QUENCHING AND PHOTOBLEACHING OF EXCITED POLYCYCLIC AROMATIC HYDROCARBONS BY CARBON TETRACHLORIDE

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(Received May 26, 1981; in revised form July 7, 1981)

Summary

The singlet quenching and photobleaching of several aromatic polycyclic hydrocarbons by carbon tetrachloride was investigated. The quenching rate constants were determined from fluorescence quenching measurements. The values obtained in ethanol range from 1.2×10^{10} M^{-1} s^{-1} to 2×10^6 M^{-1} s^{-1} for fluorene and coronene respectively. These values depend markedly on the solvent polarity (*e.g.* the quenching rate constant of perylene increases from 2×10^7 M^{-1} s^{-1} to 1.24×10^9 M^{-1} s^{-1} from cyclohexane to acetonitrile) and the characteristics of the substituents (*e.g.* values of 2×10^{10} M^{-1} s^{-1} and 1.2×10^8 M^{-1} s^{-1} were obtained for the quenching of 1-methoxynaphthalene and 1-cyanonaphthalene respectively). In most cases investigated, the singlet quenching leads to efficient photocleavage of the hydrocarbon.

The results obtained can be interpreted in terms of a quenching mechanism involving charge transfer from the donors to the carbon tetrachloride. The photobleaching yield is not related to the rate of the quenching process and is determined by the para-localization energies for the transannular addition.

1. Introduction

Carbon tetrachloride is known to be an efficient quencher for several fluorescent compounds [1 - 6]. Similarly, this compound is also able to quench the excited triplet state of aromatic [6, 7] and carbonyl [8] compounds. The quenching process has usually been explained in terms of an exciplex mechanism which involves partial transference of charge from the donor to the carbon tetrachloride molecule [1 - 4, 6]. This process frequently leads to efficient photobleaching, in most cases from the excited singlet state [5, 6]. Nevertheless, photochemical reaction also takes place from the triplet state in the photolysis of 2-pentanone [8]. In this case, as well as in the quenching of ketone singlets [1], the reaction involves as a

first step the dissociation of the C—Cl bond in carbon tetrachloride. In the present work we report the data obtained in a study of the quenching of the excited singlet state of several polycyclic hydrocarbons by carbon tetrachloride in order to clarify the factors which determine both the quenching rate and the photobleaching efficiency of the process.

2. Experimental details

Fluorescence measurements were carried out in a 204-S Perkin–Elmer spectrofluorimeter. All quenching experiments except those employing coronene and phenanthrene were carried out in air. The only criteria used for the purity of the polycyclic hydrocarbons were their absorption and fluorescence spectra. At the low concentrations employed (usually less than 10^{-5} M), the possible presence of impurities cannot play any significant role.

Bleaching experiments were carried out either in nitrogen or air employing light from a medium pressure mercury burner. Nearly monochromatic light was obtained at the main emission lines by filtering the light through suitable filters or employing a 33-86-38 Bausch and Lomb monochromator. The bleaching of the hydrocarbons was followed by the changes in absorbance at the wavelength of their maximum absorption. Valerophenone in benzene (ϕ_{butene} = 0.3 [9]) and 2-heptanone in *iso*-octane ($\phi_{acetone}$ = 0.2 [9]) were employed as actinometers at 3660 Å and 2970 Å respectively. All measurements were carried out at room temperature (approximately 20 °C). The bleaching in the absence of carbon tetrachloride was always considerably smaller than that in the presence of this compound. The solvents (Merck, p.a.) and the carbon tetrachloride (Merck, for fluorescence spectroscopy) were employed as purchased.

3. Experimental results

Carbon tetrachloride quenches the fluorescence of all the compounds considered. Typical Stern–Volmer plots are shown in Fig. 1. The values of $k_Q\tau$ obtained in ethanol from this type of plot are given in Tables 1 and 2. Table 3 gives similar results obtained in solvents of various polarities. The τ values required to obtain the reported values of k_Q were taken from the literature [12, 13]. When the lifetime in air was not available, it was estimated from the lifetime in nitrogen and the relationship between the fluorescence yields in air and in nitrogen. The quenching of perylene fluorescence in acetonitrile and cyclohexane by carbon tetrachloride was measured from pure acetonitrile to pure carbon tetrachloride. The values of $\phi_{F1}{}^0/\phi_{F1}$ obtained are given in Fig. 2.

The photobleaching of the compounds considered showed either isosbestic points or an unchanged spectral shape during the hydrocarbon
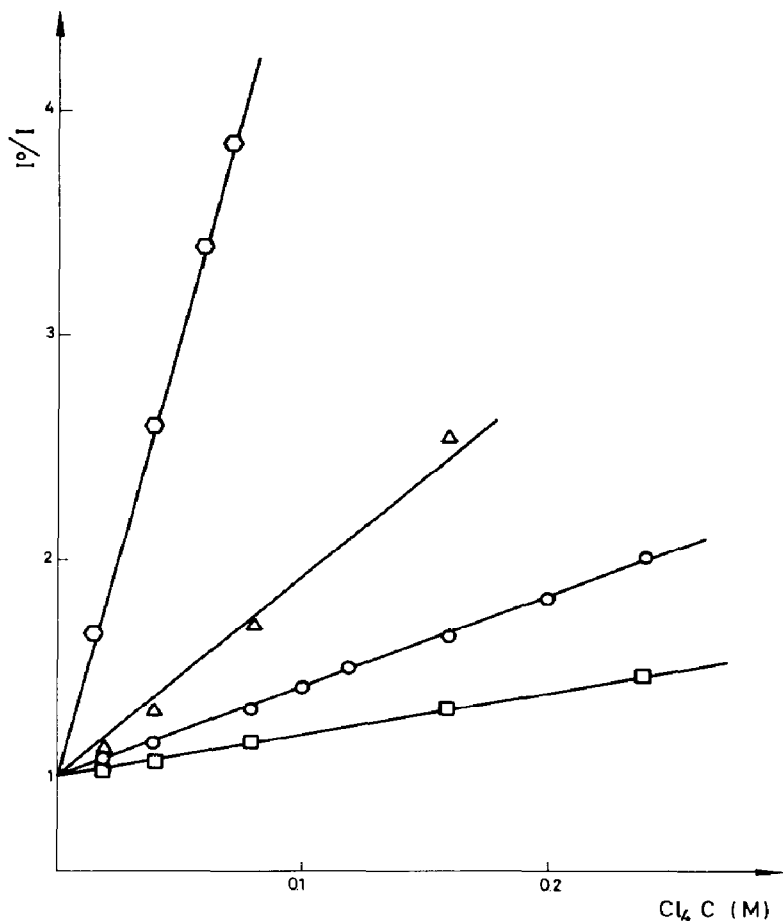
Fig. 1. Stern—Volmer plot from fluorescence measurements: ○, naphthalene (excitation, 285 nm; emission, 330 nm); △, anthracene (excitation, 350 nm; emission, 405 nm); o, benzo(α)pyrene (excitation, 370 nm; emission, 407 nm); □, benz(a)anthracene (excitation, 320 nm; emission, 390 nm).

consumption. The only exception was benz(a)anthracene photolysed at 313 nm. In this case the change in the spectra at long irradiation times suggested a significant photoconsumption of the primary products. However, isosbestic points were observed when the same compound was irradiated at 366 nm. The monitoring wavelength, the wavelength of the isosbestic points and the fraction of the initial absorbance remaining at the monitoring wavelength at long irradiation times are given in Table 4. The concentration C of the parent compound at a given time can be obtained from

$$C = \frac{A/A_0 - \alpha}{1 - \alpha} C_0 \tag{1}$$

where A_0 is the initial absorbance, A is the absorbance at time t and α is the relationship between the final and initial absorbances. Plots of $\ln(C_0/C)$

TABLE 1

Fluorescence quenching data obtained in ethanol

Donor	E_s (kJ mol^{-1})	IP[a] (eV)	λ_{exc}; λ_{emis}	$k_Q\tau$ (M^{-1})	k_Q ($\times 10^9$ M^{-1} s^{-1})
Benzene	460	9.23	260; 282	62	4.8
Biphenyl	412	8.21	300; 340	55	9.2
			310; 335		
Fluorene	397	7.78	290; 315	82	12
Naphthalene	384	8.13	320; 335	102	4.9
			285; 330		
Acenaphthene	382	7.66	305; 335	160	11.8
			320; 335		
Phenanthrene	346	7.80	320; 375	4.0[b]	0.07
			337; 375		
Chrysene	332	7.61	300; 382	2.1	0.17
Pyrene	322	7.41	330; 395	7.5	0.38
Anthracene	319	7.43	350; 405	9.6	2.12
Benz(a)anthracene	310	7.45	320; 390	2.2	0.12
Dibenz(a,h)-anthracene	303	7.80	330; 395	0.37	0.027
Benzo(α)pyrene	297	7.12	370; 407	4.3	0.27
Fluoranthene	295	7.80	345; 435	0.18	0.005
Benzo(ghi)perylene	294	7.19	370; 435	0.74	0.02
			340; 450		
Coronene	279	7.34	315; 450	0.56[b]	0.002
Perylene	275	7.00	413; 442	1.30	0.33
Tetracene	254	7.01	450; 475	0.19	0.043
			450; 485		
			450; 510		
Rubicene	222[c]	6.11[d]	435; 550	0.056	0.007
Triphenylene	352	7.86	305; 350	0.67	0.052
			335; 350		

[a] From ref. 10.
[b] Value obtained in nitrogen.
[c] Estimated from the onset of the first absorption band.
[d] From ref. 11.

against time were nearly linear at low absorbances, showing that the bleaching can be considered as first order in the hydrocarbon. For the conditions employed, this dependence can be attributed to the change in absorbed light intensity. This type of plot is shown in Fig. 3.

The photobleaching quantum yields in 10% carbon tetrachloride solution in ethanol obtained from the initial decrease in hydrocarbon concentration are also given in Table 4. These values were obtained in air. The bubbling of nitrogen only produced a moderate increase in the photobleaching without changing the spectra of the final products significantly. The photobleaching rates depend on the carbon tetrachloride concentration. Plots of the reciprocal rate against the reciprocal carbon tetrachloride concentration are shown in Fig. 4 for anthracene and benzo(α)pyrene.

TABLE 2

Effect of substituents on k_Q in naphthalene derivatives

Substituent	k_Q $(\times 10^9 \text{ M}^{-1} \text{ s}^{-1})$
None	5.7
1-Methoxy	19.8
1-Hydroxy	18.8
1-Acetate	8.25
1-Methyl	5.24
1-Cyano	0.12
2-Methoxy	15.3
2-Hydroxy	14.4
2-Acetate	8.3
2-Methyl	6.5
2-Chloro	1.4
2-Cyano	0.2

Solvent, acetonitrile.

The photobleaching of perylene in acetonitrile was measured under conditions of nearly quantitative singlet quenching (carbon tetrachloride concentration, 0.5 - 10 M) and for these conditions was nearly independent of the carbon tetrachloride concentration.

Triplet quenching experiments for phenanthrene were carried out in acetonitrile by following the triplet decay (monitored at 455 nm [14]) as a function of the added carbon tetrachloride. (These measurements were carried out in the laser facilities of the National Research Council of Canada. A description of the equipment has been given elsewhere [15].) A value of $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for the phenanthrene triplet quenching rate constant.

4. Discussion

4.1. Fluorescence quenching

The quenching of anthracene fluorescence by carbon tetrachloride has been found to be sensitive to the wavelength employed [4], an effect attributed to ground state complexes. The occurrence of these complexes is indicated by curvatures in the Stern–Volmer plots and by changes in the absorption spectra as a function of added carbon tetrachloride. Both effects were absent in the present work for all compounds studied. Furthermore, the measurements were carried out employing excitation light of long wavelengths, where the effect of the complexes is minimal [4], and the $k_Q\tau$ values were independent of the excitation and monitoring wavelengths. The results obtained can then be interpreted in terms of the process

$$^1\text{A} + \text{Cl}_4\text{C} \rightarrow \text{quenching} \tag{2}$$

TABLE 3

Effect of the solvent on k_Q

Compound	Solvent	k_Q ($\times 10^9$ M^{-1} s^{-1})
Fluorene	Acetonitrile	15
	Ethanol (95%)	12
	Cyclohexane	9.5
Naphthalene	Acetonitrile:H$_2$O (3:1)	4.7
	Acetonitrile	5.7
	Ethanol (95%)	3.2
	Tetrahydrofuran	3.6
	Benzene	2.4
	Cyclohexane	0.3
Benz(a)anthracene	Acetonitrile:H$_2$O (3:1)	0.78
	Acetonitrile	0.23
	Ethanol (95%)	0.11
	Tetrahydrofuran	0.09
	Benzene	0.09
	Cyclohexane	0.04
Phenanthrene	Acetonitrile:H$_2$O (3:1)	0.37
	Acetonitrile	0.20 (0.17)[a]
	Ethanol	0.07
	Cyclohexane	0.012
Perylene	Acetonitrile	1.24
	Ethanol	0.34
	Cyclohexane	0.02
Tetracene	Acetonitrile	0.095
	Ethanol	0.043
	Benzene	0.017
	Cyclohexane	0.004
Triphenylene	Acetonitrile	0.07
	Ethanol	0.051
	Cyclohexane	0.028

[a]Obtained from the change in triplet quantum yield.

The values of log k_Q obtained are plotted against the singlet energies in Fig. 5, which shows that a weak correlation exists between log k_Q and the singlet energy; two main factors must be considered, however.

(i) Large values of k_Q are obtained even for some compounds (*e.g.* perylene) whose singlet energies are considerably smaller than the strength of the C—Cl bond (305 kJ mol^{-1}). For these compounds the main quenching reaction path cannot involve a breaking of the C—Cl bond as is found in other systems [1, 8].

(ii) There is a wide scatter in the data and, for a given singlet energy, the values of k_Q can differ by more than two orders of magnitude.

Most of the main departures from the correlation between log k_Q and E_s can be explained in terms of the ionization potentials IP of the donors. For example the large values obtained for perylene, benz(a)anthracene and acenaphthene and the low value of phenanthrene can be at least partially
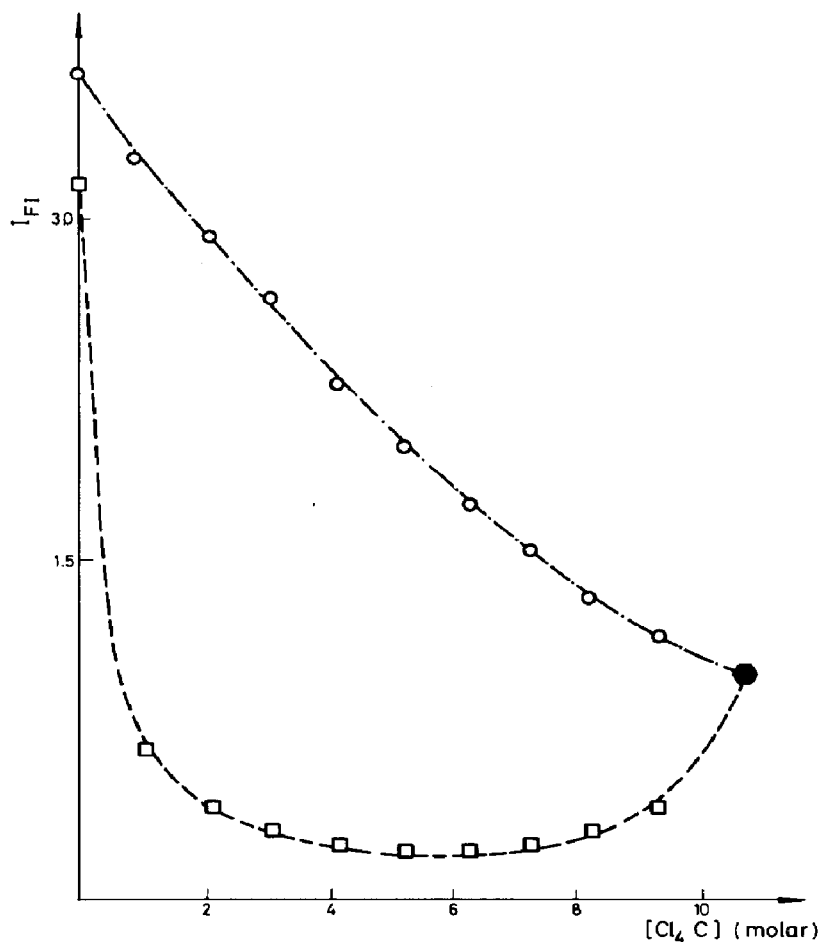
Fig. 2. Change in perylene fluorescence yield as a function of carbon tetrachloride concentration in the following solvents: □, acetonitrile; ○, cyclohexane; ●, bulk carbon tetrachloride.

explained in terms of their ionization potentials (low for perylene, benz(a)-anthracene and acenaphthene and relatively high for phenanthrene). This dependence together with the change in k_Q with the substitution in the naphthalene derivatives (see Table 2) and the change in k_Q with the solvent (see Table 3) suggest a quenching mechanism involving the formation of a charge transfer complex. For this mechanism the values of k_Q, E_s and IP are generally related by an expression such as [1, 2]

$$\ln k_Q = \alpha - \frac{\beta(\text{IP}_D - \text{EA}_A - C - P - E_s)}{kT} \qquad (3)$$

where IP_D is the donor ionization potential, EA_A is the acceptor electron affinity, C is the Coulomb energy and P is the polarization energy of the separated charges. For the quenching of alkyl-substituted benzenes [3] and acetone [1] by carbon tetrachloride a linear relation was found between

TABLE 4

Photobleaching quantum yields

Compound	λ_{irrad}; λ_{monit} (nm)	$\lambda_{isosbestic}$ (nm)	α	$\phi_{bleaching}$ [a]	$\phi_{bleaching}^{\infty}$ [b]
Anthracene	366; 355	384	< 0.1	1.0	1.0
Tetracene	435; 471	c	—	0.17[d]	1.05
Benzo(α)pyrene	366; 383	386	0.22	0.48	0.60
					0.63[e]
Benz(a)anthracene	366; 338	368	< 0.1	0.4	0.60
Benzo(ghi)perylene	366; 380	386, 342	0.4	0.16	0.57
Perylene	366; 434	438, 421, 414	0.36	0.2	0.34
					0.35[e]
Chrysene	313; 318	325	0.21	0.12[f]	0.22
Dibenz(a,h)anthracene	313; 332	c	—	0.036[f]	0.17
Fluoranthene	366; 355	—	—	< 0.01[g]	< 0.06
Phenanthrene	297; 293	296	0.3	≈ 0.04	≈ 0.07
Triphenylene	297; 284	288	h	≈ 0.02	≈ 0.05

[a] Obtained in ethanol as solvent; carbon tetrachloride concentration, 1 M; hydrocarbon concentrations, between 1×10^{-5} and 1×10^{-4} M.
[b] Obtained from eqn. (8).
[c] No significant change in the spectra shape observed during the bleaching.
[d] Obtained employing perylene as a reference and assuming $\phi_{bleaching}$ for this compound at 435 nm is equal to that obtained at 366 nm.
[e] From Fig. 4.
[f] Obtained employing benz(a)anthracene as a reference and assuming $\phi_{bleaching}$ for this compound at 313 nm is equal to that obtained at 366 nm.
[g] No measurable bleaching observed.
[h] Conversion too low to allow an estimation of α.

In k_Q and $IP_D - E_s$, implying that $C + P$ can be considered as nearly constant (or at least proportional to $IP_D - E_s$). The data given in Table 1 show only an extremely weak correlation between $\log k_Q$ and $IP_D - E_s$. This can be due either to a different quenching mechanism or to the assumptions involved in expecting a linear relation between $IP_D - E_s$ and $\log k_Q$. With regard to the first possibility, the effect of substituents and the effect of the solvent would strongly support a quenching mechanism involving a complex with significant charge separation. The data of Table 2 show that, for the naphthalene derivatives, there is a noticeable increase in k_Q when the donor capacity of the substituent increases. This change is much larger than that expected from the possible changes in E_s (by comparison with Fig. 5) and can be ascribed to changes in IP_D. Naphthalene and naphthalene derivatives can be assumed then to quench carbon tetrachloride, as do benzene derivatives [1], by a charge transfer mechanism.

The data of Table 3 are also compatible with a quenching mechanism involving significant charge separation. This table shows that, for the donors considered, there is a noticeable increase in k_Q when the dielectric constant of the solvent increases. It is interesting to note that for the same donors
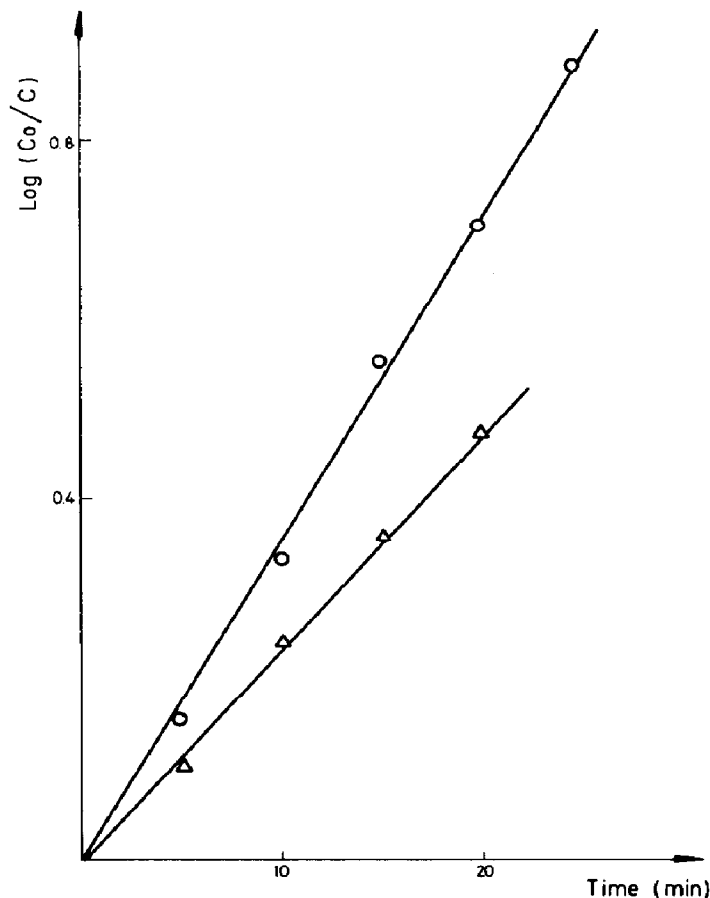
Fig. 3. Plot of log (C_0/C) (from eqn. (1)): O, anthracene; △, benzo(α)pyrene.

there is no dependence of k_Q on the solvent when di-*tert*-butyl peroxide, which quenches by a different mechanism, is employed as quencher [16].

The absence of a linear relationship between log k_Q and $IP_D - E_s$ can be explained in terms of the requirements that must be fulfilled in order to obtain this type of correlation. It is assumed in eqn. (2), through the term IP_D, that an electron is totally removed from the donor. This is an extreme assumption. Regarding this point it is interesting to note that our results indicate that a change in E_s is more significant than a similar change in IP. Our values of log k_Q could be correlated better with $\alpha IP - E_s$ where α is a factor smaller than unity. For example, if α is taken as 0.7, a reasonably good correlation is obtained that even includes the available data for the quenching of triplet states (Fig. 6). The scatter observed in this figure can be explained by the implicit assumption that the term $C + P$ is nearly constant. When the donors change as much as they do in the present work, this assumption cannot be valid since both the polarizability of the molecule and the coulombic interaction must depend on the molecular characteristics. In conclusion, we consider that the dominant quenching pathway involves a mechanism of partial charge transfer from the aromatic donor to the carbon
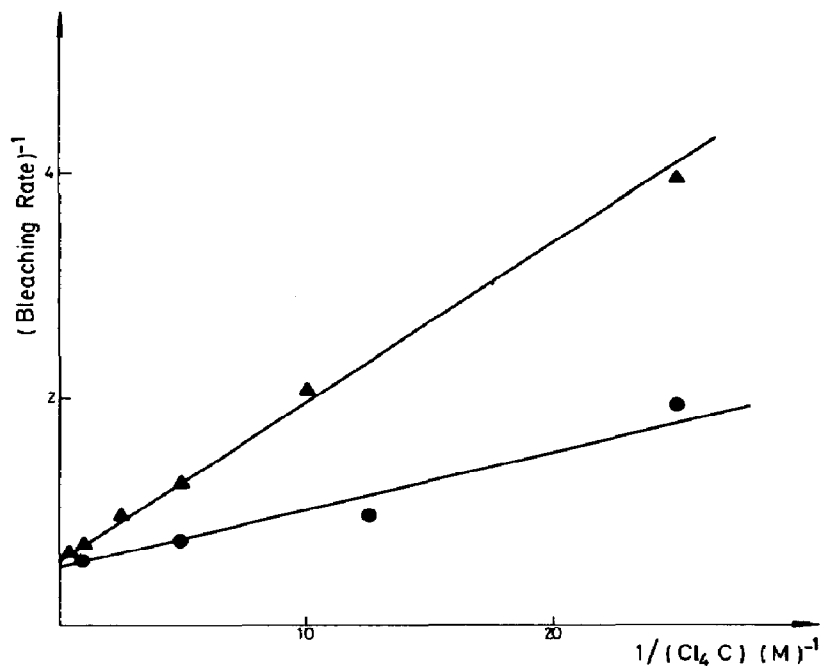
Fig. 4. Plot of the inverse photobleaching rate (in arbitrary units) against the inverse of the carbon tetrachloride concentration: ●, anthracene; ▲, benzo(α)pyrene.
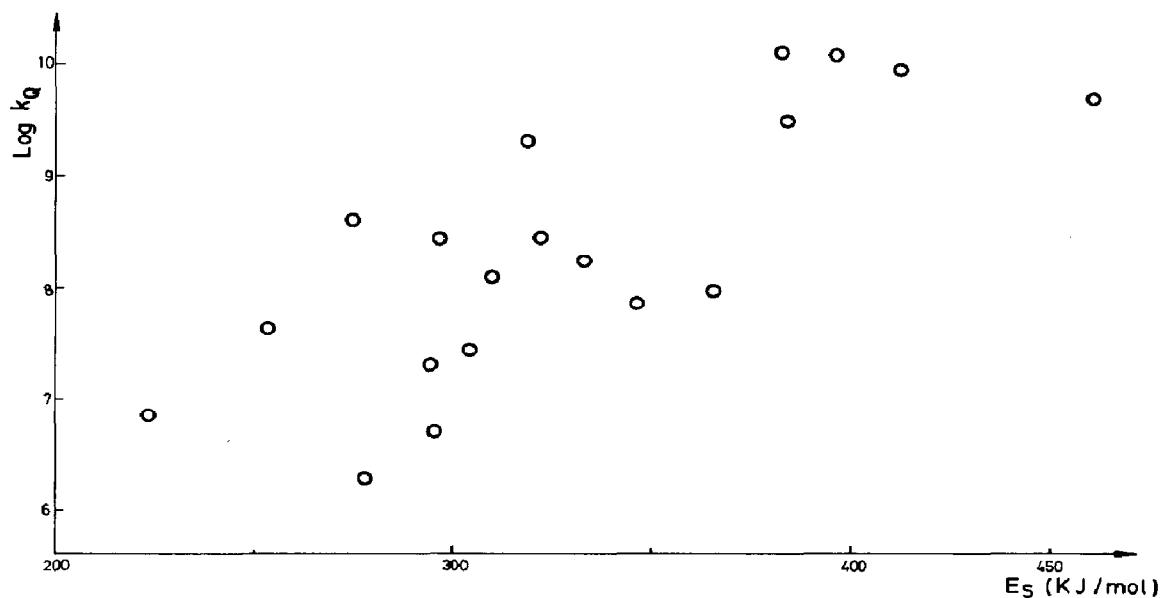

Fig. 5. Plot of log k_Q against the donor's singlet energy.

tetrachloride, as previously proposed for benzene [3] and anthracene [4], and that the poor correlation between log k_Q and $IP_D - E_s$ does not invalidate this conclusion. The fact that the available triplet data show a similar dependence on the ionization potential and excited state energy of the donor
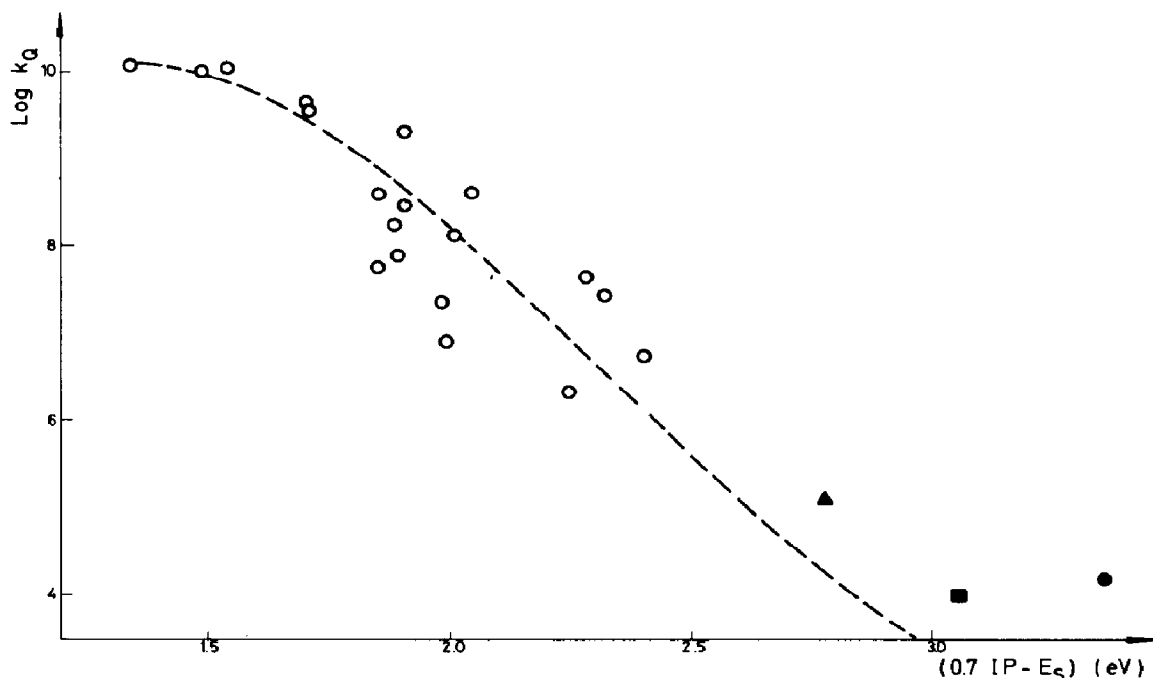
Fig. 6. Plot of log k_Q against $0.7 \mathrm{IP} - E_s$: ▲, triplet naphthalene in cyclohexane [17]; ●, triplet anthracene in benzene [5]; ■, triplet phenanthrene in acetonitrile (this work).

suggests that triplet quenching also takes place by a similar mechanism. Nevertheless, it has to be considered that the data for naphthalene and anthracene were obtained in non-polar solvents, where the rate of quenching can be considerably slower than in ethanol. In spite of this, the data, particularly those for anthracene, clearly lie above the best fit for the singlet processes. This difference can be explained in terms of the lower energy of the triplet intermediate and could be significant since only partial charge transfer takes place at the critical configuration.

The results of Fig. 3 show that an increase in the quencher concentration in acetonitrile beyond approximately 5 M increases the fluorescence intensity and hence the singlet lifetime. A similar dependence has been observed in other systems [18] and has been explained in terms of a change in the rate of the unimolecular photoprocesses induced by the change in solvent. In the present system these results can again be explained in terms of a "solvent effect" of the quencher. At very high carbon tetrachloride concentrations its effect as solvent (and the decrease in k_Q due to the decrease in polarity) is more significant than the change in quencher concentration (i.e. $k_Q[Q]$ decreases when $[Q]$ increases). The data obtained with cyclohexane as solvent are also compatible with this explanation.

4.2. Photobleaching

The photobleaching of anthracene has been attributed to a singlet reaction [5].

The results obtained in the present work confirm this conclusion. A simple mechanism comprising the reactions

$$A + h\nu \rightarrow {}^1A \tag{4}$$

$${}^1A \rightarrow A + h\nu \tag{5}$$

$${}^1A \rightarrow {}^3A \tag{6}$$

$${}^1A + Cl_4C \rightarrow \text{bleaching} \tag{2}$$

leads to

$$\frac{1}{\text{rate}} = a + \frac{a}{k_Q\tau} \frac{1}{[Cl_4C]} \tag{7}$$

The rate of photobleaching was measured, as a function of carbon tetrachloride concentration, using anthracene, benzo(α)pyrene and perylene. The data obtained fitted eqn. (7) (see Fig. 4 for the data obtained for anthracene and benzo(α)pyrene). The values of $k_Q\tau$ obtained by this method (9.3 M^{-1}, 4.1 M^{-1} and 1.46 M^{-1} for anthracene, benzo(α)pyrene and perylene respectively) are in complete agreement with those obtained from fluorescence measurements (see Table 1). This agreement indicates that, under our experimental conditions, only photobleaching from the excited singlet is taking place. Furthermore, the moderate increase in the photobleaching rates when air is excluded is also compatible with a predominantly singlet photoreaction.

The values of $\phi_{\text{bleaching}}$ given in Table 4 were obtained under conditions of partial singlet quenching. The values under conditions of total quenching can be obtained by extrapolation to infinite carbon tetrachloride concentration (see Fig. 4) or by using the equation
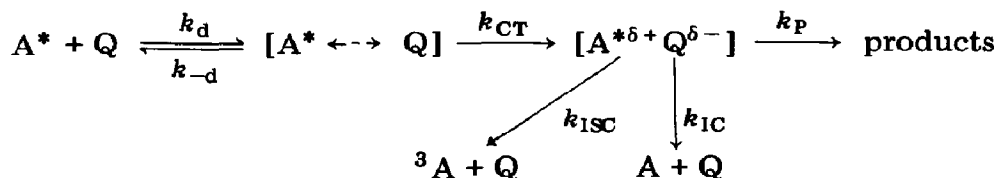
$$(\phi_{\text{bleaching}})_{\infty} = \phi_{\text{bleaching}} \left(1 + \frac{1}{k_Q\tau[Q]}\right) \tag{8}$$

The values obtained using eqn. (8) are also given in Table 4. They agree satisfactorily with those obtained by extrapolation to infinite carbon tetrachloride concentration.

The values of $\phi_{\text{bleaching}}$ obtained do not show a simple relationship with the singlet energy, the ionization potential or the value of k_Q. Furthermore, the fact that $\phi_{\text{bleaching}}$ for perylene is almost the same in 0.5 M carbon tetrachloride in acetonitrile up to pure carbon tetrachloride shows that the bleaching rate under conditions of nearly total quenching is not affected by the solvent polarity. However, the results obtained for the acenes and their derivatives can be explained in terms of differences in the para-localization energies for a transannular addition [19]. Similarly, the lack of fluoranthene photobleaching can also be explained in terms of its large aromaticity. The trend in photobleaching therefore parallels the Diels—Alder reactivity [19]. In

this respect it is interesting to note that the same conclusion can be reached for the rate of photo-oxidation of aromatic hydrocarbons [19, 20].

Thus the present results can be explained in terms of the following simplified scheme:

$$A^* + Q \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [A^* \leftarrow \rightarrow Q] \xrightarrow{k_{CT}} [A^{*\delta+}Q^{\delta-}] \xrightarrow{k_P} \text{products}$$

with branches labeled k_{ISC} leading to $^3A + Q$ and k_{IC} leading to $A + Q$.

where the complex $A^{\delta+}Q^{\delta-}$ involves partial charge transfer. The quenching rate given by

$$k_Q = k_d \frac{k_{CT}}{k_{CT} + k_{-d}}$$

depends on the singlet energy and partially on the ionization potential of the hydrocarbon. Furthermore, it increases when the solvent polarity increases. However, the photobleaching quantum yield for total quenching given by

$$\phi^{\infty}_{\text{bleaching}} = \frac{k_P}{k_P + k_{IC} + k_{ISC}}$$

correlates, at least for the acene derivatives, with the same parameters as the 1,4-Diels–Alder addition and can be considered as nearly solvent independent.

Further discussion of the photobleaching mechanism requires a complete analysis of the photoproducts. This type of work is at present being pursued in our laboratory.

For some of the compounds considered, particularly phenanthrene, fluoranthene and triphenylene, most of the quenching processes are unreactive. This means that $k_{IC} + k_{ISC} \gg k_P$. In order to evaluate the relative relevance of k_{IC} and k_{ISC} for phenanthrene we measured the change in the triplet quantum yield as a function of carbon tetrachloride concentration [14]. This type of measurement allows an evaluation of k_Q and ϕ_T and, by extrapolation to infinite carbon tetrachloride concentration, of $k_{ISC}/(k_{ISC} + k_{IC} + k_P)$. The value of k_Q obtained is included in Table 3 and agrees with that obtained by fluorescence quenching. The ϕ_T obtained at high carbon tetrachloride concentrations indicates that less than 5% of the quenching leads to assisted intersystem crossing. We can then conclude that, in the absence of photoreduction, assisted internal conversion is the main decay path of the intermediate. A similar result has been obtained in the quenching of 2,5-diphenyl oxazole singlets by carbon tetrachloride [6].

Acknowledgment

Thanks are given to Dr. J. C. Scaiano for allowing us the use of his laser photolysis equipment.

References

1 R. O. Loufty and A. C. Somersall, *Can. J. Chem.*, *54* (1976) 760.
   J. O. Paulik, P. I. Plocard, A. C. Somersall and J. E. Guillet, *Can. J. Chem.*, *51* (1973) 1435.
2 J. Klein, V. P. Plazanet and G. Laustriat, *J. Chim. Phys. Phys.-Chim. Biol.*, *67* (1970) 302.
3 D. Soperstein and E. Levin, *J. Chem. Phys.*, *62* (1975) 3560.
4 W. R. Ware and C. Lewis, *J. Chem. Phys.*, *57* (1972) 3546.
5 F. A. Carroll and D. G. Whitten, *J. Phys. Chem.*, *80* (1976) 2046.
6 T. Takahashi, K. Kikuchi and H. Kokubun, *J. Photochem.*, *14* (1980) 67.
7 S. Kusuhara and R. Hardwick, *J. Chem. Phys.*, *41* (1964) 2386, 3943.
8 E. A. Lissi and M. V. Encina, *J. Photochem.*, 3 (1974) 237.
9 J. C. Scaiano, E. Lissi and M. V. Encina, *Rev. Chem. Intermed.*, 2 (1978) 139.
10 R. M. Edges and F. A. Madsen, *J. Chem. Phys.*, *28* (1958) 950.
11 R. Morales, *Thesis*, Universidad de Chile, 1981.
12 J. B. Birks and I. H. Munro, *Prog. React. Kinet.*, *4* (1967) 239.
13 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.
14 E. J. Land, *Proc. R. Soc. London, Ser. A*, *305* (1968) 457.
15 R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, *82* (1978) 2064.
16 M. V. Encina and E. A. Lissi, to be published.
17 S. Ander, H. Blume, G. Heinrich, D. Schulte-Frohlinde, *J. Chem. Soc., Chem. Commun.*, (1968) 745.
18 J. C. Scaiano, *J. Am. Chem. Soc.*, *102* (1980) 7747.
19 D. Biermann and W. Schmidt, *J. Am. Chem. Soc.*, *102* (1980) 3163, 3173.
20 B. Stevens, S. R. Pérez and J. A. Ors, *J. Am. Chem. Soc.*, *96* (1974) 6846.