SOLVENT ISOTOPE EFFECTS ON THE QUENCHING OF PORPHYRIN FLUORESCENCE BY ELECTRON ACCEPTORS IN ALCOHOLS OR WATER

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(Received May 21, 1985; in revised form December 9, 1985)

Summary

The quenching of porphyrin fluorescence by oxidants in alcohols and water was found to be static. It is shown that the quenching constants in deuterated solvents are lower than those in non-deuterated solvents. The quenching in such systems is suggested to be due to the formation of complexes in which the donor and the acceptor are bound to the molecules of the medium. The effect of deuteration on the constants for the quenching of fluorescence is accounted for by the variation in the rate of electron transfer in the molecular complexes under study.

1. Introduction

The fluorescence of tetrapyrrol pigments in solution is quenched by electron acceptors [1]. The quenching process is satisfactorily described by the Stern—Volmer equations [1 - 3]

$$\frac{\varphi_0}{\varphi} = 1 + \kappa C \tag{1}$$

and

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 C \tag{2}$$

In eqns. (1) and (2), φ_0, φ and τ_0, τ are the the fluorescence quantum yields and lifetimes in the presence and absence of quencher respectively, κ is the quenching constant, k_q is the rate constant of quenching and C is the quencher concentration. The quenching constants increase on increasing the electron-acceptor and electron-donor properties of the excited molecules. This indicates that the quenching processes are governed by electron transfer from the excited molecule to the acceptor [1, 4, 5]. In this case, singlet radical ion pairs are believed to be formed, which decay practically com-

pletely on recombination [5, 6]. "Free" radical ions result from the reactions of triplet excited molecules [7].

In the majority of solvents, the quenching of porphyrin fluorescence is dynamic. With relatively strong electron acceptors, the quenching rate is controlled by the diffusion of the reacting molecules [8]. In alcohols, static quenching makes a marked contribution to excited state deactivation [8]. The present paper shows that analogous static quenching may also take place in aqueous solutions. Judging from the data obtained, static quenching in hydroxylic solvents results from the formation of complexes whose electron acceptor and electron donor are bound to each other by alcohol or water molecules or their associates. The electron-transfer rate in such complexes decreases in deuterated solvents. Analysis of the quenching of porphyrin fluorescence by oxidants in hydroxylic solvents is presented in this paper.

2. Experimental details

Pheophytin a, meso-tetraphenylporphin (H$_2$TPhP), tetra-4-tert-butyl-phthalocyanin (H$_2$Pc) and their metal derivatives used in this study were prepared by the procedure reported in refs. 9 - 12. Quinones and nitro compounds purified by recrystallization or sublimation were chosen as quenchers. The fluorescence spectra were recorded using apparatus similar to that described in ref. 13. The excitation wavelength was chosen to eliminate light absorption by the quencher. The fluorescence decay was studied using a pulse fluorometer (the flash time did not exceed 2 ns). Fluorescence lifetimes were measured by the method of single-photon counting, using a time–amplitude ORTEC transformer and a multichannel NOKIA analyser. The quenching of fluorescence is described satisfactorily by eqns. (1) and (2). The decay of fluorescence of tetrapyrrol pigments in the presence and absence of quencher was found to be exponential.

The equilibrium constants K_c of complexation of porphyrins with quinones were obtained spectrophotometrically. On increasing the quencher concentration in solution, the intensities of the absorption bands for the porphyrins diminish. Simultaneously, some broadening in these bands was observed. The complexation constants were determined using the equation [14]

$$\frac{C_{A_0} C_{D_0} l}{\Delta D(C_{A_0} + C_{D_0})} = \frac{1}{K_c \Delta \epsilon (C_{A_0} + C_{D_0})} + \frac{1}{\Delta \epsilon} \tag{3}$$

where l is the length of the cell, $\Delta \epsilon = \epsilon_c - \epsilon_D - \epsilon_A$ where ϵ_c, ϵ_D and ϵ_A are the extinction coefficients of the complex, the donor and the acceptor respectively, ΔD is the change in the optical density of the solution and C_{A_0} and C_{D_0} are the initial concentrations of the reactants. Equation (3) permits K_c to be determined through varying the optical density, even for those spectral regions where the absorption bands of the donor, acceptor and complex overlap. According to eqn. (3) the experimental curves are

linearized in the coordinates $(C_{A_0}C_{D_0}/D(C_{A_0} + C_{D_0}), 1/(C_{A_0} + C_{D_0}))$. The intercept on the y axis and the slope of the straight line were used to calculate the K_c. The complexation constants of porphyrins with electron acceptors thus obtained are listed in Table 1.

TABLE 1

Constants of complexation of porphyrins with electron acceptors measured spectrophotometrically

Quencher	K_c (l mol^{-1})			
	Toluene	Acetone	Ethanol	Isopropanol
p-Benzoquinone	0.46	0.43	2.8	2.9
p-Chloranil	6	23		
p-Dichlorobenzene	10	8		
m-Dichlorobenzene	1.1	0		
Toluquinone	1.4			2.5

3. The results and their analysis

3.1. Some specific features of fluorescence quenching of porphyrins in alcohols and water

A plot of the rate constant k_q for the quenching of pheophytin a fluorescence by toluquinone against the solvent fluidity $1/\eta$ is presented in Fig. 1. On increasing the viscosity of the medium, k_q was found to decrease. This suggests that the rate of quenching in this system is controlled by the diffusion of the reactants. For the majority of solvents, κ also decreases with an increase in $1/\eta$ (Fig. 2). As the fluorescence lifetimes of pheophytin a are not affected by the nature of the solvent (see Table 2), the influence of viscosity on κ seems to be due to the variation in the rate of diffusion. An analogous drop in κ was also observed in some other systems (see Tables 2 - 4). Such effects are considered in detail in ref. 8.

In most cases $\kappa > k_q\tau_0$ (see Table 3). For the majority of solvents, however, $\kappa - k_q\tau_0$ is small, which may be largely associated with non-steady-state diffusion effects [15]. Besides, the magnitude of κ depends on the static quenching constants. In fact, in all cases when a drop in the fluorescence intensity is due to both static and dynamic quenching, the overall quenching process is described by the equation [2, 3]

$$\frac{\varphi_0}{\varphi} = (1 + VC)(1 + k_q\tau_0 C) \tag{4}$$

where V is the static quenching constant. The dependence of φ_0/φ on C is practically linear at low concentrations of the quencher. In this case, the quenching constant may be expressed as the sum of static and dynamic quenching:
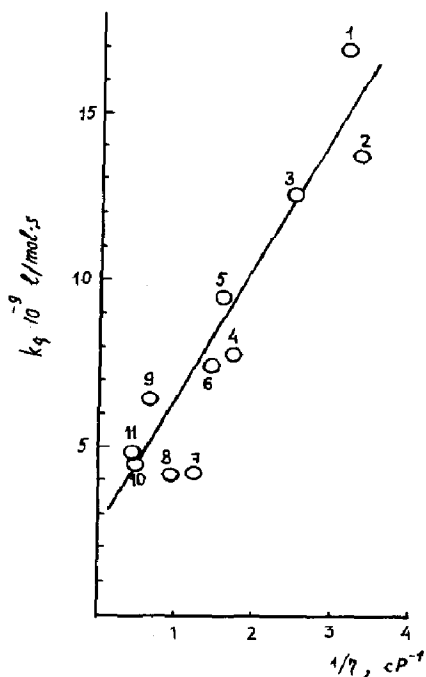
Fig. 1. Plot of the rate constant k_q of fluorescence quenching of pheophytin a by tolu-quinone against the viscosity η of the medium: 1, acetone; 2, hexane; 3, heptane; 4, toluene; 5, benzene; 6, nonane; 7, o-xylene; 8, ethanol; 9, dodecane; 10, tetradecane; 11, isopropanol.
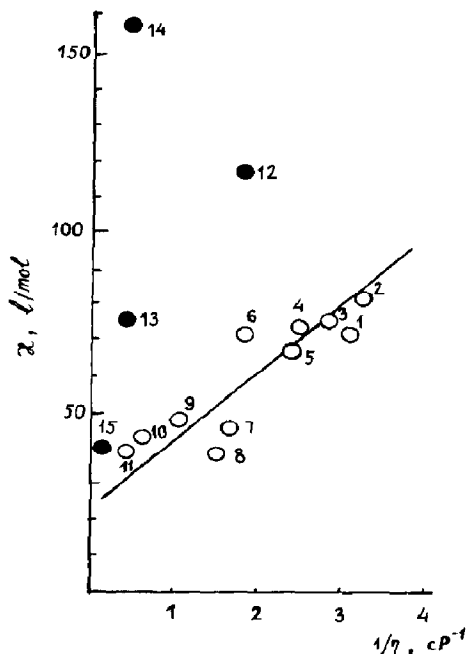
Fig. 2. Plot of the constant κ of fluorescence quenching of pheophytin a by toluquinone against the viscosity η of the medium: 1, acetone; 2, hexane; 3, acetonitrile; 4, methyl ethyl ketone; 5, heptane; 6, octane; 7, toluene; 8, benzene; 9, decane; 10, dodecane; 11, tetradecane; 12, methanol; 13, n-propanol; 14, isopropanol; 15, n-hexanol.

$$\kappa \approx V + k_q \tau_0 \tag{5}$$

In the simplest case, V equals the constant of formation of a non-fluorescent complex between donor and acceptor molecules in the ground state.

It follows from Table 1 that the constants K_c of complexation of porphyrins with the electron acceptors used are small. They are comparable with $(\kappa - k_q \tau_0)$ (see Table 3). These findings suggest that the measured values of κ are close to those limiting values of the quenching constant that would be obtained if they were determined by diffusion-controlled deactivation of excited molecules by electron acceptors.

Again, the quenching constants for lower alcohols are much higher than the values shown in Fig. 2. For alcohols, the $(\kappa - k_q \tau_0)$ were also found to be very high (Table 3). This indicates that the quenching of porphyrin fluorescence by electron acceptors is more static in alcohols compared with other solvents. However, the constants of complexation of porphyrins with electron acceptors in alcohols, determined spectrophotometrically, are small.

TABLE 2

Constants of fluorescence quenching of pheophytin a by electron acceptors in various solvents at room temperature

Solvent	$1/\eta$ (cP^{-1})	τ_0 (ns)	κ (l mol^{-1})					
			1	2	3	4	5	6
Hexane	3.24	5.4	125	42				
Acetone	3.10	7.2	125	51				105
Acetonitrile	2.82		50					100
Methyl ethyl ketone	2.48		146	35				87
Heptane	2.42	5.5	137	38				
Octane	1.85		85	38				
Toluene	1.7	5.8	61	43	45	15	68	77
Benzene	1.54	5.2	62	33				74
Cumene	1.26		30	47				
Benzonitrile	0.75		40	30				67
Dodecane	0.60	5.4	43	47				
Tetradecane	0.44	5.6	30	39				
Methanol	1.82		64	81				
Ethanol	0.88	6.0	30	91				120
Propanol	0.43		38	113				
Isopropanol	0.42	6.2	72	115	80	29	86	192
Isopentanol	0.20		30	48				
n-Hexanol	0.18		42	52				65

The numbering of the quenchers used is (1) p-benzoquinone, (2) 1,4-naphthoquinone, (3) o-dinitrobenzene, (4) p-nitrophenol, (5) p-dinitrobenzene and (6) p-chloranil.

TABLE 3

Constants of fluorescence quenching of pheophytin a by toluquinone in various solvents

Solvent	κ (l mol^{-1})	$k_q\tau_0$ (l mol^{-1})	$\kappa - k_q\tau_0$ (l mol^{-1})
Hexane	80	75	5
Heptane	75	70	5
Nonane	62	40	22
Dodecane	50	35	15
Tetradecane	40	25	15
Benzene	41	50	−9
Toluene	44	45	−1
o-Xylene	38	25	13
Acetone	72	55	17
Isopropanol	160	30	130
Ethanol	62	25	37

TABLE 4

Constants of fluorescence quenching of porphyrins by electron acceptors in various solvents

| Solvent	κ (l mol^{-1})						
	A, 1	B, 3	C		D, 5	E, 5	F, 7
			3	5			
Hexane	107						
Acetone	87						13
Acetonitrile	110						
Methyl ethyl ketone	71	17					11
Heptane	82						
Toluene	41		19	47	6	60	
Benzene	40	11					
Cumene		8					
Dodecane	35						
Tetradecane	36						
Methanol	102				83		
Ethanol	37						
Propanol	44						
Isopropanol	56	25	53	112	56	83	
Water							27

The numbering of the quenchers is as in Table 2. In addition, (7) phthalic anhydride, (A) H$_2$PhC, (B) H$_2$TPhP, (C) ZnTPhP, (D) TPhPGaOH, (E) AlClPhC, (F) dialanylamid-*meso*-porphyrin-IX-methyl-gluconate (DAA).

They cannot account for high κ values (Table 3). Static quenching in alcohols is likely to be due to the formation of at least two types of complexes differing in stability. The formation of A-type complexes is revealed by a change in the absorption spectra. As a rule, A complexes are of low stability (Table 1) and therefore cannot be responsible for the high static quenching constants in alcohols. The abnormally high values of κ in these solvents are accounted for by the formation of the more stable B-type complexes. However, these are not observed spectroscopically.

A and B complexes presumably have different structures. All the data obtained indicate that A complexes are charge transfer complexes. It is possible that in the B complexes the porphyrin and oxidant molecules are far apart, so that their interaction cannot be detected spectroscopically. It is evident that the formation of B complexes involves alcohol molecules or associates. In fact, alcohol molecules can form coordinated bonds with metalloporphyrins [9], as well as hydrogen bonds with non-metal pigments and quenchers. Presumably, such complexes have one of the following structures:

$H{\cdots}[O{-}H]_n{\cdots}O{=}\langle\ \rangle{=}O$

I

$Me{\cdots}[O{-}H]_n{\cdots}O{=}\langle\ \rangle{=}O$
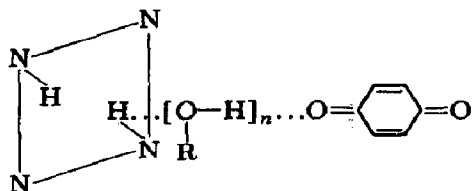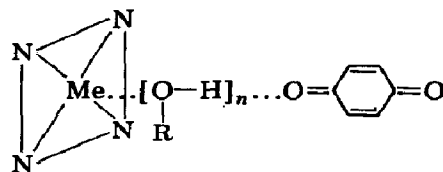
II

Analogous complexes are formed in aqueous solvents. At any rate, the constants of quenching of water-soluble-porphyrin fluorescence by phthalic anhydride in water are higher than those in other classes of solvents (Table 4). The validity of the proposed structures I and II is confirmed by the fact that abnormally high static quenching constants are not observed in the quenching of anthracene, perylene or pyrene (whose molecules are not involved in specific interactions with alcohols) fluorescence by electron acceptors.

3.2. Effect of alcohol deuteration on quenching constants

The constants for the quenching of porphyrin fluorescence by electron acceptors decrease when hydrogen is substituted by deuterium in the hydroxyl moieties of the alcohols and on passing from water to heavy water. The magnitude κ_H/κ_D of the isotope effect may be as high as 3.3 which considerably exceeds the experimental error. Substitution of hydrogen by deuterium at the carbon atom was found to affect negligibly the quenching constants. This follows from the quenching of pheophytin a fluorescence by 1,4-naphthoquinone in completely deuterated methanol and in methanol only containing deuterium in its hydroxyl group (Table 5). The observed isotope effect cannot be accounted for by changes in the fluorescence life-times of the porphyrins. For instance, τ_0 for pheophytin a, on passing from a non-deuterated to a deuterated solvent, does not change by more than a factor of 1.2 (Table 5). The magnitude of κ_H/κ_D is as a rule higher than this. Variations in τ_0 from the deuteration of the alcohols can be attributed to a dye-to-alcohol isotope exchange. In the deuteration of porphyrins it is known that the rates of non-radiative transitions from S_1 states slow down [16].

The deuteration of solvents slightly affects their viscosity [17]. As a consequence, the revealed isotope effects cannot be associated with a change in the rate constant of diffusion and are due only to variations in the static quenching constant, this appearing in expression (5) for κ. This assumption is confirmed by the data for the effect of temperature on κ in both non-deuterated and deuterated alcohols.

3.3. Temperature effects on the constants for quenching of porphyrin fluorescence by electron acceptors

The shape of the plot of κ against temperature is determined by the nature of the medium. A temperature effect on the constants for the

TABLE 5

Constants of fluorescence quenching of porphyrins in alcohols and deuterated alcohols at room temperature

Porphyrin	Quencher	Solvent	τ_0 (ns)	κ (l mol^{-1})	κ_H/κ_D
Pheophytin a	Toluquinone	CH$_3$OH	6.3	115	1.85
		CH$_3$OD	6.1	62	
Pheophytin a	Toluquinone	(CH$_3$)$_2$CHOH	6.3	160	2.42
		(CH$_3$)$_2$CHOD	5.5	66	
Pheophytin a	1,4-Naphthoquinone	CH$_3$OH	6.3	80	2.86
		CH$_3$OD	6.1	28	
Pheophytin a	1,4-Naphthoquinone	CH$_3$OD	6.1	28	0.8
		CD$_3$OD	6.1	35	
Pheophytin a	1,4-Naphthoquinone	(CH$_3$)$_2$CHOH	6.3	120	2
		(CH$_3$)$_2$CHOD	5.5	60	
TPhPGaOH	n-Dinitrobenzene	CH$_3$OH		84	1.55
		CH$_3$OD		54	
ZnTPhP	o-Dinitrobenzene	(CH$_3$)$_2$CHOH		51	2
		(CH$_3$)$_2$CHOD		25	
ZnTPhP	n-Dinitrobenzene	(CH$_3$)$_2$CHOH		99	1.7
		(CH$_3$)$_2$CHOD		56	
DAA	Phthalic anhydride	H$_2$O		27	1.7
		D$_2$O		13	
DAA	Eu(CH$_3$COO)$_3$	H$_2$O		67	3.3
		D$_2$O		20	

quenching of pheophytin a fluorescence by toluquinone in dodecane is described satisfactorily by the Arrhenius equation (Fig. 3) in the studied temperature range of 290 - 357 K. As mentioned above, the fluorescence quenching in a given system is mainly dynamic and its rate is limited by diffusion. According to refs. 9, 18 and 19 the fluorescence lifetimes of tetrapyrrol pigments are not much affected by temperature. Therefore, the effect of temperature on κ is mainly due to the change in the rate of diffusion. As a result, for κ in dodecane the observed activation energy has about the same order of magnitude as that of the solvent viscous flow [20].

A different dependence of κ on temperature was found to exist in isopropanol (Fig. 4). In this case, the effect of temperature on κ is described by a V-shaped curve. Analogous results have been obtained for other alcohols. The curve in Fig. 4 can be interpreted using expression (5) for the fluorescence quenching constant. It is evident that in the high temperature region

$$k_q\tau_0 \gg V \qquad \kappa \approx k_q\tau_0 \qquad (6)$$

This part of the curve obeys the Arrhenius equation. The corresponding energy of activation (13 kJ mol^{-1}) is close to the activation energies of diffusion-controlled processes. The rate constants of quenching decrease
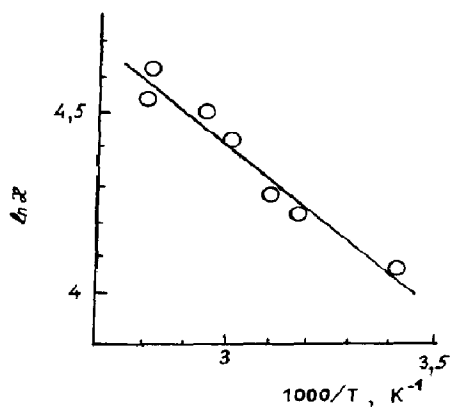
Fig. 3. Plot of the constant of fluorescence quenching of pheophytin a by toluquinone against temperature in dodecane.
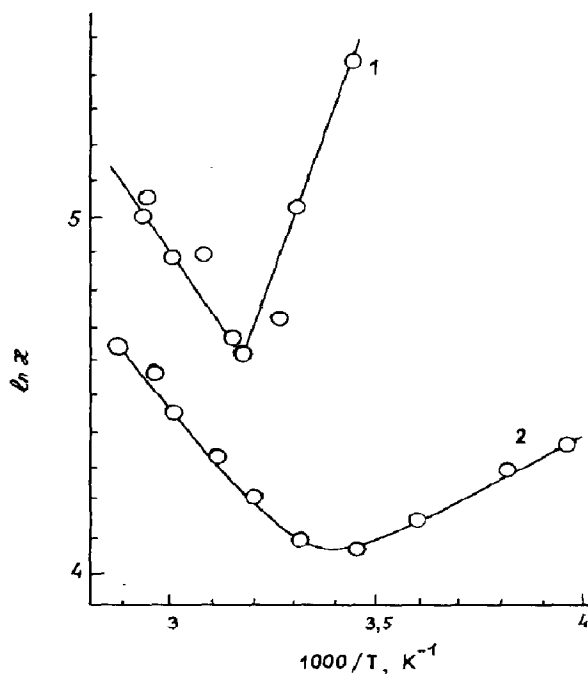
Fig. 4. Plot of the constant of fluorescence quenching of pheophytin a by toluquinone against temperature in $(CH_3)_2CHOH$ (1) and $(CH_3)_2CHOD$ (2).

with a drop in temperature; correspondingly, the stability of complexes I and II increases, these being responsible for the static quenching of porphyrin fluorescence in alcohols. Therefore, in the low temperature region

$$k_q \tau_0 \ll V \qquad \kappa \approx V \tag{7}$$

The slope of this part of the curve is determined by the enthalpies of complexation of molecules in the ground state and the activation energy of electron transfer in the complex. This topic will be considered in detail below.

An analogous V-shaped dependence of κ on temperature was revealed in deuterated isopropanol (Fig. 4). In the high temperature region, the activation energy of quenching for deuterated isopropanol was found to be 10.5 kJ mol^{-1} which is close to that for non-deuterated isopropanol. The small discrepancy in the values of κ observed here (Table 4) can be attributed to differences in the corresponding values of τ_0 (Table 5). Besides, expression (5) is likely to be less valid for non-deuterated isopropanol compared with the deuterated compound because of its larger static quenching constant V.

The alcohol deuteration affects appreciably the slope of the low temperature region (Fig. 4). The observed activation energy in non-deuterated

isopropanol is equal to 26 kJ mol^{-1} and in deuterated isopropanol it is 4.3 kJ mol^{-1}. This suggests that the magnitude of the isotope effect depends on temperature. At low temperatures, κ_H/κ_D can be very large (Fig. 4).

The data obtained for the effect of temperature on κ_H and κ_D confirm the assumption that the isotope effects are associated mainly with the variation in the static quenching constant.

4. Discussion

As mentioned above, the static quenching of porphyrin fluorescence by electron acceptors in alcohols is accounted for by formation of complexes in which the donor and acceptor molecules in the ground state do not appreciably interact. It is reasonable to suggest that such complexes can fluoresce and that their fluorescence spectra will not differ markedly from those for "free" porphyrins. However, the fluorescence quantum yield for these complexes will be much lower as their excitation can initiate electron transfer from donor to acceptor.
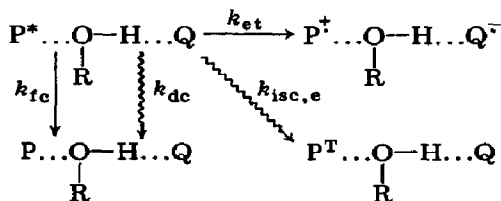
The proposed model allows the experimental data considered above to be analysed. Consider the following kinetics scheme:

$$P + Q \overset{K_p}{\underset{}{\rightleftharpoons}} PQ \tag{I}$$

$$PQ + h\nu \longrightarrow (PQ)^* \tag{II}$$

$$(PQ)^* \overset{k_{fc}}{\longrightarrow} P + Q + h\nu \tag{III}$$

$$(PQ)^* \overset{k_{dc}}{\longrightarrow} PQ \tag{IV}$$

$$(PQ)^* \overset{k_{et}}{\longrightarrow} P^+Q^- \tag{V}$$

$$(PQ)^* \overset{k_{isc}}{\longrightarrow} (PQ)^T \tag{VI}$$

$$P + h\nu \longrightarrow P^* \tag{VII}$$

$$P^* \overset{k_f}{\longrightarrow} P + h\nu \tag{VIII}$$

$$P^* \overset{k_{isc}}{\longrightarrow} P^T \tag{IX}$$

$$P^* + Q \xrightarrow{k_q} P + Q \tag{X}$$

$$P^* \xrightarrow{k_d} P \tag{XI}$$

$$(PQ)^* + Q \xrightarrow{k_{qc}} PQ + Q \tag{XII}$$

where PQ stands for complex I or complex II.

According to this mechanism the fluorescence quenching under steady state conditions is described by the equation

$$\frac{\varphi_0}{\varphi} = (1 + K_p C)(1 + k_q \tau_0 C)\theta \tag{8}$$

where

$$\theta = \frac{1}{1 + K_p C \tau_c / \tau_0} \tag{9}$$

In eqns. (8) and (9), K_p is the constant of formation of either complex I or complex II. The formation of weaker common charge transfer complexes was not taken into account. In addition, $\tau_0 = 1/(k_f + k_d + k_{isc})$ is the lifetime of porphyrin molecules in the absence of the quencher, $\tau_k = 1/(k_{fc} + k_{dc} + k_{isc,c} + k_{et} + k_{qc}[Q])$ is the lifetime of an excited complex and $\tau = 1/(k_f + k_d + k_{isc} + k_q[Q])$ is the lifetime of excited porphyrin molecules in the presence of the quencher. In deriving eqn. (8), it was assumed that the concentration of the porphyrin was much less than that of the quencher and that the extinction coefficients for the porphyrin and the complex are equal in the spectral regions in which the quencher molecules do not absorb light. We also assume that the rate constants of deactivation for porphyrin and complex molecules are similar:

$$k_{fc} \approx k_f \qquad k_{dc} \approx k_d \qquad k_{isc} \approx k_{isc,c} \tag{10}$$

The quenching rate constants k_q and k_{qc} should differ if only because of steric factors brought about by the acceptor molecule complexing with the porphyrin. However, these differences cannot be very high. Therefore, for simplicity, we assume $k_{qc} \approx k_q$. With these simplifications, eqns. (8) and (9) show that the process is essentially dynamic, providing the rate constant of electron transfer is small for both complexes I and II.

The effective constant κ of quenching equals the slope of the plot of φ_0/φ against C at $C = 0$:

$$\frac{d(\varphi_0/\varphi)}{dC}\bigg|_{C=0} = \kappa = K_p\left(1 - \frac{\tau_0^c}{\tau_0}\right) + k_q \tau_0 \tag{11}$$

In eqn. (11) $\tau_0^c = 1/(k_{fc} + k_{dc} + k_{isc,c} + k_{et})$ is the lifetime of the excited complex $(PQ)^*$ in the absence of quenching [18].

It follows from eqns. (3) and (11) that the static quenching constant may be expressed as

$$V = K_p \left(1 - \frac{\tau_0^c}{\tau_0} \right) \tag{12}$$

It is reasonable to expect that the lifetime τ_0^c of the excited complex is shorter than the lifetime τ_0 of the excited porphyrin, and therefore $V < K_p$. Taking into account eqn. (10), the static quenching constant may be written as

$$V \approx K_p \frac{k_{et}}{1/\tau_0 + k_{et}} \tag{13}$$

where $k_{et}/(1/\tau_0 + k_{et})$ may be designated the quantum yield of ion-state formation in the photoexcitation of complex I or complex II.

At low temperatures

$$K_p \frac{k_{et}}{1/\tau_0 + k_{et}} \gg k_q \tau_0$$

The slope E_v of the plot of $\ln \kappa$ against $1/T$ in this temperature region is, in general, variable because $1/\tau_0$ and k_{et} are differently affected by temperature. However, τ_0 is almost constant and at sufficiently low temperatures:

$$k_{et} \ll 1/\tau_0 \qquad V \approx K_p k_{et} \tau_0 \qquad E_v \approx \Delta H_p - E_{et} \tag{14}$$

where ΔH_p is the enthalpy of complexation for the complex PQ and E_{et} is the activation energy of electron transfer in the complex. At higher temperatures, an inverse inequality may hold true:

$$k_{et} \gg 1/\tau_0 \qquad V = K_p \qquad E_v \approx \Delta H_p \tag{15}$$

Again, in the low temperature region, where the quenching constant increases with decreasing temperature, no appreciable bends in the plots of $\ln \kappa$ against $1/T$ were observed. This can be attributed to the fact that our measurements were performed over a narrow temperature range. It is also possible that expression (15) holds for those temperatures at which $k_q \tau_0 \gg V$ and the bend for V is masked by the dependence of k_q on temperature.

The above relationships enable the revealed isotope effects to be analysed. Consider the possible reasons.
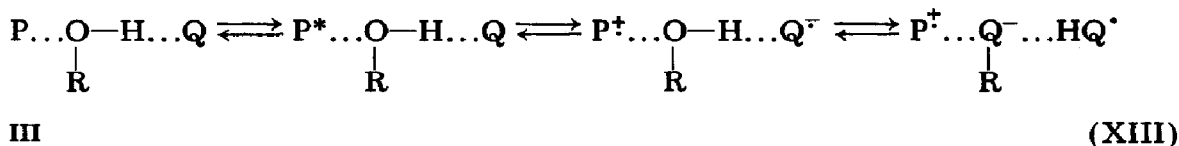
Isotopic substitution may influence the stability of coordinated bonds and hydrogen bonds and therefore the stability of complexes I and II. However, such effects cannot be large. The substitution of hydrogen by deuterium in alcohols is accompanied by an increase in the energy of the hydrogen bond by a relatively small amount (about 0.4 kJ mol^{-1}) [21]. In the systems under study, isotopic substitution was found to decrease the quenching constants and the isotope effects proved to be much higher.

For instance, for isopropanol

$$E_v^H - E_v^D = -21.7 \text{ kJ mol}^{-1}$$

The effect of isotopic substitution on the stability of coordinated bonds between alcohols and the metalloporphyrin is likely to be less than the effect on the stability of the hydrogen bonds. Thus a decrease in the fluorescence quenching constant in the deuteration of an alcohol may be largely due to the variation in the rate constant k_{et} of electron transfer from the excited molecule to the oxidant.

One may assume that k_{et} is the effective constant describing the overall process:

$$\text{P}...\overset{|}{\underset{R}{O}}-H...Q \rightleftharpoons \text{P*}...\overset{|}{\underset{R}{O}}-H...Q \rightleftharpoons \text{P}^{\ddagger}...\overset{|}{\underset{R}{O}}-H...Q^{\top} \rightleftharpoons \overset{+}{\text{P}}...\overset{|}{\underset{R}{Q}}^{-}...HQ^{\bullet}$$

III   (XIII)

Immediately after the electron transfer, a proton or deuteron transfer may occur in complexes I and II. The rate of transfer of the deuteron is less than that of the proton [22]. Therefore, the deuteron transfer is less able to compete with the electron reverse transfer from the radical anion to the radical cation. As a result, a lower fluorescence quenching constant should be obtained. However, such isotope effects cannot have an important bearing on κ. The fact is that the electron transfer in many of the systems under study is an extremely exothermal process. So the change in free energy ΔG_{et} of electron transfer between excited pheophytin a and toluquinone is about 55 kJ mol^{-1}. These calculations were carried out using the corresponding electrochemical potentials and energies of singlet-excited-state pheophytin a [5] by employing the standard equation [23]. Therefore, in scheme (XIII) the second stage is irreversible. Besides, the solvent isotope effect was also observed in the quenching by a europium salt (Table 4), i.e. in a system for which scheme (XIII) is hardly fully applicable.

The effect of the solvent isotope composition on κ seems to be due mainly to the variation in the rate of formation of the primary radical ion pair III. A number of publications [24 - 27] deal with solvent isotope effects in outer-sphere electron transfer processes.

The influence of isotopic substitution on the rate of electron transfer is a quantum effect [28]. It results from a change in the Frank−Condon factors on deuteration of the molecules of the first coordination sphere [29, 30]. It follows from eqn. (12) that such an isotope effect should be observed when $k_{et} \geqslant 1/\tau_0$. For porphyrins $\tau_0 \leqslant 10^{-8}$ s (Tables 2 and 5; see also refs. 9, 18 and 19). Therefore, k_{et} should be of the order of 10^9 s^{-1}. According to the simplest model of electron tunnelling transfer, k_{et} diminishes on increasing the donor-to-acceptor distance R [31]:

$$k_{et} = \nu \exp(-2R/L) \tag{16}$$

For atomic and molecular systems, ν cannot much exceed 10^{15} s^{-1} [32]. According to eqn. (16) the rate of electron transfer depends on the decay factor L which is determined by the overlap between the wavefunction "tails" of the electron donor and the electron acceptor. For a series of molecules L has been found to be 1.5 ± 0.1 Å [32]. The calculations performed using eqn. (16) indicate that when $k_{et} \approx 10^{9}$ s^{-1} the donor and acceptor must be about 10 Å apart. These results lead to the conclusion that in complexes I and II the reactant molecules are bound by alcohol dimers.

Acknowledgments

References

1 I. I. Dilung and I. N. Chernik, *Zh. Fiz. Khim.*, *37* (5) (1963) 1100.
2 S. L. Bondarev and G. P. Gurinovich, *Opt. Spektrosk.*, *26* (4) (1974) 687.
3 P. J. McCartin, *J. Am. Chem. Soc.*, *85* (1963) 2021.
4 G. R. Seely, *J. Phys. Chem.*, *73* (1969) 125.
5 G. R. Seely, *Photochem. Photobiol.*, *27* (1978) 639.
6 M. Crouterman and D. Holten, *Photochem. Photobiol.*, *25* (1977) 85.
7 A. K. Chibisov, *Usp. Khim.*, *50* (7) (1981) 1169.
8 E. I. Kapinus, I. Yu. Kucherov and I. I. Dilung, *Teor. Eksp. Khim.*, *18* (5) (1982) 572.
9 G. P. Gurinovich, A. N. Sevchenko and K. N. Solovev, *Spectroscopy of Chlorophyll and Related Compounds*, Nauka i Teknika, Minsk, 1968.
10 A. Treibs and N. Höberle, *Lieb. Ann. Chem.*, *713* (1968) 183.
11 J. W. Buchler, G. Eikelman, L. Puppe and K. Ruhbook, *Lieb. Ann. Chem.*, *745* (1971) 135.
12 S. A. Mikhalenko, S. V. Barkanov, O. L. Lebedev and E. A. Lukyanets, *Zh. Obshch. Khim.*, *41* (12) (1971) 2736.
13 S. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.
14 E. N. Guryanova, I. P. Goldstein and I. P. Romm, *Donor–Acceptor Bonds*, Khimiya, Moscow, 1973.
15 W. R. Ware and J. S. Novros, *J. Phys. Chem.*, *70* (1966) 3246.
16 A. G. Gradishko and V. N. Knyuksto, *Opt. Spektrosk.*, *44* (1978) 458.
17 I. B. Rabinovich, *Isotope Effect on Physico-Chemical Properties of Liquids*, Nauka, Moscow, 1968.
18 A. N. Terenin, in *Photosynthesis Problems*, Isd. A.N. S.S.S.R., Moscow, 1958.
19 B. M. Dzhagarov and G. P. Gurinovich, *Opt. Spektrosk.*, *30* (1971) 425.
20 A. Weissberger, E. Proskauer, J. A. Riddik and E. E. Toops, *Organic Solvents*, Wiley-Interscience, New York, 1955.
21 M. P. Shakhparonov, *Introduction to Modern Theory of Solutions*, Vysshaya Shkola, Moscow, 1978.
22 L. Melander and W. H. Saunders, *Reaction Rates of Isotopic Molecules*, Wiley, New York, 1980.
23 D. Pehm and A. Weller, *Ber. Bunsenges Phys. Chem.*, *73* (1969) 834.

24 J. Hudis and R. W. Dodson, *J. Am. Chem. Soc.*, *78* (1956) 911.
25 A. M. Zwickel and H. Taube, *Discuss. Faraday Soc.*, *78* (1956) 911.
26 M. M. Itzkovitz and F. R. Nordmeyer, *Inorg. Chem.*, *14* (1975) 2124.
27 W. J. Weaver and T. T. Li, *J. Phys. Chem.*, *87* (1983) 1153.
28 E. Buhks, J. Jortner and G. Navon, *J. Phys. Chem.*, *85* (1981) 3759.
29 E. Buhks, J. Jortner and G. Navon, *J. Phys. Chem.*, *85* (1981) 3763.
30 J. Ulstrup and J. Jortner, *J. Chem. Phys.*, *63* (1975) 4358.
31 S. Strauch, G. McLendon and T. McCuire, *J. Phys. Chem.*, *87* (1983) 3579.
32 E. G. Petrov, *Charge Transfer Physics in Biosystems*, Naukova Dumka, Kiev, 1984.