TRIPLET–TRIPLET ENERGY TRANSFER FROM BENZOPHENONE TO TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II) CHLORIDE IN ACETIC ACID: RELEVANCE OF TRIVIAL ABSORPTION EFFECTS

G. FAVARO, F. MASETTI and R. RAMADORI

Dipartimento di Chimica, Università di Perugia, 06100 Perugia (Italy)

(Received July 2, 1978)

Summary

Energy transfer from benzophenone to $Ru(bipy)_3^{2+}$ has been studied in acetic acid by phosphorescence quenching of the donor and phosphorescence sensitization of the acceptor. A general method is described for the correction of trivial effects on the Stern–Volmer plots when both absorption and emission spectra of the donor overlap the absorption spectrum of the acceptor. The combination of intensity and lifetime data indicates that the quenching is not simply diffusional.

1. Introduction

Arylketones have found widespread use as sensitizers for photoluminescence and photochemistry in different solvents.

This paper presents a preliminary study to test the possibility of using arylketones as sensitizers in acetic acid. In previous work we used biacetyl as quencher for triplet ketones in benzene and water solution. Such a quencher cannot be used in acetic acid since it gives a scarcely reproducible phosphorescence signal. This investigation has been carried out by utilizing benzophenone (B) as the triplet donor and tris(2,2'-bipyridine)ruthenium(II) chloride ($Ru(bipy)_3^{2+}$) as the acceptor. Acetic acid has been found to have the prerequisites for a photophysical study, since it can be easily purified and is a reasonable solvent for ions as well as for organic compounds. Benzophenone and $Ru(bipy)_3^{2+}$ both display phosphorescence emission in room temperature acetic acid solution. This combination of properties makes it possible to study energy transfer by observing either emission quenching of the donor or emission sensitization of the acceptor. However, to rationalize our experimental data we had to overcome the difficulties arising from the overlapping of the spectra of the two partners. Therefore we were forced to correct both the quenched emission of the donor and the sensitized emission of the acceptor for trivial absorption effects. Comparison of the results from intensity measurements with decay time data suggests that the quenching mechanism for this system may not be simple.

2. Experimental

Benzophenone (J. T. Baker) was recrystallized from water–ethanol. The $Ru(bipy)_3Cl_2$ (G. F. Smith Chemical Co.) was used without further purification. Acetic acid (Carlo Erba RPE) was purified by the method described in the literature for similar purposes [1].

All the measurements were carried out in acetic acid solution at room temperature (20 ± 2 °C) which was de-aerated by bubbling with pure nitrogen. Concentrations of the acceptor ranged from 1.87×10^{-6} M to 3.7×10^{-5} M and those of the donor, which were held constant in each experimental run, ranged from 7.43×10^{-3} to 2.7×10^{-2} M in separate runs.

Emission intensity measurements were performed using a Hitachi–Perkin–Elmer MPF-3 spectrofluorimeter. The excitation was performed with 360 nm light and the emission intensities were measured at 450 nm and 595 nm, the emission maxima of donor and acceptor respectively.

A solution of quinine sulphate in 1 N H_2SO_4 was used as the standard to determine the luminescence quantum yield.

Quenching by lifetime measurements was carried out by means of the decay time apparatus described elsewhere [2]. The decays were exponential over at least two to three half-lives. Reproducibility of the mean lifetimes was within 4%.

3. Results and discussion

In order to discuss the results and the corrections introduced we shall make reference to the following scheme, which can be generally referred to a donor (D)–acceptor (A) couple where both absorb the incident light and the donor emission spectrum overlaps the acceptor absorption spectrum:
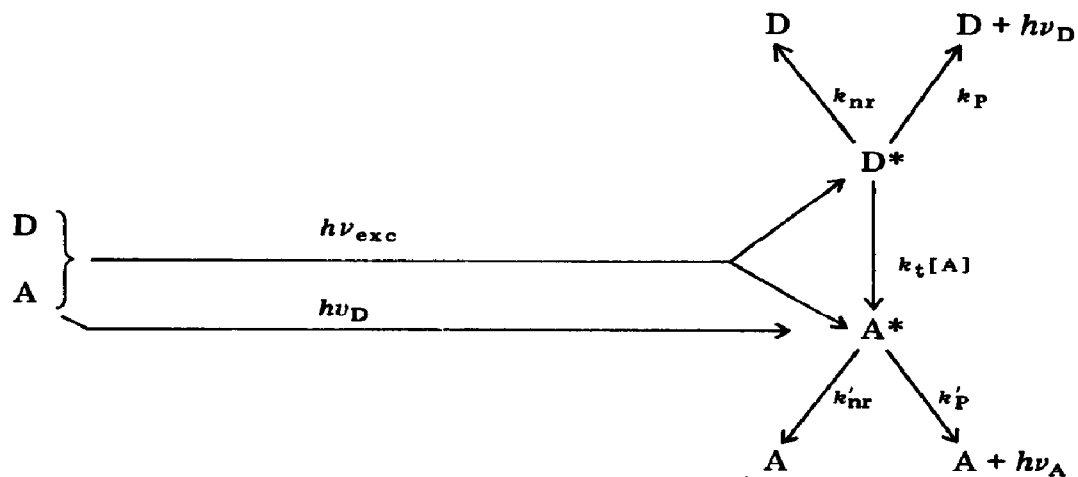
This situation is illustrated in Fig. 1 for the benzophenone donor and $Ru(bipy)_3^{2+}$ acceptor. In the scheme k_P and k_{nr}, k_P' and k_{nr}' are the rate
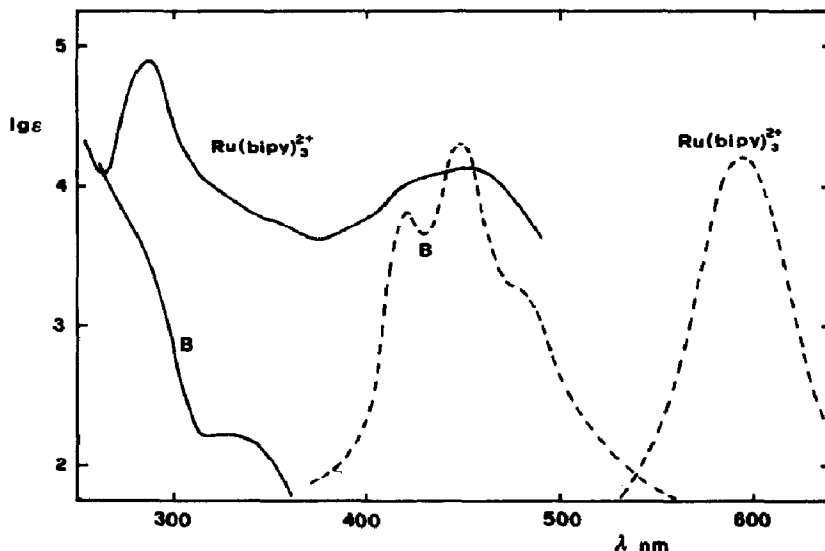
Fig. 1. Absorption (solid curve) and emission (broken curve) spectra of benzophenone and Ru(bipy)$_3^{2+}$ in acetic acid solution. The uncorrected emissions are normalized with respect to each other.

parameters of the radiative and non-radiative deactivations of the donor and the acceptor respectively; k_t is the rate parameter for the bimolecular quenching process. This situation implies that the phosphorescence intensity of the donor decreases with increasing acceptor concentration more rapidly than expected from energy transfer only, since the acceptor acts as an inner filter at the exciting wavelength and absorbs trivially the light emitted by the donor. In contrast, the sensitized phosphorescence intensity of the acceptor is due to three contributions: (i) energy transfer; (ii) direct excitation; (iii) trivial absorption of the light emitted by the donor. Therefore it appeared necessary to correct the experimental intensity values before introducing them into the appropriate Stern–Volmer equations.

The fraction I_D of the light absorbed by the donor varies with the acceptor concentration according to the equation

$$I_D = \frac{\epsilon_D[D]}{\epsilon_D[D] + \epsilon_A[A]} I = \frac{A_D}{A} I \tag{1}$$

where I is the total absorbed light and A_D and A are the absorbances at the exciting wavelength for the donor and for the total system respectively [3]. Since the emission intensity is proportional to the intensity of the absorbed light, the experimental ratio $(P^0/P)_{expt}$ of the luminescence of the donor in the absence and in the presence of the acceptor must be multiplied by the intensity ratio I_D/I_D^0 of the light absorbed by the donor in the presence and in the absence of the acceptor. This factor can be expressed in terms of the absorbances A and A_D and the transmittances T and T_D of the solution containing both D and A and of that containing the donor alone:

$$\frac{I_D}{I_D^0} = \frac{I}{I_D^0} \frac{A_D}{A} = \frac{(1-T)A_D}{(1-T_D)A} \tag{2}$$

The further reduction of the intensity ratio, owing to the reabsorption by the acceptor of the light emitted by the donor, can be accounted for by multiplying the experimental ratio $(P^0/P)_{expt}$ by the transmittance T' of the solution at the wavelength of analysis of the emitted light. The following equation was therefore used to obtain corrected P^0/P values for the intensity quenching data:

$$\frac{P^0}{P} = \left(\frac{P^0}{P}\right)_{expt} \frac{(1-T)A_D}{(1-T_D)A} T' \tag{3}$$

where the spectrophotometric parameters must be evaluated for the effective path length of the exciting and emitted light, which is estimated to be 5 mm when 10 mm path optical cells are used[†].

Experiments were carried out which were designed to eliminate the possibility of errors arising for the finite bandpass of the excitation and emission monochromators and the photometric precision of the spectrophotometric data. Three kinds of experiments were carried out: (i) measurements of phosphorescence intensity of $Ru(bipy)_3^{2+}$ in the presence of an inner filter (2-OH-benzophenone) which does not sensitize using different slit amplitudes; (ii) quenching measurements at different wavelengths, which imply different contributions of trivial absorption; (iii) measurements of the phosphorescence of benzophenone by inserting grey filters of different transmittance in the emission path. All these experiments led us to the conclusion that the factors introduced to correct the experimental data give results that are completely reliable.

The diagrams of Fig. 2 illustrate the relevance of inner filter and trivial absorption effects for the benzophenone–$Ru(bipy)_3^{2+}$ system under our experimental conditions. While the experimental points show an upward curvature, the corrected data appear to fit fairly well the normal Stern–Volmer equation

$$\frac{P^0}{P} = 1 + K_{SV}^Q [Ru(bipy)_3^{2+}] \tag{4}$$

where the Stern–Volmer constant K_{SV}^Q is equal to the product $k_t \tau^0$ of the bimolecular rate parameter for the triplet lifetime of the donor.

Concerning the emission intensity measurements of acceptor, the last of the three contributions (sensitized phosphorescence, directly excited phosphorescence and phosphorescence excited by trivial absorption of the donor emission) is certainly negligible in our system. In fact, the phosphorescence quantum yield of benzophenone in acetic acid was found to be 2×10^{-3}, a value too low to give an appreciable contribution to the total emission.

[†]A similar formula is reported in the literature [4] which differs from that obtained by us only in the evaluation of T and T_D which are considered through the whole path length of the cell (1 cm).
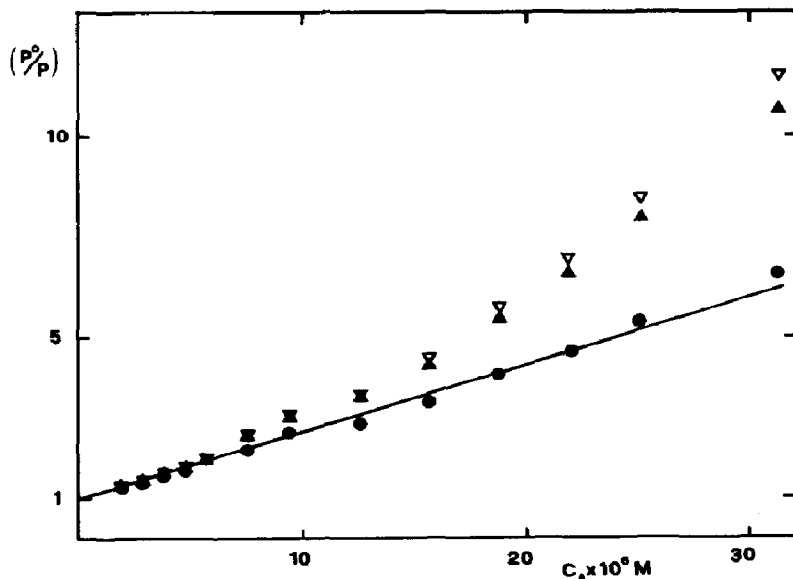
Fig. 2. Stern—Volmer plots of phosphorescence quenching for the benzophenone—Ru(bipy)$_3^{2+}$ system: △, observed intensity ratios $(P^0/P)_{expt}$;▼, intensity ratios corrected for inner filter effect on exciting light; ●, P^0/P values corrected for both the inner filter effect and trivial absorption of emitted light.

Therefore we can reasonably consider that the experimental intensity value is due essentially to the sum of the other two terms. Since both are affected by the inner filter effect of the two components on each other, the corrected sensitized phosphorescence P can be related to the experimental value P_{expt} by the equation

$$P_{expt} = P\,\frac{(1-T)A_D}{(1-T_D)A} + P^0\,\frac{(1-T)A_A}{(1-T_A)A} \tag{5}$$

where T, T_D, A and A_D have the meanings given earlier, T_A and A_A are the transmittance and absorbance at the exciting wavelength of a solution containing the acceptor alone, and P^0 is the emission intensity of the acceptor excited by the same wavelength and obtained from a calibration plot in separate experiments under the same experimental conditions.

From eqn. (5) the corrected P value is given by

$$P = P_{expt}\,\frac{(1-T_D)A}{(1-T)A_D} - P^0\,\frac{(1-T_D)A_A}{(1-T_A)A_D} \tag{6}$$

Since in this case the corrections applied for direct excitation and inner filter effect operate in opposite directions, the first increasing and the second decreasing the experimental intensity, the difference between the experimental and the corrected points may not be great, as shown in Fig. 3 for the B—Ru(bipy)$_3^{2+}$ system by the sensitization Stern—Volmer plot:

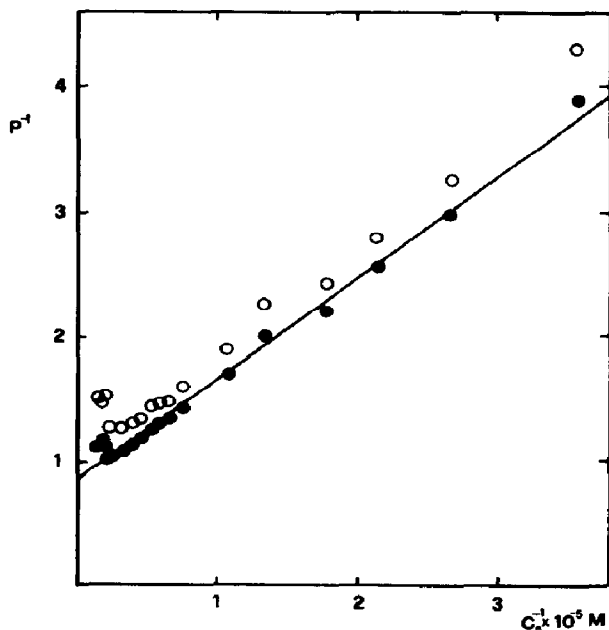$$P^{-1} = K\left(1 + \frac{1}{K_{SV}^S[\text{Ru(bipy)}_3^{2+}]}\right) \tag{7}$$

Fig. 3. Stern—Volmer plots for phosphorescence sensitization of the benzophenone—Ru(bipy)$_3^{2+}$ system: ○, uncorrected P_{expt} values; ●, corrected P values.

where K is a constant which includes the triplet yield of the donor, the triplet lifetime of the acceptor, the rate of light absorption and an instrumental factor [5 - 7].

Table 1 illustrates the results obtained from measurements of corrected quenching $K_{SV}{}^Q$ and sensitization $K_{SV}{}^S$ at different donor concentrations. Lack of sensitivity of K_{SV} values to the concentration effect demonstrates that no self-quenching [7] occurs for benzophenone in acetic acid, at least in the concentration range explored.

Although the corrections on the intensity quenching data amount to 50% at the higher quencher concentrations, and those on sensitized intensity only to 15%, the $K_{SV}{}^S$ values show a lower reproducibility, probably due to

TABLE 1

Values of Stern—Volmer constants at different donor concentrations obtained from measurements of phosphorescence quenching $K_{SV}{}^Q$ and sensitized phosphorescence $K_{SV}{}^S$ for the benzophenone—Ru(bipy)$_3^{2+}$ system in acetic acid

[B] × 10^3 (M)	$K_{SV}{}^Q$ × 10^{-4} (M^{-1})	$K_{SV}{}^S$ × 10^{-4} (M^{-1})
7.43	16.0	11.4
13.25	16.0	10.0
16.05	15.6	9.2
20.7	15.0	9.5
23.7	14.8	12.0
27.0	15.8	10.3

additional effects of the two opposite corrections. However, even if trivial corrections are significant, the discrepancy between the values of $K_{SV}{}^Q$ ($(15.5 \pm 0.5) \times 10^4$ M^{-1}) and $K_{SV}{}^S$($(10 \pm 1) \times 10^4$ M^{-1}) appears to be larger than the experimental error. Although energy transfer clearly takes place, as is shown by the occurrence of the sensitized emission of the acceptor, other mechanisms could play some role in the quenching of the donor emitting state. In order to acquire more information about the possibility of the occurrence of a mixed mechanism, quenching experiments by decay time measurements were performed. This procedure yields the true K_{SV} value directly, free of any contributions from trivial absorption or competing quenching mechanisms, by means of a decay time Stern–Volmer plot:

$$\frac{\tau^0}{\tau} = 1 + K_{SV}{}^\tau [\mathrm{Ru(bipy)}_3^{2+}] \tag{8}$$

where τ and τ^0 are respectively the triplet lifetimes of B in the presence and in the absence of quencher. Figure 4 shows a comparison between the observed intensity ratios $(P^0/P)_{expt}$ and the decay time ratios τ^0/τ. The results from the three different methods are compared in Table 2. By far the most interesting feature is the clear-cut difference (about 40%) between the $K_{SV}{}^\tau$ and $K_{SV}{}^Q$ values which cannot be explained by the experimental error since the uncertainty is within 2 - 3%. The inescapable implication is that some quenching occurs by a mechanism different from energy transfer.

Knowledge of the emission lifetime also makes it possible to calculate the bimolecular rate constant $k_t = K_{SV}/\tau^0$ for the quenching process and the
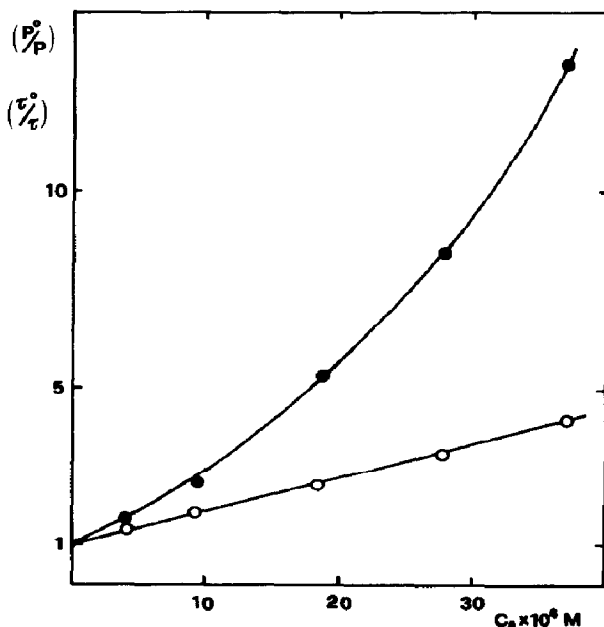

Fig. 4. Comparison of the trends of observed intensity ratios (●) and lifetime ratios (○) vs. $\mathrm{Ru(bipy)}_3^{2+}$ concentration.

TABLE 2

Comparison of mean K_{SV} values for the benzophe-none–Ru(bipy)$_3^{2+}$ system obtained by different methods

$K_{SV}^Q \times 10^{-4}$ (M^{-1})	$K_{SV}^S \times 10^{-4}$ (M^{-1})	$K_{SV}^\tau \times 10^{-4}$ (M^{-1})
15.5 ± 0.5	10 ± 1	8.9 ± 0.2

unimolecular rate constant $k_P = \phi_P/\tau^0$ for the radiative deactivation of the excited state. A general summary of the photophysical parameters of the benzophenone triplet in acetic acid, including some literature values, is given in Table 3. The agreement with the literature data may be considered reasonable for τ^0, but very poor for ϕ_P and k_P which influence each other. We believe that our ϕ_P value is more reliable since it has been obtained in relation to a typical fluorescence standard like quinine sulphate, while the literature value [1] was obtained by taking as standard the phosphorescence of benzophenone in carbon tetrachloride, a solvent which gives scarcely reproducible phosphorescence data (see later). Concerning the rate parameter k_t the observed discrepancy is not surprising, since it was obtained with different quenchers. While the interaction of triplet benzophenone with naphthalene may be considered to be diffusion controlled ($k_{diff} = 4.95 \times 10^9$ M^{-1} s^{-1} [1]), it is well known that inorganic complexes may give rise to lower rate parameters which specifically depend on the characteristics of the quencher [8].

Inspection of Table 4, where the triplet lifetime of benzophenone in different solvents is reported, shows that the dielectric constant of the solvent has an increasing effect on the lifetime, with the exception of carbon tetrachloride, a solvent for which the data are more uncertain. The reasonably high triplet lifetime in acetic acid, together with the absence of self-quenching processes, makes this solvent particularly suitable for carrying out sensitization by benzophenone. Another factor is that acetic acid is a good solvent for many compounds, whereas water, for example, in which the triplet lifetime is higher [7], is a poor solvent for many organic compounds.

TABLE 3

Photophysical parameters of triplet benzophenone in acetic acid

$\tau^0 \times 10^6$ (s)	$\phi_P \times 10^3$	k_P (s^{-1})	$\nu_{0,0} \times 10^{-3}$ (cm^{-1})	$k_t \times 10^{-9}$ (M^{-1} s^{-1})
31 ± 3	2 ± 0.2	65 ± 10	23.9	2.9 ± 0.3
43.9 ± 0.6[a]	10 ± 1[a]	288[a]	23.8[a]	5.57[a,b]

[a]Data from ref. 1;   [b]Quencher, naphthalene.

TABLE 4

Triplet lifetime of benzophenone in different solvents

$\tau^0 \times 10^6$ (s)			
Benzene	Carbon tetrachloride	Acetic acid	Water
5.3[a]	16[b]	31	230[f]
6.9[b]	94[c]	44[e]	200[g]
	124[d]		

[a]Data from ref. 6; [b]data from ref. 9; [c]data from ref. 10; [d]data from ref. 11; [e]data from ref. 1; [f]data from ref. 7; [g]data from ref. 12.

Further work is in progress on different arylketones with the aim of extending the results obtained in this preliminary paper and to establish definitely the existence and the nature of the mixed quenching mechanism.

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