40. Photoionization of Naphthalene and Anthracene in Acetonitrile

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Naphthalene and anthracene undergo a monophotonic ionization process in MeCN to produce the radical cations in low quantum yields (around 0.06 for anthracene). This reaction originates from the relaxed singlet excited state S_1, and it is not due to traces of H_2O in the solvent.

Introduction. – The photoinduced ionization of aromatic molecules in MeCN has been reported to occur with monophotonic excitation for a variety of compounds which absorb at relatively short wavelength (249 nm in laser-flash-photolysis experiments) [1]. The presence of radical ions was established by absorption spectrophotometry following ns laser excitation, but in some cases the assignment is not unambiguous, when the radical cation and the radical anion have similar spectra, as in the case of alternant hydrocarbons such as naphthalene [2]. Since some molecules like *p*-chloranil (2,3,5,6-tetrahydro-2,5-cyclohexadiene-1,4-dione; **CA**) undergo a *reverse* photoinduced electron transfer (*i.e.* electron capture) in MeCN [3], and others like perylene undergo bimolecular electron transfer in the excimer leading to an ion pair [4], it is important to establish unequivocally the nature of the transient species. This has been the first object of the research described in this paper. Following the identification of the primary photoproduct in the case of naphthalene, we have extended our observations to anthracene which can be photoexcited with light of much longer wavelength (*e.g.* 355 nm); this allows to study the influence of the photon energy on the electron transfer process.

Results. – *1-Methylnaphthalene* (**1-MN**). Compound **1-MN** has been selected for this study, because the radical cation and the radical anion have substantially different absorption spectra [2]. The anion shows a broad absorption band extending to over 1000 nm, while the onset of absorption by the cation is at about 820 nm. A 2.3×10^{-4} M solution of **1-MN** in deoxygenated MeCN irradiated with the 266-nm fourth-harmonic of the YAG laser shows a transient absorption at 700 nm but not at 900 nm *(Fig. 1)*. The same observation is made in the **1-MN/CA** system, where 4.2×10^{-3} M **CA** is excited by the 355-nm third-harmonic of the laser, in the presence of 5×10^{-3} M **1-MN**. In this case, photoexcited **CA** acts as the electron acceptor from ground-state **1-MN**, and no transient absorption at 900 nm (corresponding to **1-MN**$^{\cdot -}$) is observed. It is, therefore, concluded that photoexcited **1-MN** in MeCN undergoes an ionization to produce only **1-MN**$^{\cdot +}$ and $(MeCN)_n^{\cdot -}$. The presence of charge carriers is demonstrated by the transient photocurrent observed under these conditions *(Fig. 2)* which incidentally decays with the same rate as the optical signal of *Fig. 1*.

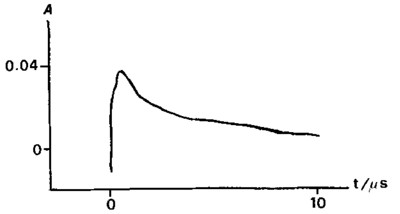


Fig. 1. *Transient absorptions (A) at 700 nm and at 900 nm of a deoxygenated solution of 2.3 × 10^{-4}* M 1-MN *in MeCN* (266-nm laser excitation)

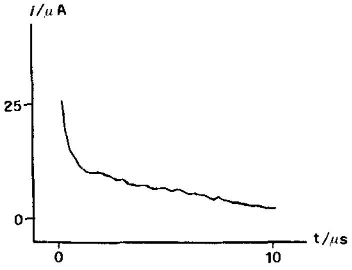


Fig. 2. *Transient photocurrent (i) of a deoxygenated 2.3 × 10^{-4}* M *solution of* 1-MN *in MeCN*

Anthracene (**A**). The radical cation and anion of **A** have very similar absorption spectra in the VIS and NIR, so that they cannot be distinguished purely on spectroscopic grounds [2]. When a 1.23 × 10^{-4} M deoxygenated solution of **A** in MeCN is irradiated with the 355-nm laser pulse, a transient absorption is obtained with a peak near 700 nm corresponding to the ion radicals' spectra *(Fig. 3)*. When this same solution is saturated with oxygen, the initial absorbance of the radical cation $A^{\cdot+}$ decreases by a factor of 0.53; the fluorescence intensity of **A** decreases by a factor of *ca.* 0.48 under the same conditions, with both steady-state and laser-flash excitation. The close agreement between these figures confirms the involvement of the relaxed (fluorescent) state S_1 of **A** in the photoionization process.

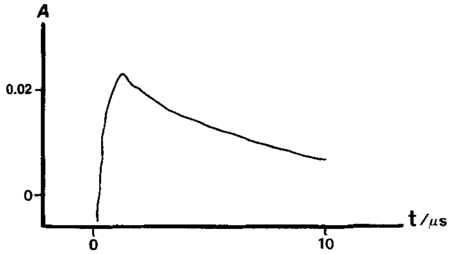


Fig. 3. *Transient absorption (A) at 700 nm of a deoxygenated solution of 1.23 × 10^{-4}* M **A** *in MeCN* (355-nm laser excitation)

The presence of charge carriers is established by the observation of the transient photocurrent *(Fig. 4)*, and from the initial optical density at 700 nm the quantum yield of radical ion(s) formation is estimated as 0.065.

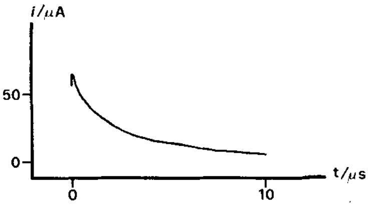


Fig. 4. *Transient photocurrent (i) of a deoxygenated 1.23 × 10^{-4}* M *solution of* **A** *in MeCN*

The initial optical density at 700 nm decreases linearly with the laser pulse energy, suggesting a monophotonic process *(Fig. 5)*. When the concentration of **A** is decreased, the ion yield decreases slowly, following the fraction of excitation light absorbed *(Fig. 6)*; this shows that the electron-transfer process is not bimolecular, *e.g.*

$$\mathbf{A}^* + \mathbf{A} \rightarrow \mathbf{A}^{\cdot+} + \mathbf{A}^{\cdot-}$$

as in the case of perylene [4]. The monomolecular participation of **A** is further confirmed by the lack of a growing-in of the 700-nm transient absorption at short times.

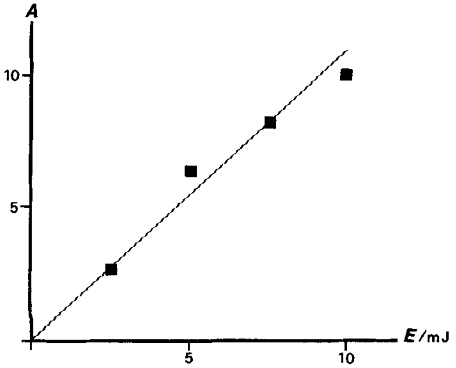


Fig. 5. *Initial absorbance (A) of the transient at 700 nm as a function of laser excitation energy (E)*

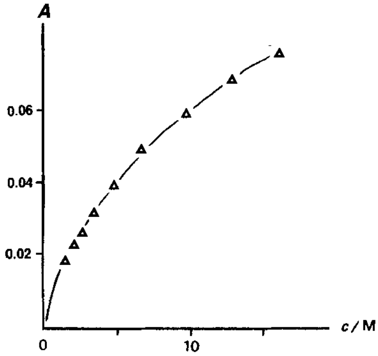


Fig. 6. *Effect of the concentration (c) of* **A** *on the initial absorbance (A) of the 700-nm transient*

The 700-nm transient must, therefore, be either $\mathbf{A}^{\cdot+}$ or $\mathbf{A}^{\cdot-}$ (it cannot be due to a mixture of the ions). It will be shown below that it must be $\mathbf{A}^{\cdot+}$ on energetic grounds; this is similar to the case of 1-MN discussed above. In mixtures of benzene (PhH) and MeCN, this initial absorption decreases with decreasing MeCN mole fraction, as shown in *Fig. 7*. The decrease is not linear, but extrapolates to *ca.* 0.22 PhH mole fraction. This behaviour is similar to the case of perylene and the same explanation may be suggested: not all the MeCN molecules in the solvation shell of **A** are equivalent, and electron transfer occurs only to preferred sites which maximize the electrostatic stabilization energy.

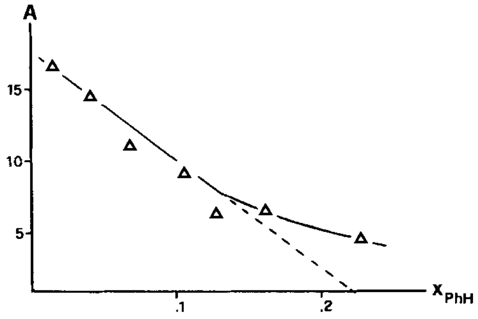


Fig. 7. *Initial absorbance (A) of the 700-nm transient as a function of PhH/MeCN mixture composition* (x_{PhH} = benzene mole fraction)

In view of the effect of molecular oxygen on the transient absorption and on the photocurrent, the possible involvement of the triplet state T_1 of **A** has to be considered. The initial absorbance at 420 nm and the decay time are the same in PhH and in MeCN (about 20 μs under our experimental conditions); thus, T_1 decays by quenching and by T-T annihilation in both solvents and does not seem to participate in the electron-transfer process. It should be added that no quenching of the fluorescence of **A** in MeCN compared to PhH could be observed, but the ion yield is so low (~ 6.5%) that it would be difficult to measure such small changes quantitatively.

When the laser pulse at 266 nm is used, the transient absorption at 700 nm is proportional simply to the pulse intensity, showing that the excess energy of *ca.* 1.1 eV on going from 355 to 266 nm has no influence on the electron-transfer process.

Under irradiation conditions, the absorption spectrum of **A** in PhH or in MeCN decreases as a result of the well known photodimerization. The same spectral changes are observed in both solvents, the ratio of the quantum yields corresponding simply to the ratio of the solvents' viscosities. No new overall photoreaction is observed in MeCN, so that the charges must recombine to restore the initial molecules.

The decay of the $\mathbf{A}^{\cdot +}$ absorption follows second-order kinetics, as expected for the charge recombination process. The rate constant for ion recombination is 2.24×10^{10} s^{-1} M^{-1}, and this corresponds closely to the diffusion-controlled limit in MeCN near 300 K (from the *Debye* equation, it is calculated as 1.91×10^{10}, from the modified equation according to *Osborne* and *Porter* as 2.87×10^{10} s^{-1} M^{-1} [5]).

The calculated figures apply, however, to neutral particles only, and the diffusion-controlled recombination of particles of opposite charges can be expected to be roughly twice faster from the *Debye-Eigen* equation [6]; an exact figure cannot be quoted here, because the size of the negative ion is not firmly established (it could be the dimer $(MeCN)_2^{\cdot -}$ rather than the monomer $MeCN^{\cdot -}$). In any case, the recombination rate comes close to the diffusional limit, even if it does not quite reach it.

The effect of added H_2O to the solutions of **A** in MeCN has also been investigated. At H_2O mole fractions > 0.02, the hydrated electron is observed by its absorption at 800 nm; this absorption increases with added H_2O to reach a maximum for a H_2O mole fraction of *ca.* 0.1. The 700-nm absorption which results from the superimposed spectra of $\mathbf{A}^{\cdot +}$ and of the hydrated electron behaves similarly *(Fig. 8)*. In the absence of added H_2O, $\mathbf{A}^{\cdot +}$ is still

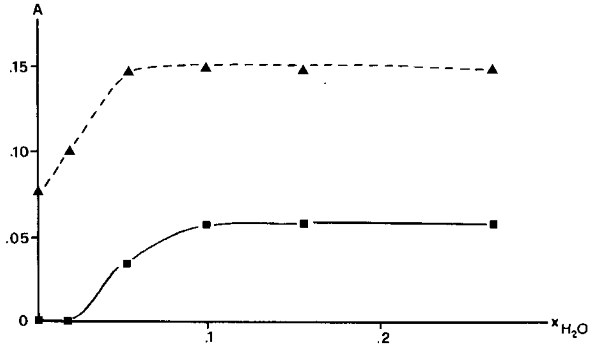


Fig. 8. *Effect of added H_2O (x_{H_2O} = water mole fraction) in MeCN on initial absorbance (A) of radical cation at 700 nm (▲) and of hydrated electron at 800 nm (■)*

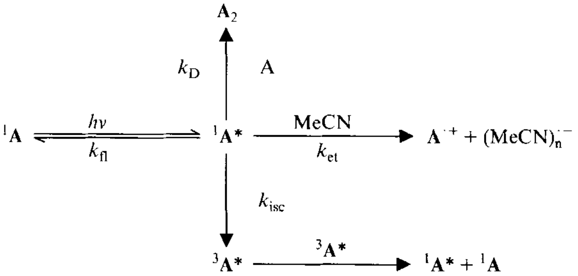
present, when the hydrated electron cannot be observed, and it can be concluded that the electron-transfer process is not due to trace impurities of H_2O in MeCN.

These measurements have been repeated with specially dried MeCN[1]) of which the H_2O content was measured as 8 ppm by *Karl-Fischer* titration. No rise of the absorption of $A^{\cdot +}$ could be detected within the time resolution of our system (about 20 ns), and the initial ion yield was unchanged.

Effect of Electron Scavengers. When bromobenzene (PhBr) is added to deoxygenated solutions of **A** in MeCN, the decay of the photocurrent becomes much slower, although its initial value is only slightly increased *(Fig. 9)*. This can be understood from the fact that most of the photocurrent in MeCN results from the highly mobile solvated electrons ($MeCN_n^{\cdot -}$) which recombine relatively rapidly with $A^{\cdot +}$; in the presence of PhBr, these solvated electrons are trapped by this scavenger.

It is probable that oxygen has a similar effect, and in addition it quenches $^1A^*$ by formation of the endoperoxide.

The overall scheme for the photoreactivity of **A** in MeCN can, therefore, be summarized as follows:



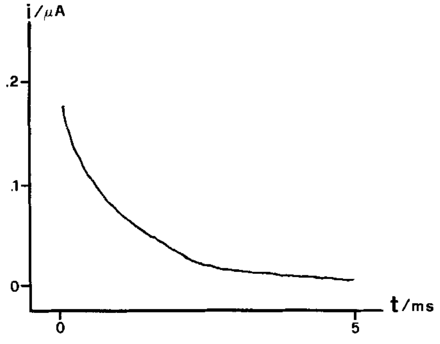


Fig. 9. *Time dependance of transient photocurrent (i) of a deoxygenated MeCN solution of* **A** (1.23 × 10^{-4} M) *with* 8 × 10^{-4} M *PhBr*

Discussion. – *Energy Balance and Rate Constants.* In the case of **A**, the rate constant k_{et} for photoionization in MeCN can be estimated from the observed ion yield and the competitive rate constants of deactivation by fluorescence and intersystem crossing [7]:

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[1]) A two-step drying procedure over 3-Å molecular sieve was used for this experiment; the details will be described elsewhere.

$$k_{\mathrm{fl}} = 2 \times 10^8\ \mathrm{s}^{-1}$$
$$k_{\mathrm{isc}} = 3.35 \times 10^8\ \mathrm{s}^{-1}$$
$$k_{\mathrm{ct}} = k_{\mathrm{ion}}\ [\mathrm{MeCN}]_{\mathrm{eff}} = 1.4 \times 10^7\ \mathrm{s}^{-1}$$

Although the molar concentration of neat MeCN is 19M, it has been suggested that only those solvent molecules in contact with the thinnest regions of the aromatic system are actually efficient in the electron-transfer process [4]. The concentration $[\mathrm{MeCN}]_{\mathrm{eff}}$ is then approximately 5M and the second-order rate constant k_{ion} becomes $3 \times 10^6\ \mathrm{s}^{-1}\ \mathrm{M}^{-1}$.

The energy balance of photoionization is $\Delta E = +0.34$ eV from the *Rehm-Weller* equation with the modified *Coulomb* term [8]:

$$\Delta E = E_{\mathrm{ox}} - E_{\mathrm{red}} - E^* + C$$

with $E_{\mathrm{ox}}(\mathrm{A}) = 0.95$ V (*vs.* SCE), $E_{\mathrm{red}}(\mathrm{MeCN}_{\mathrm{liq}}) = -3.5$ V (*vs.* SCE), the excited state energy E^* being 3.3 eV for the singlet state S_1 of **A** and

$$C = -\frac{e^2}{2\,n^2\,(r_{\mathrm{A}} + r_{\mathrm{MeCN}})}$$

where n is the mean refractive index of **A** and MeCN, and r_{A}, r_{MeCN} are the 'radii' of **A** and MeCN, respectively, in the contact-charge-separated state. In the present instance, we take $r_{\mathrm{A}} = 1.7$ Å (the half thickness of a planar π system) and $r_{\mathrm{MeCN}} = 2.74$ Å.

Although this reaction is slightly endergonic, it agrees with the relatively low photoionization rate constant $k_{\mathrm{ion}} = 3 \times 10^6\ \mathrm{s}^{-1}\ \mathrm{M}^{-1}$. It is in fact in broad agreement with the unimolecular rate constant for electron transfer as function of energy balance (for $\Delta E = +0.37$ V; [9]: $k_{\mathrm{ct}} = 5 \times 10^7\ \mathrm{s}^{-1}\ \mathrm{M}^{-1}$).

The reverse process of electron capture by $^1\mathrm{A}^*$ from MeCN is highly endergonic, $\Delta E = +2.6$ eV with the same *Coulomb* term; it is, therefore, of no significance. On the other hand, the process of bimolecular electron transfer (similar to the case of perylene [6])

$$^1\mathrm{A}^* + \mathrm{A} \rightarrow \mathrm{A}^{\cdot +} + \mathrm{A}^{\cdot -}$$

should be energetically favourable ($\Delta E = -1.1$ eV). It does not occur in the case of **A**, probably because the excimer collapses very rapidly to the photodimer in all solvents.

Reactive State(s). The monophotonic ionization of **A** in MeCN could occur in principle from the thermalized excited singlet S_1 or triplet T_1, or from a non-relaxed (FC) singlet S_n. This last intermediate can be eliminated on the grounds of the similar relative efficiencies for 355-nm and 266-nm excitation. An involvement of T_1 is not consistent with the absence of the growing-in of the radical cation's absorption at short times; under our experimental conditions the triplet-triplet absorption in deoxygenated solutions has a lifetime of 20 µs, whereas the radical cation's absorption starts to decay immediately after the flash of ~ 25 ns duration. In addition, monophotonic ionization from the triplet is unlikely because of the energy balance: the T_1 state of **A** is 1.45 eV below the S_1 state for which the ΔG_{ct} was already calculated as +0.34 eV.

Our results point to the thermally relaxed singlet excited state as the most probable intermediate. The fact that no fluorescence quenching can be observed reliably in going from PhH to MeCN solvent can be ascribed to the low ion yield; in addition repopulation of the S_1 state may result from ion recombination.

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