

in the original optimization of procedures, but not yet for a silyl ether derivative.

6. Molecular mechanics calculations also account for the experimental finding that the nominally free rotation of the side chain C-17 to C-20 bond is in fact restricted so that the C-20 hydrogen is pointing to the β -face of the steroid.

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Pressure Effects on the Dynamic Quenching by Oxygen of Singlet and Triplet States of Anthracene Derivatives in Solution

Hiroya Yasuda,[†] Andrew D. Scully,[†] Satoshi Hirayama,^{*,†} Masami Okamoto,^{*,†} and Fujio Tanaka[‡]

Contribution from the Laboratory of Chemistry and Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan, and Faculty of Integrated Arts and Sciences, The University of Osaka Prefecture, Mozu-umemachi, Sakai, Osaka 591, Japan. Received February 2, 1990

Abstract: The mechanism for the quenching by oxygen of the singlet and triplet states of several anthracene derivatives in methylcyclohexane (MCH) under pressures of up to 700 MPa was investigated. The value for the rate constant of fluorescence quenching, k_q^S , at 0.1 MPa is found to vary from $(3.2 \pm 1.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 9,10-dicyanoanthracene (DCNA) to $(2.88 \pm 0.27) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for 9-methylanthracene (MEA), whereas values for the rate constant of the triplet-state quenching process, k_q^T , at 0.1 MPa are similar for each of the anthracenes, being in the range $(3.0\text{--}3.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The values for k_q^S and k_q^T decrease with increasing pressure, mainly as a result of the increase in viscosity of the solvent that accompanies the pressure increase. A linear relation between $\ln k_q^S$ and $\ln \eta$ is found for anthracene (A) and MEA, with slopes of -0.57 ± 0.04 and -0.64 ± 0.02 , respectively. However, plots of this relation show a distinct downward curvature for 9,10-dichloroanthracene (DCLA) and DCNA. It is also found that $\ln k_q^T$ does not vary linearly with $\ln \eta$ for any of the derivatives examined. The activation volumes of k_q^S for A and MEA are estimated to be in the range $12\text{--}14 \text{ cm}^3 \text{ mol}^{-1}$. These values are about 2 times larger than those determined for k_q^T , but are only half of the value reported for the activation volume of the viscosity of MCH. The ratio of k_q^T to k_q^S for MEA and DCLA at 0.1 MPa is reasonably close to the predicted value of 1/9 and increases with pressure, reaching a value of approximately 4/9 for DCLA at 700 MPa. These results suggest that, in addition to $^1(\text{AO}_2)^*$, encounter complexes of the form $^3(\text{AO}_2)^*$ or $^5(\text{AO}_2)^*$, for which the total spin angular momentum is not conserved, may come to play an important role in the quenching of the triplet state as the pressure is increased. Dynamic aspects of the fluorescence quenching are also discussed in terms of the transient decay feature characterized by the $t^{1/2}$ function predicted by the Smoluchowski model.

Introduction

Molecular oxygen is an efficient quencher of the electronically excited states of many organic molecules. In most cases, the quenching by oxygen is so efficient that the reaction rate is believed to be diffusion-limited. However, quenching rate constants reported in the literature vary from compound to compound, for example, $3.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for *p*-methoxybiphenyl and $4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for fluoranthene.¹ Despite this wide range of magnitudes, it is often claimed that a quenching reaction is diffusion-controlled if the rate constant exceeds a value of approximately $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, or sometimes even a value smaller than this. This also appears to be the case for quenchers other than oxygen. It is important that a clear distinction is made between fully diffusion-controlled reactions and those that are nearly diffusion-controlled, since in the latter case the quenching efficiency is less than unity. When the probability is less than 1, the quenching reaction is not infinitely fast and encounter complexes with rather long lifetimes may become involved in the reaction. Consequently, a detailed investigation into the quenching mechanism, especially the structure

and stability of such encounter complexes, is required.^{2,3}

In a recent comprehensive review, Saltiel and Atwater discussed in detail the mechanism by which molecular oxygen quenches electronically excited states in solution.¹ According to their proposed mechanism (in which a charge-separated state is not included⁴), it is concluded that the maximum value of the rate constant for quenching of the singlet states of organic compounds is approximately $2.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This is almost 9 times larger than that estimated for the triplet states due to the favorable spin statistical factor for the former, assuming that the total spin angular momentum is conserved upon quenching. For aromatic compounds whose electronic states are of $\pi\pi^*$ nature, the rate constants for quenching of the singlet states always appear to be larger than those for the corresponding triplet states.¹ However, the ratios of these values have not been examined extensively for

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[‡]Faculty of Engineering and Design, Kyoto Institute of Technology.

[§]University of Osaka Prefecture.

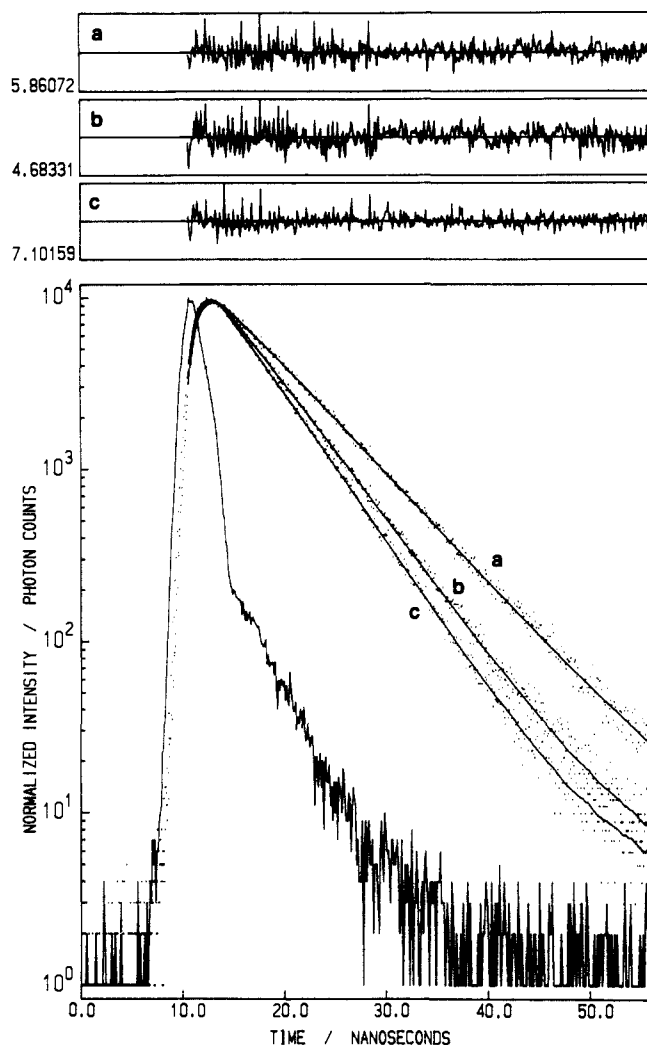


Figure 1. Fluorescence decay curves measured for MEA (1.0×10^{-5} M) (---) in (a) deaerated and (b) aerated MCH solutions at 100 MPa and 25 °C. Both decay curves are described satisfactorily by a single-exponential function (—). For comparison, the decay curve measured for MEA in a deaerated solution of MCH at 0.1 MPa is also shown (c). Residuals corresponding to the fitted curves are displayed in the upper panels.

any specific molecule as a function of external parameters. Such a study is necessary in order to provide a complete understanding of the so-called "diffusion-controlled" quenching process by molecular oxygen.

The application of pressure is one very useful technique for studying the diffusional process, since the viscosity of the solvent can be changed continuously over a wide range while other properties of the solvent are kept practically constant. The aim of this work, therefore, was to study the effects of pressure on the quenching by molecular oxygen of both singlet and triplet states of some anthracene derivatives in order to provide some insight into the detailed mechanism of this "diffusion-controlled" process. Anthracene derivatives were used because, for these molecules, the electronic nature, singlet-state lifetime, and triplet yield can be varied widely by introducing different types of substituents while the molecular diameters (i.e., the hard-sphere collisional cross-section) remain almost constant.

Experimental Section

Zone-refined anthracene (A) (Wako Pure Chemical Industries Ltd.) was used as received. 9-Methylanthracene (MEA), 9,10-dichloroanthracene (DCLA), and 9,10-dimethylanthracene (DMEA) (Aldrich Chemical Co. Inc.) were purified by recrystallization and then by thin-layer chromatography (TLC). 9,10-Dicyanoanthracene (DCNA)⁵ and

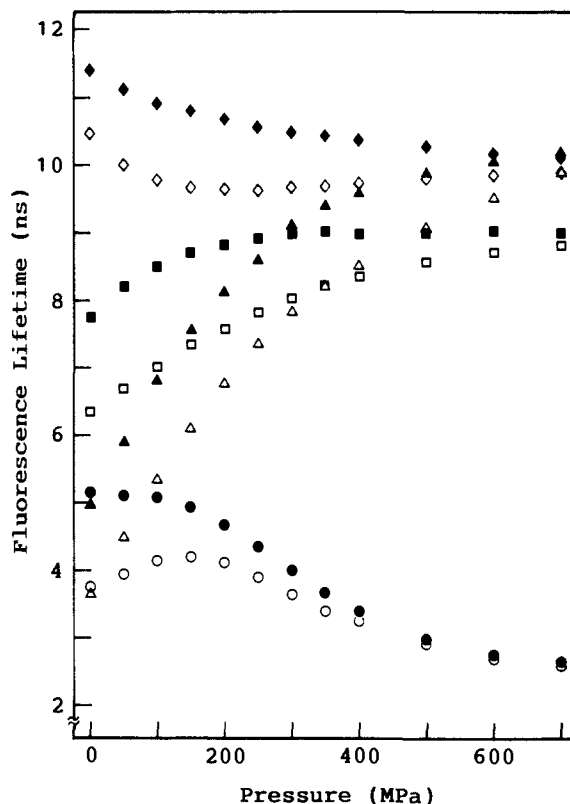


Figure 2. Fluorescence lifetimes of A (●; ○), MEA (▲; △), DCLA (■; □), and DCNA (◆; ◇) as a function of pressure at 25 °C. Solid and open symbols represent the deaerated and aerated solutions, respectively.

9-acetylanthracene (ACA)⁶ were synthesized according to the literature and were purified by recrystallization prior to purification on a TLC plate. Spectroscopic grade methylcyclohexane (MCH) (Dojin Pure Chemicals Co.) was used as received. The sample solutions were deaerated by bubbling with solvent-saturated nitrogen gas for 20 min. This procedure was found to be sufficient to remove dissolved oxygen by comparing the fluorescence lifetime measured at 0.1 MPa with that for a solution that was degassed by using repeated freeze-pump-thaw cycles. The temperature of the sample solutions was kept at 25.0 ± 0.1 °C. The concentration of oxygen in air-equilibrated MCH (2.5×10^{-3} M) was determined by gas chromatography with a column of 5-Å molecular sieve. This value was obtained by calibration against the value reported for cyclohexane (2.3×10^{-3} M).⁷ The change in concentration accompanying the volume change that occurs by applying pressure was corrected for by using the compressibility of MCH.⁸

The experimental details for the high-pressure apparatus used for the triplet-triplet (T-T') absorption measurements and for the fluorescence decay measurements were described in previous papers.^{9,10} The applied pressure was calibrated against a managan gauge. The fluorescence decay curves were measured by using the technique of time-correlated single-photon counting and have a channel width of 111 ps. The experimentally obtained fluorescence decay curves were analyzed by using an iterative nonlinear least-squares method as reported previously.¹¹ The fluorescence decay curves were also analyzed according to the $t^{1/2}$ function based on the Smoluchowski model for diffusion-controlled reactions^{2,3} in a manner similar to that described in a previous paper.¹²

Results and Discussion

Pressure Effects on the Fluorescence Lifetime. The effects of pressure on the fluorescence lifetime were examined in both aerated and deaerated solutions at a concentration of ca. 10^{-5} M for each anthracene derivative. The concentration was kept low

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Table I. Rate Parameters for the S₁ and T₁ States of A in MCH at 25 °C

pressure/ MPa	τ_f^0 /ns	τ_f /ns	τ_T /ns	$k_q^S/10^9$ M ⁻¹ s ⁻¹	$k_q^T/10^9$ M ⁻¹ s ⁻¹	k_q^T/k_q^S
0.1	5.15 ± 0.07	3.76 ± 0.06	106.4	28.7 ± 2.8	3.76	0.13 ± 0.02
50	5.10 ± 0.07	3.94 ± 0.06	115.0	22.1 ± 2.4	3.33	0.15 ± 0.02
100	5.07 ± 0.07	4.13 ± 0.06	125.6	16.7 ± 2.2	2.96	0.18 ± 0.03
150	4.93 ± 0.07	4.18 ± 0.06	138.1	13.2 ± 2.1	2.63	0.20 ± 0.04
200	4.66 ± 0.07	4.10 ± 0.06	152.3	10.4 ± 2.2	2.34	0.22 ± 0.05
250	4.34 ± 0.06	3.90 ± 0.06	169.3	9.1 ± 2.2	2.06	0.23 ± 0.06
300	3.99 ± 0.06	3.64 ± 0.06	189.4	8.3 ± 2.5	1.82	0.22 ± 0.07
350	3.66 ± 0.05	3.38 ± 0.05	213.5	7.7 ± 2.3	1.59	0.21 ± 0.07
400	3.38 ± 0.05	3.24 ± 0.05	240.3	4.3 ± 2.6	1.39	0.33 ± 0.20
500	2.98 ± 0.05	2.92 ± 0.05		(2.3 ± 3.1)		
600	2.74 ± 0.04	2.69 ± 0.04		(2.2 ± 2.8)		
700	2.65 ± 0.04	2.60 ± 0.04		(2.3 ± 2.9)		

Table II. Rate Parameters for the S₁ and T₁ States of MEA in MCH at 25 °C

pressure/ MPa	τ_f^0 /ns	τ_f /ns	τ_T /ns	$k_q^S/10^9$ M ⁻¹ s ⁻¹	$k_q^T/10^9$ M ⁻¹ s ⁻¹	k_q^T/k_q^S
0.1	4.97 ± 0.07	3.66 ± 0.05	111.5	28.8 ± 2.7	3.59	0.13 ± 0.02
50	5.92 ± 0.08	4.48 ± 0.06	118.8	20.8 ± 1.9	3.23	0.16 ± 0.02
100	6.81 ± 0.10	5.33 ± 0.07	125.1	15.2 ± 1.6	2.97	0.20 ± 0.03
150	7.56 ± 0.11	6.11 ± 0.08	140.2	11.4 ± 1.4	2.59	0.23 ± 0.03
200	8.12 ± 0.12	6.77 ± 0.10	152.6	8.7 ± 1.3	2.33	0.27 ± 0.05
250	8.59 ± 0.13	7.36 ± 0.11	170.9	6.8 ± 1.2	2.04	0.30 ± 0.06
300	9.11 ± 0.14	7.82 ± 0.11	190.2	6.2 ± 1.0	1.82	0.29 ± 0.06
350	9.38 ± 0.15	8.21 ± 0.12	210.1	5.2 ± 1.0	1.61	0.31 ± 0.07
400	9.58 ± 0.15	8.50 ± 0.13	237.6	4.5 ± 1.0	1.41	0.32 ± 0.08
500	9.88 ± 0.15	9.07 ± 0.14		3.0 ± 0.9		
600	10.04 ± 0.16	9.51 ± 0.14		1.8 ± 0.9		
700	10.18 ± 0.16	9.88 ± 0.15		1.0 ± 0.8		

Table III. Rate Parameters for the S₁ and T₁ States of DCLA in MCH at 25 °C

pressure/ MPa	τ_f^0 /ns	τ_f /ns	τ_T /ns	$k_q^S/10^9$ M ⁻¹ s ⁻¹	$k_q^T/10^9$ M ⁻¹ s ⁻¹	k_q^T/k_q^S
0.1	7.74 ± 0.06	6.35 ± 0.06	134.5	11.3 ± 1.0	2.97	0.26 ± 0.03
50	8.19 ± 0.06	6.68 ± 0.05	138.0	10.6 ± 0.8	2.78	0.26 ± 0.03
100	8.50 ± 0.06	7.01 ± 0.05	144.0	9.3 ± 0.7	2.58	0.28 ± 0.03
150	8.69 ± 0.07	7.33 ± 0.05	157.1	7.7 ± 0.7	2.31	0.30 ± 0.03
200	8.82 ± 0.06	7.57 ± 0.05	168.6	6.7 ± 0.6	2.11	0.31 ± 0.03
250	8.92 ± 0.07	7.82 ± 0.06	180.7	5.5 ± 0.6	1.93	0.35 ± 0.04
300	8.98 ± 0.07	8.02 ± 0.06	205.3	4.6 ± 0.6	1.68	0.37 ± 0.05
350	9.02 ± 0.07	8.19 ± 0.06	223.3	3.8 ± 0.6	1.52	0.40 ± 0.06
400	8.97 ± 0.07	8.34 ± 0.06	240.8	2.8 ± 0.5	1.39	0.45 ± 0.09
500	8.99 ± 0.07	8.56 ± 0.06		1.8 ± 0.5		
600	9.02 ± 0.06	8.70 ± 0.06		1.3 ± 0.4		
700	8.98 ± 0.12	8.81 ± 0.06		0.7 ± 0.6		

in order to minimize the effects of reabsorption on the fluorescence lifetime.¹³ Figure 1 shows the fluorescence decay curves measured for deaerated MCH solutions of MEA at 0.1 and 100 MPa and for an aerated MCH solution of MEA at 100 MPa. In all cases, the fluorescence decay curve is described satisfactorily by a single exponential. Figure 2 illustrates the pressure dependence of the fluorescence lifetime for A, MEA, DCLA, and DCNA. The difference between the reciprocals of the fluorescence lifetimes $\tau_f(P)$ and $\tau_f^0(P)$, which represent the fluorescence lifetimes at the pressure P in the aerated and deaerated solutions, respectively, yields the rate constant for quenching of the excited singlet state (S₁), $k_q^S(P)$, if the concentration of dissolved oxygen is known. This is expressed by the following equation:

$$1/\tau_f(P) - 1/\tau_f^0(P) = k_q^S(P)[O_2] \quad (1)$$

The largest value of $k_q^S(P)$ was found for MEA at 0.1 MPa ((2.88 ± 0.27) × 10¹⁰ M⁻¹ s⁻¹), and this value is almost 10 times larger than that for DCNA ((3.2 ± 1.1) × 10⁹ M⁻¹ s⁻¹). The values of $k_q^S(P)$ for A, MEA, and DCLA at 0.1 MPa are in good agreement with those reported in the literature.¹ The values obtained for $k_q^S(P)$ are summarized in Tables I–IV, together with other relevant data.

Table IV. Rate Parameters for the S₁ State of DCNA in MCH at 25 °C

pressure/ MPa	τ_f^0 /ns	τ_f /ns	$k_q^S/10^9$ M ⁻¹ s ⁻¹
0.1	11.41 ± 0.17	10.47 ± 0.16	3.2 ± 1.1
50	11.12 ± 0.17	10.01 ± 0.15	3.8 ± 1.1
100	10.92 ± 0.16	9.78 ± 0.15	4.0 ± 1.1
150	10.81 ± 0.16	9.68 ± 0.15	3.9 ± 1.1
200	10.68 ± 0.16	9.65 ± 0.15	3.6 ± 1.1
250	10.57 ± 0.16	9.63 ± 0.15	3.2 ± 1.1
300	10.49 ± 0.16	9.66 ± 0.15	2.8 ± 1.1
350	10.44 ± 0.16	9.68 ± 0.15	2.5 ± 1.0
400	10.37 ± 0.16	9.73 ± 0.15	2.1 ± 1.0
500	10.27 ± 0.15	9.80 ± 0.15	1.5 ± 1.0
600	10.16 ± 0.15	9.85 ± 0.15	(1.0 ± 1.0)
700	10.12 ± 0.15	9.88 ± 0.15	(0.8 ± 1.0)

In the deaerated solution, the fluorescence lifetime of A is shortened as the pressure increases, and this shortening is accompanied by a concomitant increase in the lowest triplet-state yield.¹⁴ This effect has been ascribed to enhancement of the rate of intersystem crossing (ISC) with increasing pressure.¹⁴ On the

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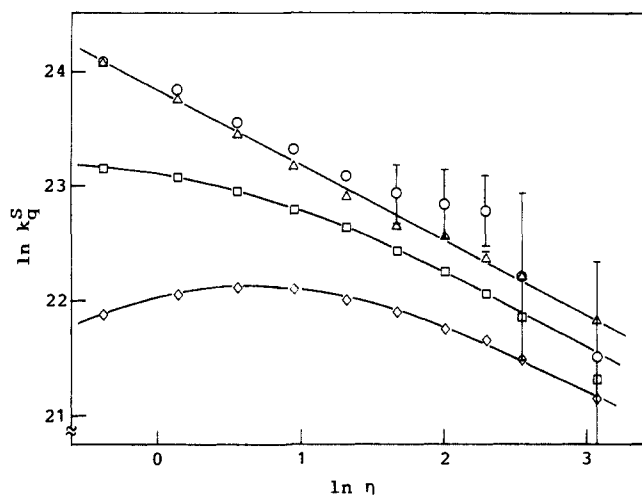


Figure 3. Plots of $\ln k_q^S$ vs $\ln \eta$ for A (O), MEA (Δ), DCLA (\square), and DCNA (\diamond). The relation is linear only for A ($\alpha = -0.57 \pm 0.04$) and MEA ($\alpha = -0.64 \pm 0.02$). Activation volumes calculated at 0.1 MPa are listed in Table VI.

other hand, the fluorescence lifetime of MEA increases monotonically with pressure and appears to reach a maximum value of approximately 10 ns. A remarkable viscosity dependence for the fluorescence lifetime of MEA has been reported by Blatt et al.¹⁵ In the present case, however, the viscosity of MCH increases only moderately with pressure,⁸ suggesting that the increase in the fluorescence lifetime with pressure is not due to changes in viscosity alone. The fluorescence quantum yield of MEA must be substantially less than unity even at 700 MPa, since the fluorescence lifetime at 700 MPa is significantly shorter than the radiative lifetime, τ_r , of MEA (≈ 14.8 ns).¹⁶ Behavior similar to MEA was found for DCLA, whose lifetime increases from 7.74 ± 0.06 ns at 0.1 MPa to 8.98 ± 0.12 ns at 700 MPa, as shown in Figure 2. The increase in τ_f for this compound is accompanied by a decrease in the triplet-state yield, as reported previously.¹⁴ Again, the fluorescence lifetime at 700 MPa is shorter than the radiative lifetime ($\tau_f = 11.4$ ns at 77 K).¹⁶ In contrast to the three compounds described earlier, the τ_f of DCNA, which, at 0.1 MPa, is almost equal to τ_r , decreases monotonically with pressure, presumably because of an increase in the refractive index of MCH.¹⁷

In aerated solutions, the effect of pressure on the fluorescence lifetimes of MEA, DCNA, and DCLA is similar to that found for deaerated solutions. However, anomalous behavior occurs in the case of A, where the value for τ_f assumes a maximum value of 4.2 ns at 150 MPa. This unusual variation of τ_f with increasing pressure is attributed to contributions by two opposing effects, namely retardation of the quenching due to viscosity increase and promotion as a result of an enhanced rate of ISC.¹⁴ As the pressure is increased further, the difference between $\tau_f(P)$ and $\tau_f^0(P)$ diminishes. This is attributed to less favorable quenching by oxygen in solvents of higher viscosity. Consequently, an unavoidable increase in the uncertainty associated with $k_q^S(P)$ arises as the pressure increases, and this is indicated by the error bars in Figure 3.

Pressure Effects on the Triplet-State Lifetime. The lifetimes of the lowest triplet states (T_1) were determined from the decay of the T-T' absorption. The triplet-state lifetimes of the anthracenes in deaerated solutions at ambient temperatures vary from a few hundred microseconds to 1 ms. Because of this relatively long lifetime, oxygen quenching of T_1 is extensive, reducing the lifetimes substantially (≈ 100 ns) in air-saturated solutions. In both cases (aerated and deaerated), however, the decay curves are described satisfactorily by a single exponential function. The

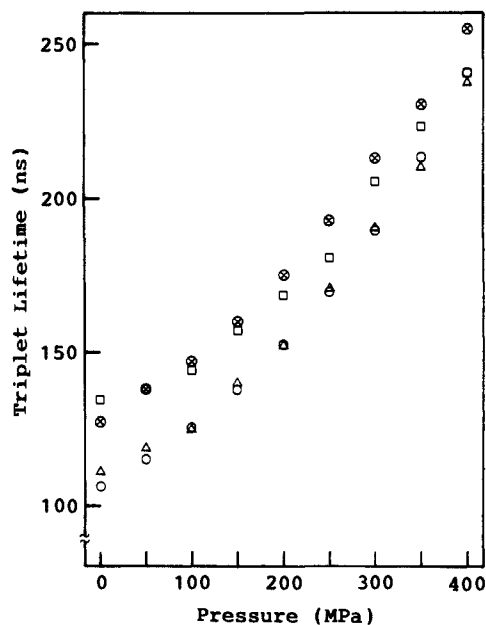


Figure 4. Triplet-state lifetimes of A (O), MEA (Δ), DCLA (\square), and ACA (\otimes) as a function of pressure at 25 °C.

Table V. Rate Parameters for the T_1 State of ACA in MCH at 25 °C

pressure/ MPa	τ_T /ns	$k_q^T/10^9$ $M^{-1} s^{-1}$
0.1	127.6 ± 4.2	3.13
50	138.1 ± 3.5	2.78
100	147.0 ± 2.0	2.53
150	159.8 ± 2.0	2.27
200	175.2 ± 4.2	2.03
250	192.6 ± 3.0	1.82
300	212.9 ± 3.1	1.62
350	230.4 ± 5.6	1.48
400	254.8 ± 10.1	1.32

triplet-state lifetimes obtained in the air-saturated solutions are plotted against pressure in Figure 4 for A, MEA, DCLA, and ACA. 9,10-Dicyanoanthracene did not yield a measurable amount of T_1 upon direct excitation to S_1 , and hence, its lifetime was not obtained.

The rate constant for quenching of T_1 , k_q^T , was calculated from eq 3, in which the term $1/\tau_T^0(P)$ in eq 2 is neglected, since $\tau_T^0(P)$ is significantly longer than $\tau_T(P)$. The values obtained for $k_q^T(P)$

$$1/\tau_T(P) - 1/\tau_T^0(P) = k_q^T(P)[O_2] \quad (2)$$

$$1/\tau_T(P) = k_q^T(P)[O_2] \quad (3)$$

are listed in Tables I–V. Since ACA does not fluoresce in solution at room temperature, only τ_T and k_q^T are given in Table V. Very fast ISC is responsible for the lack of fluorescence from this molecule.^{18,19} Despite the large differences in the pressure dependence of the fluorescence lifetimes for these compounds, their quenched triplet lifetimes are of the same magnitude and all show a very similar pressure dependence.

Both $k_q^S(P)$ and $k_q^T(P)$ decrease with increasing pressure because of an increase in the viscosity of the solvent, but neither varies in accordance with the generally accepted Debye equation:

$$k_q = 8RT/2000\eta \quad (4)$$

When $\ln k_q^S(P)$ is plotted against $\ln \eta$, reasonably good linear correlations are obtained for A and MEA, with slopes of -0.57 ± 0.04 and -0.64 ± 0.02 , respectively (see Figure 3). The same plot for DCLA and DCNA is distinctly nonlinear. It has been

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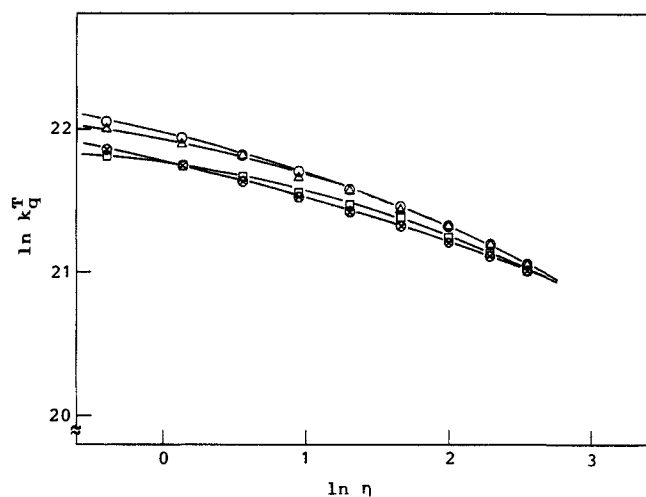


Figure 5. Plots of $\ln k_q^T$ vs $\ln \eta$ for A (O), MEA (Δ), DCLA (\square), and ACA (\odot). Activation volumes calculated at 0.1 MPa are listed in Table VI.

Table VI. Activation Volumes for the Quenching by Oxygen of the S_1 and T_1 States of Anthracene Derivatives in MCH at 25 °C and 0.1 MPa^a

compd	$\Delta V_q^{*,S}/$ $\text{cm}^3 \text{ mol}^{-1}$	$\Delta V_q^{*,T}/$ $\text{cm}^3 \text{ mol}^{-1}$
A	12 ± 1 (12 ± 2)	6.1 ± 0.1
MEA	14 ± 1 (12 ± 2)	5.8 ± 0.1
DCLA	(6 ± 1)	5.1 ± 0.1

^aThe numbers in parentheses are the activation volumes calculated by using quadratic analysis.²⁴ The activation volume calculated from the pressure dependence of the viscosity of MCH is $24 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$. The quenching of $^1\text{O}_2$ by β -carotene has the activation volume of $10 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$, which is similar to those for the quenching of S_1 of A and MEA by oxygen.

reported²⁰ that for the diffusion of small molecules, such as oxygen, in solution the diffusion coefficient, D , is nonlinear with respect to T/η , but instead is proportional to T/η^α where α is less than unity. For k_q^T , however, even after due consideration for the small size of oxygen, $\ln k_q^T$ does not yield a simple relation to $\ln \eta$ and always shows a convex deviation as shown in Figure 5. This result suggests that the mechanism for quenching by oxygen for S_1 of A and MEA is different from that for T_1 of these molecules.

The different effects of pressure on k_q^S and k_q^T are reflected in the significantly different activation volumes that are given in Table VI. Activation volumes, ΔV^* , of the order of 12–14 $\text{cm}^3 \text{ mol}^{-1}$ are often found for purely diffusion-controlled reactions involving small molecules.²¹ The values found for the fluorescence quenching of DCLA and the triplet-state quenching of the anthracene derivatives studied in this work are approximately half of this value. At present, we have no satisfactory explanation for this discrepancy. It is also interesting to note the similarity of the values for $\Delta V_q^{*,S}$ and $\Delta V_q^{*,T}$ in the case of DCLA. 9,10-Dicyanoanthracene behaves anomalously since a negative activation volume is obtained at 0.1 MPa, which implies that the quenching rate constant should increase with increasing viscosity.

Quenching Mechanism. The value of $k_q^S(0.1)$ for MEA is 9 times larger than that of DCNA. If the quenching by oxygen is purely collisional and has a quenching probability of unity for both DCNA and MEA, then their collision diameters must differ by a factor of 3. This is unreasonably large for these molecules, whose molecular frameworks are almost identical. Thus, it appears that the probability of quenching per encounter is significantly less than unity for DCNA.

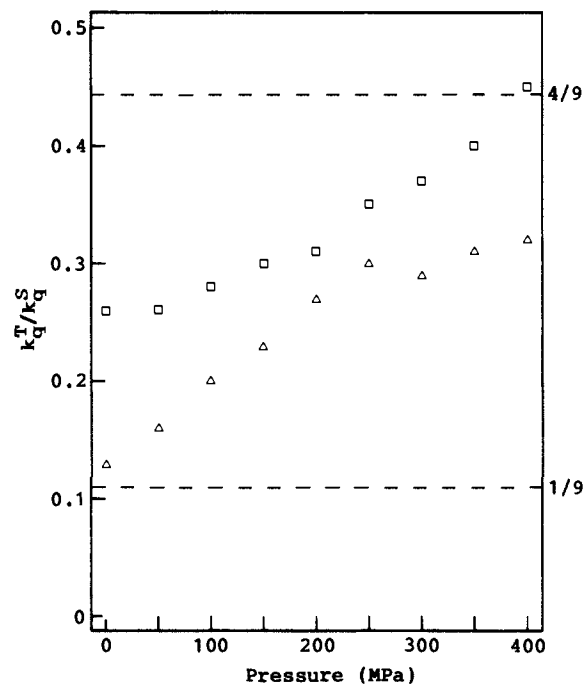
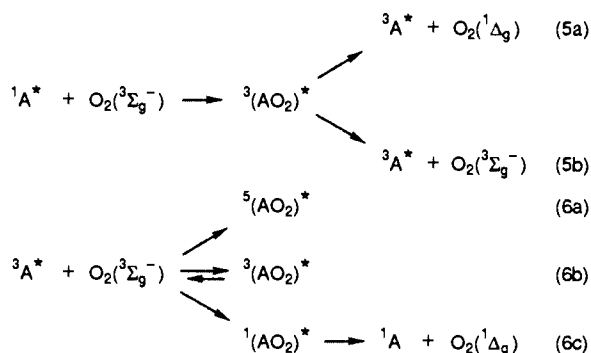


Figure 6. Pressure effect on the ratio of k_q^T to k_q^S for DCLA (\square) and MEA (Δ).

The generally accepted mechanisms for quenching by oxygen can be written as follows:



The presence of the charge-transferred state in nonpolar solvents has been neglected. Also, the inefficient process leading directly to the ground state, ^1A , is not considered here.⁴ If processes 5a and 6c dominate for the singlet- and triplet-state quenching, respectively, and if these are both diffusion-controlled reactions, then the ratio of the two quenching rate constants, as determined by spin statistics, is equal to 1/9.¹ The ratio at 0.1 MPa for the quenching of MEA and DCLA is reasonably close to this value (see Figure 6) and is consistent with values reported previously for the quenching by oxygen of other anthracene derivatives.¹ However, the ratio increases with increasing pressure for each derivative and reaches a value of approximately 4/9 in the case of DCLA, as is seen from Figure 6. From this result, together with the nonlinearity of the plots of $\ln k_q^T$ vs. $\ln \eta$ observed for all of the anthracenes studied in this work, it is concluded that the quenching of the electronically excited states by oxygen is not governed simply by diffusional collision with the excited molecule and spin statistics.

The fact that k_q^T is less suppressed by increasing pressure than k_q^S may be explained as follows. At low pressures, the dissociation of the complex ${}^3(\text{AO}_2)^*$ to the initial state (eq 6b) is so fast that the process does not lead to the quenching of ${}^3\text{A}^*$ but to the regeneration of ${}^3\text{A}^*$. However, at higher pressures, the process that regenerates ${}^3\text{A}^*$ is retarded because of a positive activation volume associated with that process allowing ISC from ${}^3(\text{AO}_2)^*$ to ${}^1(\text{AO}_2)^*$ to become competitive. Once ${}^1(\text{AO}_2)^*$ is formed, it

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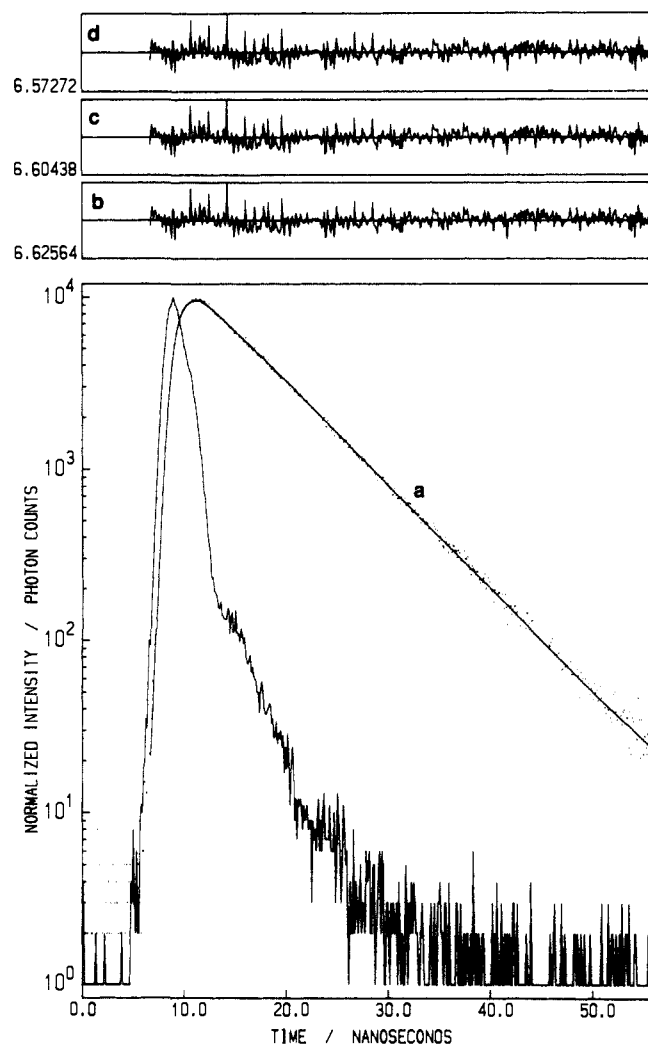


Figure 7. Fluorescence decay curve of DMEA (1.0×10^{-5} M) in an air-saturated MCH solution at 0.1 MPa and 25 °C (---) and fitted curve obtained from $t^{1/2}$ analysis (—) ($a = 0.141 \text{ ns}^{-1}$, $b = 6.1 \times 10^{-4} \text{ ns}^{-1/2}$, $\delta\text{SH} = -87 \text{ ps}$). Residuals for $t^{1/2}$ analysis (b), single-exponential analysis with value of δSH fixed at the value obtained from $t^{1/2}$ analysis (c), and single-exponential analysis with δSH adjustable ($\delta\text{SH} = -89 \text{ ps}$) (d) are shown in the upper panels.

leads to quenching (eq 6c) without the regeneration of $^3\text{A}^*$. As a result, any decrease in k_q^T associated with an increase in viscosity may be partly canceled by the participation of this extra quenching process. Since k_q^T does not vary appreciably from derivative to derivative at any pressure, the short-lived encounter complex $^3(\text{AO}_2)^*$ appears to play a similar role in the quenching process for each of the anthracene derivatives examined.

Decay Curve Features Associated with Diffusion-Controlled Quenching. The linear relation found between $\ln k_q^S$ and $\ln \eta$ for A and MEA suggests that the quenching by oxygen of S_1 for these molecules is a diffusion-controlled process. However, other independent experimental evidence is required in order to verify the diffusion-controlled nature of this reaction. One method of identifying a diffusion-controlled process involves analysis of fluorescence decay curve features. When a reaction in condensed phase occurs very rapidly, the transient effect, i.e., time-dependent diffusion, must be taken into consideration.² In such cases, as was demonstrated by Nemzek and Ware,²² the time dependence

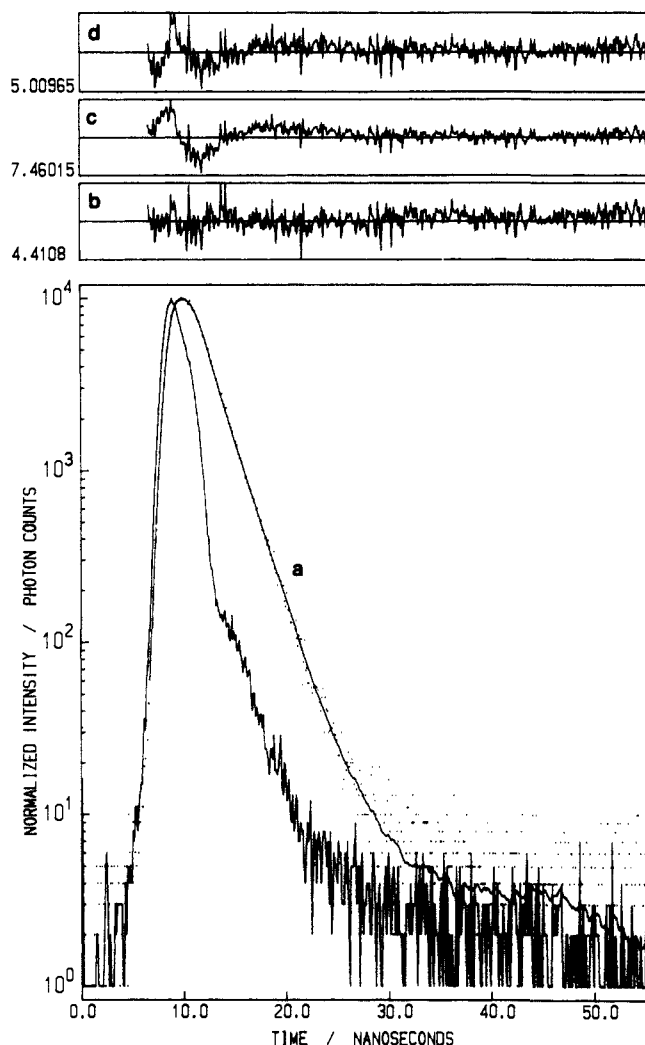


Figure 8. Fluorescence decay curve of DMEA (1.0×10^{-5} M) in an oxygen-saturated MCH solution at 0.1 MPa and 25 °C (---) and fitted curve obtained from $t^{1/2}$ analysis (—) ($a = 0.427 \text{ ns}^{-1}$, $b = 0.162 \text{ ns}^{-1/2}$, $\delta\text{SH} = 52 \text{ ps}$). Residuals for $t^{1/2}$ analysis (b), single-exponential analysis with value of δSH fixed at the value obtained from $t^{1/2}$ analysis (c), and single-exponential analysis with δSH adjustable ($\delta\text{SH} = 134 \text{ ps}$) (d) are shown in the upper panels.

of the excited state, $F(t)$, can be described by the following equation:

$$F(t) = F(0) \exp[-t/\tau_0 - 4\pi R_{\text{eff}} D_{\text{AQ}} N[\text{Q}]t \{1 + 2R_{\text{eff}}/(\pi D_{\text{AQ}}t)^{1/2}\}] \quad (7)$$

$$F(t) = F(0) \exp(-at - 2bt^{1/2}) \quad (7a)$$

$$a = 1/\tau_0 + 4\pi R_{\text{eff}} D_{\text{AQ}} N[\text{Q}] \quad (7b)$$

$$b = 4(R_{\text{eff}})^2 (\pi D_{\text{AQ}})^{1/2} N[\text{Q}] \quad (7c)$$

The term that is proportional to $t^{1/2}$ represents the transient effect and dominates at short times in the fluorescence decay. The terms R_{eff} and D_{AQ} are the effective collisional diameter and the mutual diffusion constant of the excited molecule and quencher, respectively. The other terms have the same definitions as those given by Nemzek and Ware.²²

A $t^{1/2}$ analysis of the fluorescence decay of DMEA in an air-saturated MCH solution ($[\text{O}_2] = 2.5 \text{ mM}$) yields a good fit to the data, as shown in Figure 7. However, the value of b obtained from this analysis ($b = 6.1 \times 10^{-4} \text{ ns}^{-1/2}$) is 2 orders of magnitude smaller than that calculated on the basis of the Stokes–Einstein relation (with slip),² where the molecular radii of DMEA and oxygen were taken to be 0.4 and 0.2 nm, respectively,⁴ and by

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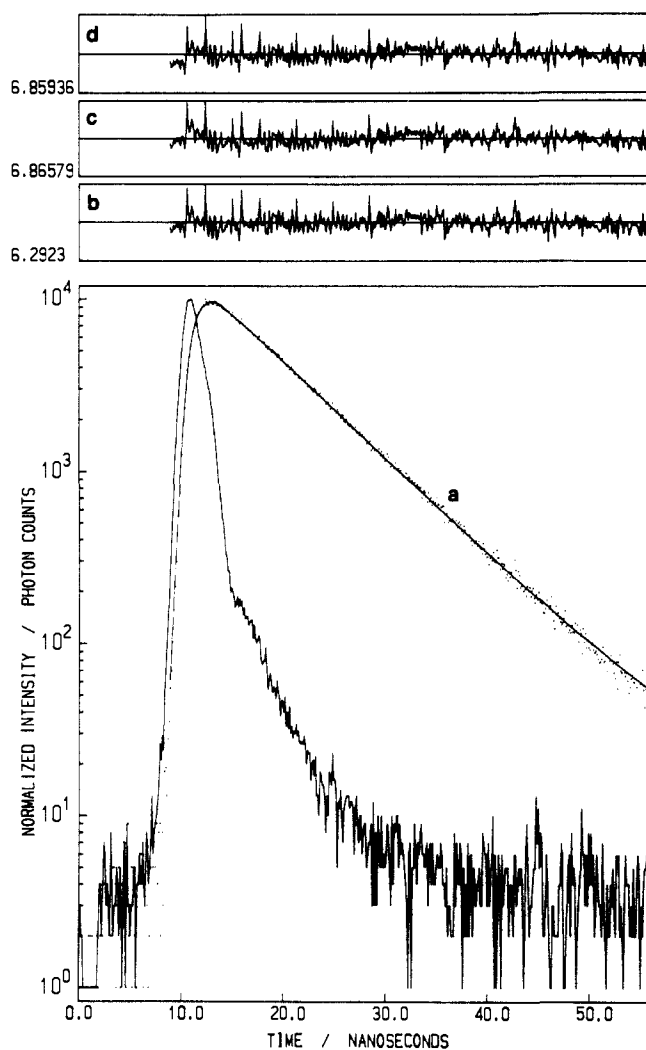


Figure 9. Fluorescence decay curve of DCNA (1.0×10^{-5} M) in an oxygen-saturated MCH solution at 0.1 MPa and 25 °C (•••) and fitted curve obtained from $t^{1/2}$ analysis (—) ($a = 0.129 \text{ ns}^{-1}$, $b = 1.1 \times 10^{-2} \text{ ns}^{-1/2}$, $\delta\text{SH} = -42 \text{ ps}$). Residuals for $t^{1/2}$ analysis (b), single-exponential analysis with δSH fixed at the value obtained from $t^{1/2}$ analysis (c), and single-exponential analysis with δSH adjustable ($\delta\text{SH} = -22 \text{ ps}$) (d) are shown in the upper panels.

assuming that the quenching process is diffusion-controlled, with the experimentally determined quenching rate constant being $2.66 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

Also shown in Figure 7 are the residuals for single-exponential analysis in which the time-zero shift parameter, δSH , is fixed at the same value as the optimized value obtained from the $t^{1/2}$ analysis (Figure 7c) and where it is permitted to vary freely (Figure 7d). The value of δSH is expected to be similar for both $t^{1/2}$ analysis and single-exponential analysis. A large discrepancy ($\gg 20 \text{ ps}$) between the value of δSH for these two methods of analysis implies that single-exponential analysis is inappropriate.

It is seen from Figure 7 that the quality of fitting in all three cases is comparable, with the optimized values of δSH for both the $t^{1/2}$ and single-exponential analyses being very similar. This result indicates that even under these experimental conditions, in which the fluorescence decay time is approximately half the unquenched value, the degree of quenching that occurs before the steady state is attained is minimal. Consequently, the deviation of the data from single-exponentiality is negligible.

A $t^{1/2}$ analysis of the fluorescence decay of DMEA in an oxygen-saturated solution of MCH ($[\text{O}_2] = 16 \text{ mM}$) gives a significantly better fit to the data than single-exponential analyses in which the value of δSH is either fixed at the optimized value obtained from the $t^{1/2}$ analysis or allowed to be freely adjustable (Figure 8). Furthermore, the values for a and b , from which values for R_{eff} and D_{AO} may be calculated, obtained from the $t^{1/2}$ analysis are in reasonable agreement with those predicted by using the same method as that described for the case of the air-saturated MCH solution. The values of R_{eff} and D_{AO} obtained from the $t^{1/2}$ analysis are 1.2 nm and $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively.

When the probability of reaction is very low, such as that found in the case of DCNA (≈ 0.1), the transient term can be neglected^{2,3} and the fluorescence decay curve should remain single exponential, even for an oxygen-saturated MCH solution. Figure 9 shows the fluorescence decay for DCNA in an oxygen-saturated MCH solution at 0.1 MPa. The quality of fitting by $t^{1/2}$ analysis and single-exponential analysis is comparable. Also, the value of b obtained from the $t^{1/2}$ analysis ($b = 1.1 \times 10^{-2} \text{ ns}^{-1/2}$) is 1 order of magnitude smaller than that expected if the values of R_{eff} and D_{AO} for DCNA in MCH are similar to those obtained experimentally for DMEA in an oxygen-saturated MCH solution. These results provide further support for the earlier contention that the probability of reaction between DCNA and oxygen is significantly less than unity.

The acquisition of data for the quenching of T_1 by oxygen is based on the absorption technique. The decay curves obtained by using this method are not of sufficiently good quality to allow a nonexponential analysis similar to that applied to the fluorescence quenching decay data. When sufficient progress has been made with this technique, it may be possible to confirm that more than one kinetic process is involved in the quenching of T_1 .

In conclusion, it has been shown in this work that diffusional quenching processes can be studied in detail by examining these processes as a function of pressure. Evidence has been presented that suggests that the mechanism for quenching by oxygen for S_1 of A and MEA is different from that of T_1 for these molecules. Also, it is proposed that at pressures greater than 0.1 MPa the encounter complex ${}^3(\text{AO}_2)^*$ participates in the process of quenching by oxygen of T_1 for the anthracene derivatives studied in this work. Furthermore, the application of pressure may also prove useful for facilitating the examination of processes that are characterized by the transient effect.

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Registry No. A, 120-12-7; MEA, 779-02-2; DCLA, 605-48-1; DMEA, 781-43-1; DCNA, 1217-45-4; oxygen, 7782-44-7.