

## SOLVENT EFFECT ON THE DEACTIVATION OF EXCITED NAPHTHALENE DERIVATIVES BY UNSATURATED COMPOUNDS

M. V. ENCINAS and E. A. LISSI

*Departamento de Química, Facultad de Ciencia, Universidad de Santiago de Chile, Santiago (Chile)*

(Received April 30, 1984; August 13, 1984)

### Summary

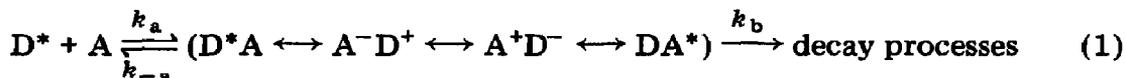
The quenching rate constants for the deactivation of several naphthalene derivatives by a wide range of unsaturated compounds have been measured in various solvents ranging from *n*-hexane to water. The magnitude of the dependence of the rate on the solvent is determined by the extent of the dipolar contribution to the exciplex stability. For processes between excited aromatics and quenchers of widely different electron affinity, the quenching rate constant changes by more than two orders of magnitude on going from non-polar to highly polar solvents. In polar solvents the quenching rate constants measured in aprotic and protic solvents and in aqueous mixtures correlate with the  $E_T(30)$  number of the solvent.

### 1. Introduction

The interaction of excited aromatic hydrocarbons with mono-olefins and diolefins has been investigated for several years [1]. These systems constitute a classic example of excited state quenching mediated by exciplex formation [2].

Relevant questions to be answered for such systems are how the quenching rate constants depend on the characteristics (*i.e.* excitation energy and multiplicity, ionization potential and electron affinity) of the donor and acceptor, and how it is affected by the properties of the medium in which the process is carried out [3 - 18]. This information is required for the evaluation of the contribution of charge transfer structures to the stability of the excited intermediate. Furthermore, a more complete description of the system must clarify which properties (*i.e.* lifetime, fluorescence yields and photoreaction paths and yields) are due to the exciplex [5, 7, 9, 10, 12 - 14, 19, 20] and which are due to the bimolecular processes (such as exciplex quenching) in which the intermediate can participate [21].

The quenching of an excited aromatic compound by an acceptor whose excited energy lies above that of the donor can be represented by the simplified equation



where  $k_b$  includes all irreversible decay processes. The relative contribution of structures such as  $A^-D^+$  and/or  $D^-A^+$  to the stability of the exciplex intermediate depends upon the relative electron-acceptor and electron-donor properties of the excited aromatic and the quencher. Most of the systems investigated were assumed to interact mainly through exciplexes dominated either by  $A^-D^+$  [6, 10, 12] or  $A^+D^-$  [3 - 5, 8, 9, 12, 13, 21 - 23] contributions but the turning point (*i.e.* the point at which the mechanism changes [12, 24, 25]) was not characterized. The other unresolved aspect of the interaction is the role played by the solvent, and the possible relationship between the quenching rate and the solvent properties as a function of the relative contributions of the structures depicted in eqn. (1). The early work of Taylor and Hammond [11] has shown that, as in thermal reactions [26], the extent of the effect of the solvent upon the quenching rate constant can be employed as a rough indication of the contribution of charge transfer structures (either  $D^+A^-$  or  $D^-A^+$ ) to the exciplex stability. Nevertheless, later investigations of other systems that also interact by charge transfer mechanisms [9, 24, 25, 27 - 29] indicate that the degree of solvent dependence of the quenching rate constant is only poorly related to the polarity of the excited intermediate. Furthermore, in those systems where the quenching process is solvent dependent, the solvent property that determines the quenching rate constant seems to depend on the donor-acceptor pair under consideration [30 - 34].

The present work was carried out with two aims: first, to find the dependence of the singlet quenching rate constants of several naphthalene derivatives on the quencher characteristics of a variety of unsaturated compounds ranging from electron-rich olefins (*e.g.* 2,5-dimethyl-2,4-hexadiene) to electron-deficient olefins (*e.g.* dicyanoethylene), and secondly to evaluate the solvent dependence of the measured rates over a wide range of solvents and solvent mixtures (from *n*-hexane to water).

## 2. Experimental details

2,3-Dimethylnaphthalene (DMN), naphthalene (N), 2-methoxy naphthalene (2-MON), 2-cyanonaphthalene (2-CN) and 1-cyanonaphthalene (1-CN) were purchased from Aldrich and were purified by vacuum sublimation. The quenchers employed were of the highest purity commercially available. They were vacuum distilled prior to use.

The singlet quenching rate constants were determined by measuring the donor fluorescence intensity as a function of the quencher concentration. These measurements were carried out in air or in nitrogen-bubbled solutions at room temperature using a Perkin-Elmer LS-5 spectrofluorometer.

The singlet lifetimes  $\tau_s$  of 1-CN, 2-CN, N and 2-MON were taken from the literature [10, 11, 13, 19]. The values of  $\tau_s$  for DMN in those solvents where literature data were unavailable were derived from the relative fluorescence intensities in the solvent considered and a reference solvent with known  $\tau_s$ . Benzene ( $\tau_s = 78$  ns) [35] was employed as the reference for non-protic solvents and ethanol ( $\tau_s = 78$  ns) [36] was used for protic solvents or solvent mixtures. The fluorescence yields were corrected to take into account differences in the refractive indices of the solvents considered:

$$\tau = \tau_{\text{ref}} \frac{\phi_{f1}}{(\phi_{f1})_{\text{ref}}} \left( \frac{f_{\text{ref}}}{f} \right)^2$$

where  $f$  is the refractive index of the solvent and  $f_{\text{ref}}$  is the refractive index of the reference solvent. In this method it is assumed that the fluorescence rate constant is independent of the solvent. This assumption is supported by the small change in  $k_{f1}$  found for several methyl-substituted naphthalenes when the solvent is changed from a hydrocarbon to 96% ethanol [35].

The concentrations of the naphthalene derivatives were always less than  $10^{-3}$  M.

### 3. Results and discussion

The relative contributions of  $D^-A^+$  and  $D^+A^-$  to the exciplex stability depend on the donor and acceptor properties of D and A, and can be determined for a given A from the effect of substituents in D and for a given  $D^+$  from the effect of the double-bond electronic density upon the exciplex stability. This stability can be measured by the exciplex enthalpy of formation [13 - 15] and has been related to the position of the exciplex fluorescence band [5, 9, 22]. From the simplified kinetic scheme given in eqn. (1), the experimental quenching constant  $k_Q$  is given by

$$k_Q = k_a \frac{k_b}{k_{-a} + k_b} \quad (2)$$

Since the value of  $k_a$  is generally large and near the diffusion-controlled limit [12 - 15], the rate of the quenching process will be determined by  $k_b/k_{-a}$  and can be expected to increase when the stability of the exciplex increases (owing to a decrease in  $k_{-a}$ ) and/or when the rate of the deactivation processes (measured by  $k_b$ ) increases.  $k_Q$  values for the quenching of the 2-CN singlet by several unsaturated compounds in ethanol are given in Table 1. The quenching rate constants obtained for N, DMN and 2-MON are also given in Table 1. These values are given relative to those measured with 2-CN.

The results shown in Table 1 allow exciplexes in which  $D^+A^-$  contributions predominate to be distinguished from those in which  $D^-A^+$  contributions predominate. This distinction can be made in terms of the relative

TABLE 1

 $k_Q$  values obtained in ethanol at 25 °C

Quencher	Ionization potential (eV)	$(k_Q)_{2-CN}$ ( $\times 10^9 M^{-1} s^{-1}$ )	$(k_Q)_N^a$ ( $\times 10^9 M^{-1} s^{-1}$ )	$(k_Q)_{DMN}^a$ ( $\times 10^9 M^{-1} s^{-1}$ )	$(k_Q)_{2-MON}^a$ ( $\times 10^9 M^{-1} s^{-1}$ )
2,5-Dimethyl-2,4-hexadiene	7.84	10.1	—	0.15	0.14
2,3-Dimethyl-2-butene	8.42	5.5	0.003	0.005	0.02
Vinyl pyrrolidone	—	5.5	0.03	0.006	0.024
Styrene	8.47	4.4	0.027	0.03	0.1
cis-1,3-Pentadiene	8.65	5.0	—	—	—
Isoprene	8.85	1.9	0.012	0.009	0.011
Cyclopentene	9.01	0.23	—	0.14	0.23
Cyclohexene	9.1	0.1(0.25 <sup>b</sup> )	—	0.08	0.044
2-Hexene	9.15	0.063	—	—	—
trans-3-Hexene	9.14	0.01	—	0.8	0.70
Vinyl acetate	9.19	0.028	—	0.38	0.57
1-Hexene	9.46	<0.006	—	—	—
n-Butyl methacrylate	—	0.055	2.0	6.5	18
Methyl methacrylate	—	0.056	1.9	7.7	20
Tetrachloroethylene	9.32	0.071	1.13	3.9	11.2
Trichloroethylene	9.45	0.04	—	1.0	1.7
trans-Dichloroethylene	9.65	0.012	—	1.1	1.2
Dibutyl maleate	—	2.1	—	3.3	3.9
Acrylonitrile	10.9	0.010	4.3	28	100
Methacrylonitrile	—	0.008	—	64	54
Fumarionitrile	11.16	7.0	—	1.14	1.5

<sup>a</sup> Values relative to that of 2-CN.<sup>b</sup> Value obtained employing 1-CN.

values obtained, for a given quencher, when substituted naphthalenes with various electron affinities are considered. For those quenchers with  $(k_Q)_{2-CN}$  values larger than the quenching rate constants obtained for the other naphthalene derivatives, it can be considered that a charge transfer complex ( $CN^-A^+$ ) dominates the exciplex [12, 24, 27]. In contrast, when  $(k_Q)_{DMN}$  and  $(k_Q)_{2-MON}$  are larger than  $(k_Q)_N$  and  $(k_Q)_{2-CN}$ , it can be considered that, at least for the former compounds, the aromatic compounds act as electron donors [24, 27]. The exciplex structure of olefins with intermediate ionization potentials (IPs) (about 9.20 eV) will be determined by the aromatic electronegativity. Vinyl acetate (IP, 9.19 eV) and *trans*-3-hexene (IP, 9.14 eV) show similar  $k_Q$  values with 2-CN and 2-MON. Therefore it can be considered that polar structures play only a minor role in these compounds and/or that the main contributors to 2-CN quenching are the  $2-CN^-A^+$  structures, whereas  $2-MON^+A^-$  predominates in the quenching of 2-MON. The small magnitude of the solvent effect on  $k_Q$  (see Section 4) observed in these systems is compatible with these considerations.

The quenching mechanism can also be inferred from the dependence of  $k_Q$  on the IP of the quencher. The data obtained in the quenching of 2-CN are plotted against the olefin IP in Fig. 1. These data show that, for quenchers of low IP,  $k_Q$  decreases when the quencher IP increases. However, no correlation of  $k_Q$  with the IP of the quencher is observed for quenchers with IPs above about 9.2 eV. The quenching rate for these olefins can be expected to correlate with the electron affinity of the quencher. This type of dependence is shown in Fig. 2 for 2-MON. A similar correlation is ob-

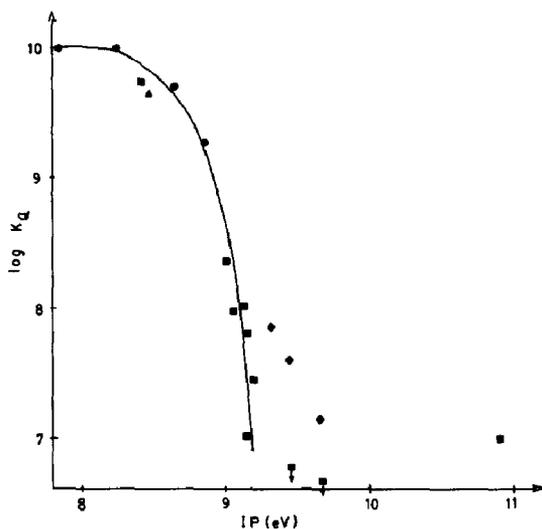


Fig. 1. Dependence of the quenching of 2-CN fluorescence by unsaturated compounds on the quencher IP (solvent, ethanol): ■, mono-olefins; ●, diolefins; ▲, styrene; ◆, chloroethylenes.

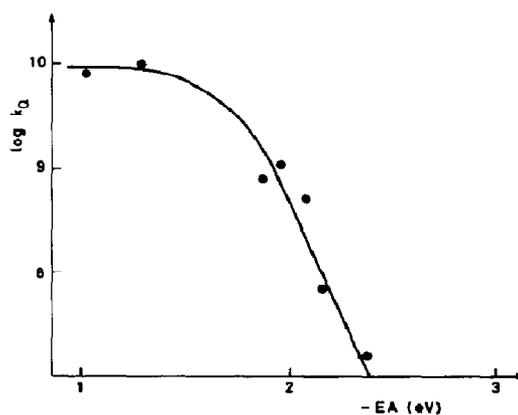


Fig. 2. Dependence of the quenching of 2-MON fluorescence on the quencher electron affinity.

served in the quenching of DMN. In contrast, the data obtained for 2-CN correlate very poorly with the quencher electron affinities. In particular, it should be noted that the chloroethylenes are considerably faster quenchers than acrylonitrile despite their smaller electron affinities.

The data given in Fig. 1 show that mono-olefins, diolefins and styrene show similar behaviour. This implies that only the  $D^*A$  and  $D^-A^+$  structures determine the quenching rate and that no significant role is played by  $DA^*$ .

#### 4. Dependence of $k_Q$ on the solvent polarity

The dependence of  $k_Q$  on the solvent was evaluated for several excited aromatic-quencher pairs over a wide range of solvents. The systems studied comprised exciplexes dominated by  $D^+A^-$  contributions (*i.e.* DMN-butyl methacrylate and DMN-acrylonitrile) and exciplexes dominated by  $D^-A^+$  contributions (*i.e.* 1-CN-cyclohexene). Some measurements were also carried out for systems where the exciplex could comprise several contributions of similar weight (*i.e.* DMN-*trans*-3-hexene and DMN-vinyl acetate). In these systems the effect of the solvent upon  $k_Q$  is very small. For example, for DMN and *trans*-3-hexene  $k_Q$  changes by less than a factor of 2 when the solvent changes from *n*-heptane to acetonitrile or ethanol. Similarly, the quenching rate constant for the deactivation of DMN by vinyl acetate in *n*-hexane was almost identical with that measured in methanol or in a 60vol.%methanol-40vol.%water mixture.

Systems containing an electron-rich aromatic and an electron-deficient olefin show a strong solvent dependence. For example, the rate constant for the quenching of DMN by butyl methacrylate changes from  $10^7 \text{ M}^{-1} \text{ s}^{-1}$  in *n*-hexane to  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in 50vol.%methanol-50vol.%water. This change is even larger than that observed in the deactivation of 2-methylnaphthalene by *N*-methylpiperidine [37], and is among the largest observed in bimolecular photoprocesses taking place through exciplex intermediates.

The systems considered in the present work are unlikely to undergo specific interactions with the solvent (*i.e.* to form hydrogen bridges) and thus allow the processes in protic and aprotic solvents to be compared. The values of  $k_Q$  measured for these systems correlate poorly with most factors generally employed to characterize the solvent such as the macroscopic dielectric constant [32], the vibrational structure of pyrene absorption bands [38], the dipolar moment of the solvent [31] and the polarity-polarizability parameter of the solvent [39]. When correlations between  $k_Q$  and these parameters were attempted the protic solvents showed  $k_Q$  values considerably larger than those predicted from the dependence observed in aprotic solvents. The data obtained correlated much better with empirical spectroscopic parameters such as that derived from the solvatochromic band of pyridinium-*N*-phenolbetaine [26, 40]. In terms of this effect the solvent is characterized by its  $E_T(30)$  value which is defined as the transition energy (in kilocalories per mole) of the probe intramolecular charge transfer band.

The relationship between  $\log k_Q$  and  $E_T(30)$  is shown in Figs. 3 and 4 for the DMN-acrylonitrile and DMN-*n*-butyl methacrylate systems. In these figures we have plotted  $\log k_Q$  instead of the more usual relationship  $\log k_Q/(k_{dif} - k_Q)$  owing to the lack of  $k_{dif}$  values for several of the solvent mixtures employed. In any case a plot of  $\log \{k_Q/(k_{dif} - k_Q)\}$  would further increase the solvent dependence observed at high  $E_T(30)$  values. The value of  $k_Q$  for the DMN-acrylonitrile pair measured in water ( $(3.5 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) was not included in Fig. 3 since it implies that the process is almost diffusion controlled. The data could also be correlated, at least for the pure solvents, in terms of the solvent acceptor numbers or Kosover's  $Z$  parameter since they vary linearly with the  $E_T(30)$  parameter [40, 41]. The following discussion will be based on the  $E_T(30)$  parameter owing to the fact that it has been measured for the solvent mixtures employed in the present work.

The data shown in Figs. 3 and 4 are for protic and aprotic solvents as well as for water-protic solvent and water-aprotic solvent mixtures [42]. A clear relationship between  $\log k_Q$  and  $E_T(30)$ , particularly at large  $E_T(30)$  values, is observed in both systems considered. The  $E_T(30)$  value is one of the scales most generally used to characterize the solvent [26] but has only been applied to correlate photochemical data involving intramolecular charge transfer processes [30, 31, 43]. The betaine dye exhibits (i) a large permanent dipole moment suitable for detecting dipole-dipole and dipole-induced dipole interactions between solute and solvent, (ii) a large polarizable  $\pi$  electron system suitable for detecting dispersion interactions

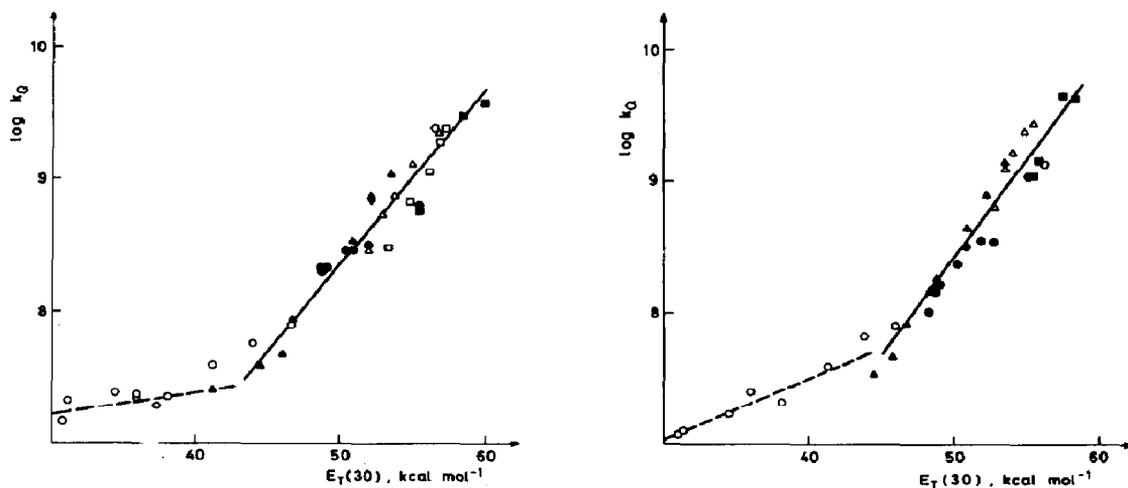


Fig. 3. Dependence of the rate constant for the quenching of DMN by acrylonitrile on the solvent parameter  $E_T(30)$ :  $\circ$ , non-protic solvents;  $\bullet$ , protic solvents;  $\blacksquare$ , water-methanol mixtures;  $\triangle$ , water-ethanol mixtures;  $\square$ , water-acetonitrile mixtures;  $\blacktriangle$ , water-dioxane mixtures;  $\blacklozenge$ , water-dimethylformamide.

Fig. 4. Dependence of the rate constant for the quenching of DMN by *n*-butyl methacrylate on the solvent parameter  $E_T(30)$ :  $\circ$ , non-protic solvents;  $\bullet$ , protic solvents;  $\blacksquare$ , water-methanol mixtures;  $\triangle$ , water-ethanol mixtures;  $\blacktriangle$ , water-dioxane.

and (iii) a highly basic electron pair donor centre (the phenolic oxygen atom) suitable for specific hydrogen-bond interactions with protic solvents. This last characteristic makes the  $E_T(30)$  value strongly dependent on the solvent hydrogen bonding power [31]. The fact that the present  $k_Q$  values correlate with the  $E_T(30)$  parameter could imply that the quenching rate constant is also sensitive to the capacity of the medium to form hydrogen bridges. This is a rather unexpected finding for a process involving an aromatic compound and an olefin. Nevertheless, Bowman *et al.* [10] have concluded from results obtained in the quenching of naphthalene by acrylonitrile in acetonitrile and *tert*-butanol that the exciplex must undergo some specific types of interaction that only hydroxylic solvents can provide. An alternative explanation could be sought in the smaller entropy change required to orientate, in the surroundings of a dipolar exciplex, a protic solvent that has a much higher degree of order than an aprotic solvent [13].

The data given in Figs. 3 and 4 were obtained from pure solvents and aqueous mixtures. The  $E_T(30)$  values of the mixtures approximately follow the percentage of water, and the  $k_Q$  values closely follow the behaviour of the  $E_T(30)$  parameter. The  $E_T(30)$  values of mixtures of alcohols and aprotic solvents (*i.e.* methanol-acetonitrile and methanol-dimethylformamide) are much larger than those of the pure solvents [42, 44]. This unusual behaviour is not shown by the quenching data since in these mixtures  $\log k_Q$  changes almost linearly with the volume percentage of the protic solvent.

The plot of  $\log k_Q$  versus  $E_T(30)$  gives, at large  $E_T(30)$  values, slopes of  $0.15 \text{ kcal}^{-1}$  and  $0.11 \text{ kcal}^{-1}$  for butyl methacrylate and acrylonitrile respectively.

The linear relationship between  $\log k_Q$  and  $E_T(30)$  breaks down for solvents characterized by low  $E_T(30)$  values. This is particularly noticeable for the DMN-acrylonitrile system in which changing the solvent from *n*-hexane ( $E_T(30) = 31$ ) to ethyl acetate ( $E_T(30) = 38$ ) barely modifies  $k_Q$ . Similar behaviour has been found in other systems containing dipolar exciplexes. For example, Kuzmin *et al.* [27] measured the rates of 1,2-benzanthracene triplet quenching by *p*-bromonitrobenzene in 27 solvents ranging from *n*-pentane to formamide and found that the values of  $k_Q$  were almost solvent independent up to  $E_T(30)$  values of 38. A close relationship between  $\log k_Q$  and  $E_T(30)$ , with a slope of  $0.097 \text{ kcal}^{-1}$ , was obtained at higher  $E_T(30)$  values.

The dependence of  $k_Q$  on the solvent for systems involving exciplexes with significant  $D^-A^+$  contributions is shown in Figs. 5 and 6. These figures show that the magnitude of the solvent effect on  $k_Q$  is related to the difference between the electron affinities of the donor and the quencher. The  $k_Q$  for the 1-CN-cyclohexene pair changes by nearly two orders of magnitude and exhibits fair correlation with the  $E_T(30)$  parameter of the solvent. No change in the  $k_Q$  of the DMN-1,3-octadiene system is observed on going from *n*-hexane to acetonitrile, but a moderate increase in  $k_Q$  with  $E_T(30)$  values is obtained for solvents with higher  $E_T(30)$  values.

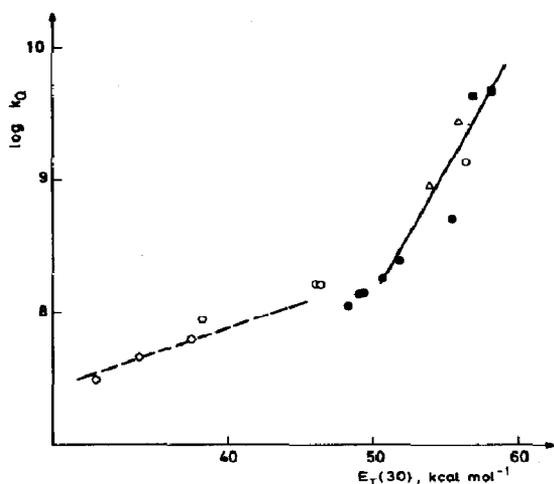


Fig. 5. Solvent dependence of  $k_Q$  for the quenching of 1-CN by cyclohexene: O, non-protic solvents; ●, protic solvents; Δ, ethanol-water mixtures; ■, methanol-water mixtures.

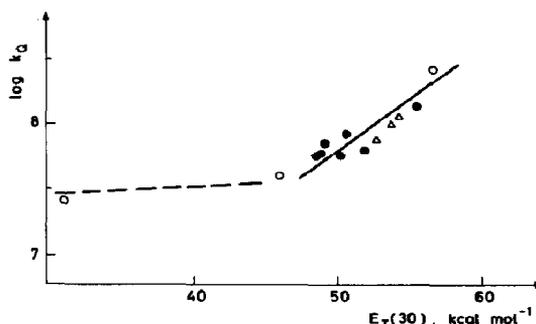


Fig. 6. Solvent dependence of  $k_Q$  for the quenching of DMN by 1,3-octadiene: O, non-protic solvents; ●, protic solvents; Δ, water-ethanol mixtures.

It can be concluded from the previous discussion that in those systems where a noticeable solvent dependence of  $k_Q$  is observed the best correlation is obtained between  $\log k_Q$  and the  $E_T(30)$  parameter of the solvent. The onset of the dependence is related to the difference between the electron affinities of the donor and the quencher, and takes place at higher  $E_T(30)$  values as this difference decreases. In some systems no significant solvent effect is observed over the whole range of solvents employed. Since the  $E_T(30)$  value is a measure of the capacity of the solvent to stabilize dipolar structures, the increase in the quenching rate with the solvent  $E_T(30)$  number may be due to a slower rate of back exciplex dissociation and/or to faster exciplex decay to produce an ion pair. The contribution of ion pair formation to the exciplex lifetime (and hence to  $k_Q$ ) has been found to be significant in very polar solvents [45].

In solvents with reduced polarity radical ion formation ceases to be an important degradation pathway [46] and the main role of the solvent is to stabilize the exciplex, leading to a reduced back dissociation rate. O'Connor and Ware [13] have found that, in the quenching of 1-CN by 1,2-dimethylcyclopentene, the rate constant for the dissociation reaction changes by about two orders of magnitude when the solvent is changed from hexane to ethyl acetate. This change accounts almost completely for the observed differences between the two solvents.

Lewis and Hoyle [9] have performed a detailed study of the effect of the solvent on  $k_Q$  and the behaviour of the exciplex in the deactivation of diphenylvinylene carbonate by 2,5-dimethyl-2,4-hexadiene. These researchers found that increasing the solvent polarity can decrease the rates of the

reactions that deactivate the exciplex. If a similar dependence were present in the system under investigation here, the change in the exciplex back dissociation with the solvent polarity would have to be even larger than that indicated by the observed change in the experimental quenching constant. Nevertheless, it must be considered that the systems studied by Lewis and Hoyle [9] involve exciplexes with only a small degree of charge transfer character.

The marked change in slope observed in the plots of  $\log k_Q$  against the  $E_T(30)$  number of the solvent may indicate a change in the structure of the exciplex [9] or may correspond to the solvent polarity required to make ion pair formation the main decay process for the polar exciplex. The formation of a solvated ion pair in polar solvents could even occur directly without the formation of a transient with a finite lifetime [9, 47]. Different quenching mechanisms in polar and non-polar solvents have also been proposed by Mieus *et al.* [37] for the quenching of 2-methylnaphthalene by aliphatic amines.

### Acknowledgments

We thank Dr. Fernando Ibáñez for measuring the  $E_T(30)$  values in some solvents and solvent mixtures. Financial support from the Dirección de Investigaciones Científicas y Tecnológicas, Universidad de Santiago, and the Fondo Nacional de Ciencias (Grant 515/82) is acknowledged.

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