are observable in carbonyl compounds [20]. For several measurements under equivalent conditions using the normal argon ($[O_2] \leq 2$ vol.ppm) the lifetime and I_P/I_F ratios are as follows: $\tau_P = 283.2 \pm 13.0 \mu s$ and $I_P/I_F = 25.1 \pm 1.0$ (12 values) in benzene; $\tau_P = 359.7 \pm 9.5 \mu s$ and $I_P/I_F = 23.2 \pm 1.3$ (five values) in acetonitrile. For the solvent cyclohexane five measurements lead to $\tau_P = 179.0 \pm 12.4 \mu s$ and $I_P/I_F = 12.3 \pm 0.3$. It is noteworthy that (a) the I_P/I_F ratios are higher than those reported in the literature (Table 1), indicating smaller oxygen and/or impurity concentrations and (b) the standard deviations are much smaller using this simple degassing method under our precautionary conditions. Furthermore, the data measured by Jones *et al.* [8] and Turro (ref. 8, note 8) fit the correlation shown in Fig. 1. As a result of our investigations the determination of

[†]See footnote to p. 54.

the phosphorescence lifetimes only requires measurement of the I_P/I_F ratios. Using eqn. (5) or eqn. (6) the lifetimes in benzene or acetonitrile can easily be calculated.

For the calculation of the phosphorescence quantum yield the corrected emission spectra were integrated. The ratio A_P/A_F of the calculated areas for the phosphorescence and fluorescence emission corresponds to the ratio ϕ_P/ϕ_F of the quantum yields. The value of A_P/A_F for 0.02 M biacetyl in benzene is 14.7 and that for 0.2 M biacetyl in benzene is 17.8. The smaller A_P/A_F value of the 0.2 M biacetyl solution is due to the inner filter effect, because part of the fluorescence emission is absorbed at wavelengths shorter than 470 nm. With $\phi_P/\phi_F = 14.7$ and $\phi_F = 0.0025$ [2, 5] the calculated phosphorescence quantum yield is 0.037 (0.05 [5]).

4. Conclusion

We have shown that simple purification procedures of biacetyl and use of argon purging as the degassing method result in reproducible phosphorescence intensities. By means of our correlation between the ratios of the phosphorescence to the fluorescence intensities and phosphorescence lifetimes it is possible to calculate accurate phosphorescence lifetimes for biacetyl in benzene and acetonitrile only by steady state emission measurements. These lifetimes correspond to the experimental conditions under investigation, when sources of error such as impurities in the biacetyl and incomplete removal of oxygen are taken into account.

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