QUENCHING AND REVERSIBLE ENERGY TRANSFER KINETICS INVOLVING TWO EXCITED DONOR STATES

G. FAVARO

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

(Received June 4, 1982; in revised form January 5, 1983)

Summary

A Stern–Volmer-type analysis is presented for donor–acceptor systems where two different donor excited states are involved in the quenching and reversible energy transfer processes. Special cases are discussed where the treatment of the experimental data allows the kinetic parameters to be determined.

1. Introduction

In a study of the bimolecular interactions between arylketones [1] we proposed a mechanism involving two excited donor states, where both reversible energy transfer and chemical quenching can occur, to explain the experimental data on quenching which lead in some cases to non-linear Stern–Volmer (SV) kinetics. Even though different types of behaviour in the SV plots such as linearity, upward curvature and downward curvature are observed, we believe that the same general scheme can be used to describe all the cases found experimentally owing to the similarity of the donor-quencher systems examined. Differences in the triplet energies and/or the lifetimes of the partners can lead to the different types of behaviour observed because some processes prevail over others. Therefore, in addition to the general mechanism, which is very complicated, we shall present some limiting cases which can reasonably be assumed to operate in the systems that we have studied.

Although many investigations of the kinetics of non-linear SV plots involving two excited donor states which are deactivated by the same quencher have been reported [2 - 7], the reversibility of the energy transfer process and the consequent possibility of investigating the quenching mechanism by interchanging the roles of donor and quencher for the two partners have not been considered. Reversibility is included here because evidence has been obtained for its occurrence in back transfer experiments [1]. We shall confine our analysis to donor–quencher systems where only the phosphorescence emission from the lowest triplet state of the donor can be observed, as

is the case in our experimental studies. We shall also assume that the triplet energy of the quencher is intermediate with respect to, or lower than, those of the excited states of the donor. Even though the theory is developed in terms of triplet states and is based on quenching and sensitization measurements of phosphorescence, it can be applied to any two excited states of a donor following quenching and sensitization of either emission or photoreaction.

2. General mechanism

The general mechanism is illustrated in Fig. 1. It is assumed that reversible interconversion occurs between the upper and the lower excited states
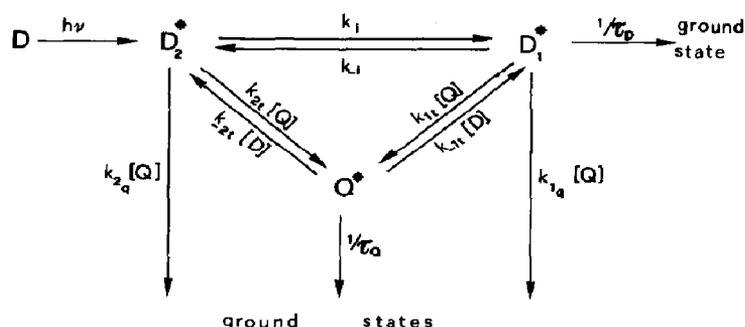
Fig. 1.

D_2^* and D_1^* of the donor and that reversible energy transfer to the quencher can occur from both the excited states. These processes are assumed to be competitive with the quenching and decay processes. Steady state analysis of $[D_2^*]$, $[D_1^*]$ and $[Q^*]$ yields the following expressions for the quenching of the phosphorescence emission of the donor:

$$\frac{\phi_D^0}{\phi_D} = 1 + \left(\left[(k_{1q} + k_{1t})\tau_D + (k_{-1t} + k_{-2t})k_{1q}\tau_D\tau_Q[D] + \right.\right.$$

$$+ (1 + k_{-1}\tau_D) \left\{ \frac{k_{2q} + k_{2t}}{k_i} + \frac{(k_{-1t} + k_{-2t})k_{2q}\tau_Q[D]}{k_i} \right\} \left] [Q] + \right.$$

$$+ \left\{ \frac{(k_{1q} + k_{1t})(k_{2q} + k_{2t})\tau_D}{k_i} + \frac{(k_{1q} + k_{1t})k_{-2t}k_{2q}\tau_D\tau_Q[D]}{k_i} + \right.$$

$$+ \frac{(k_{2q} + k_{2t})k_{-1t}k_{1q}\tau_D\tau_Q[D]}{k_i} \right\} [Q]^2 \right) \times$$

$$\times \left\{ 1 + (k_{-1t} + k_{-2t})\tau_Q[D] + \frac{k_{-1t}k_{2t}\tau_Q[D][Q]}{k_i} \right\}^{-1} \tag{1}$$

where $\phi_D{}^0/\phi_D$ represents the quenching ratio for the emission from $D_1{}^*$ and the parameters have the same meaning as indicated in Fig. 1.

By interchanging the roles of donor and quencher of the two partners when the quencher is directly excited by irradiation, the following equation is obtained for the sensitized phosphorescence of the donor:

$$\phi_D{}^{-1} = K\Bigg\{1 + k_{1q}\tau_D[Q] +$$
$$+ \frac{(1 + k_{-i}\tau_D + k_{1t}\tau_D[Q] + k_{1q}\tau_D[Q])k_{-2t}k_{2q}[Q] + k_{-i}k_{-1t}k_{2q}\tau_D[Q]}{k_i k_{-1t} + k_i k_{-2t} + k_{-1t}k_{2t}[Q] + k_{-1t}k_{2q}[Q]} +$$
$$+ \frac{(k_i + k_{2t}[Q] + k_{2q}[Q])(1 + k_{1t}\tau_D[Q] + k_{1q}\tau_D[Q]) + k_{-i}\tau_D(k_{2q} + k_{2t})[Q]}{\tau_Q[D](k_i k_{-1t} + k_i k_{-2t} + k_{-1t}k_{2t}[Q] + k_{-1t}k_{2q}[Q])}\Bigg\}$$
$$(2)$$

where K is a constant including the triplet lifetime of D and the quantum yield of excited Q^*. Despite its complexity this equation yields a linear trend for $\phi_D{}^{-1}$ and $[D]^{-1}$. However, eqn. (1) shows that the experimental quenching ratio is a function of the quencher concentration of the type

$$f([Q]) = 1 + \frac{L[Q] + M[Q]^2}{N + R[Q]} \tag{3}$$

This equation predicts SV-type plots with an oblique asymptote. By solving for the oblique asymptote, the following equations are obtained for the final slope and intercept of the asymptote extrapolated to $[Q] = 0$:

asymptote slope = $\{(k_{1q} + k_{1t})(k_{2q} + k_{2t})\tau_D + (k_{1q} + k_{1t})k_{-2t}k_{2q}\tau_D\tau_Q[D] +$
$$+ (k_{2q} + k_{2t})k_{-1t}k_{1q}\tau_D\tau_Q[D]\}(k_{-1t}k_{2t}\tau_Q[D])^{-1} \tag{4}$$

asymptote intercept = $1 + (\{k_{2q} + k_{2t} + (k_{-1t} + k_{-2t})k_{2q}\tau_Q[D]\} \times$
$$\times [(1 + k_{-i}\tau_D)k_{-1t}k_{2t}\tau_Q[D] -$$
$$- k_i\tau_D\{(k_{1q} + k_{1t})(1 + k_{-2t}\tau_Q[D]) + k_{-1t}k_{1q}\tau_Q[D]\}]) \times$$
$$\times (k_{-1t}k_{2t}\tau_Q[D])^{-2} \tag{5}$$

Depending on the relative values of the kinetic parameters and/or the concentration of the donor, the following can hold in eqn. (5):

$$(1 + k_{-i}\tau_D)k_{-1t}k_{2t}\tau_Q[D] \gtreqless k_i\tau_D\{(k_{1q} + k_{1t})(1 + k_{-2t}\tau_Q[D]) + k_{-1t}k_{1q}\tau_Q[D]\} \tag{6}$$

In consequence, the intercept of the asymptote can be larger than, smaller than or equal to unity and the plots can curve downwards, curve upwards or be linear. The complexity of these equations implies that only qualitative information can be obtained from the shape of the plots.

3. Special cases

The energy differences and lifetimes of the three excited states may be such that there is no competition between some of the processes in Fig. 1. Furthermore substituent effects and steric factors [8] may be important in determining the efficiency of the quenching processes. If the situation is such that the energy of Q^* is intermediate between the energies of D_2^* and D_1^*, the back transfer from Q^* to D_2^* or the direct transfer from D_1^* to Q^* or both may be negligible ($k_{-2t} = 0$ and/or $k_{1t} = 0$) because they are endothermic. Conversely, if the triplet energy of the quencher is lower than the energies of both excited states of the donor, back transfer processes, particularly to the higher excited state D_2^*, may become inefficient ($k_{-2t} = 0$ and possibly $k_{-1t} = 0$). Furthermore, if the energy gap between D_2^* and D_1^* is large, the thermal conversion of the lowest triplet may also be inefficient ($k_{-i} = 0$).

Some of the above restrictions give a quenching expression of the same type as eqn. (3) (case (a)). There are also specific conditions which reduce eqn. (3) to one of the following expressions:

$$f([Q]) = 1 + \frac{L[Q]}{N + R[Q]} \tag{7}$$

(case (b)) or

$$f([Q]) = 1 + L[Q] + M[Q]^2 \tag{8}$$

(case (c)).

3.1. Case (a)

The simplest formulation for eqn. (3) is obtained when the processes governed by the parameters k_{-2t}, k_{1t}, k_{-i} and k_{2q} are inefficient. This means that all endothermic processes are ignored and only the lower state D_1^* is considered to be quenchable. This case is of some interest because, at least in principle, the kinetic parameters can be obtained. The equation for quenching is

$$\frac{\phi_D^0}{\phi_D} = 1 + \left[\left\{ \frac{k_{2t}}{k_i} + k_{1q}\tau_D(1 + k_{-1t}\tau_Q[D]) \right\}[Q] + \frac{k_{1q}k_{2t}\tau_D(1 + k_{-1t}\tau_Q[D])[Q]^2}{k_i} \right] \times$$

$$\times \left(1 + k_{-1t}\tau_Q[D] + \frac{k_{-1t}k_{2t}\tau_Q[D][Q]}{k_i} \right)^{-1} \tag{9}$$

and the equation for sensitized phosphorescence is

$$\phi_D^{-1} = K \left(1 + k_{1q}\tau_D[Q] + \frac{1 + k_{1q}\tau_D[Q]}{k_{-1t}\tau_Q[D]} \right) \tag{10}$$

The expressions for the slope and intercept of the asymptote of the SV quenching plot are

$$\text{asymptote slope} = k_{1q}\tau_D + \frac{k_{1q}\tau_D}{k_{-1t}\tau_Q[D]} \tag{11}$$

$$\text{asymptote intercept} = 1 + \frac{(k_{2t}/k_i)k_{-1t}\tau_Q[D] - k_{1q}\tau_D(1 + k_{-1t}\tau_Q[D])}{(k_{2t}/k_i)(k_{-1t}\tau_Q[D])^2} \tag{12}$$

If the final slope of the asymptote can be experimentally determined at different donor concentrations, $k_{1q}\tau_D$ and $k_{-1t}\tau_Q$ values can be obtained as the intercept and the intercept-to-slope ratio respectively of the linear plot of the asymptote slope *versus* $[D]^{-1}$ according to eqn. (11). Insertion of these values in eqn. (12) allows k_{2t}/k_i to be obtained from the intercept of the asymptote. Comparison with the values of K_{SV} obtained from the sensitization measurements should confirm the $k_{-1t}\tau_Q$ value. Depending on the relative values of the kinetic parameters and/or on the donor concentration, the conditions which determine the behaviour of the curvature of the plots are

$$\frac{k_{2t}/k_i}{k_{1q}\tau_D} \gtreqless \frac{1 + k_{-1t}\tau_Q[D]}{k_{-1t}\tau_Q[D]} \tag{13}$$

These conditions lead to downward curving plots, linear plots or upward curving plots respectively. A linear plot with intercept equal to unity corresponds to the situation where the quenching rate is just balanced by the back transfer rate. Figure 2 shows how variations in k_{2t}/k_i (from 5×10^4 to 0.2×10^2 M^{-1}) for constant $k_{1q}\tau_D$ (10^3 M^{-1}) and $k_{-1t}\tau_Q[D]$ (0.5) change the shape of the quenching plot from a downward curve ($k_{2t}/k_i < 3 \times 10^3$ M^{-1}) through a linear plot ($k_{2t}/k_i = 3 \times 10^3$ M^{-1}) to an upward curve ($k_{2t}/k_i > 3 \times 10^3$ M^{-1}). Since the final slopes of the asymptotes, which depend only on $k_{1q}\tau_D$ and $k_{-1t}\tau_Q[D]$ (eqn. (11)), should be the same for all the curves shown in Fig. 2, it can be seen that the higher is the value of k_{2t}/k_i, the lower are the [Q] values required to determine the asymptote slope. This determination appears to be impossible for curves 5 and 6 ($k_{2t}/k_i = 5 \times 10^2$ M^{-1} and $k_{2t}/k_i = 0.2 \times 10^2$ M^{-1}) which are far from asymptotic linearity because the coefficients of the quadratic concentration terms in eqn. (9) are extremely small. Figure 3 shows how a linear plot can be transformed into an upward or a downward curving plot by varying $k_{-1t}\tau_Q$ or [D]. It is of particular interest that for a given donor–quencher system an increase in [D] causes the plots to curve downwards whilst a decrease in [D] has the opposite effect. For example, Fig. 3 shows for $k_{-1t}\tau_Q = 10^3$ M^{-1} what is obtained when the donor concentration required for the plot to be linear ([D]= 10^{-3} M; $k_{-1t}\tau_Q[D] = 1$) is increased ([D] = 5×10^{-3} M; $k_{-1t}\tau_Q[D] = 5$) or decreased ([D] = 0.2×10^{-3} M; $k_{-1t}\tau_Q[D] = 0.2$) by a factor of 5. The possibility of linearizing a plot by changing the donor concentration (this can only be done for $k_{2t}/k_i > k_{1q}\tau_D$) may offer an alternative to the method of determining k_{2t}/k_i as the slope of the linear plot.
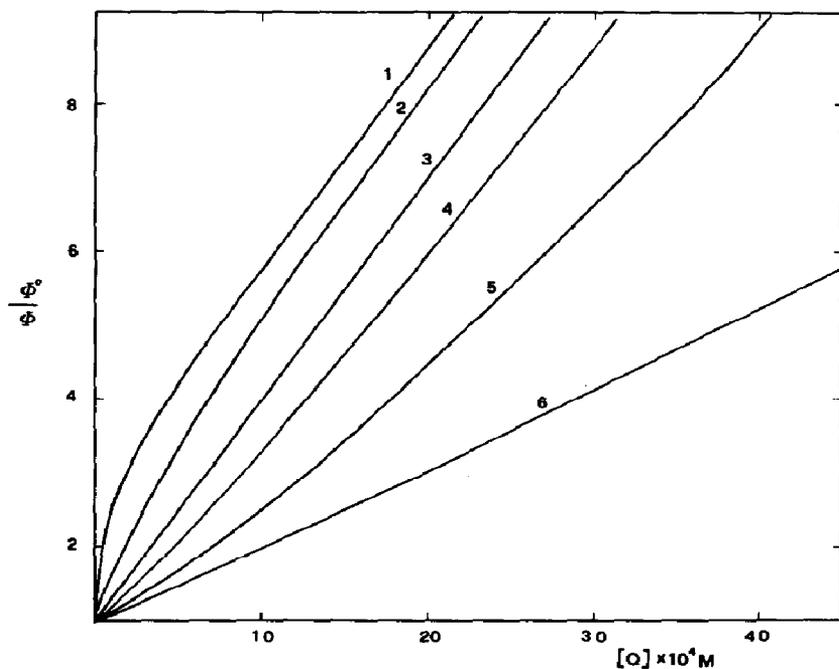
Fig. 2. Quenching plots obtained using eqn. (9). The effect of variations in k_{2t}/k_i for constant $k_{1q}\tau_D$ (10^3 M^{-1}) and $k_{-1t}\tau_Q[D]$ (0.5): curve 1, 5×10^4 M^{-1}; curve 2, 10^4 M^{-1}; curve 3, 3×10^3 M^{-1}; curve 4, 1.5×10^3 M^{-1}; curve 5, 5×10^2 M^{-1}; curve 6, 0.2×10^2 M^{-1}.
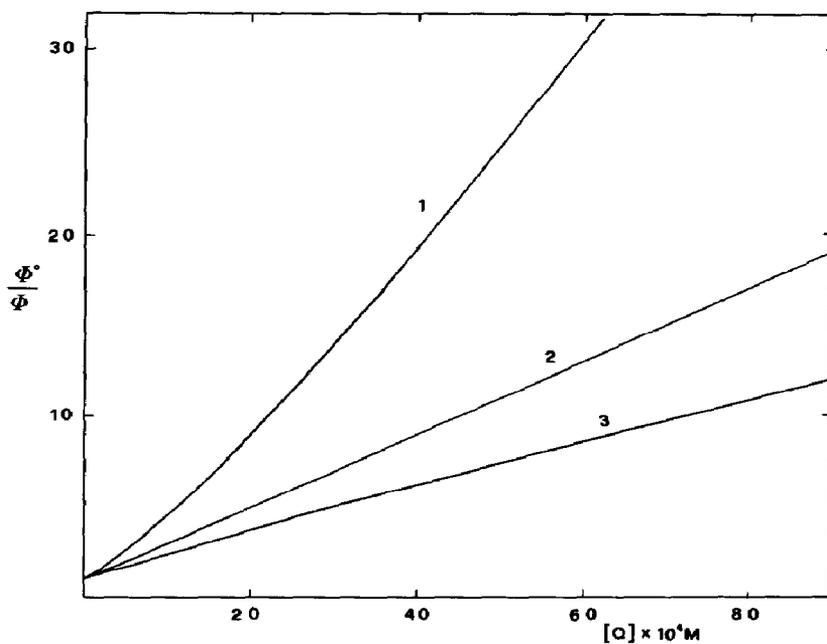
Fig. 3. Quenching plots obtained using eqn. (9). The effect of variations in $k_{-1t}\tau_Q[D]$ for constant k_{2t}/k_i (2×10^3 M^{-1}) and $k_{1q}\tau_D$ (10^3 M^{-1}): curve 1, 0.2; curve 2, 1; curve 3, 5.

3.2. Case (b)

Equation (7) produces a downward curving SV plot with a horizontal asymptote. The limiting conditions required to produce this situation are $k_{1t} = 0$ and $k_{1q} = 0$. This means that the lowest excited state D_1^* deactivates only through monomolecular processes. The kinetic parameters are easily obtained from the treatment of the experimental data when the additional conditions $k_{-2t} = 0$ and $k_{-i} = 0$ are introduced. These assumptions are reasonable because the processes neglected are both endothermic. The equation for quenching now becomes

$$\frac{\phi_D{}^0}{\phi_D} = 1 + \frac{\{k_{2t}/k_i + (k_{2q}/k_i)(1 + k_{-1t}\tau_Q[D])\}[Q]}{1 + k_{-1t}\tau_Q[D] + (k_{-1t}k_{2t}/k_i)\tau_Q[D][Q]} \tag{14}$$

and the equation for sensitized phosphorescence becomes

$$\phi_D{}^{-1} = K\left(1 + \frac{1}{k_{-1t}\tau_Q[D]}\right) \tag{15}$$

SV-type plots given by eqn. (14) are shown in Fig. 4 for k_{2t}/k_i and k_{2q}/k_i constant and equal to 10^4 M^{-1} and for $k_{-1t}\tau_Q[D]$ varying in the range 0.1 - 9. It can be seen that, when quenching and energy transfer are competitive, the higher is the value of $k_{-1t}\tau_Q[D]$ the lower are the values of the quencher concentration at which the horizontal asymptote is reached. Therefore, for a given donor–quencher system variations in the donor concentration can help to identify such a mechanism. Figure 5 shows that the plots deviate
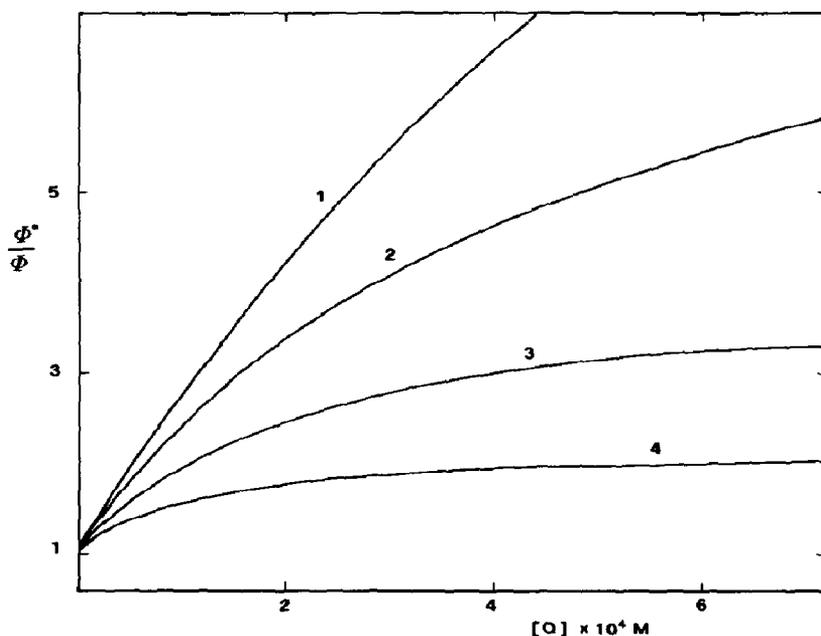
Fig. 4. Quenching plots obtained using eqn. (14). The effect of variations in $k_{-1t}\tau_Q[D]$ for constant k_{2t}/k_i and k_{2q}/k_i (both equal to 10^4 M^{-1}): curve 1, 0.1; curve 2, 0.3; curve 3, 1; curve 4, 9.
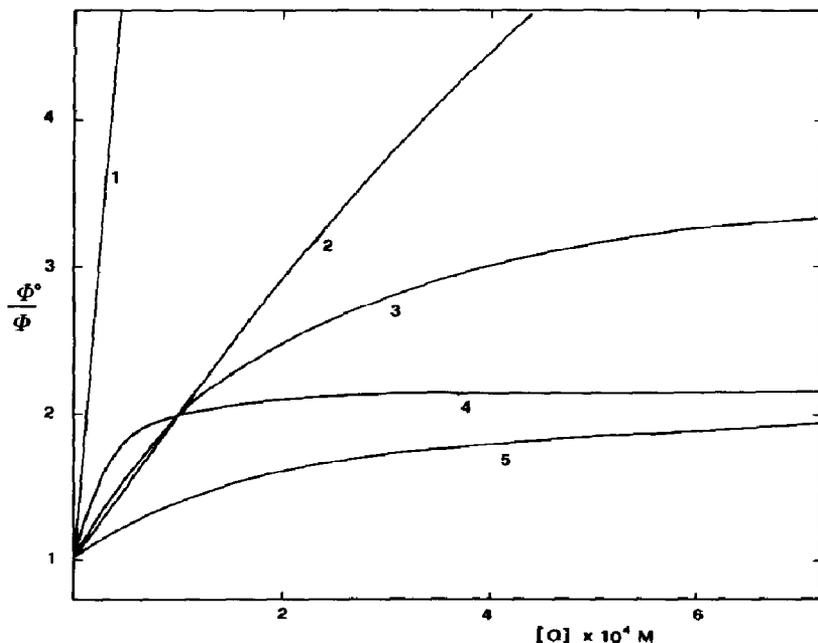
Fig. 5. Quenching plots obtained using eqn. (14). The effect of variations in k_{2t}/k_i and k_{2q}/k_i for $k_{-1t}\tau_Q[D] = 1$: curve 1, $k_{2t}/k_i = 10^4$ M^{-1} and $k_{2q}/k_i = 10^5$ M^{-1}; curve 2, $k_{2t}/k_i = 10^3$ M^{-1} and $k_{2q}/k_i = 10^4$ M^{-1}; curve 3, $k_{2t}/k_i = k_{2q}/k_i = 10^4$ M^{-1}; curve 4, $k_{2t}/k_i = 10^5$ M^{-1} and $k_{2q}/k_i = 10^4$ M^{-1}; curve 5, $k_{2t}/k_i = 10^4$ M^{-1} and $k_{2q}/k_i = 10^3$ M^{-1}.

only slightly from linearity when quenching prevails over energy transfer ($k_{2t} < k_{2q}$) and that they attain the horizontal asymptote at low quencher concentrations where energy transfer is the most important process ($k_{2t} > k_{2q}$). The value for the horizontal asymptote can be obtained from eqn. (14):

$$\text{horizontal asymptote} = 1 + \frac{k_{2t}/k_i + (k_{2q}/k_i)(1 + k_{-1t}\tau_Q[D])}{k_{-1t}k_{2t}\tau_Q[D]} \tag{16}$$

In order to check that the experimental data fit the proposed mechanism and to obtain the kinetic parameters, it is best to linearize eqn. (14) by using its reciprocal form:

$$\frac{\phi_D}{\phi_D{}^0 - \phi_D} = \frac{k_{-1t}k_{2t}\tau_Q[D]}{k_{2t} + k_{2q}(1 + k_{-1t}\tau_Q[D])} + \frac{k_i(1 + k_{-1t}\tau_Q[D])}{\{k_{2t} + k_{2q}(1 + k_{-1t}\tau_Q[D])\}[Q]} \tag{17}$$

from which the plot of $\phi_D/(\phi_D{}^0 - \phi_D)$ against $[Q]^{-1}$ yields a straight line with the ratio

$$\frac{\text{slope}}{\text{intercept}} = \frac{k_i}{k_{2t}} + \frac{k_i}{k_{2t}k_{-1t}\tau_Q[D]} \tag{18}$$

Measurements performed using various donor concentrations would allow the parameters k_i/k_{2t} and $k_{-1t}\tau_Q$ to be determined as the intercept and

intercept-to-slope ratio of the linear plot produced by eqn. (18). Then k_{2q}/k_i could be estimated using eqns. (16) or (17). The value of K_{SV} for the back sensitization of the phosphorescence of D by the quencher obtained from eqn. (15) should confirm the $k_{-1t}\tau_Q$ value.

3.3. Case (c)

Mathematically the limiting condition that reduces the general quenching equation (eqn. (1)) to an SV-type equation like eqn. (8) is either $k_{2t} = 0$ or $k_{-1t} = 0$. However, the absence of energy transfer from the higher triplet state of the donor ($k_{2t} = 0$) appears unlikely because the process is exothermic. However, a very short lifetime of D_2^* or efficient competition by chemical quenching would reduce the energy transfer efficiency to a negligibly small value. Conversely, if the triplet energy of the quencher is lower than the energies of both excited states of the donor, back transfer from D_1^* ($k_{-1t} = 0$) may not occur. This implies that the back transfer to D_2^* ($k_{-2t} = 0$) is also impossible. Under these conditions the expression for quenching is

$$\frac{\phi_D^0}{\phi_D} = 1 + \left\{ (k_{1q} + k_{1t})\tau_D + \frac{k_{2q} + k_{2t}}{k_i} \right\}[Q] + \frac{(k_{1q} + k_{1t})(k_{2q} + k_{2t})\tau_D[Q]^2}{k_i} \quad (19)$$

Obviously, back sensitization of the donor phosphorescence cannot be observed. The upward curvature of the plot produced by eqn. (19) is determined by the relative importance of the bimolecular processes of D_1^* ($(k_{1q} + k_{1t})\tau_D$) and of D_2^* ($(k_{2q} + k_{2t})/k_i$), the sum of which represents the coefficient of $[Q]$ and the product of which represents the coefficient of $[Q]^2$. Mathematically, the curvature is more marked for $(k_{1q} + k_{1t})\tau_D = (k_{2q} + k_{2t})/k_i$ as shown in Fig. 6 where $(k_{1q} + k_{1t})\tau_D$ is constant and $(k_{2q} + k_{2t})/k_i$ ranges from 10^2 to 10^4 M^{-1} (or vice versa). The coefficients of $[Q]$ and $[Q]^2$ can be determined by a computer fit and can then be solved for $(k_{1q} + k_{1t})\tau_D$ and $(k_{2q} + k_{2t})/k_i$. However, the quenching and energy transfer parameters cannot be separated and the same experimental result is achieved when only one of these processes is operative for each excited state. The occurrence of both quenching and energy transfer can only be assessed if the excited quencher undergoes some observable process (emission and/or photoreaction).

4. Remarks and examples

It can be seen that in the cases examined the quenching plots are much more indicative of the complexity of the mechanism than are the back sensitization plots. However, a combination of quenching and back sensitization experiments can be used to determine which type of complexity leads to departure from normal SV kinetics, which might otherwise be ascribed to different causes [4]. Moreover, the back sensitization results enable a comparison of the kinetic parameters obtained by different methods to be made.
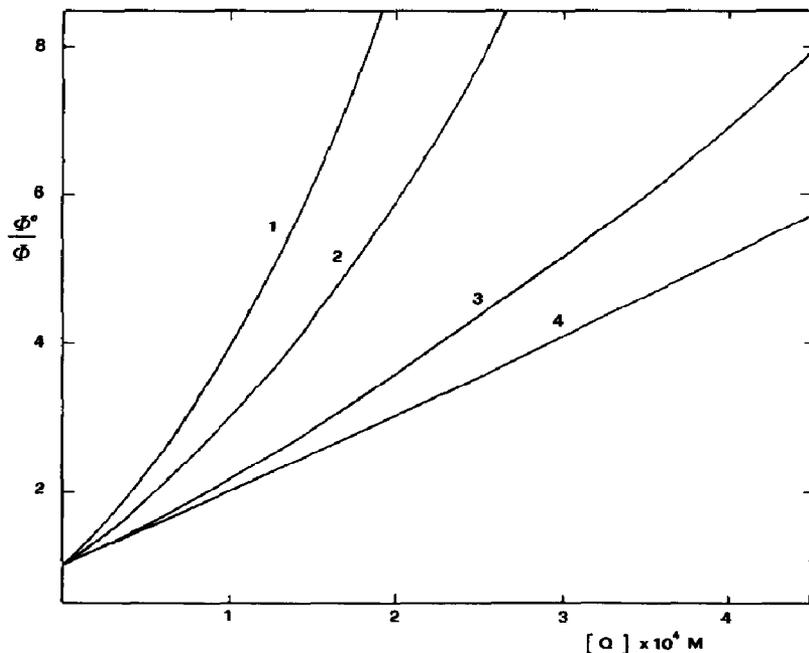
Fig. 6. Quenching plots obtained using eqn. (19). The effect of variations in $(k_{1q} + k_{1t})\tau_D$ or $(k_{2q} + k_{2t})/k_1$ for constant $(k_{1q} + k_{1t})\tau_D$ (10^4 M^{-1}): curve 1, 10^4 M^{-1}; curve 2, 5 $\times$ 10^3 M^{-1}; curve 3, 10^3 M^{-1}; curve 4, 10^2 M^{-1}.

However, even though the analysis of the experimental results can provide all the kinetic parameters of interest for the special cases examined, far more data are required for this analysis than for the treatment of normal SV kinetics. Slight deviations from linearity may be difficult to detect either because of the uncertainty of the measurements or because intensity ratio values larger than 7 - 8 cannot be measured with precision. When the quenching is followed for low values of intensity ratios only, the SV plots may appear to be linear but the experimental SV constant is not simply equal to the product of the quenching parameter and the lifetime of the donor.

Examples of cases (a), (b) and (c) have been found for arylketones as donors and in some situations it has been possible to determine the kinetic parameters.

The 4-carboxy-benzophenone (D)–2-amino-benzophenone (Q) system which exhibits SV plots with upward curvature fits an equation of the form of eqn. (3) well, but L, M, N and R cannot be resolved for the individual kinetic parameters because there is not enough experimental information to decide whether limiting conditions hold and what they are. Similar behaviour is exhibited when 3-benzoylpyridine is used as the donor.

A downward curving plot with a horizontal asymptote has been obtained using 3-benzoylpyridine as the donor and 4-hydroxybenzophenone or 4,4'-dimethoxybenzophenone as quenchers. This behaviour is illustrated in Fig. 7. The best fit curve for the limiting conditions of case (b) (full curve)
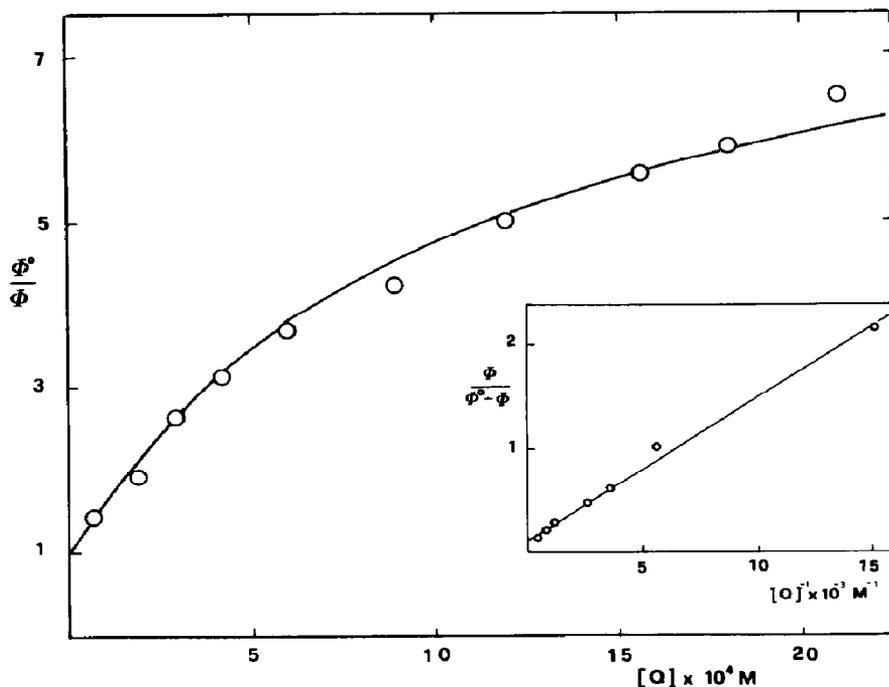
Fig. 7. Experimental results (○) and best fit curve (———) obtained using eqn. (14) for the quenching of 3-benzoylpyridine phosphorescence by 4-hydroxybenzophenone in acetic acid solution. The inset shows the same data treated using eqn. (17).

was constructed using the following set of parameters: $k_{2t}/k_i = 4.45 \times 10^3$ M^{-1}; $k_{2q}/k_i = 7.0 \times 10^3$ M^{-1} and $k_{-1t}\tau_Q[D] = 3.17$.

Examples of case (c) have been reported for the quenching of some arylketones (benzophenone, 4,4'-dichlorobenzophenone and 3-benzoyl-pyridine) by $Ru(bpy)_3^{2+}$. The cation in fact possesses an excited triplet state due to charge transfer to the ligand [9], the energy of which (48 kcal) is far enough below those of the ketone donors (approximately 68 kcal for the lowest triplets) to rule out back transfer to the donor. In this case it is assumed that energy transfer occurs from one state of the ketone and quenching occurs from the other state. Kinetic analysis of the experimental data for the quenching of the intensity and duration of the donor emission and for the sensitized quencher emission allows the two contributions to be separated and the kinetic parameters to be obtained [10].

Other systems examined gave rise to quenching SV plots which appeared to be linear. However, the effect of donor concentration on the experimental SV constant and the back sensitization experiments indicated that a complex mechanism, such as that discussed here, might be operative. It can be seen from eqns. (9) and (14) that linear plots can be obtained when the quadratic concentration terms are negligibly small, at least for low quenching ratio values. However, the experimental SV constant depends on the donor concentration through the relation

$$K_{SV}^{-1} = \frac{1 + a[D]}{b + c[D]} \tag{20}$$

where the analytical coefficients represent the kinetic parameters or some combination of them. It should be noted that the same equation is obtained, without approximations, when the higher triplet state of the donor is not involved in the interaction whereas the lower undergoes both quenching and reversible energy transfer. A detailed analysis of the effect of donor concentration on the 4-carboxybenzophenone (D)–4,4′-dimethoxybenzophenone (Q) system allowed the kinetic parameters for direct and back transfer to be obtained by substituting the experimental data in eqn. (20) [1].

References

1 G. Favaro and F. Masetti, *J. Photochem.*, *15* (1981) 241.
2 J. C. Dalton and N. J. Turro, *Mol. Photochem.*, *2* (1970) 133.
3 P. J. Wagner, *Mol. Photochem.*, *3* (1971) 23.
4 P. J. Wagner, in A. A. Lamola (ed.), *Creation and Detection of the Excited State*, Vol. 1A, Dekker, New York, 1971, p. 173.
5 M. D. Shetlar, *Mol. Photochem.*, *6* (1974) 143, 167, 191.
6 P. J. Wagner and T. Nakahira, *J. Am. Chem. Soc.*, *96* (1974) 3668.
7 P. J. Wagner, *J. Photochem.*, *10* (1979) 387.
8 S. G. Cohen, A. Parola and G. H. Parson, *Chem. Rev.*, *73* (1973) 141.
9 J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, *98* (1976) 4835.
10 G. Favaro and F. Masetti, *J. Phys. Chem.*, *83* (1979) 2129.