

## ELECTRON TRANSFER FROM EXCITED MOLECULES OF ANTHRACENE DERIVATIVES TO METHYLVIOLGEN. GENERATION OF THE CATION-RADICAL AND HYDROGEN

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Received June 19th, 1986

The quantum yields of formation of the methylviologen cation-radical were measured, the effect of pH was studied, and the possibility of photogeneration of hydrogen was examined for systems with disodium 1,5- or 1,8-anthracenedisulphonate in aqueous media or 9-acetylanthracene in micellar media of sodium dodecyl sulphate, in the presence of methylviologen, triethanolamine, and colloidal platinum.

Electron transfer from aromatic hydrocarbons to methylviologen ( $MV^{2+}$ ) proceeds readily from their singlet and triplet states<sup>1,2</sup>. Previously<sup>3</sup> we investigated the formation of the CT complexes between  $MV^{2+}$  and three anthracene derivatives, *viz.* disodium 1,5- and 1,8-anthracenedisulphonate (ADS) and 9-acetylanthracene (9-AA) in aqueous and micellar media. The observed quenching of fluorescence was interpreted in terms of its dynamic (electron transfer) and static (CT complex formation) components. In the present work, conditions for the formation of the relatively stable methylviologen cation-radical ( $MV^{\cdot+}$ ) are studied and the possibility of photogeneration of hydrogen in the presence of colloidal platinum is examined.

### EXPERIMENTAL

The purification of ADS (Research Institute for Organic Syntheses, Pardubice-Rybitví) and preparation and purification of 9-AA have been described<sup>3</sup>. Sodium dodecyl sulphate (DS) of purity better than 99% (Pierce) was used as received. Methylviologen dichloride (Aldrich) was crystallized twice from a water-ethanol 4 : 1 mixture. Triethanolamine (TEA) of reagent grade purity (Lachema, Brno) was used without additional treatment. Solutions were made up from redistilled water. 9-AA was dissolved in micellar medium of SDS ( $0.5 \text{ mmol l}^{-1}$ ) in a UC005 AJ 1 ultrasonic bath (Tesla, Vráble) at 35°C for 60 min; the undissolved fraction was collected on an S4 glass filter. Phosphate buffer was used for pH adjustment, controlled by means of an OP 109 ionometer (Radelkis, Budapest). Electronic absorption spectra were scanned on a Perkin-Elmer 330 spectrophotometer over the region of 200–750 nm.

Photolysis experiments were performed using  $10 \times 10 \times 40$  mm quartz cells closed with septa through which argon was fed for 20 min by means of syringe needles. Samples were exposed to radiation of an XBO 101 xenon discharge lamp or an HBO 200 mercury discharge lamp, accommodated in housings equipped with quartz optics (Carl Zeiss, Jena). For quantitative

experiments, the radiation from the discharge lamps was filtered through a UVSIF 365 filter. The intensity of the excitation radiation ( $\lambda_{ex}$  365 nm) was determined with a conventional ferri-oxalate actinometer.

Colloidal solution of platinum was obtained by a 4 hours' reduction of 74.7 mg of  $K_2PtCl_6$  in 500 ml of water with 60 ml of a 1% solution of potassium citrate under boil.<sup>4</sup> For removing foreign ions and lowering conductivity, the solution was stirred for 24 h with Amberlite MB-3 ion exchanger at room temperature. Experiments with hydrogen generation were carried out in an elliptic photoreactor fitted with an N86UV fluorescent lamp, emitting radiation over the region of 320–360 nm. 100 ml of solution containing 50 ml of the colloidal platinum solution prepared was exposed to radiation in a quartz tube 20 mm in inner diameter. The hydrogen volume increment was measured with an azotometer of 3 ml volume. Formation of hydrogen was proved by chromatographic analysis on a Chrom IV apparatus (Laboratorní přístroje, Prague) fitted with a column 3.6 m long, packed with 13 X molecular sieve.

## RESULTS AND DISCUSSION

Irradiation of solutions of the anthracene derivatives in the presence of  $MV^{2+}$  and TEA at pH 7.0, 7.8, 8.7, and 10.2 and bubbled with argon induces a progressive increase in the absorbance of the blue  $MV^{\dot{+}}$  cation-radical (Fig. 1). The electronic absorption spectrum is consistent with published data<sup>5-7</sup> for this species. Typical is the broad band at 460–780 nm with its maximum at 605 nm and the rather narrow band at 340–410 nm with its maximum at 395 nm which exhibits a pronounced vibronic structure. The  $MV^{\dot{+}}$  cation-radical formed is highly sensitive to the presence of oxygen in the solution. After the irradiation, the samples were bubbled with air. The absorption by  $MV^{\dot{+}}$  vanished and the absorption spectrum showed no marked decrease in the absorbance of the anthracene derivative after the irradiation, which

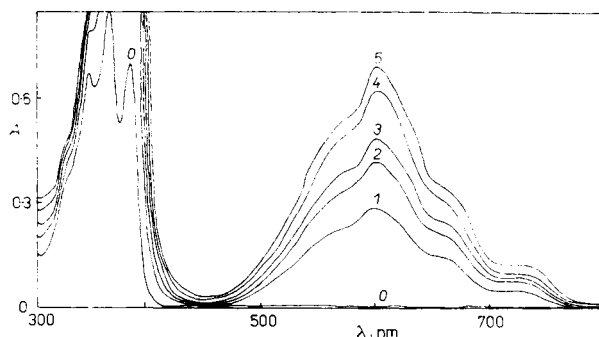


FIG. 1

Time increase in absorbance of  $MV^{\dot{+}}$  in a system of 1,8-ADS ( $0.2 \text{ mmol l}^{-1}$ ),  $MV^{2+}$  ( $0.2 \text{ mmol l}^{-1}$ ), and TEA ( $10 \text{ mmol l}^{-1}$ ) in water at pH 7.8;  $\lambda_{ex}$  365 nm,  $d = 1 \text{ cm}$ . Exposure, min: 0 0; 1 2; 2 3; 3 4; 4 6; 5 12

might occur as a result of the possible side reactions. The increase in absorbance of  $MV^{\ddagger}$  in the long-wavelength band region (602 nm) during the irradiation by light of 365 nm wavelength is shown in Fig. 2. In all cases, a rapid absorbance increase occurs in the starting stage, later the increase rate slows down to become nearly constant. The actinometrically determined intensity of the entering photolytic radiation of 365 nm wavelength,  $I_0$ , molar absorptivity of  $MV^{\ddagger}$  at 602 nm,  $\epsilon_{MV^{\ddagger}}$  ( $(11 \pm 1) \cdot 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ , ref.<sup>6</sup>), and the basic data of the time change in absorbance at 602 nm during the irradiation, converted to absorption at the excitation wavelength, were used for the calculation of the quantum yield,  $\Phi$ , of  $MV^{\ddagger}$  formation. The intensity of the excitation radiation absorbed by the photolyte is taken with respect to the absorption by the active component (anthracene derivative) solely, because excitation of this compound only leads to the formation of the  $MV^{\ddagger}$  cation-radical. The rate of the  $MV^{\ddagger}$  concentration increase is described by the equation

$$dc_{MV^{\ddagger}}/dt = \Phi(A_0/A)I = \Phi(A_0/A)I_0(1 - 10^{-A}), \quad (I)$$

where  $A_0/A$  is the ratio of the absorbance of the anthracene derivative to the total absorbance of the solution at the excitation wavelength in the given time instant. The dimension of the entering excitation radiation  $I_0$  is  $\text{mol quant s}^{-1} \text{ l}^{-1}$ . The total

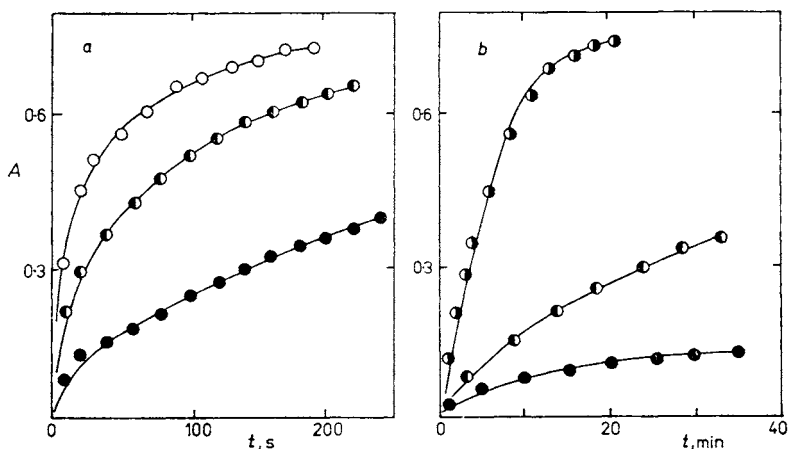


FIG. 2

Increase in absorbance of  $MV^{\ddagger}$  at 602 nm during irradiation of a system containing  $MV^{2+}$  ( $0.2 \text{ mmol l}^{-1}$ ), TEA ( $10 \text{ mmol l}^{-1}$ ) and either 1,5-ADS ( $0.2 \text{ mmol l}^{-1}$ ),  $I_0 = 4.45 \cdot 10^{16} \text{ quant} \cdot \text{s}^{-1}$  a or 9-AA ( $0.18 \text{ mmol l}^{-1}$ ) in SDS ( $50 \text{ mmol l}^{-1}$ )  $I_0 = 3.5 \cdot 10^{16} \text{ quant s}^{-1}$  b;  $\lambda_{ex}$  365 nm, pH: ● 7.0, ◐ 7.8, ○ 8.7, ● 10.2

absorbance is

$$A = A_0 + A_{MV^+} = \epsilon_A c_A + \epsilon_{MV^+} c_{MV^+} \quad (2)$$

If the concentration of the anthracene derivative can be regarded as constant, the time change in absorbance can be expressed as

$$dA/dt = \Phi I_0 (\epsilon_A \epsilon_{MV^+} c_A / A) (1 - 10^{-A}) \quad (3)$$

which integrated over the  $\langle 0, t \rangle$  interval gives

$$A_t^2 - A_0^2 = 2\Phi I_0 \epsilon_A \epsilon_{MV^+} c_A \int_0^t (1 - 10^{-A}) dt \quad (4)$$

The slope of this dependence was used to calculate the quantum yield. Since for experimental reasons the time intervals were chosen not very dense (10 s for ADS and 60 s for 9-AA), the functional dependences of the experimental values were fitted by 4th and 5th degree polynomials.

Eq. (4) is satisfied (with a correlation coefficient of 0.998) in the starting conditions of irradiation until the absorbance of  $MV^{\dot{+}}$  attains a value of approximately 0.9, which is in an exposure period of about 20 s.

The calculated quantum yields are given in Table I. It is evident that the quantum yield as well as the rate of formation of  $MV^{\dot{+}}$  depends appreciably on pH; the roughly S-shaped curve of this dependence, particularly for ADS, exhibits an inflection point in the pH 8 range.

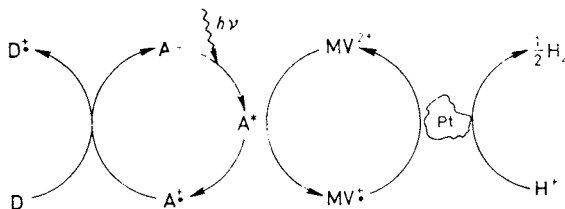
ADS in solutions fluoresce intensely<sup>3,8,9</sup>; the quantum yields of fluorescence in water are 0.14 and 0.08 for 1,5-ADS and 1,8-ADS, respectively. This fluorescence is efficiently quenched by  $MV^{2+}$  which forms CT complexes with these anthracene derivatives in their ground energy state<sup>3</sup>. We assume, taking into account the Gibbs free energy change<sup>3</sup>, that the electron transfer proceeds predominantly from the first singlet excited state. This assumption is borne out by the above results; consistent

TABLE I

Quantum yields of formation of methylviologen cationradical in dependence on pH

Compound	pH 7.0	pH 7.8	pH 8.7	pH 10.2
1,8-ADS	0.11	0.20	0.31	0.36
1,5-ADS	0.06	0.11	0.22	0.26
9-AA	0.001	0.003	0.007	0.01

with it is also the relatively low quantum yield of formation of  $MV^{\ddagger}$  during the electron transfer from excited molecules of 9-AA to  $MV^{2+}$  in the micellar medium of SDS, where the reactive excited state can only be the triplet state of the  $\pi\pi^*$  electronic configuration because the quantum yield of ISC for 9-AA is unity<sup>10</sup>.



SCHEME 1

The simplified reaction pathway 1 (Scheme 1), which applies generally to similar systems<sup>11-13</sup> where the electron donor D (TEA) is "sacrificed", should be considered within a whole complex of simultaneous reactions where the irreversible oxidation of D is a competitive reaction with respect to the electron back-transfer from  $MV^{\ddagger}$  to the anthracene derivative cation-radical  $A^{\ddagger}$ . In view of the basic properties of TEA, we suppose that the effect of pH appears mainly in the rate of this competitive reaction.

The electron transfer from  $MV^{\ddagger}$  to colloidal platinum and the generation of hydrogen are appreciably pH dependent<sup>14</sup>. The equivalence point for the  $MV^{2+}/MV^{\ddagger}$  pair lies at pH 7.63 for a hydrogen pressure of 0.1 MPa. Thus it can be expected that at lower pH, reduction of  $H_2O$  to  $H_2$  will take place in the system under study. Qualitative experiments performed in the preparative photochemical reactor with ADS as the primary electron donor A in solutions at pH 7.0 led to photo-

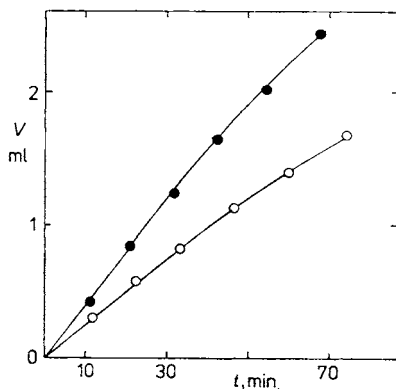


FIG. 3  
Evolution of photogenerated hydrogen in the presence of colloidal platinum for systems with ● 1,8-ADS, ○ 1,5-ADS

generation of hydrogen at rates of 2.25 and 1.35 ml h<sup>-1</sup> for 1,8-ADS and 1,5-ADS, respectively (Fig. 3).

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Translated by P. Adámek.