

ARYLKETONES AS TRIPLET DONORS AND QUENCHERS: EVIDENCE FOR CHEMICAL QUENCHING AND REVERSIBLE ENERGY TRANSFER

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Summary

Quenching measurements of phosphorescence intensity and lifetime of benzophenone and its derivatives with electron-attracting substituents by arylketones with electron-releasing substituents, carried out in acetic acid, show that the quenching rate parameter k_q depends on the structure of the two interacting partners. The k_q value increases with the electron-donating power of the substituents in the quencher, approaching the diffusional value with the strongest electron-donating groups, whilst it decreases when electron-withdrawing substituents are present in the quenched species. The first effect is explained by an interaction mechanism where a charge transfer occurs from the quencher to the excited donor. The effect of donor structure on the k_q value is ascribed to the contribution of a partial reversible energy transfer. A study of the dependence of the experimental quenching parameter on the donor concentration gives evidence for the reversible transfer process.

1. Introduction

The aromatic carbonyl compounds are known to be very efficient triplet sensitizers. However, this property can be strongly affected by structural and environmental effects. The substituent as well as the solvent can bring about changes in the configuration of the lowest excited states (see, for example, refs. 1 - 3). In non-polar solvents the majority of arylketones have lowest n, π^* triplet states [4, 5]. Strongly electron-withdrawing groups stabilize the n, π^* triplet states, whilst electron-donating substituents raise the n, π^* states and may invert the energy of the lowest triplet levels [4, 6]. Polar solvents produce the same triplet state inversion as do electron-donating groups. Since only triplets of n, π^* character have been found to exhibit efficient sensitizing power, some compounds, which work as sensitizers in non-polar solvents, become completely inefficient in a solvent of higher polarity [7].

Acetic acid, which has been found to be a convenient solvent for studying phosphorescence emissions at room temperature [8], is also a good solvent for an investigation of substituent effects because its dielectric constant (6.15) is sufficiently high to produce an inversion of the lowest states in arylketones with electron-donating substituents, but not in benzophenone and its derivatives substituted with electron-withdrawing groups. In a previous paper [7] we have shown that those ketones which have π, π^* lowest triplets, with a charge transfer character, do not sensitize the emission of a suitable acceptor ($\text{Ru}(\text{bipyridine})_3^{2+}$) but they act as quenchers of the n, π^* triplet ketones.

Since only the n, π^* ketones exhibit phosphorescence emission in acetic acid at room temperature [7], in order to elucidate the mechanism of this interaction, quenching measurements of phosphorescence intensity and lifetime of n, π^* arylketones such as benzophenone (B), 3-benzoylpyridine (3-BP), 4,4'-dichlorobenzophenone (4,4'-ClB) and 4-carboxybenzophenone (4-COOHB) by ketones with electron-donating substituents (4,4'-dimethoxybenzophenone (4,4'-CH₃OB), 4-hydroxybenzophenone (4-OHB), 4-aminobenzophenone (4-NH₂B), 4,4'-bis(dimethylamino)-benzophenone (4,4'-N(CH₃)₂B), 2-hydroxybenzophenone (2-OHB) and 2-aminobenzophenone (2-NH₂B)) were performed in this solvent.

2. Experimental

2.1. Materials

B (J. T. Baker), 4-COOHB, 2-OHB, 2-NH₂B (Aldrich), 4-OHB and 4-NH₂B (Fluka) were purified by recrystallization from water-ethanol. 4,4'-ClB (K and K) was recrystallized from *n*-hexane; 4,4'-CH₃OB (Eastman) was recrystallized from ethanol; 3-BP (Aldrich) was recrystallized from light petroleum. 4,4'-N(CH₃)₂B (Fluka) was purified by the method described by Schuster *et al.* [9].

Acetic acid (Carlo Erba RPE) was purified by the method suggested in the literature [8] when used for similar purposes.

2.2. Equipment

Absorption spectral measurements were performed on a Unicam SP 500/2 spectrophotometer or a Perkin-Elmer Coleman 572 spectrophotometer.

Emission intensity measurements were performed using a Hitachi-Perkin-Elmer MPF-3 spectrofluorimeter. An accessory for phosphorescence measurements was used for the spectra at low temperature.

The apparatus for the decay time measurements has been previously described in detail [10]. It uses as an exciting source an Osram XBO 150 W xenon lamp, operating at 16 kV in a free running mode, and a photomultiplier (Philips 150 AVP)-oscilloscope (Tektronix 546) system for monitoring the light emitted.

2.3. Experimental conditions

All the quenching measurements were performed at room temperature (20 ± 2 °C), the solutions having been carefully deaerated by bubbling with pure nitrogen. The concentrations of the quenchers ranged from 10^{-6} to 10^{-3} M, depending on their quenching efficiency. Those of the ketone donors, which were held constant in each experimental run, ranged from 6.6×10^{-3} to 8×10^{-3} M; this gave an absorbance of about 0.8 at the exciting wavelength, which was necessary for the donor to absorb the major portion of the exciting light. To investigate the possibility of a reversible energy transfer in the system 4-COOHB (donor (D)) + 4,4'-CH₃OB (quencher (Q)), the concentration of the donor was varied from 3.3×10^{-4} to 6.6×10^{-3} M. Preliminary measurements showed that the absorption spectra for all donors and quenchers follow the Lambert-Beer law and the absorption spectra of solutions containing both the donor and the quencher were found to be additive with respect to the spectra of the individual compounds. This excludes the occurrence of stable associations in the ground state. Comparison with literature data of absorption spectra [3, 11] and ground and excited state pK values [3, 11, 12] for the amino and hydroxy derivatives indicated that protonation and deprotonation do not occur in acetic acid either in the ground state or, probably, in the excited state.

2.4. Lifetime measurements

Lifetime measurements were performed in solutions of the donor, either alone or in the presence of the quenchers. The exciting light was passed through a Corning CS 7-54 filter (transmittance 250 - 400 nm) and the phosphorescence was observed through a Corning CS 3-73 cut-off filter. The phosphorescence decay curves, followed over three half-lives, were clearly first order. This excludes the occurrence of triplet-triplet annihilation. The reproducibility was within 3% for the same solution and within 10% for different solutions. The values measured can be considered to be accurate to within 20% because of the presence of residual oxygen, the concentration of which is of the order of 10^{-6} M in a nitrogen-saturated solution [13]. Only for 3-BP, because of its shorter-lived triplet, is the accuracy of the same order as the experimental uncertainty.

2.5. Emission intensity measurements

The excitation was performed with 360 nm light, which represents the best compromise of maximum absorption by the donors and minimum absorption by the quenchers. The quenching of the donor phosphorescence was observed at the emission maxima: 448 nm for B, 452 nm for 4,4'-ClB, 455 nm for 3-BP and 465 nm for 4-COOHB. Because of the overlapping of the absorption spectra of the donors and quenchers at the exciting wavelength, all the experimental intensity ratios $(P^0/P)_{\text{exp}}$ were corrected for trivial absorption effects using the formula [14, 15]

$$\frac{P^0}{P} = \left(\frac{P^0}{P} \right)_{\text{exp}} \frac{(1 - T)A_D}{(1 - T_D)A} \quad (1)$$

where A , A_D and T , T_D represent respectively the absorbance and transmittance at the exciting wavelength of a solution containing both donor and quencher and of a solution containing the donor alone. Only with 2-NH₂B and 4,4'-N(CH₃)₂B as quenchers was a further correction necessary because of the overlapping of the absorption spectra of the quenchers with the emission spectra of the donors. This was achieved by multiplying eqn. (1) by the transmittance of the solution at the wavelength of analysis of the emitted light [14, 15]. Assuming that the fluorimeter slits were centred on the fluorescence cell face, all the spectrophotometric quantities were referred to the half-cell thickness. Control experiments, designed to check the reliability of the corrections and to exclude the possibility of errors arising from the finite bandpass of the excitation and emission monochromators and the photometric accuracy of the spectrophotometric data, have been described in a previous paper [14]. The linearity of the Stern-Volmer (SV) plots, achieved in most cases by correcting the experimental data, and the agreement between the results obtained by intensity quenching measurements and those obtained by lifetime quenching measurements (which do not need any correction) are an *a posteriori* confirmation of the reliability of the corrections applied. Even though the correlation coefficients of the SV plots are very good ($r > 0.990$, obtained by a least-squares fitting of the experimental data to eqn. (2) with the requirement that the intercept is unity), the reproducibility of the quenching constants k_q^{ob} observed, reported in Table 1, is not better than 10%. In any case, the inaccuracy caused by the presence of residual oxygen does not affect the k_q^{ob} values, since it influences both lifetime and intensity measurements, in the presence and in the absence of quencher, to the same extent.

3. Results

3.1. Effect of quencher structure on k_q^{ob}

Quenching measurements of phosphorescence intensity and decay time by six quenchers (4,4'-CH₃OB, 4-OHB, 4-NH₂B, 4,4'-N(CH₃)₂B, 2-OHB and 2-NH₂B) were carried out for each of the four donors (B, 3-BP, 4,4'-ClB and 4-COOHB). The corrected P^0/P values, inserted in the SV equation

$$\frac{P^0}{P} = 1 + K_{SV}^{ob}[Q] \quad (2)$$

gave linear trends, with the exceptions of the systems 3-BP + 2-NH₂B and 4-COOHB + 2-NH₂B which showed an upward curvature and of the systems 3-BP + 4,4'-CH₃OB and 3-BP + 4-OHB which showed a downward curvature.

All the decay time plots for quenching were found to be linear, following the SV-type equation

$$\frac{1}{\tau_D^0} = \frac{1}{\tau_D} + k_q^{ob}[Q] \quad (3)$$

where τ_D^Q and τ_D represent the triplet lifetime of the donor in the presence and in the absence of the quencher respectively.

The kinetic parameter k_q^{ob} observed was obtained by dividing the SV constant K_{SV}^{ob} observed from eqn. (2) by the triplet lifetime of the donor and/or from eqn. (3). The k_q^{ob} values obtained by the different methods were in excellent agreement, except in those cases where non-linearity was observed in the intensity SV plots. For these systems the k_q^{ob} values reported in Table 1 refer to lifetime measurements, whilst the other values are the average of those obtained from the two experimental methods. In the cases where agreement was found the occurrence of static quenching can be definitely excluded. By way of illustration, the behaviour of B with the four *p*-substituted quenchers is shown in Fig. 1. The quenching rate parameter increases with increasing electron-releasing power of the substituents, approaching the diffusional value ($k_{diff} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [8]) with the strongest electron-donating groups. This trend is qualitatively followed by the other donors; it

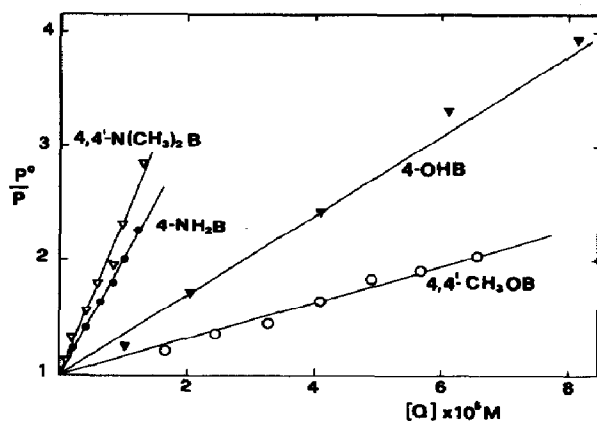


Fig. 1. SV plots for the quenching of the benzophenone phosphorescence by four *p*-substituted derivatives.

TABLE 1

Kinetic parameters for the quenching of arylketone donors by arylketone quenchers in acetic acid at room temperature

| Quencher | k_q^{ob} ($\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) values for various donors | | | |
|---|--|-----------------|--------------|--------------|
| | B | 3-BP | 4,4'-ClB | 4-COOHB |
| (τ (μs)) | (35 \pm 4) | (7.4 \pm 0.5) | (26 \pm 1) | (41 \pm 2) |
| 4,4'-CH ₃ OB | 0.43 | 0.38 | 0.16 | 0.08 |
| 4-OHB | 1.2 | 1.1 | 1.3 | 0.35 |
| 4-NH ₂ B | 3.0 | 2.4 | 3.1 | 2.5 |
| 4,4'-N(CH ₃) ₂ B | 3.7 | 4.2 | 4.6 | 3.0 |
| 2-OHB | 2.7 | 2.2 | 3.3 | 2.1 |
| 2-NH ₂ B | 3.5 | 2.4 | 3.7 | 3.1 |

is illustrated in Fig. 2 by a tentative correlation diagram of $\log k_q^{ob}$ versus σ_p^+ of the substituents [16] in the quencher. The dependence of the quenching rate parameter on the substituents may indicate a contribution to the interaction mechanism by a charge transfer process from the quencher to the excited donor through a so-called n-type exciplex [17]. Electron transfer between the π system of the aromatic ring of the quencher and the half-filled n orbital of the triplet state of the donor should in fact be facilitated by electron-releasing substituents in the quencher.

3.2. Effect of the donor structure on k_q^{ob}

The effect of substituents in the donor molecule is not so evident. The comparison, however, is more puzzling here because the uncertainty in the lifetime measurements can affect the k_q^{ob} data for the various donors differently. Only with 4,4'-CH₃OB as acceptor does the k_q^{ob} value appear to decrease regularly as the electron-withdrawing power of the donor substituent increases. For the other quenchers it can only be stated that 4-COOHB, the donor with the strongest electron-withdrawing substituent, shows the lowest k_q^{ob} values. This behaviour cannot support the hypothesis of an n-type interaction, since a decrease in the charge density in the donor should increase the charge transfer from the quencher in the n-type exciplex. However, the decrease in the k_q^{ob} values with decreasing triplet energy of the donors, as shown by the qualitative trends of Fig. 3, suggests that there could be a contribution from reversible energy transfer in the donor-quencher interaction.

Reversible energy transfer is expected to occur with a reasonable probability when the donor triplet energy is only very slightly above or even below that of the quencher. Moreover, since reversible energy transfer

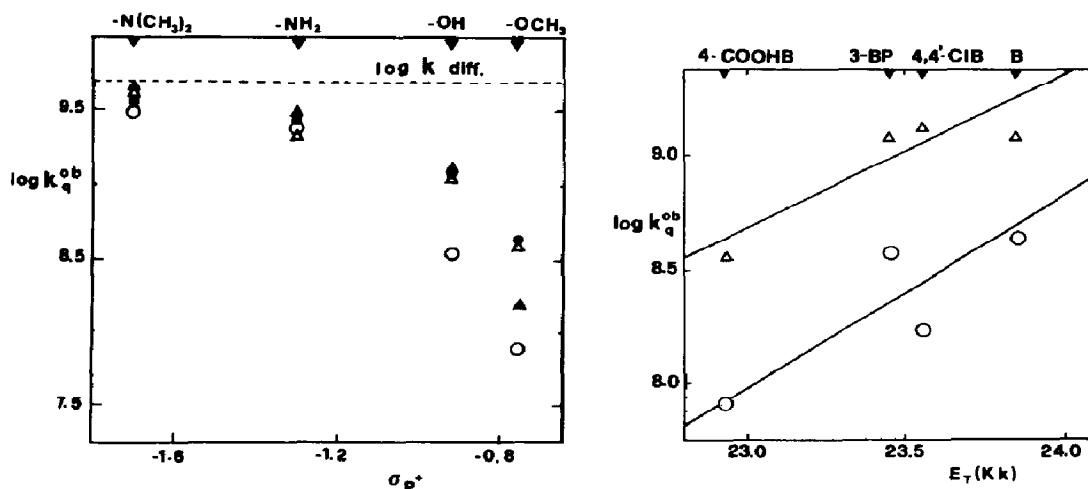


Fig. 2. A correlation diagram of σ_p^+ values for the substituents in the quencher with the quenching rate constants: ●, B; △, 3-BP; ▲, 4,4'-CIB; ○, 4-COOHB.

Fig. 3. A correlation diagram of the triplet energies of the donors with the quenching rate constants for the quenchers 4,4'-CH₃OB (○) and 4-OHB (△).

requires a collision of the excited quencher with the ground state donor, it will be more efficient with a long-lived excited acceptor and its efficiency will be enhanced as the donor concentration increases [18].

3.3. Effect of concentration on k_q^{ob}

In order to determine whether reversibility is important in the interaction mechanism, the effect of donor concentration on k_q^{ob} was studied for the system 4-COOHB (donor) + 4,4'-CH₃OB (quencher); this system was chosen because it has the lowest k_q^{ob} value. Moreover, it is possible to excite the donor at a wavelength (370 nm) where the absorbance of the quencher is very low. In this way the correction for trivial absorption effects can be maintained within a reasonable value and at very low concentrations of the donor.

The results obtained from intensity and decay time measurements are illustrated in Fig. 4. It can be seen that the slopes of the SV diagrams decrease as the concentration of the donor increases.

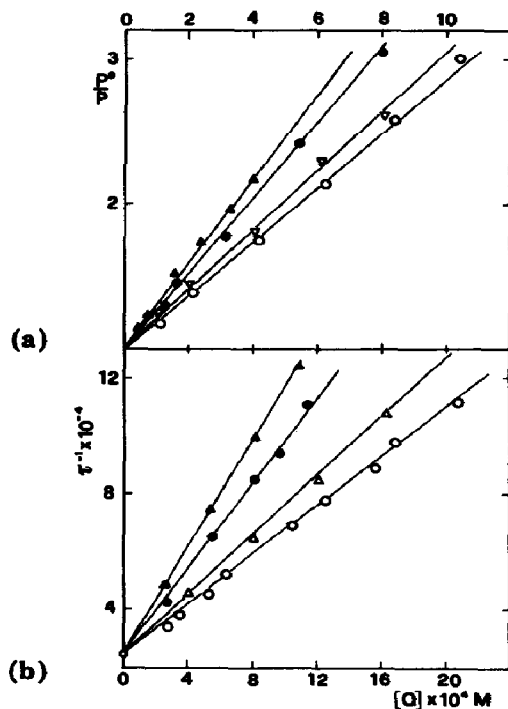


Fig. 4. Effect of the donor concentration $[D]$ on the intensity (a) and decay time (b) quenching for the system 4-COOHB (D) + 4,4'-CH₃OB (Q). (a) \blacktriangle , $[D] = 6.9 \times 10^{-4} \text{ M}$; \bullet , $[D] = 1.7 \times 10^{-3} \text{ M}$; ∇ , $[D] = 3.4 \times 10^{-3} \text{ M}$; \circ , $[D] = 6.6 \times 10^{-3} \text{ M}$. (b) \blacktriangle , $[D] = 6.7 \times 10^{-4} \text{ M}$; \bullet , $[D] = 1.3 \times 10^{-3} \text{ M}$; Δ , $[D] = 4.0 \times 10^{-3} \text{ M}$; \circ , $[D] = 6.6 \times 10^{-3} \text{ M}$.

Following a simple kinetic scheme, where k_t and k_{-t} are the kinetic parameters for the direct and back transfer respectively and τ_D and τ_Q are the triplet lifetimes of the two partners, the equation which is obtained under steady irradiation is [18]

$$\frac{P^0}{P} = 1 + \frac{k_t \tau_D [Q]}{1 + k_{-t} \tau_Q [D]} \quad (4)$$

From this equation, the SV constant K_{SV}^{ob} observed is equal to $k_t \tau_D / (1 + k_{-t} \tau_Q [D])$. Therefore a plot of $(K_{SV}^{ob})^{-1}$ versus $[D]$ should be linear with $(k_t \tau_D)^{-1}$ as the intercept and $k_{-t} \tau_Q$ as the slope/intercept ratio:

$$(K_{SV}^{ob})^{-1} = (k_t \tau_D)^{-1} + \frac{k_{-t} \tau_Q [D]}{k_t \tau_D} \quad (5)$$

However, the experimental data for the system under study do not fit this equation, as shown by the plot given in Fig. 5.

3.4. Back sensitization experiments

Since only the donor is phosphorescent in acetic acid at room temperature, there is another possibility for testing the occurrence of the back transfer. By directly exciting the quencher (4,4'-CH₃OB), it should be possible to obtain the sensitization of the donor phosphorescence if intersystem crossing to the triplet state is a non-negligible process for the acceptor. This means inverting the donor-acceptor roles of the two partners. To avoid misunderstanding we shall continue to indicate 4-COOHB as the donor and 4,4'-CH₃OB as the quencher or acceptor. The experimental situation is very crucial since there is no spectral region where irradiation of the quencher can be performed without directly exciting the phosphorescence of the donor. We chose $\lambda = 330$ nm as the exciting wavelength, which represents the best compromise of maximum absorption by 4,4'-CH₃OB and minimum absorption by 4-COOHB ($\epsilon_Q/\epsilon_D = 21$). The concentration of the quencher was 2×10^{-4} M and those of the donor ranged from 3.3×10^{-4} to 1×10^{-3} M. The phosphorescence intensity values at each donor concentration were corrected by taking into account the facts that they are the sum of two contributions (sensitized phosphorescence and directly excited phosphorescence of the donor) and that both components are reduced by trivial absorption effects [14]. In addition, the extent of quenching of the directly excited phosphorescence can be evaluated by comparison with the quenching ratio of donor phosphorescence when excited at a wavelength (370 nm) where the absorption of the quencher is negligible. The corrected intensity values, treated according to the sensitization SV equation (eqn. (6)) (where K is a constant which includes kinetic parameters of the acceptor, the triplet yield and lifetime and instrumental factors [5]), gave the plot shown in Fig. 6, from which $K_{SV}^{ob} = 730 \text{ M}^{-1}$ was obtained.

$$P^{-1} = K \left(1 + \frac{1}{K_{SV}^{ob} [D]} \right) \quad (6)$$

Despite the good linearity of the plot, this value can be considered to be indicative only of the order of magnitude of K_{SV}^{ob} because of the crucial conditions under which the measurements were performed. However, it does give additional evidence for the reversible energy transfer.

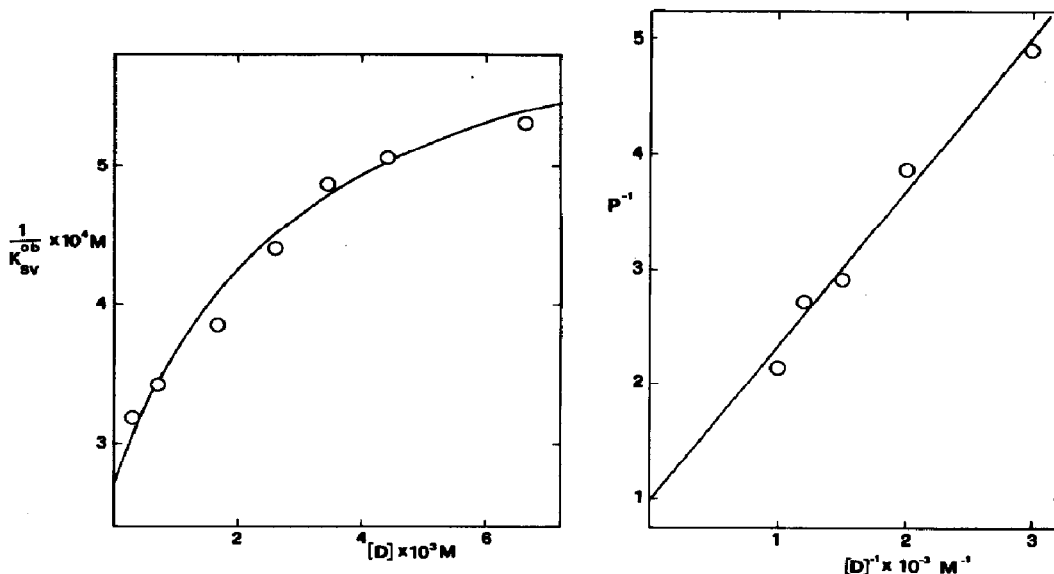


Fig. 5. Intensity quenching data treated according to eqn. (5): —, best-fitting curve obtained using the parameters of Table 2 (eqn. (7)).

Fig. 6. SV plot (eqn. (6)) for the donor (4-COOHB) phosphorescence sensitized by the quencher (4,4'-CH₃OB).

4. Discussion

The lack of sensitizing power and phosphorescence emission at room temperature for the ketones which work as quenchers implies either that triplets are not formed or that they are quite short lived and/or have a very small radiative transition probability. However, the quenchers, like the donors, exhibit phosphorescence emission at liquid nitrogen temperature. These emissions, which will be described in detail in a separate paper [19], show the presence of at least two components which are characterized by different spectral distributions and lifetimes. The triplet energies for the quenchers are of the same order of magnitude as (or even higher than) those for the donors. It should be noted that, of the two components, one exhibits n, π^* character and the other exhibits π, π^* character and that their relative energies are inverted in the quenchers (lower π, π^* state) relative to the donors (lower n, π^* state). The change in the role of the arylketones from sensitizers to quenchers parallels the inversion of triplet levels indicated by spectroscopy. Low temperature spectroscopy shows not only that the triplets are formed for the quenchers as well but also that they possess the energetic requisites to work as sensitizers. Their behaviour at room temperature could be predominantly the result of a very fast deactivation of the lowest π, π^* triplets through interaction with the solvent.

Taking into account kinetic and spectroscopic data, a mechanism for the quenching of arylketones by each other can be proposed as a working

hypothesis. Its reliability can be considered to be reasonable on the basis of the experimental data for which it is able to account. The question can be raised as to whether a unique mechanism can explain all the results or whether different mechanisms are responsible for the behaviour of the various partners, taking into account the fact that the correlations observed are qualitative and that some contrast exists between the effect of substituents in the quencher and the effect of substituents in the donor molecules.

We believe that the occurrence of reversible energy transfer is highly probable for the system 4-COOHB + 4,4'-CH₃OB on the basis of both concentration effects and back sensitization. Moreover, the energetic situation indicated by spectroscopy makes the back transfer slightly exothermic. However, the results illustrated in Fig. 5 require a more complicated mechanism than that leading to eqns. (4) and (5). All we can say in this respect is that the experimental data in Fig. 5 fit an equation of the type

$$(K_{SV}^{ob})^{-1} = \frac{1 + M[D]}{N + L[D]} \quad (7)$$

i.e. the corresponding curve should cross the abscissa ($[D] = 0$) at $1/N$ and should show a horizontal asymptote ($[D] \rightarrow \infty$) equal to M/L .

A kinetic analysis of the bimolecular interaction showed that such a dependence of K_{SV}^{ob} on the donor concentration may be justified by assuming the simultaneous occurrence of three processes: (i) energy transfer from the excited donor to the quencher; (ii) back transfer from the excited quencher to the donor; (iii) chemical quenching of the donor by the quencher. The simplest mechanism including these processes is illustrated by the schematic diagram shown in Fig. 7; straight-line arrows refer to radiative transitions, wavy arrows stand for radiationless transitions and broken-line arrows indicate bimolecular interactions. k_t and k_{-t} indicate the rate parameters for the direct and back transfer respectively and k_q indicates the rate parameter for the chemical quenching. Following this scheme eqn. (8) is obtained, where τ_D and τ_Q are the triplet lifetimes of the donor and quencher respectively.

$$\frac{P^0}{P} = 1 + \frac{\{(k_q + k_t)\tau_D + k_q k_{-t} \tau_D \tau_Q [D]\} [Q]}{1 + k_{-t} \tau_Q [D]} \quad (8)$$

This equation is expected to give a linear trend of the quenching ratios *versus* $[D]$ at constant donor concentration, as found experimentally. The reciprocal of the SV constant observed

$$(K_{SV}^{ob})^{-1} = \frac{1 + k_{-t} \tau_Q [D]}{(k_q + k_t)\tau_D + k_q k_{-t} \tau_D \tau_Q [D]} \quad (9)$$

is in agreement with eqn. (7) where the analytical coefficients are expressed in terms of kinetic parameters. These coefficients were evaluated by a trial and error method to build up the curve given in Fig. 5; the best-fitting values, together with their kinetic meaning, are reported in Table 2. Some kinetic parameters for the system under study are listed in Table 3.

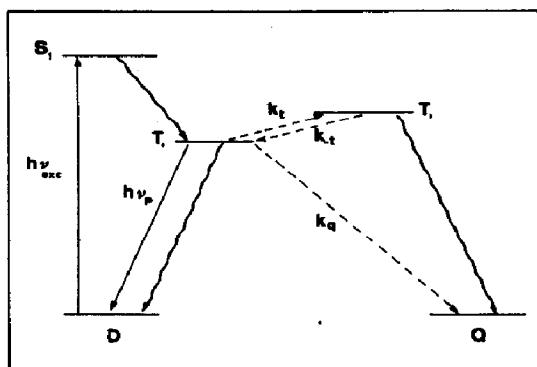


Fig. 7. Energy level scheme for chemical quenching and reversible energy transfer: \longrightarrow , radiative steps; \rightsquigarrow , radiationless transitions; \dashrightarrow , intermolecular processes.

TABLE 2

Parameters used for obtaining the curve in Fig. 5 (eqn. (7)) (system 4-COOHB (D) + 4,4'-CH₃OB (Q)) and their kinetic meaning (eqn. (8))

| Parameters | | Estimated values |
|------------|----------------------------|----------------------------------|
| Eqn. (7) | Eqn. (8) | |
| M | $k_{-t}\tau_Q$ | $0.8 \times 10^3 \text{ M}^{-1}$ |
| N | $(k_q + k_t)\tau_D$ | $3.7 \times 10^3 \text{ M}^{-1}$ |
| L | $k_q k_{-t} \tau_Q \tau_D$ | $1.2 \times 10^6 \text{ M}^{-2}$ |
| L/M | $k_q \tau_D$ | $1.5 \times 10^3 \text{ M}^{-1}$ |
| $N - L/M$ | $k_t \tau_D$ | $2.2 \times 10^3 \text{ M}^{-1}$ |

TABLE 3

Kinetic parameters for the system 4-COOHB (D) + 4,4'-CH₃OB (Q)

| τ_D^a (μs) | τ_Q^b (μs) | k_q ($\text{M}^{-1} \text{ s}^{-1}$) | k_t ($\text{M}^{-1} \text{ s}^{-1}$) |
|------------------------------|------------------------------|--|--|
| 41 ± 2 | > 0.2 | 3.7×10^7 | 5.4×10^7 |

^a Directly measured.

^b Limiting value estimated by assuming the diffusional value for k_{-t} .

When the back transfer becomes less probable, because the triplet energy is too low and/or because the triplet lifetime of the quencher is too short, the quenching equation assumes the classical form of the SV equation with K_{SV}^{ob} equal to $k_q \tau_D$, or to $k_t \tau_D$ or to the sum of both.

However, this scheme does not explain the non-linear quenching data found for the four systems cited earlier. There are various possibilities for interpreting downward and upward curvatures of the SV plots. Some can be excluded *a priori*. A downward curvature could in fact arise if the donor emission is the sum of two contributions, one coming from an unquenched state and the other coming from a quenched state (see, for example, ref. 20),

but this should lead to different quenching ratios P^0/P by changing the wavelength of analysis, owing to a different spectral distribution for the two emissions. This was not observed, even with the highest quencher concentrations. Sensitized emission of the quencher can also be excluded on the basis of the same experimental evidence. Transient effects [21], which should cause an upward curvature of the SV plots in low viscosity solvents ($\eta < 3$ cP; $\eta \approx 1.3$ cP for acetic acid), can be excluded because of the relatively long-lived triplets of the donors ($\tau_D > 10^{-6}$ s). The same kind of departure from normal SV kinetics would be produced by static quenching. Even though any evidence of donor–quencher association is lacking and the concentrations used are rather low, it cannot be definitely excluded that a percentage of excited donor molecules, formed with a quencher molecule as a nearest neighbour, can lead to competitive occurrence of static quenching.

However, the involvement of an upper non-luminescent excited state of the donor could satisfactorily explain all the experimental findings. Three possibilities can be recognized.

(1) The upper state contributes only to the chemical quenching, whilst reversible energy transfer occurs only from and to the lowest triplet state.

(2) The upper state is involved both in energy transfer and in chemical quenching, whilst the back transfer occurs to the lowest triplet of the donor.

(3) The upper state transfers its excitation energy to the quencher from which the energy is transferred back to the lowest state of the donor, which can also be chemically quenched.

Maintaining the same meaning as that stated earlier for the kinetic parameters k_q , k_t , k_{-t} , τ_D and τ_Q and assuming that the upper triplet converts to the lowest state (k_{-ic}) and can also be thermally populated (k_{-ic}) by it, the following equations are obtained for the phosphorescence quenching from possibilities (1), (2) and (3) respectively:

$$\frac{P^0}{P} = 1 + \frac{\{k_q/k_{ic}(1 + k_{-ic}\tau_D)(1 + k_{-t}\tau_Q[D]) + k_t\tau_D\}[Q] + k_q/k_{ic}k_t\tau_D[Q]^2}{1 + k_{-t}\tau_Q[D]} \quad (10)$$

$$\frac{P^0}{P} = 1 + \frac{(1 + k_{-ic}\tau_D)\{k_t + k_q(1 + k_{-t}\tau_Q[D])\}[Q]}{k_{ic}(1 + k_{-t}\tau_Q[D]) + k_t k_{-t}\tau_Q[D][Q]} \quad (11)$$

$$\frac{P^0}{P} = 1 + \frac{\{k_t(1 + k_{-ic}\tau_D) + k_q k_{ic}\tau_D(1 + k_{-t}\tau_Q[D])\}[Q] + k_q k_t\tau_D(1 + k_{-t}\tau_Q[D])[Q]^2}{k_{ic}(1 + k_{-t}\tau_Q[D]) + k_t k_{-t}\tau_Q[D][Q]} \quad (12)$$

The first of these equations gives rise to an upward curvature at high quencher concentrations. The second produces a downward curvature. From the third equation a curve with an oblique asymptote is expected, the slope of which depends on the relative magnitudes of the kinetic parameters.

Under conditions of sufficiently low concentrations, *i.e.* when the terms containing $[Q]^2$ and/or $[Q][D]$ are negligible, all three equations give rise to linear SV plots, with a dependence of K_{sv}^{ob} on $[D]$ corresponding to eqn. (7). In any case it can be demonstrated that, for certain relative values of the kinetic parameters, experimental trends may be obtained which are far from having reached their asymptotes and thus appear to be linear [22, 23]. Equations (10) and (11) can explain, separately, the two kinds of non-linearity found experimentally, whilst eqn. (12) can explain both, depending on the particular kinetic and energetic situation, where either chemical quenching (downward curvature) or back transfer (upward curvature) can be neglected.

It is clearly difficult, without other evidence, to decide by which kinetic scheme the experimental data should best be treated. The different dependences of the sensitized K_{sv}^{ob} value on the donor concentration could give a good indication [23]. Unfortunately it was experimentally impossible to explore a sufficiently large range of donor concentrations to obtain a meaningful set of data. Under the experimental conditions used in the sensitization measurements, the K_{sv}^{ob} value can be calculated using the parameters of Table 2 and the appropriate kinetic equation for each scheme [23]. The differences between the calculated values ($K_{sv}^{ob} = 590 \text{ M}^{-1}$ (Fig. 7), 550 M^{-1} (possibility (1)), 800 M^{-1} (possibility (2)), 590 M^{-1} (possibility (3))) and that found experimentally ($K_{sv}^{ob} = 730 \text{ M}^{-1}$) are less than 25%. This deviation is largely within what we believe to be the experimental uncertainty ($\pm 50\%$); therefore, we cannot exclude any of the mechanisms considered.

5. Conclusions

The results of this work show that the substituent in arylketones, by determining the character and the energy of the lowest triplet states, is the most important factor in defining their role as donors or quenchers in a solvent of intermediate polarity, such as acetic acid.

Even though no definite conclusion can be drawn about the specific interaction mechanism between the arylketones studied, there is sufficient evidence to state that a two-way mechanism — a chemical quenching and a reversible energy transfer — is operative.

Following this hypothesis, various factors can be envisaged which should or should not be determining in discriminating between the different behaviours of the donor–quencher systems. Some can be accounted for experimentally. Strong electron-releasing substituents in the quencher should facilitate the charge transfer interaction responsible for the chemical quenching. This can be considered to be the prevalent means for quenching by amino and dimethylamino derivatives, for which the k_q^{ob} value approaches the diffusional value with all the donors. Relatively long-lived triplets of the quencher and similar triplet energies for both the donor and the quencher should favour the reversible energy transfer. Only the second of these factors is susceptible to

experimental control. 4,4'-CH₃OB and 4-OHB, which possess triplet energies (measured at liquid nitrogen temperature) near to those of the donors, display k_q^{ob} values which are smaller than the diffusional value; they are particularly small with 4-COOHB where the back transfer becomes more exothermic. No effect of the triplet lifetime of the donor is expected to favour one or other mechanism. This can be easily checked by comparing the τ and k_q^{ob} values reported in Table 1.

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