FORMATION OF CT COMPLEXES AND ELECTRON TRANSFER FROM EXCITED MOLECULES OF ANTHRACENE DERIVATIVES TO METHYLVIOLOGEN IN AQUEOUS AND MICELLAR MEDIA

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Disodium 1,5- and 1,8-anthracenedisulphonate (ADS) and 9-acetylanthracene form coloured CT complexes with methylviologen (MV^{2+}) in aqueous and micellar media. The complex formation constants and molar absorptivities were determined by the Benesi–Hildebrandt method. In the fluorescence quenching, its static component plays the major role. The dynamic quenching component is determined by the rate constant of electron transfer from the S_1 state of ADS to MV^{2+}.

Solar energy conversion and storage are attracting ever-increasing interest. Among promising processes is the photolysis of water to hydrogen, or hydrogen and oxygen, making use of photo-redox reactions of organic compounds[1-4].

In the present work, attention is paid to systems involving photoexcited molecules of anthracene derivatives, *viz.* disodium 1,5- and 1,8-anthracenedisulphonate (ADS) and 9-acetylanthracene (9-AA), as electron donors and methylviologen (N,N-dimethyl-4,4-dipyridinium chloride, MV^{2+}) as an electron acceptor.

Electron transfer from aromatic hydrocarbons to MV^{2+} proceeds easily from their singlet and triplet excited states[5]. Johansen and coworkers[6] observed that the 9-anthracenecarboxylate anion in its triplet excited state reduces MV^{2+} very efficiently to the cation-radical $MV^{+\cdot}$ which is capable of reducing water to hydrogen. By efficient energy transfer from excited molecules of tris(2,2'-dipyridyl)ruthenium(II) to this anthracene derivative, generation of hydrogen was achieved with a quantum yield as high as 0·85 (ref.[6]).

EXPERIMENTAL

1,5-ADS and 1,8-ADS (Research Institute for Organic Syntheses, Pardubice-Rybitví) was crystallized four times from a 3 : 1 (v/v) ethanol–water mixture (twice with additions of activated carbon). 9-AA was prepared by the Friedel–Crafts reaction from anthracene and acetyl chloride[7] and recrystallized three times from ethanol; m.p. 75—76°C (published: 75°C). The purity of the compound was checked by thin layer chromatography on Silufol 365 plates (Kavalier, Sázava) using 95% ethanol for ADS and a benzene–ethanol system for 9-AA. Sodium dodecyl sulphate (SDS) (Pierce) was of purity 99% or better.

Solutions were made up using redistilled water and distilled ethanol. 9-AA in a solution of SDS (50 mmol l^{-1}) was sonicated for 60 min at 35°C in a UC 005 A31 ultrasonic bath (Tesla, Vráble). The undissolved 9-AA was collected on an S4 glass filter.

Electronic absorption spectra were scanned on a Perkin–Elmer 330 spectrophotometer at room temperature, fluorescence spectra were run on a homemade apparatus[8] comprising an OSA optical spectral analyzer (B & M Spektronic, Munich) fitted with a SIT 500 vidicon. The measurements on the OSA apparatus were performed in the spectra accumulation mode using standard routines of a WP-4 process computer (B & M). The intensities of the fluorescence maxima and the integral intensities over the 380—475 nm range were determined from the records. The times of fluorescence quenching were measured with an LIF 200 instrument (Zentrum für wissenschaftlichen Gerätebau, Berlin) using an IGT 50 nitrogen laser working at a 50 kW power and 500 ps FWHM. The signals were detected with a BCI 280 boxcar integrator.

RESULTS AND DISCUSSION

The electronic absorption spectra of ADS and 9-AA resemble each other closely (Fig. 1). In the long-wavelength spectral range, there is observed an absorption band with a pronounced vibronic structure, typical of anthracene and its simple derivatives[9]. Five vibronic transitions can be well distinguished. The 0–1 transition is the most intense and lies at 365 nm. The shape, relative intensities, and positions of maxima of the vibronic bands do not vary appreciably in dependence on the solvent used. The spectrum of 9-AA in the micellar media of SDS does not vary appreciably either. Another band, considerably more intense, appears in the 250 nm range; it exhibits no marked vibronic structure. In the presence of MV^{2+} in concentrations of $0.1 - 8$ mmol l^{-1}, aqueous solutions of ADS and micellar ethanolic

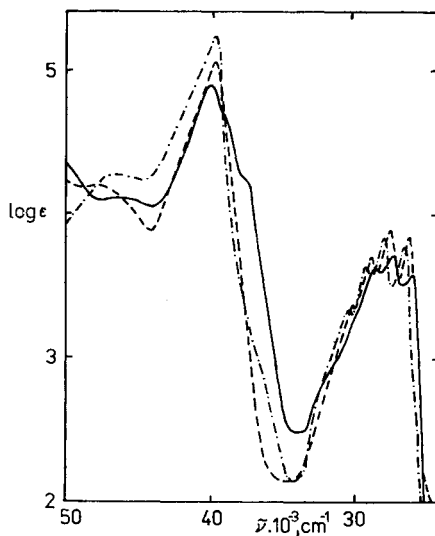

FIG. 1

Electronic absorption spectra of anthracene derivatives. ——— 1,8-ADS in water, ————— 1,5-ADS in water, —·—·— 9-AA in ethanol

solutions of 9-AA display a new, concentration-dependent band in the 400 — 570 nm region (Fig. 2a).

It is well known that aromatic hydrocarbons form CT complexes with compounds with a pronounced charge distribution over their molecules or possesing a positive charge. Aryldiazonium salts[10], tetracyanoethylene[11], etc., can serve as the acceptors. In our case, negatively charged solvated molecules of ADS react with positively charged molecules of MV^{2+}. The newly appearing absorption band in the 400 to 570 nm range is also observed in solutions containing 9-AA and MV^{2+}. We assume that this is due to electron transition associated with charge transfer[10,11], for which a broad band without a vibronic structure is typical. The complex formation constant K_{CT} and the molar absorptivity at a wavelength λ, ε_λ, can be determined by the Benesi––Hildebrandt method[12] using Eq. (1)

$$c_A/A_\lambda = \left[1/(K_{CT}\varepsilon_\lambda)\right](1/c_{MV^{2+}}) + (1/\varepsilon_\lambda),\qquad(1)$$

where c_A and $c_{MV^{2+}}$ are concentrations of the anthracene derivative and MV^{2+}, respectively, and A_λ is the absorbance of the former at wavelength λ. The validity of this relation for the systems studied is illustrated in Fig. 3, and the K_{CT} and values so obtained are given in Table I. The complex formation constants are considerably
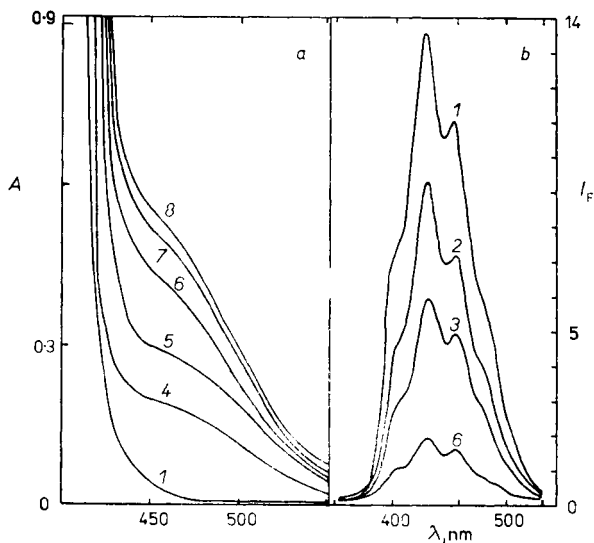

FIG. 2

a Increase in absorbance of CT complex for 1,8-ADS (0·5 mmol l^{-1}) and b decrease of fluorescence band (λ_{ex} = 365 nm). $c_{MV^{2+}}$, mmol l^{-1}: 1 0; 2 0·2; 3 0·75; 4 1; 5 2; 6 4; 7 6; 8 8

higher than those[13] for the pyrene–MV^{2+} system in methanol ($K_{CT} = 3\cdot4\,l\,mol^{-1}$) or in the micellar media of $0\cdot1$M-SDS ($K_{CT} = 704\,l\,mol^{-1}$). Another example is the anthracene–p-chlorobenzenediazonium tetrafluoroborate system in acetonitrile and $0\cdot1$M-SDS, $K_{CT} = 0\cdot6$ and $210\,l\,mol^{-1}$, respectively[10]. For ADS, this can be explained in terms of a strong electrostatic interaction of the oppositely charged molecules, the mutual alignments with the MV^{2+} molecules suiting better to the stability of the CT complex in the case of 1,5-ADS. The conditions for the formation of the CT complex are also very favourable in SDS micelles, where the molecules of 9-AA are solvated predominantly inside the micelles while the molecules of MV^{2+} are bound to the Stern's negatively charged layers of the micelles by electrostatic forces

TABLE I

Spectral and kinetic parameters of interaction of disodium 1,5- and 1,8-anthracenedisulphonate in water and 9-acetylanthracene in sodium dodecyl sulphate (a) and in ethanol (b) with methylviologen

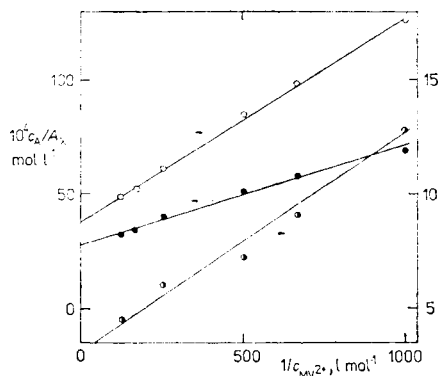| Parameter	1,5-ADS	1,8-ADS	9-AA	
			a	b
ε_{CT}, $l\,mol^{-1}\,cm^{-1}$	346	262	343	183
λ_{CT}, nm	440	440	450	450
K_{CT}, $l\,mol^{-1}$	705 ± 10	462 ± 10	292 ± 10	$15\cdot3 \pm 5$
τ_0, ns	$2\cdot82 \pm 0\cdot02$	$1\cdot25 \pm 0\cdot01$	—	—
B, $l\,mol^{-1}$	1 720	896	—	—
$k_E \doteq 10^{10}\,l\,mol^{-1}\,s^{-1}$	$1\cdot2 \pm 0\,2$	$1\cdot0$	—	—
q_f	$0\cdot14$	$0\cdot08$	—	—

FIG. 3

Benesi–Hildebrandt plot. ○ 1,8-ADS in water, ● 1,5-ADS in water, ◑ 9-AA in micellar media of SDS (50 mmol l^{-1})

The possibility that the ionization potential of 9-AA inside the negatively charged SDS micelles is lower[14] may also contribute. This concept is consistent with the model where the dynamic structure of the micelle makes it possible for water and hydrophilic molecules to penetrate into the inner hydrophobic core of the micelle[10,13,15]. In the homogeneous medium of ethanol, K_{CT} is lowest but still about five times higher than in the case of pyrene.

Fluorescence of the two ADS isomers is efficiently quenched by MV^{2+}. Experiments performed at a continuous excitation (Figs 2b, 4) and at a pulse excitation (Fig. 5) with a nitrogen laser suggest that the quenching process can be divided into the static and dynamic components; the static component is associated with the CT complex formation whereas the dynamic component is associated with the interaction of the S_1 singlet excited state with MV^{2+}, which is basically electron transfer from the S_1 state to MV^{2+}. This behaviour can be overall expressed by the equation[16]

$$I_0/I = (1 + K_{CT}c_Q)(1 + k_{ET}\tau_0 c_Q),\tag{2}$$

where I_0 and I are the fluorescence intensities at a zero concentration of quencher Q and at its concentration c_Q, respectively, k_{ET} is the rate constant of electron transfer, and τ_0 is the donor fluorescence lifetime in the absence of Q. Eq. (2) expresses a non-linear dependence of the fluorescence intensity ratio, or the fluorescence quantum yield ratio, on the concentration of quencher. From a comparison with the dynamic
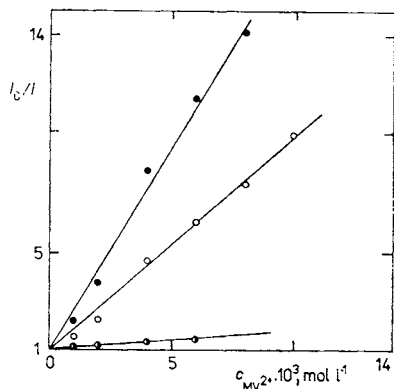

Fig. 4

Dependence of ratio of integral intensities of fluorescence on concentration of MV^{2+}.
● 1,5-ADS in water, ○ 1,8-ADS in water, ◐ anthracene in ethanol
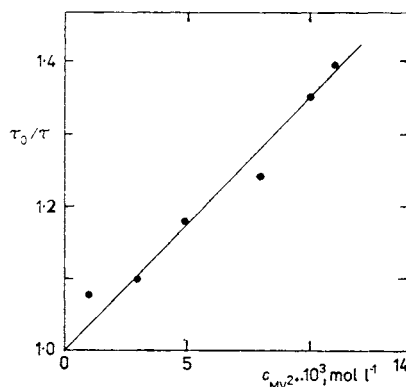
Fig. 5

Stern–Volmer relation between the ratio of fluorescence lifetimes of 1,5-ADS and concentration of MV^{2+} in water

component, which can be determined from the change in the fluorescence lifetime in dependence on the concentration of quencher, the equilibrium constant K_{CT} then can be calculated by means of the relation

$$(I_0/I)(\tau/\tau_0) = 1 + K_{CT}c_Q, \qquad (3)$$

which, in the theoretical concept, corresponds to the value found by the Benesi––Hildebrandt method. The very good linear dependence of the ratio of integral intensities of fluorescence (I_0/I) on the concentration of MV^{2+} over a rather wide region of $c_{MV^{2+}} = 0.05 - 4$ mmol l^{-1}, is illustrated in Fig. 4, the slopes B of the dependences are given in Table I. The slope for the quenching of fluorescence of unsubstituted anthracene in ethanol is about one order of magnitude lower, viz. 215 l mol^{-1} (Fig. 4).

The dynamic quenching component (Fig. 5) brings about shortening of the fluorescence lifetime with increasing concentration of MV^{2+}. The Stern–Volmer relation is linear, the slope of the dependence of τ_0/τ on $c_{MV^{2+}}$ is 31·74 l mol^{-1} and the rate constant of electron transfer from the S_1 state of 1,5-ADS is $k_{ET} = 1·2 . 10^{10}$ l . mol^{-1} s^{-1}, a value about twice as high as the diffusion-limited rate constant in aqueous medium at 20°C, 6·5 . 10^9 l mol^{-1} s^{-1} (ref.[17]). For 1,8-ADS, for which the fluorescence lifetime is 1·25 ns, the fluorescence quenching in the subnanosecond region could not be examined experimentally with a sufficient accuracy; we estimate that the rate consant k_{ET} for the S_1 state of 1,8-ADS is in the order of 10^{10} l mol^{-1} . s^{-1}.

The experimental data obtained can be discussed in terms of Scheme 1, where in addition to the CT complex, formation of an exciplex during the interaction of the S_1 and T_1 excited states of the anthracene derivatives MV^{2+} is assumed. For simplicity, the common structure of the exciplex generated from both the S_1 and T_1 states
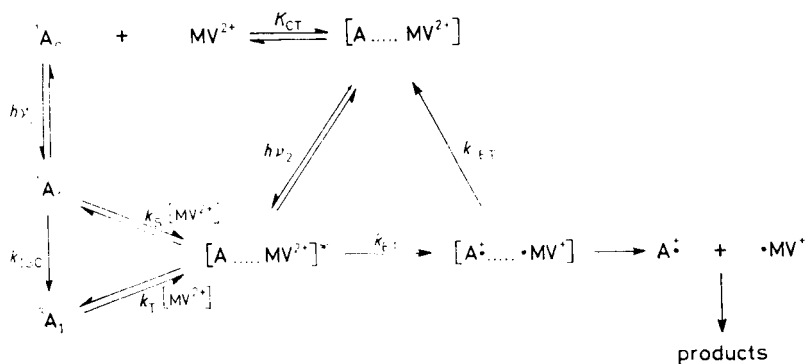
Scheme 1

is shown. Moreover, we suppose that the structure of the CT excited state approaches closely that of the exciplex. In agreement with published data[18,19], the electron transfer takes place in the collision configuration of the exciplex giving rise to the geminal ion pair $[A^{+} \ldots \cdot MV^{+}]$, particularly in polar medium. The separate solvated ions then react further with molecules of the medium (including oxygen) to give the starting compounds and decomposition products.

The diference between the slopes for fluorescence quenching B (Fig. 4) and the slope for the dynamic quenching (Fig. 5) suggests that the static quenching component reflects considerably more complex processes associated with the formation of, e. g., 1 : 1 and 1 : 2 or 2 : 1 CT complexes or exciplexes. The fluorescence intensity is also lowered appreciably by the absorbance increase of the CT complex in the excitation and fluorescence regions.

The contributions of the singlet and triplet excited states to the exciplex formation and electron transfer are determined principally by the probability of intersystem transition (ISC) and change in the Gibbs energy ΔG of activation of the system for electron transfer[20], expressed by the equation

$$\Delta G = E_{1/2}(A/A^{+}) - E_{0,0}(A) - E_{1/2}(MV^{+}/MV^{2+}) + \Delta G_E, \qquad (4)$$

where $E_{1/2}$ are the oxidation and reduction potentials of the anthracene derivative and MV^{2+} (-0.45 eV), respectively, $E_{0,0}$ is the energy of the 0–0 transition for the S_1 or T_1 state of the electron donor, and ΔG_E is the free energy of Coulomb interaction between the radical-ions.

For anthracene, where $E_{1/2}(A/A^{+}) = +1.5$ eV (ref.[21]), $^1E_{0,0} = 3.31$ eV and $^3E_{0,0} = 1.85$ eV (ref.[22]), the free energies calculated by Eq. (4) are -1.36 eV for the S_1 state and $+0.010$ eV for the T_1 state (disregarding the ΔG_E term). Thus from the thermodynamic point of view, the electron transfer is only possible from the S_1 state of anthracene. In this approximation, the difference between the reactivities of the S_1 and T_1 states is determined primarily by the magnitude of the singlet––triplet splitting; this is rather high for anthracene as compared to other aromatic hydrocarbons[23]. This concept is consistent with the results obtained, e.g., for the quenching of fluorescence of acridine orange[22]. In our experiments with ADS, the interaction is between oppositely charged species, and the ΔG_E term in Eq. (4) can no more be ignored; since the effect is electrostatic attraction, this term is negative and contributes to the possibility of electron transfer from both the S_1 and T_1 states. This is indicated by the k_{ET} value (Table I). The reactivity of ADS in the triplet excited states is being studied[24]. For 9-AA the ISC quantum yield approaches unity[25]. Results so far obtained indicate that the electron transfer to MV^{2+} occurs predominantly from the T_1 state and seems to be promoted by the micellar medium of SDS (ref.[24]).

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