



SOLVENT EFFECTS AS A DIAGNOSTIC TEST FOR RADIATIONLESS MECHANISMS

Oxygen and nitric oxide singlet and triplet quenching efficiencies of aromatic compounds in polar and nonpolar solvents are reported. Solvent effects depend on the electronic energy of the electronic states, but are only strong for triplet states of high electronic energy. An increase in solvent polarity increases the triplet quenching rate for O_2 and decreases the quenching rate for NO. The results are interpreted in terms of the weak and strong coupling situation of radiationless transitions and reveal that solvent effects can provide a test to distinguish between these two nonradiative cases.

1 — INTRODUCTION

Theories of radiationless transitions reveal that the coupling strength of the nuclear modes in electronic states determines the mechanism of nonradiative processes [1,2]. For small nuclear coordinate displacements (weak coupling case) radiationless transition rate constants decrease with an increase in the energy-gap of the electronic states, *i.e.*, follow a normal energy-gap law. In contrast, for strong coordinate displacements (strong coupling case), radiationless transitions follow an inverse energy-gap law [3]. The elucidation of nonradiative mechanisms is generally based on the electronic energy dependence of the nonradiative rates. However solvent polarity affects the electronic state energies and can also be employed as a tool to distinguish between weak and strong coupling situations.

Fig. 1 presents the potential energy curves of a diatomic oscillator in the ground and in an excited state for weak and strong coupling situations. Increasing solvent polarity is assumed to decrease the energy-gap between the excited and ground states, because, commonly, excited states have an higher charge-transfer character than ground states. For the weak coupling case fig. 1 shows that an increase in solvent polarity leads to a decrease on the barrier of energy and width of the oscillators and, consequently, increases the nonradiative rate constants [2]. For the strong coupling situation the opposite

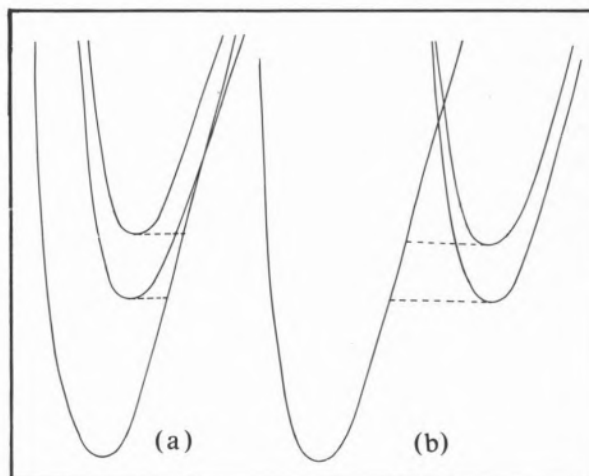


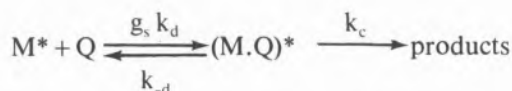
Fig. 1

Relative positions of the potential energy curves in the weak coupling (a) and strong coupling (b) situations

effect is observed since increasing solvent polarity increases the energy barrier and the barrier width Δx and decreases the nonradiative rates. This solvent effect can still be enhanced by an increase of the oscillator displacements with increasing polarity, particularly if the change in bond lengths between ground and excited states is associated with a transfer of charge. Therefore theory predicts opposite solvent effects on nonradiative rates for the weak and strong coupling cases and for the last situation the effect is expected to be of a larger magnitude.

2 — MECHANISMS OF OXYGEN AND NITRIC OXIDE QUENCHING OF AROMATIC MOLECULES

The rates of quenching of excited aromatic molecules by paramagnetic species can depend on molecular parameters [4,5] and this has been interpreted in terms of the following mechanism



where $(M.Q)^*$ is a transient complex between the excited molecule M^* and the quencher Q via which overall spin could be conserved. The quenching rate is given by

$$k_q = g_s k_d \frac{k_c}{k_{-d} + k_c}$$

where g_s is a spin statistical factor, k_d the diffusion rate, k_{-d} the dissociation rate of the complex and k_c the rate of electronic relaxation (internal conversion) of the initially formed excited state of the quenching complex. Fig. 2 presents the relevant electronic states of the quenching complexes. The significant differences between the two quenchers, apart from the spin multiplicity factors, resides in the fact that O_2 has low lying electronic states that can be involved in the quenching process, whereas NO has no such states. The dependence of k_q on molecular parameters is attributed to the radiationless rate constant k_c , because k_d and k_{-d} depend on solvent viscosity, but are virtually independent of the hydrocarbon nature; k_c is weakly dependent on electronic matrix factors [3,6,7] and is strongly

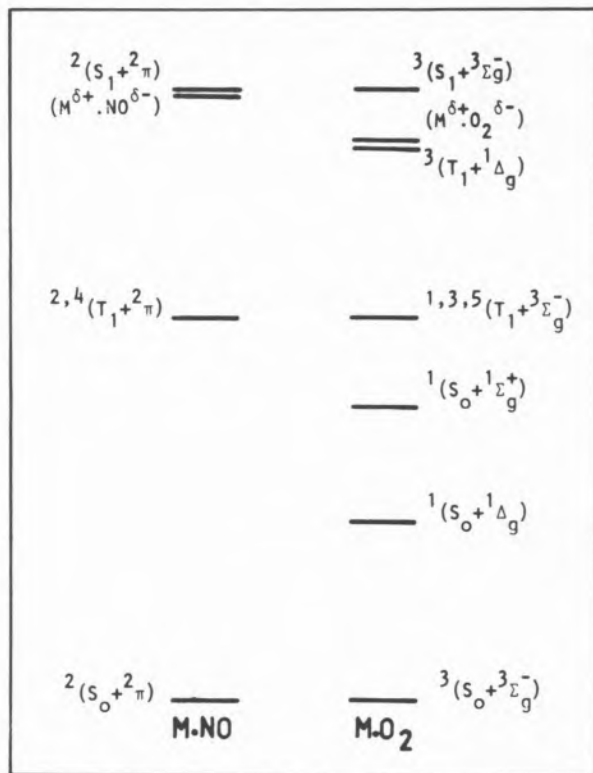


Fig. 2

Electronic energy states of the quenching complexes of aromatic molecules with NO and with O_2

affected by Franck-Condon factors of the radiationless conversions between the states of the quenching complexes.

When $k_c \gg k_{-d}$ ($k_{-d} \cong 10^{12} \text{ s}^{-1}$) the quenching rates are only controlled by diffusion and spin factors, but when $k_c \ll k_{-d}$ the quenching rates are proportional to k_c . Singlet quenching of aromatic molecules by O_2 and NO is diffusion controlled, since for both quenchers $g_s = 1$. Triplet states have quenching rate constants much smaller than $g_s k_d$. For O_2 the k_c rates are controlled by the Franck-Condon factors of CH stretching vibrations of the aromatic compounds which have a coordinate displacement of $R \cong 0$ and, consequently, are in the weak coupling situation. The same behaviour is found with NO quenching for triplet energies $< 14500 \text{ cm}^{-1}$. However for higher energies k_c is controlled by the NO distension which suffers a strong displacement between ground and excited states and follows an inverse energy-gap law. Therefore quenching of aromatic triplets by paramagnetic species appears to be a good model system to investigate the use of solvent effects for probing radiationless mechanisms.

3 — SOLVENT EFFECTS IN SINGLET AND TRIPLET QUENCHING

Solvent effects arise through changes in viscosity and polarity, but only the last parameter influences the electronic states energies of the quenching complexes and is relevant for the present study. Consequently solvent effects are only considered for solvent of comparable macroscopic viscosities, η , but with different dielectric constants, ϵ . Previous studies on solvent effects in NO quenching considered such an effect as anomalous and no satisfactory interpretation was provided [5,7] because: i) no theoretical model for the interpretation of experimental data was available at the time [3] and ii) no reliable data for gas solubilities was available, at least in relative terms.

Here we report the fluorescence and triplet quenching efficiencies of several aromatic molecules by O_2 and NO in *n*-hexane and acetonitrile. Difficulties in finding literature solubility coefficients of the two gases in acetonitrile and the strong discrepancies (*ca.* 2 times) reported for the solubility of NO in *n*-hexane [5,8] have lead us to determine all the solubility coefficients at low pressures by gas chromatography [9]. The solubility values are presented in Table 1 together with solvent viscosities and dielectric constants.

The solvent effects for the singlet quenching have been determined by us through lifetime and Stern-Volmer measurements (Table 2) whereas the solvent effects for triplet quenching (Table 3) were estimated from the data of PORTER and coworkers [4,5] once corrected for the solubility coefficients of Table 1. The data reveal that solvent polarity has very little influence on singlet quenching, but for triplet states strong and opposite effects are observed for O_2 and NO at high triplet energies. For triplet energies below 15000 cm^{-1} no solvent effect is found.

Charge-transfer states are located below the singlet states for oxygen [10]. Any increase in solvent polarity will increase the energy-gap between S_1 and CT states and should decrease the quenching rates. The small solvent effect observed for O_2 reveal a minor (*ca.* 10-15%) CT state contribution for the overall quenching process, in agreement with the findings of GIJZEMAN [7]. The coupling magnitude of two electronic states is proportional to the

Table 1
Gas Solubility Coefficients and Solvent Properties

| Solvent | $\eta/\text{cp}^{\text{a}}$ | ϵ^{a} | Gas solubility $\text{s}/10^{-5}\text{ mol l}^{-1}\text{ Torr}^{-1}$ | |
|------------------|-----------------------------|-----------------------|--|-------------------|
| | | | O_2^{b} | NO ^{b)} |
| <i>n</i> -hexane | 0.300 | 1.88 | 2.0 | 1.9 |
| acetonitrile | 0.325 | 37.5 | 1.1 | 1.2 |
| acetone | 0.304 | 20.7 | — | $2.15^{\text{c)}$ |

a) J. A. RIDDICK and W. B. BUNGER, «Organic Solvents — Physical Properties and Methods of Purification», 3rd edn. in Techniques of Organic Chemistry, ed. A. Weissberger, vol. 2 (Wiley, Interscience, New York 1970).

b) Ref. [9].^c estimated from the data of ref. [5] corrected through the data of refs. [8] and [9].

Table 2
Solvent Effects for Singlet Quenching in Acetonitrile and *n*-Hexane

| Compounds | E_{S_1}/cm^{-1} | $k_q(\text{acet})/k_q(\text{hex})$ | |
|-------------|--------------------------|------------------------------------|------|
| | | O_2 | NO |
| Naphthalene | 32200 | 0.85 | 0.98 |
| Pyrene | 26900 | 0.9 | 1.0 |
| Perylene | 23000 | 0.75 | 0.95 |

Table 3
Solvent Effects for Triplet Quenching in Acetonitrile and in Hexane^{a)}

| Compounds | E_T/cm^{-1} | $k_q(\text{acet})/k_q(\text{hex})$ | |
|----------------------|----------------------|------------------------------------|------------------|
| | | O_2 | NO |
| Chrysene | 20 000 | 2.3 | 0.1 |
| 1,2-benzanthracene | 16 500 | — | 0.15 |
| 3,4-benzpyrene | 14 800 | 0.9 | — |
| 3,4:8,9-dibenzpyrene | 12 000 | — | $1.0^{\text{b)}$ |

a) Data of refs. [4] and [5] corrected with the solubility coefficients of Table 1.

b) In acetone and hexane.

inverse square of the electronic energy-gap and, therefore, the absence of solvent effects for NO implies that its CT state is very far or is virtually isoenergetic with S_1 . Since the NO affinity is higher, but not much different from the one of oxygen (NO 0.024 eV; O_2 0.44 eV [11]) the last hypothesis is the reasonable one.

In the triplet quenching only the highest triplet states ($> 15000\text{ cm}^{-1}$) are sufficiently close to the CT states in order to possess any significant charge-transfer character. The relative positions of $^1(T_1 + ^3\Sigma_g)$ and $^1(S_0 + ^1\Sigma_g)$ for O_2 and $^2(T_1 + ^2\pi)$ and $^2(S_0 + ^2\pi)$ for NO are solvent dependent with the highest state shifting to lower energies with increasing polarity. The increase in the O_2 quenching rate of chrysene triplet corresponds to an energy stabilization of *ca.* 800 cm^{-1} from hexane to acetonitrile. With NO an even higher stabilization energy (*ca.* 950 cm^{-1}) is estimated at a constant R, but such an estimation is not consistent with the higher energy of the NO charge-transfer state. Acetonitrile seems to borrow some of its effects from an increase in the NO displacement, because an increase in the transfer of charge in the quenching complex increases the bond length of the NO moiety.

Although O_2 can suffer a transfer of charge similar to the one of NO, oxygen quenching does not present an inverse energy-gap behaviour. Two reasons can be invoked for such a situation: i) energy gaps between the electronic states in the quenching complexes are much smaller for O_2 than for NO and this favours the Franck-Condon factors of non-displaced oscillators such as the CH modes; ii) for the same amount of charge transfer the increase in O_2 bond length is smaller than in NO; in fact the relevant bond lengths O_2^- (0.126 nm) [12], O_2 (0.1207) and O_2^+ (0.1123) [13] reveal that the increase in bond length between O_2^- and O_2 is smaller than the one between O_2 and O_2^+ , molecules isoelectronic with NO^- and NO.

In conclusion the present results reveal that solvent effects for the weak and strong coupling situations of nonradiative transitions are of opposite signs

and, when of a large magnitude provide an indication of the underlying radiationless mechanisms.

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SUMÁRIO

Efeitos de solvente na Análise dos Mecanismos de Transições Não-radiativas.

Estudam-se os efeitos de polaridade do solvente nas constantes cinéticas de supressão de singuletos e tripletos excitados de compostos aromáticos pelo oxigénio e pelo monóxido de azoto. O efeito de solvente depende da energia dos estados electrónicos e só é apreciável com tripletos de alta energia electrónica. Um aumento da polaridade do solvente aumenta as constantes de supressão pelo O_2 enquanto diminui as constantes de supressão pelo NO. Os resultados são interpretados com base nos mecanismos de acoplamento fraco e forte para transições não-radiativas, e revelam que noutros sistemas os efeitos do solvente podem ajudar a distinguir entre estes dois tipos de mecanismos.