PHOTOPHYSICAL PROPERTIES OF BENZIL IN SOLUTION: TRIPLET STATE DEACTIVATION PATHWAYS

LUCIA FLAMIGNI[†], FRANCESCO BARIGELLETTI, SERGIO DELLONTE and GIORGIO ORLANDI[†]

Istituto di Fotochimica e Radiazioni d'Alta Energia del Consiglio Nazionale delle Ricerche, Via de' Castagnoli 1, 40126 Bologna (Italy)

Summary

The fluorescence and phosphorescence from benzil in dilute benzene and cyclohexane solutions (2×10^{-4} M) were studied by both conventional luminescence and time-correlated single-photon techniques in the temperature range 8 - 69 °C. The fluorescence ($\lambda = 502$ nm) did not show a substantial temperature dependence and was free from thermal and triplet–triplet annihilation delayed contributions at the low concentration used. The phosphorescence ($\lambda = 562$ nm) was temperature dependent and its decay was controlled by an activation energy ($E_a = 7.4 \pm 0.5$ kcal mol^{-1}) which was slightly larger than the spectroscopic singlet–triplet splitting (6.1 kcal mol^{-1}). The photophysical parameters derived from the lifetimes of the two emissions are not consistent with the model of thermal equilibration between S_1 and T_1.

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1. Introduction

Benzil and other aromatic α dicarbonyls have been extensively studied because of the large geometric distortion of the lowest excited states with respect to the ground state. Direct evidence for the presence of these distortions has been provided by time-resolved studies in semisolid glasses where distinct emissions from relaxed and unrelaxed excited states have been observed [1 - 3].

The emission of benzil in solution consists of phosphorescence and fluorescence, the latter being reportedly composed of a prompt and a delayed component [4]. The energy separation between the lowest singlet and triplet states as determined by spectral analysis is 2150 cm^{-1} [5, 6]. The fluorescence spectrum displays a Stokes shift of 5650 cm^{-1} with respect to absorption in 3-methylpentane at 27 °C [5]. Upon excitation to S_1 both S_1

[†] Also affiliated to Istituto Chimico "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy.

and T_1 emissions are observed at relative intensities depending on the temperature [4, 7]. Studies of emission quantum yields at several temperatures have suggested that the S_1 and T_1 states are thermally equilibrated and that at room temperature most of the decay of T_1 proceeds via S_1 [7].

Following these observations we have considered measurements of the decay times of the fluorescence and phosphorescence of benzil in cyclohexane and benzene solutions at a low concentration and at temperatures ranging from 20 to 69 °C to be of interest. The aim was to determine all the parameters relative to the decay of S_1 and T_1 and to compare them with the proposed equilibration model.

2. Experimental details

Benzene and cyclohexane (R. S. Carlo Erba) were of fluorometric grade and were used as purchased. Benzil (Aldrich, Gold Label) was sublimated under vacuum. Deaerated samples were sealed under vacuum after repeated freeze–pump–thaw cycles in 1 cm fluorescence cells.

The fluorescence and phosphorescence decays were detected using a single-photon time correlation apparatus. A thyratron-gated flashlamp filled with nitrogen with a full width at half-maximum of about 3 ns was used to excite the sample at both 316 nm and 337 nm. The emission was detected at right angles using a Philips 56 TVP/03 photomultiplier cooled to −20 °C. A 502 nm narrow-band interference filter (Balzers) and a 475 nm cut-off were used to select the fluorescence emission wavelength and a 604 nm narrow-band interference filter (Balzers) in combination with a 570 nm cut-off and an IR absorbing Schott glass filter (Ealing) was used to detect phosphorescence. The accumulated data were fed into a Z80-based Cromemco microcomputer for processing. Fluorescence decays were analysed by deconvolution. Phosphorescence lifetimes were calculated by excluding the initial part of the decay curve to avoid contamination due to fluorescence. Both fluorescence and phosphorescence decays were fitted to a monoexponential decay function employing a non-linear least-squares procedure. The reduced χ^2 values were lower than 1.2 and the resulting residuals were regularly distributed along the time axis.

Further details about the single-photon apparatus and the deconvolution procedure are reported elsewhere [8].

The corrected luminescence spectra and the quantum yields were determined by using a model 210 Turner spectrofluorometer. Quantum yields were estimated by the cutting and weighing method taking as reference $\Phi_{PF} = 0.94 \times 10^{-3}$ for an aerated solution of benzil in benzene [7].

3. Results

Steady state luminescence spectra of aerated and deaerated 2×10^{-4} M solutions of benzil in benzene and cyclohexane at two temperatures are shown in Fig. 1. The emission spectrum of air-saturated solutions, which
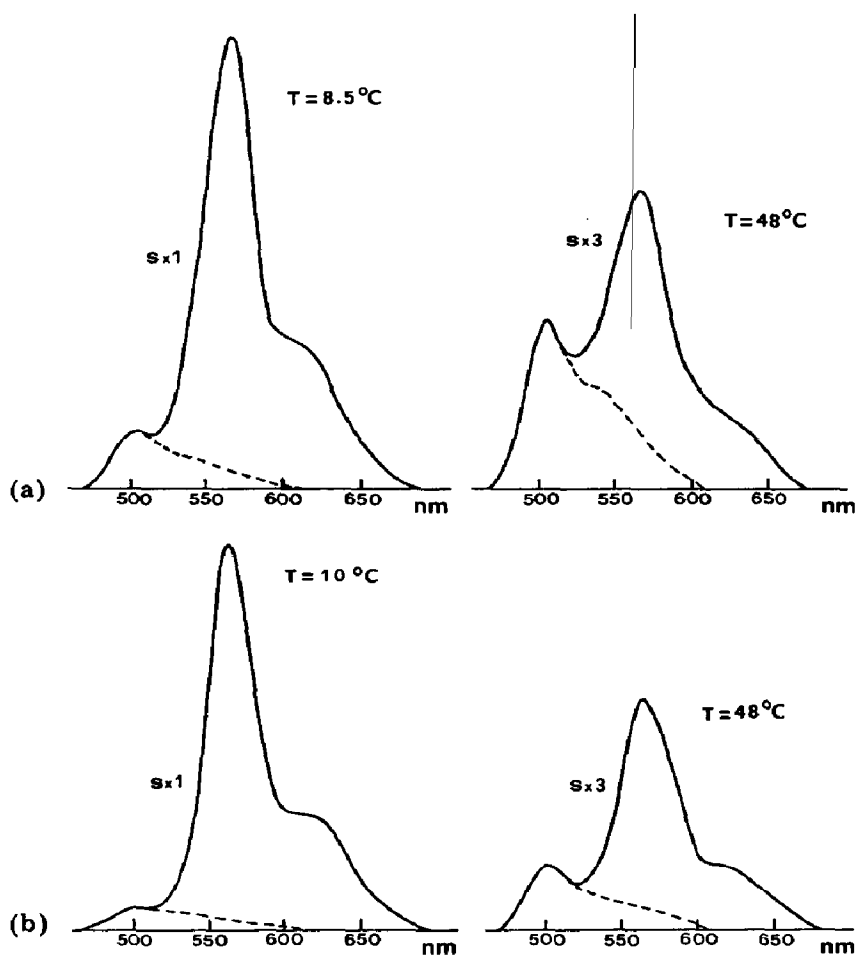
Fig. 1. Emission spectra of 2×10^{-4} M benzil in (a) benzene and (b) cyclohexane: ———, deaerated solutions; — — —, aerated solutions. The relative sensitivity is indicated. The experimental conditions were different for the benzene and cyclohexane solutions.

consists of a band at 502 nm, is due to prompt fluorescence (PF), *i.e.* to the emission of S_1 immediately following the excitation. The oxygen-free luminescence spectrum is attributed to a combination of phosphorescence (P) and fluorescence (F). The latter is composed of both PF and delayed fluorescence (DF). The bands at 562 and 620 nm, which are separated by 1670 cm^{-1} corresponding to the ground state C=O stretching frequency, belong to the phosphorescence spectrum. An estimate of the DF present can be obtained by comparison of the 502 nm peak height of the oxygen-free solution consisting of $\Phi_{PF} + \Phi_{DF}$ with that of the air-saturated solution consisting of Φ_{PF}.

The fluorescence and phosphorescence quantum yields for a 2×10^{-4} M benzil solution in benzene and cyclohexane at several temperatures are reported in Table 1. Both Φ_{PF} and $\Phi_{PF} + \Phi_{DF}$ are constant with temperature and coincide within the limits of experimental error which is 10%. Φ_{DF}, if present, is 10% or less of Φ_{PF}. The present result of $\Phi_{DF}/\Phi_{PF} \leqslant 0.1$ is in

TABLE 1

Prompt fluorescence and phosphorescence quantum yields at the reported temperatures for 2×10^{-4} M benzil in cyclohexane and benzene

Temperature (°C)	Quantum yields in cyclohexane			Temperature (°C)	Quantum yields in benzene		
	Φ_{PF} $\times 10^3$	$(\Phi_P + \Phi_{DF})$ $\times 10^3$	Φ_P $\times 10^3$		Φ_{PF} $\times 10^3$	$(\Phi_{PF} + \Phi_{DF})$ $\times 10^3$	Φ_P $\times 10^3$
10	0.94	0.94	23.3	8.5	0.94	0.94	5.8
20	0.94	0.94	15.1	21	0.94	0.94	3.1
30	0.94	0.95	10.2	30	0.94	0.94	2.0
40	0.94	0.95	6.5	38.5	0.94	0.93	1.4
48	0.94	0.94	4.8	48	0.94	0.94	1.2

The error in the determination of the quantum yields is 10%.

qualitative agreement with a reported ratio of 0.3 [7] while other sources report a Φ_{DF} even larger than Φ_{PF}. In contrast the Φ_P values vary with the temperature according to the equation

$$\Phi_P = B \exp\left(\frac{E_a}{RT}\right) \tag{1}$$

which indicates that the kinetics of the T_1 decay is of the Arrhenius type. By fitting eqn. (1) to the experimental data, we obtain $\log B = -7.4 \pm 0.4$, $E_a = 7.6 \pm 0.5$ kcal mol^{-1} and $\log B = -8.0 \pm 0.4$, $E_a = 7.4 \pm 0.5$ kcal mol^{-1} in cyclohexane and benzene solutions respectively. These energy values are slightly larger than the S_1-T_1 spectroscopic energy splitting [5] and the value found by Fang et al. [7] by plotting Φ_{DF}/Φ_{PF} against the temperature.

The fluorescence lifetime is found to be constant over the temperature range considered with τ_F values of 1.95 ± 0.05 ns and 2.1 ± 0.05 ns in cyclohexane and benzene solutions respectively.

The phosphorescence lifetimes do not exhibit a second-order component, indicating that the triplet–triplet annihilation process is not significant under our experimental conditions. The experimental error in the phosphorescence lifetime measurements is 7% or less. The rate of phosphorescence decay varies with the temperature according to the Arrhenius law

$$\frac{1}{\tau_P} = A \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

and the corresponding plots for benzene and cyclohexane solutions in the temperature range 20 - 69 °C are shown in Fig. 2. The parameters derived from the fitting are $\log A$ (s^{-1}) $= 8.8 \pm 0.4$, $E_a = 7.0 \pm 0.5$ kcal mol^{-1} and $\log A$ (s^{-1}) $= 9.6 \pm 0.4$, $E_a = 7.35 \pm 0.5$ kcal mol^{-1} for cyclohexane and benzene solutions respectively. The values of E_a obtained by steady state and kinetic experiments are in rather good agreement.

These results together with those reported in the literature allow an estimate of the parameters of the S_1 and T_1 deactivation paths and a discussion of the relevant mechanism.
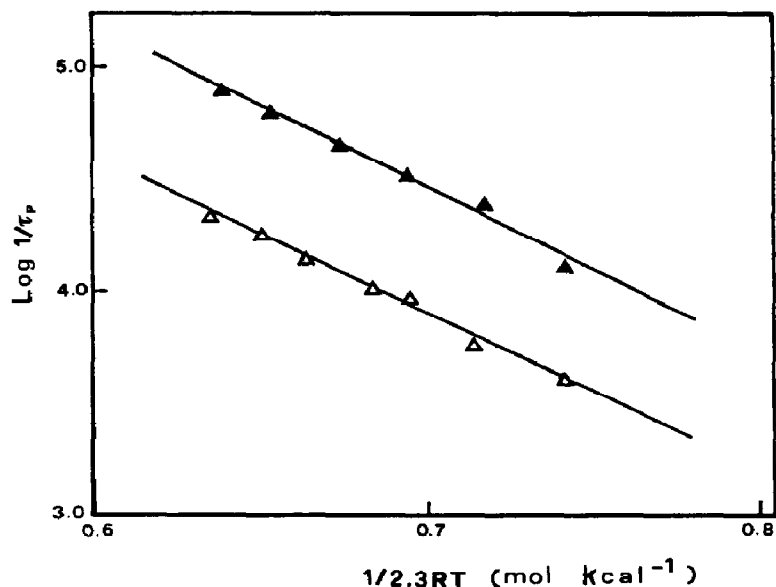
Fig. 2. Benzil phosphorescence lifetimes *vs.* temperature: ▲, 2×10^{-4} M benzil in benzene; △, 2×10^{-4} M benzil in cyclohexane.

4. Discussion

4.1. Photophysical parameters

The paths for the decay of S_1 (see Fig. 3) are $S_1 \rightsquigarrow S_0$ internal conversion (IC), $S_1 \rightsquigarrow T_1$ intersystem crossing (ISC) and $S_1 \rightarrow S_0$ fluorescence with the rate constants k_{IC}, k_{ISC} and k_r respectively. The τ_F value reported in the previous section together with the values of the quantum yields Φ_F [7] and Φ_{ISC} [9] determine the three rate constants. All these parameters are reported in Table 2. The value obtained for k_r is in agreement with that obtained by an equation of the Birks and Dyson and Strickler and Berg type [10] which relates the radiative rate constant to the absorption coefficient:

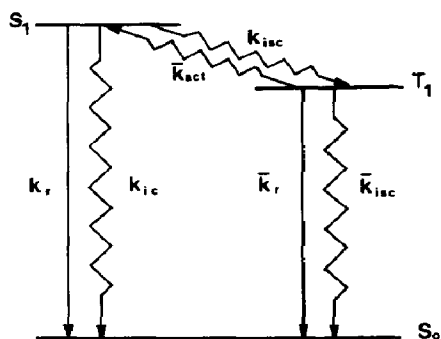$$k_r = 3 \times 10^{-9} \nu_{max}^2 \epsilon_{max} \, \Delta\nu_{1/2} \tag{3}$$

Fig. 3. Schematic energy level diagram for benzil.

TABLE 2

Photophysical parameters for the fluorescence and phosphorescence decay of benzil at 20 °C in benzene

Singlet parameters	Triplet parameters
$\tau_F = 2.1 \times 10^{-9}$ s	$\tau_P = 80 \times 10^{-6}$ s
$\Phi_{PF} = 0.94 \times 10^{-3}$ [7]	$\Phi_P = 3.1 \times 10^{-3}$
$\Phi_{ISC} = 0.92$ [9]	$\Phi_{ISC} < 3.1 \times 10^{-3}$ [6]
$k_r = 4.5 \times 10^5$ s^{-1}	$\Phi_{act} \approx 0.995$
$k_{IC} = 3.81 \times 10^7$ s^{-1}	$\bar{k}_r = 39$ s^{-1}
$k_{ISC} = 4.38 \times 10^8$ s^{-1}	$\bar{k}_{ISC} < 39$ s^{-1}
	$\bar{k}_{act} = 1.25 \times 10^4$ s^{-1}

Here ν_{max} and ϵ_{max} are the wavelength and the extinction coefficient at the absorption maximum and $\Delta\nu_{1/2}$ is the width at half-maximum of the $S_0 \rightarrow S_1$ absorption band. If we take $\nu_{max} = 25\,600$ cm^{-1}, $\epsilon_{max} = 56$ M^{-1} cm^{-1} and $\Delta\nu_{1/2} = 5000$ cm^{-1}, we find $k_r = 5.3 \times 10^5$ s^{-1} in good agreement with the value obtained from the measurement of Φ_F and τ_F.

The decay of T_1 is due to the phosphorescence, the $T_1 \rightsquigarrow S_0$ ISC and a thermally activated decay, the nature of which will be discussed later, with rate parameters $\bar{k}_r$, $\bar{k}_{ISC}$ and $\bar{k}_{act}$ respectively. Our present results indicate that $\bar{k}_{act}$ is the dominant rate parameter at room temperature and the low temperature data suggest that $\bar{k}_{ISC}$ is negligible with respect to $\bar{k}_r$. Our values of Φ_P and τ_P at room temperature (20 °C) give $\bar{k}_r$ values of 39 ± 4 s^{-1} and 60 ± 7 s^{-1} in benzene and cyclohexane solutions respectively. These values should be compared with the $\bar{k}_r$ value of 66 s^{-1} obtained by Parker and Joyce [4] in perfluoromethylcyclohexane solutions. All the rate constants are collected in Table 2.

4.2. Mechanism of T_1 decay

We now discuss the mechanism of the activated decay of T_1 which contributes 99% of the total decay of T_1. Since $\ln(\Phi_P/\Phi_F)$ depends linearly on $1/T$, it is tempting to propose that the activated decay of T_1 represents the back ISC $T_1 \rightsquigarrow S_1$ [4, 5, 7] although there is still some doubt regarding this mechanism [4].

To verify this hypothesis we have considered the model of equilibrated S_1 and T_1 in detail. In dilute solutions where T–T processes are absent the decay of equilibrated S_1 and T_1 is described by the scheme in Fig. 3 where $\bar{k}_{act} = k_{ISC} \exp(-\Delta E/RT)$ and $\Delta E = E(S_1) - E(T_1)$. The total singlet and triplet rate parameters are

$$k_S = k_{IC} + k_r + k_{ISC}$$
$$k_T = \bar{k}_{ISC} + \bar{k}_r + \bar{k}_{act}$$

(4)

Following the excitation in the S_1 state, the response function of fluorescence decay given by application of the Birks treatment of excimer emission to a ground state concentration-independent process is [11]

$$i_r = k_r \left\{ c_1 \exp\left(-\frac{\lambda_1}{t}\right) + c_2 \exp\left(-\frac{\lambda_2}{t}\right) \right\} \tag{5}$$

where

$$c_1 = \frac{\lambda_2 - k_S}{\lambda_2 - \lambda_1}$$

$$c_2 = \frac{k_S - \lambda_1}{\lambda_2 - \lambda_1} \tag{6}$$

$$\lambda_{1,2} = 0.5[k_S + k_T \pm \{(k_S - k_T)^2 + 4k_{ISC}\bar{k}_{act}\}^{1/2}]$$

where λ_1 is obtained by using the minus sign and λ_2 is obtained by using the plus sign. Under the same excitation conditions the response function for phosphorescence is

$$\bar{i}_r = \bar{k}_r k_{ISC} \frac{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)}{\lambda_2 - \lambda_1} \tag{7}$$

Both i_r and $\bar{i}_r$ undergo a two-exponential decay. However, since λ_2 is much greater than λ_1 on a microsecond scale $\bar{i}_r$ is proportional to $\exp(-\lambda_1 t)$, while on the nanosecond scale the microsecond component is lost and i_r is proportional to $\exp(-\lambda_2 t)$. Integrating with respect to eqns. (5) and (6) we obtain the quantum yields of fluorescence and phosphorescence. The fluorescence quantum yield is

$$\Phi_F = \int_0^\infty i_r \, dt$$

$$= \frac{k_r c_2}{\lambda_2} + \frac{k_r c_1}{\lambda_1} \tag{8}$$

The first term $k_r c_2/\lambda_2$ is the contribution of the fast decay and corresponds to Φ_{PF}. The second term $k_r c_1/\lambda_1$ is due to the slow decay and corresponds to Φ_{DF}. The phosphorescence quantum yield is

$$\Phi_P = \int_0^\infty \bar{i}_r \, dt$$

$$= \frac{\bar{k}_r K_e}{k_r + k_{IC} + (\bar{k}_r + \bar{k}_{ISC})K_e} \tag{9}$$

where $K_e = k_{ISC}/k_T$.

In our system k_r, k_{ISC}, k_{IC} and $\bar{k}_r$ are known and $\bar{k}_{ISC}$ is assigned values in the range $0 - \bar{k}_r$. In the model of equilibrated S_1 and T_1

$$\bar{k}_{act} = \bar{k}_{ISC} \exp\left(-\frac{\Delta E}{RT}\right)$$

with $E \approx 6$ - 7 kcal mol^{-1} according to the spectroscopic and kinetic results. If the model is valid, by using these values and eqns. (5), (7), (8) and (9) we should be able to reproduce both the steady state and the kinetic behaviour of the system. The results of the calculations are not in agreement with the experimental observations. In particular the model predicts a ratio Φ_{DF}/Φ_{PF} of about 10 which is much larger than the value of 0.1 or less reported here and in previous work [4, 7]. Furthermore the frequency factor of the phosphorescence decay is calculated to be almost two orders of magnitude smaller than that determined experimentally. A discrepancy between the model and the results is found for any set of acceptable rate constants used in the computation.

It must be concluded that the triplet deactivation cannot involve the back crossing to the emitting singlet S_1. Rather, it must involve the crossing to another singlet state S_x, the nature of which is not clear. The flexibility of the molecule owing to the possibility of rotation around three quasi-single bonds may provide several minima in the lowest singlet potential energy hypersurface. The state S_x, through which T_1 deactivates, could be one of these.

Acknowledgments

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