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OXYGEN QUENCHING OF PHENANTHRENE FLUORESCENCE AND PHOSPHORESCENCE IN LOW TEMPERATURE ALCOHOL GLASSES

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Stationary and pulse methods are applied to study static quenching of phenanthrene phosphorescence and fluorescence by oxygen in glassy alcohol matrices. A procedure is proposed to obtain the parameters of exchange quenching of luminescence from experimental data. The quenching of phenanthrene phosphorescence by oxygen is shown to follow an exchange mechanism with the rate constant $k(r) = 2 \times 10^7 \exp[-2(r - 6.5)/0.55]$ s^{-1}, where r is the phenanthrene–oxygen distance. The data obtained are used to estimate the value of phenanthrene triplet excited state dynamic quenching in non-viscous liquids to be 7×10^9 M^{-1}s^{-1}, which is in keeping with the literature value of the quenching constant in benzene. The static fluorescence quenching data for phenanthrene cannot be described within a single mechanism. Some hypotheses are proposed to account for the static fluorescence quenching.

1. Introduction

Oxygen is known to be an efficient quencher of the phosphorescence and fluorescence of organic molecules in liquids and gases. The quenching of triplet states is conventionally assumed to follow the energy transfer mechanism, singlet oxygen being produced [1,2]. However, recently evidence has been obtained [3,4] that the singlet oxygen yield per quenched triplet molecule differs essentially from unity, and also that charge transfer states are important in the deactivation of high $(E_T > 16000$ cm$^{-1})$ triplet states.

Usually, oxygen quenching of excited singlet states results in the generation of excited triplet molecules [1]. So far the luminescence quenching of organic compounds has been investigated mainly in liquid solutions where the process is diffusion-controlled. The singlet excited state quenching rate constants approach the diffusion-controlled ones, whilst the triplet state quenching rate constants are 0.1–0.01 of those [1].

Information on the quenching mechanism and the dependence of the quenching rate constants on the donor–acceptor separation may be obtained from quenching studies in a solid matrix without diffusion. There are two investigations [5,6] on the static quenching of phosphorescence of naphthalene and deuteronaphthalene by O_2 and by NO in 3-methylpentane glasses. It has been concluded [5,6] that the static quenching of naphthalene phosphorescence by O_2 and NO results from intersystem crossing enhancement, the energy transfer mechanism being not essential. Note that the results and conclusions reported [5] have been seriously criticized [7] and then revised [6] in an effort to remove shortcomings. The aim of the present investigation is:

(1) to study the influence of oxygen not only on the triplet state of the donor, but on its singlet state as well;

(2) to extend the oxygen pressure range up to 100 atm;

(3) to analyze the luminescence decay kinetics by more precise equations allowing for the forbidden volume;

(4) to check the recent methods of processing of quenching kinetic data for solid solutions;

(5) to compare the data obtained with those on quenching in liquid solutions.

2. Experimental

Phenanthrene was purified by double sublimation in vacuum. Anthracene impurity detected by absorption spectra was less than 0.1%. Ethanol was boiled with NaOH and distilled [8].

The luminescence spectra were recorded using a setup consisting of a high-pressure DRSh-500 Hg lamp, high-radiance monochromator, a sample chamber, a prismatic scanning monochromator, a photomultiplier, an ENDIM X–Y recorder. Phenanthrene luminescence was excited by the 313 nm Hg line.

The phosphorescence decay kinetics were detected under pulse excitation by a nitrogen laser LGI-21 ($\lambda = 337$ nm, $\Delta t = 15$ ns). The required phosphorescence spectral region was selected with an interference filter with $\lambda = 500$ nm ($\Delta\lambda = 7$ nm). Kinetic curves were detected with a photomultiplier and a NOKIA LP 4840 multichannel analyzer.

The samples were inside a quartz cryostat with optical windows, in liquid N_2 or O_2 whose temperature was reduced by pumping. In this way it was possible to vary the temperature within 64–90.3 K. The fluorescence decay kinetic curves were detected and processed by a spectrofluorometer from Photochemical Research Associates (PRA). Samples were excited by H_2 pulse lamp filtered light ($\Delta t = 2$ ns, $\lambda = 270$ nm), the kinetic curve being recorded at a maximum of the phenanthrene fluorescence spectrum ($\lambda = 365$ nm). Fluorescence mean lifetimes were computed by a standard program from PRA. Deconvolution of kinetic data in this program is carried out with the excitation pulse shape taken into account.

The phenanthrene concentration was 10^{-3} to 10^{-2} M. Studies of the luminescence quenching in solids required high acceptor concentrations (0.1–1 M). A technique of saturating a sample with O_2 at high pressures was developed to obtain high O_2 concentrations. High pressures (up to 100 atm) were achieved by freezing a certain amount of O_2 gas into a cylindric ampoule (2–3 mm inner diameter, 1-mm-thick walls, about 1 ml volume) using a vacuum system. The ampoules were sealed, shaken repeatedly, and re-frozen until an equilibrium concentration of the dissolved O_2 was attained, which was checked by the stationary luminescence intensity of the frozen samples.

That Henry's law was obeyed was verified at O_2 pressures of 0 to 100 atm. For that purpose the samples were O_2-saturated at a definite pressure, then frozen in liquid N_2, connected to a vacuum system and pumped out. Thereafter the solution was unfrozen slowly, and the pressure of released O_2 was measured with an oil gauge.

3. Analysis of experimental data on exchange quenching

3.1. Acceptors with strong quenching effects

Usually, the rate constant of the excited state quenching by exchange mechanism is written [1] as

$$k(r) = P \exp[-2(r - R)/L], \tag{1}$$

where P is the quenching rate constant at a donor–acceptor contact, L is the decay parameter of the wave functions of the acceptor and the donor, R is the minimum distance of approach of the particles (forbidden volume radius), r is the distance between donor and acceptor molecules. The donor has its own lifetime, which is τ_0 in the absence of an acceptor. If $P\tau_0 \gg 1$, the acceptor is called strong; if $P\tau_0 \ll 1$ it is weak.

The luminescence decay kinetics obey the equation [9]

$$I(u) = I_0 \exp[-u - CH(u)], \tag{2}$$

where $u = t/\tau_0$, C is the acceptor concentration.

$$H(u) = 4\pi \int_R^\infty \{1 - \exp[-u\tau_0 K(r)]\} r^2 \, dr. \tag{3}$$

The integral in eq. (3) cannot be evaluated explicitly and, therefore, the kinetic dependences are analyzed with approximate expressions for $H(u)$. For $\rho u \leqslant 0.5$ (where $\rho = P\tau_0$) [9]

$$H(u) \simeq (\pi L^3/2)\rho(\beta^2 + 2\beta + 2)u. \tag{4}$$

If $\rho u \gg 1$, then

$$H(u) = (\pi L^3/6)\Big[(\beta + C_E + \ln \rho u)^3$$
$$+ \pi^2/2(\beta + C_E + \ln \rho u) - \psi''(1) - \beta^3\Big],$$
$$(5)$$

$$\beta = 2R/L, \qquad C_E = 0.5772,$$

$$\psi''(1) = -2.4041.$$

By analysis of the luminescence decay curves, the parameters P and L may be chosen to fit the whole set of experimental data.

Note that in the case of weak acceptors the condition $\rho u < 0.5$ holds over a wide time range and thus the kinetic curves are exponential, the rate constant being

$$K = \tau_0^{-1} + C(\pi L^3/2)(\beta^2 + 2\beta + 2)P. \qquad (6)$$

In the case of strong quenchers, the condition $\rho u \gg 1$ holds over a wide time range, and $H(u)$ may be calculated by eq. (5).

The P and L parameters are often determined by the method of kinetic curve moments [10]. For that purpose two moments are sufficient. The zeroth moment is the relative luminescence yield, η/η_0, where η_0 is the yield in the absence of quenchers; the first moment is the relative mean luminescence lifetime, τ/τ_0.

Let us see how to distinguish between strong and weak quenching by studying the changes in the moments with acceptor concentration. In the first approximation this can be expressed only with C-linear terms [9,11]:

$$\ln(\eta/\eta_0) \simeq -\alpha_\eta C, \qquad (7a)$$

$$\tau/\tau_0 \simeq 1 - \alpha_\tau C. \qquad (7b)$$

Let us consider the intermediate case of $\rho = 1$. The coefficients α_η and α_τ in this case are [9,11]

$$\alpha_\eta^0 = V\big[(3 \ln 2)/\beta + \pi^2/(2\beta^2) + 5.4092/\beta^3\big],$$

$$\alpha_\tau^0 = V\big[3/(2\beta) + (6 \ln 2)/\beta^2 + \pi^2/(2\beta^3)\big], \quad (8)$$

where $V = \frac{4}{3}\pi R^3$ is a forbidden volume. If the coefficients α_η and α_τ obey the conditions

$$\alpha_\eta > \alpha_\eta^0, \qquad \alpha_\tau > \alpha_\tau^0, \qquad (9)$$

the quenching is strong.

3.2. Errors in α_η and α_τ calculations by approximate formulae in exchange quenching

In the case of strong quenching, the quantities α_η and α_τ are [9,11]

$$\alpha_\eta = V(\gamma/\beta)^3 K_\eta, \qquad \alpha_\tau = V(\gamma/\beta)^3 K_\tau, \qquad (10)$$

where

$$\gamma = \ln \rho + \beta,$$

$$K_\eta = \Big\{\gamma^3 - \beta^3 + \pi^2\gamma + 3\beta^2 \ln[(1+\rho)/\rho]$$

$$+ 6\beta \sum_{n=1}^{\infty} \big[(-1)^n/(n^2\rho^n)\big]$$

$$+ 6 \sum_{n=1}^{\infty} \big[(-1)^{n+1}/(n^3\rho^n)\big]\Big\}/\gamma^3, \qquad (11)$$

$$K_\tau = 3\Big\{\gamma^2 + \pi^2/3 - \beta^2/(1+\rho)$$

$$+ 2\beta \ln[(1+\rho)/\rho]$$

$$+ 2 \sum_{n=1}^{\infty} \big[(-1)^n/(n^2\rho^n)\big]\Big\}/\gamma^3.$$

It has been shown [11] that α_η and α_τ can be calculated by the approximate formulae

$$\alpha_\eta' = \frac{4}{3}\pi(R_0^3 - R^3), \qquad (12a)$$

$$\alpha_\tau' = 2\pi L R_0^2, \qquad (12b)$$

where

$$R_0 = R + (L/2) \ln \rho.$$

The radius R_0 characterizes the distance at which the excited donor concentration is half of that observed for an infinite distance from the acceptors.

The errors in α_η and α_τ calculations by the approximate formulae can be estimated as follows:

$$\delta\alpha_\eta = \alpha_\eta - \alpha_\eta', \qquad \delta\alpha_\tau = \alpha_\tau - \alpha_\tau'. \qquad (13)$$

Equations (13) yield the relative error

$$\delta\alpha_\eta/\alpha_\eta = 1 - \big[1 - (\gamma/\beta)^3\big]/K_\eta,$$

$$\delta\alpha_\tau/\alpha_\tau = 1 - 3/(\gamma K_\tau). \qquad (14)$$

It has been shown [11] that for strong acceptors

the quantity α_r equals approximately the coefficient α_δ, which determines the rate of change in the slope of the luminescence decay curve with the acceptor concentration at $u = 1$. The kinetic curve is plotted in the coordinates $\ln I$ vs u. The quantity α_δ is

$$\alpha_\delta = \left[3(\gamma + C_E)^2 + \pi^2/2 \right] V/\beta^3. \tag{15}$$

The error in α_r calculation by eq. (15) is determined from

$$\delta\alpha_r/\alpha_r = 1 - \alpha_\delta/\alpha_r. \tag{16}$$

If β is within 5–20, then for $\ln \rho \geqq 5$ the errors in α_η and α_r calculations by the approximate formulae do not exceed 10%, which is within the experimental error.

4. Experimental results

4.1. Luminescence data

Phenanthrene is suitable for luminescence quenching investigations, since it gives sufficiently high and comparable quantum yield of fluorescence ($\phi_{fl} = 0.14$) and phosphorescence ($\phi_{ph} = 0.11$) [8]. The quantum yield of triplet states for phenanthrene is rather high, 0.8 [7]. That is why the quenching of excited singlet states by O_2 cannot significantly increase the triplet states yield. The energy gap between the excited singlet and triplet states of phenanthrene is 7300 cm^{-1} [7], i.e., lower than the singlet ($^1\Delta_g$) O_2 level energy, 7918.1 cm^{-1} [12]. Consequently, $^1O_2$ formation as a result of fluorescence quenching is scarcely probable. According to [7,8] at 77 K the phenanthrene fluorescence time in EPA is $\tau_{fl}^0 = 71$ ns, and the phosphorescence time is $\tau_{ph}^0 = 4.3$ s. The times measured in this investigation are $\tau_{fl}^0 = 66 \pm 2$ ns, $\tau_{ph}^0 = 3.9 \pm 0.1$ s in ethanol at 77 K, which agree fairly well with the literature data. The luminescence spectrum (fig. 1) coincides with that published [8].

Figure 1 shows phenanthrene luminescence spectra for various concentrations of dissolved O_2 (0–1.1 M). The bands within $(30-25) \times 10^3$ cm^{-1} belong to phenanthrene fluorescence; those within $(22-15) \times 10^3$ cm^{-1}, to phenanthrene phosphores-
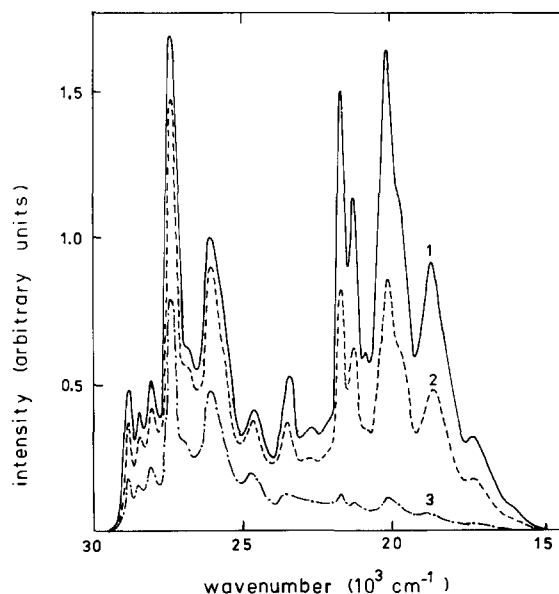

Fig. 1. Luminescence spectra of phenanthrene in ethanol at 77 K for various concentrations of dissolved O_2: (1) 0 M; (2) 0.21 M; (3) 1.1 M.

cence. The spectra overlap at $(25-22) \times 10^3$ cm^{-1}. Besides, there is also a contribution from anthracene impurity fluorescence in the spectral region $(25-22) \times 10^3$ cm^{-1}. The relative fluorescence and phosphorescence quantum yields and kinetic curves were measured in the maxima of phenanthrene fluorescence and phosphorescence spectra (365 and 500 nm, respectively) where the anthracene contribution should be negligible. Figure 1 shows that quantum yields of both phosphorescence and fluorescence decrease with increasing concentration of dissolved O_2, the phosphorescence yield falling more sharply. The decrease in the fluorescence quantum yield could be detected due to a much wider range of O_2 concentrations compared to that previously used [5,6].

4.2. Oxygen solubility

The data on O_2 solubility in ethanol (96.4%) and methanol are available up to 1 atm [13]. Therefore we verified that, within the pressure range of 1 to 80 atm, Henry's law holds with

$S = 0.19 \pm 0.01$ cm^3/cm^3 for ethanol and $S = 0.23$ ± 0.02 cm^3/cm^3 for methanol (97%).

4.3. Fluorescence quenching

The analysis of data on stationary quenching of phenanthrene fluorescence by eqs. (7a) and (12a) (fig. 2) yields the characteristic radius of 8.7 ± 0.5 Å if the forbidden volume ($R = 6.5$ Å) is taken into account. However, the fluorescence decay kinetic curves are practically exponential within the experimentally detected time range ($t = 1$–200 ns), a non-negligible non-exponentiality is observed only at 0.74 M O$_2$. A rise in O$_2$ concentration leads to a slight reduction of the fluorescence lifetime (fig. 3). Note that the lifetime τ has been calculated assuming the exponentiality of the fluorescence decay kinetic curves. Since, actually, weak non-exponentiality of the kinetic curves is detected (fig. 4, curve 4), we have studied the dependence of $\partial \ln I(u)/\partial u |_{u=1}$ on O$_2$ concentration. The tangent (α_δ) of the slope of this dependence must be identical to α_τ (section 3.2). In fact, α_τ and α_δ are the same within experimental error. Under the assumption that a change in the stationary quantum yield and the reduction of the lifetime result from the same process, we obtain $L = 0.70 \pm 0.05$ Å from eq. (12b). However, if calculated with this parameter by eq. (5), the fluorescence decay curves are substantially non-exponential over the experi-
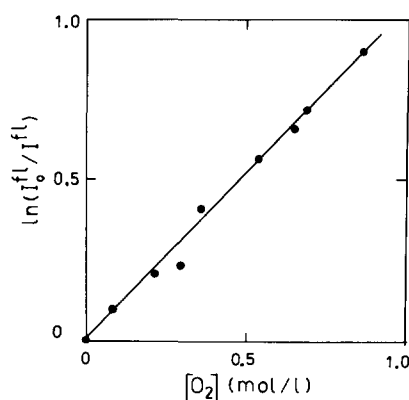
mentally detected time range (fig. 4). Note, that fig. 4 is of a qualitative illustrative character. A short (< 1 ns) non-exponential part of the theoretical curve can be obtained at $L < 0.3$ Å. In this case, however, the decrease in the mean lifetime is much less (at least by a factor of 2.5) than that
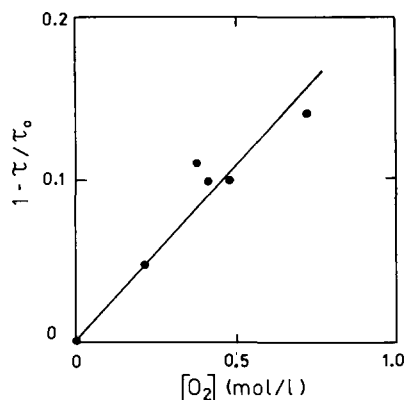
Fig. 3. Plots of phenanthrene fluorescence lifetime vs. O$_2$ concentration in ethanol at 77 K.

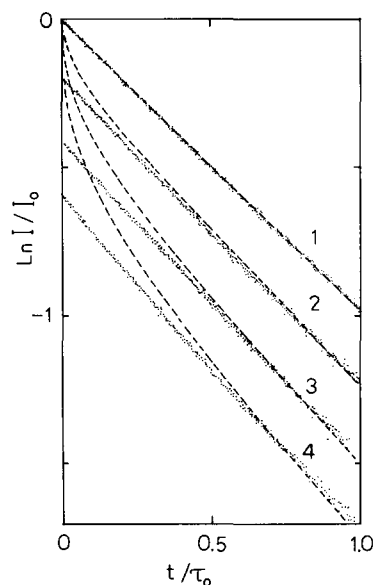Fig. 2. Plots of phenanthrene fluorescence quantum yield vs. O$_2$ concentration in ethanol at 77 K.

Fig. 4. Experimental (dots) and calculated kinetic curves of phenanthrene fluorescence decay. Calculation parameters: $L = 0.7$ Å and $P = 8.6 \times 10^9$ s^{-1}; (1) 0 M O$_2$, (2) 0.21 M O$_2$, (3) 0.48 M O$_2$, (4) 0.73 M O$_2$.

observed experimentally (fig. 3). Note that the results obtained are independent of phenanthrene concentration in the range 10^{-3}–10^{-2} M. The results cannot be described in terms of a single mechanism. Most likely, in close phenanthrene–O_2 pairs with $r < 8.7$ Å, the quenching occurs at times shorter than 2 ns, and thus we cannot detect the kinetics of this process.

The situation observed can be explained as follows. It has been proposed [2,3,14] that charge-transfer (CT) states might participate in the luminescence quenching by oxygen. The CT state energy depends on the separation distance in a pair. It is possible that for a contact of phenanthrene with O_2 the CT state has a lower energy than the singlet excited state (^1S); as the distance increases up to 8.7 Å, the energies become equal. As long as the ^1S state has a higher energy than the CT state, it can convert efficiently into the excited ^3T state via the CT states $^{1,3}D^+ \ldots O_2^-$. The CT energy is calculated by the formula

$$E_{CT} = E_{D/D^+} - E_{O_2^-/O_2} - C + E_{reorg}$$

$$= E_{CT}^0 + E_{reorg}.$$

In contrast to Smith [3], the medium reorganization energy term E_{reorg} must be added to the formula to E_{CT}, since in a frozen solution we deal with an unrelaxed state. E_{reorg} is calculated by the Marcus formula [15]

$$E_{reorg} = e^2/2(1/R_D + 1/R_A - 2/r)$$

$$\times (1/D_{op} - 1/D_{st}) \text{ eV},$$

where R_D and R_A are the radii of a donor and an acceptor molecule, respectively; r is the distance between their centres; D_{op} and D_{st} are the optical and the static dielectric constants, respectively.

For calculations let $R_D = 4.5$ Å, $R_A = 2$ Å, $D_{op} = n^2 = 1.85$, $D_{st} = 27$. In this case $E_{reorg} = 2.61 - 7.24/r$ eV. These calculations must be regarded only as a coarse estimate because the parameters for the liquid phase are employed.

It has been stated before [16] that the Marcus formula somewhat overestimates E_{reorg}. More reliable data are obtained if E_{reorg} is assumed to be about · 25% lower than that calculated by the Marcus formula. The value of E_{CT}^0 is 2.31 eV [3].
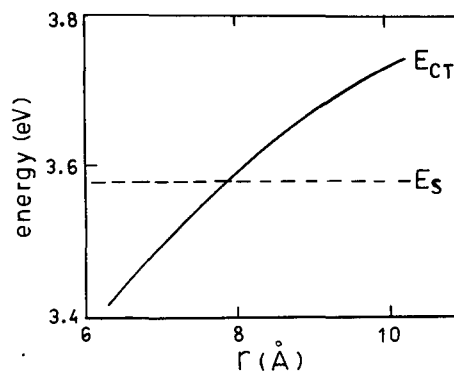

Fig. 5. Plots of the energy of a charge-transfer complex (E_{CT}) vs. the separation distance in phenanthrene$^+$–O_2^- pairs. E_s is the lowest excited singlet energy of phenanthrene.

Figure 5 shows E_{CT} vs. r calculated in this way. As seen, if $r \sim 8$ Å, E_{CT} is comparable with the singlet excited state energy (3.58 eV [7]). Thus the fluorescence quenching model proposed proves to be consistent with the experimental data.

An alternative interpretation of phenathrene fluorescence quenching is given below. If the donor–acceptor separation distance exceeds the sum of the forbidden radius and the H atom diameter, $r \geqslant R + 2R_H \simeq 9$ Å, a solvent molecule can partly (at least one of its atoms) be inserted between the donor and acceptor molecules. Thus, if $r < 9$ Å the wave functions of donors and acceptors can overlap only directly, whilst if $r > 9$ Å the interaction can be transferred indirectly through the solvent molecules. This interaction seems to be less efficient and to result only in a slight decrease of the fluorescence lifetime (fig. 3). The available experimental data do not allow one to choose between the two hypotheses.

4.4. Phosphorescence quenching

Dynamic quenching due to molecular oxygen diffusion can contribute to phosphorescence quenching even at 77 K. Figure 6 shows the intensity of phenanthrene phosphorescence dependence on temperature ($T = 63$–90.3 K) in ethanol solution at various O_2 concentrations. The intensity is seen to reach its stationary value in ethanol (96.4%) matrix at $T = 68$ K. This was the reason
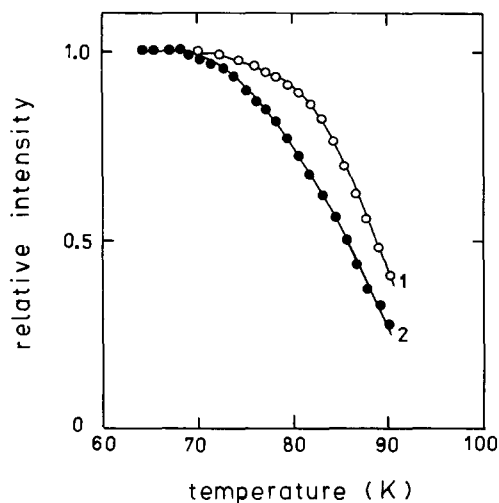
Fig. 6. Temperature dependences of the phenanthrene phosphorescence intensity in ethanol in the presence of O_2: (1) 0.21 M; (2) 0.7 M.

for obtaining all the experimental results on phenanthrene phosphorescence quenching with O_2 in ethanol only at 64 K. In methanol (97%) matrix dynamic quenching has already ceased at 77 K.

Figure 7 shows phosphorescence stationary quenching data for phenanthrene according to formula (7a). The tangent of the slope gives $\alpha_\eta =$
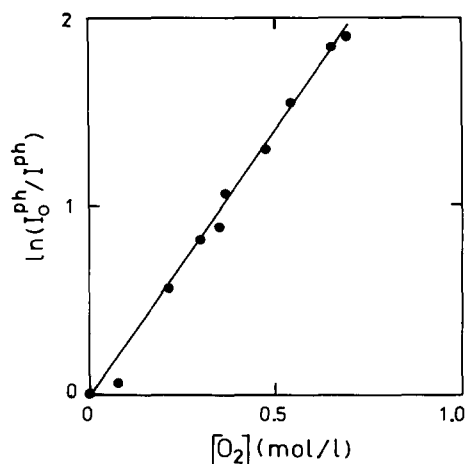
5250 ± 300 Å^3. Figure 8 shows the dependence of the phenanthrene phosphorescence mean lifetime on the dissolved O_2 concentration (7b). It has been calculated that $\alpha_\tau = 460 \pm 50$ Å^3. The forbidden volume is about 1000 Å^3. The values of R_0 and L calculated by eqs. (12) were found to be 11.5 ± 0.5 and 0.55 ± 0.05 Å, respectively. As seen from figs. 9 and 10 theoretical curves fairly well agree with the experimental data over a wide time range, from 10^{-2} to 10 s.

Thus the analysis of the scope of data on phenanthrene phosphorescence quenching with O_2 has demonstrated that quenching is by the exchange mechanism, the rate constant depending on the separation distance in a phenanthrene–O_2 pair as follows:

$$k(r) = 2 \times 10^7 \, \exp\left[-2(r - 6.5)/0.55\right] \, \text{s}^{-1}.$$

With knowledge of the static quenching parameters one can estimate the dynamic quenching rate constant anticipated in non-viscous liquids. Under very fast diffusion ($D \to \infty$) the extreme value of the quenching rate constant is determined by the expression [17]

$$k = \left(\pi L^3/2\right) P \left(2\beta + \beta^2 + 2\right).$$

It should be pointed out, however, that the value

Fig. 7. Plots of phenanthrene phosphorescence quantum yield vs. O_2 concentration in methanol at 77 K.
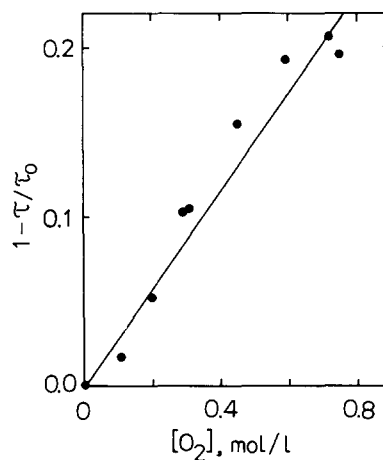

Fig. 8. The relative mean phosphorescence lifetime of phenanthrene as a function of O_2 concentration in methanol at 77 K.
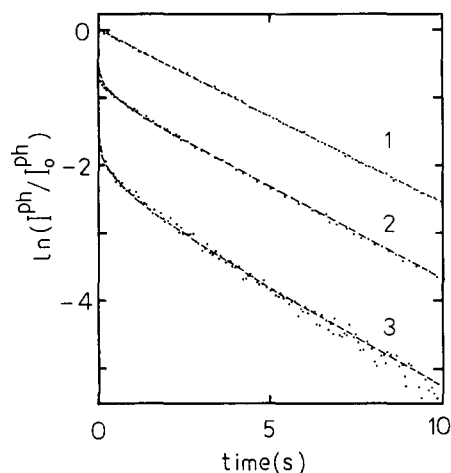
Fig. 9. Experimental (dots) and theoretical (for $L = 0.55$ Å, $P = 2 \times 10^7$ s^{-1}) kinetic curves of phenanthrene phosphorescence decay in methanol at 77 K for various O_2 concentrations: (1) 0 M; (2) 0.31 M; (3) 0.75 M.

of minimum approach distance may be chosen rather arbitrarily since molecules are, naturally, not spherically symmetric. The value of $R = 6.5$ Å is the average with respect to various relative orientations of phenanthrene and O_2 molecules. Under favorable approach of donor and acceptor molecules the R value does not exceed 4 Å. Within
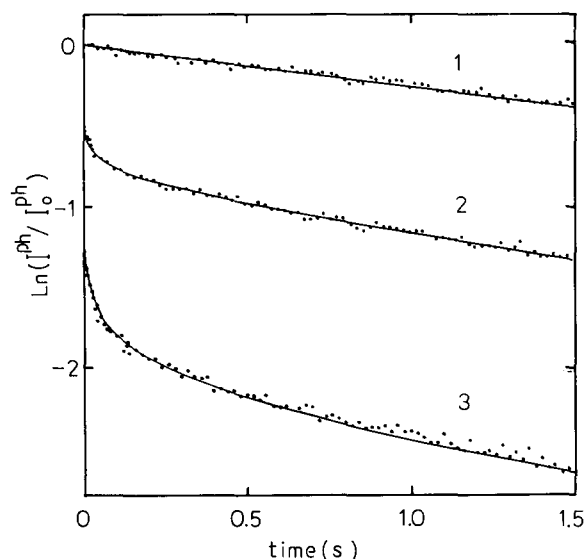

Fig. 10. Same as fig. 9.

$R = 4$ Å the constant value at contact is $P = 2 \times 10^{11}$ s^{-1}. Using this value of P one can obtain the extreme value of the dynamic quenching constant $k = 7 \times 10^9$ M^{-1} s^{-1}. The experimental value of the rate constant of phenanthrene phosphorescence quenching with O_2 measured in benzene at room temperature equals 1.33×10^9 M^{-1} s^{-1} [2].

Thus, the rate constant calculated from the experimental data on static quenching under random distribution of pairs both with respect to distance and mutual orientation is in a satisfactory agreement with the liquid phase data.

In general, two circumstances should be considered in the analysis of phosphorescence static quenching results, when the phosphorescing triplet state originates from an excited singlet one:

(i) the triplet states yield may increase in the presence of O_2;

(ii) O_2 may enhance the radiative $T_1 \rightarrow S_0$ transition intensity.

In our case point (i) cannot be of great importance, on the one hand, because of rather a high quantum yield of the triplet states (~ 0.8), and on the other hand, because the effective radius of singlet quenching (8.7 Å) is substantially less than that of triplet quenching (11.5 Å). Note that the maximum enhancement of the triplet states yield attainable at O_2 concentrations $\leqslant 0.75$ M amounts only 10%. Our experimental attempts to observe the initial growth of the phosphorescence intensity proved to be unsuccessful.

The phenomenon of the acceptor-induced radiative transitions enhancement (ii) is well-known from experimental data [18]; theoretical description of its influence upon quenching processes in rigid media is also developed [19,20]. The radiative transition enhancement may be described by the rate constant, k_r, depending on the distance between donor and an acceptor molecule according to [14]:

$$k_r = k_{r0} + P_r \exp[-2(r - R)/L],$$

where k_{r0} is the rate constant of the radiative process without acceptor, P_r is the rate constant of the acceptor-induced radiative process at a donor–acceptor contact. It follows from [14] that this process is essential when parameter $K = (P_r/k_{r0})/[\tau_0(P + P_r)] \geq 1$. There are data that the

absorption coefficient of the O_2-induced $T_1 \leftarrow S_0$ transition can be about 1 M^{-1} cm^{-1} (0.4 M^{-1} cm^{-1} for benzene [18]). Using the approximate relation $k_r \approx 10^4 \epsilon$ s^{-1} [21], one finds $k_r \approx 10^4$ s^{-1}. From the phosphorescence quantum yield data and the mean lifetime for phenanthrene it may be calculated that $k_{r0} \approx 0.025$ s^{-1}. Using these estimates and our P value, one obtains $K \approx 5 \times 10^{-3}$. Thus, in our conditions the rôle of O_2-induced triplet–singlet radiative transitions is negligible.

According to [19] the radiative $T_1 \rightarrow S_0$ transitions enhancement influences the moments of kinetics curves. For example, the ratio of the first to the second moment is less than 0.5 in this case [19]. Processing of the available experimental data shows that this ratio in our case is 0.52 ± 0.05 and implies a negligible contribution from O_2-induced $T_1 \rightarrow S_0$ transitions.

5. Conclusion

Studies on the static quenching of phenanthrene luminescence by O_2 have proved the applicability of the elsewhere [11] proposed approximate relations to obtain quenching parameters from experimental data with the forbidden volume taken into account.

It has been mentioned above that the quenching of organic molecule phosphorescence in glassy matrices by O_2 had been studied previously only by Siegel and co-workers [5,6]. R_0 and L values found by them for naphthalene phosphorescence quenching differ profoundly from those obtained for phenanthrene in this investigation: they find $R_0 = 10.1$ Å, $L = 1.3$ Å for naphthalene-h_8, and $R_0 = 9.8$ Å, $L = 1.3$ Å for naphthalene-d_8. Using these parameters one can estimate the values of the quenching rate constant at contact ($R = 4$ Å) which is $P \approx 5 \times 10^3$ s^{-1} for naphthalene and $P \approx 1 \times 10^2$ s^{-1} for deuteronaphthalene. It is seen that P values are too low to explain the high value of the quenching rate constant observed in the liquid [1]. The use of the parameters found in this investigation for static quenching of phenanthrene by O_2 allows one to explain the liquid phase quenching by the static mechanism only, without any additional assumptions.

The main difference of our results from the earlier data [5,6] is due to various L parameters (eq. (1)). It should be noted that according to the literature data $L \sim 1$ Å is typical for processes occurring by the exchange mechanism [1]. However, the detailed analysis of accessible data shows that even for the benzophenone–naphthalene pair (which is investigated more thoroughly than any other) the L values obtained by different authors vary greatly and lie between 0.66 and 1.87 Å [1]. The reasons for such differences may be the comparatively low quencher concentrations used and/or comparison of theoretical and experimental kinetic curves of phosphorescence decay in an insufficiently wide time range.

In this work the O_2 concentration was varied in a wide range, up to 1 M, corresponding to more than tenfold lowering of quantum yield. Moreover, at the parameters of R_0 and L obtained by us, experimental and theoretical phosphorescence decay curves are in a satisfactory concordance over a time range of $(10^{-3}$–$2.5)\tau_0$ (figs. 9 and 10).

The fluorescence static quenching data cannot be explained within a single model and imply two mechanisms of quenching for close ($r < 8.7$ Å) and distant ($r > 8.7$ Å) donor–acceptor pairs.

References

[1] V.L. Yermolayev, Ye.N. Bodunov, Ye.B. Sveshnikova and T.A. Shakhverdov, Bezyzluchatel'nyi perenos energii elektronnogo vozbuzhdeniya (Non-radiative electron excitation energy transfer) (Nauka, Leningrad, 1977).

[2] O.L.J. Gijzeman, F. Kaufman and G. Porter, J. Chem. Soc. Faraday Trans. II 69 (1973) 708.

[3] G.J. Smith, J. Chem. Soc. Faraday Trans. II 78 (1982) 769.

[4] A.A. Gorman, I. Hamblett and M.A.J. Rodgers, J. Photochem. 25 (1984) 115.

[5] S. Siegel and H.S. Judeikis, J. Chem. Phys. 48 (1968) 1613.

[6] P.F. Jones and S.Siegel, J. Chem. Phys. 54 (1971) 3360.

[7] J.B. Birks, Photophysics of Aromatic Molecules (Wiley, London, 1970).

[8] C.A. Parker, Photoluminescence of Solutions (Elsevier, Amsterdam, 1968).

[9] M.M. Rikenglaz and I.M. Rozman, Opt. Spectrosk. 36 (1974) 106.

[10] J. Najbar, J.B. Birks and T.D.S. Hamilton, Chem. Phys. 23 (1977) 281.

[11] N.M. Bazhin, B.I. Yakobson and A.I. Burshtein, Int. J. Quant. Chem. 16 (1979) 931.

[12] K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).

[13] Spravochnik po rastvorimosti (Handbook on Solubilities) (AN SSSR, Leningrad, 1961) Vol. 1, pp. 571–575.

[14] O.L.J. Gijzeman and F. Kaufman, J. Chem. Soc. Faraday Trans. II 69 (1973) 721.

[15] R.A. Marcus, Ann. Rev. Phys. Chem. 13 (1964) 155.

[16] S.F. Chentsov, V.V. Korolev and N.M. Bazhin, Zh. Prikl. Spektroskopii 31 (1979) 97.

[17] A.I. Burshtein, J. Lumin. 21 (1980) 317.

[18] S.P. McGlynn, T. Azumi and M. Kinoshita, Molecular Spectroscopy of the Triplet State (Prentice Hall, Englewood Cliffs, 1969).

[19] N.M. Bazhin, Chem. Phys. Lett. 69 (1980) 580.

[20] J. Najbar, Chem. Phys. Lett. 90 (1982) 154.

[21] J.G. Calvert and J.N. Pitts Jr., Photochemistry (Wiley, New York, 1966).