

Pulse Radiolysis and Simulation Computation Studies on Acridine Orange in Aqueous Solutions

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A combined pulse radiolysis-computer simulation method was applied for the elucidation of the complicated multiple H-attack on acridine orange in aqueous solutions at pH=1 to 3. The simultaneous formation of three intermediates was established: semiquinone (H-addition on the N-atom of the chromophore group), R'-species (reaction on the meso-C-atom) and H-adducts on the aromatic ring carbon. Their superimposed spectra were resolved, the individual extinction coefficients and the rate constants for their formation and decay were determined. The results are of importance in particular for understanding the decomposition of acridine orange applied as sensitizer in various devices for solar energy utilization.

1. Introduction

Acridine orange (AO, 3,6-bis-dimethylamino-acridine) has been investigated in respect of various aspects, e. g. as photosensitizer in redox devices of solar energy utilization [1, 2], as energy transfer compound in micelles [3], as well as in photophysical [4] and in biological studies [5–8]. Special interest was thereby devoted to the dye triplet and its semi-reduced form by using flash photolysis technique [9–14]. For the production of semiquinone by one electron reduction of the triplet in aqueous or methanolic solutions an appropriate electron donor (e. g. N,N,N',N'-tetramethyl-p-phenyldiamine, TMPD, etc.) was usually applied [11–14]. For semiquinone produced under such conditions in aqueous solutions at pH 3 an absorption maximum at 360 nm ($\epsilon_{360} \cong 10^3 \text{ m}^2 \text{ mol}^{-1}$) and at pH 12 a maximum at 405 nm ($\epsilon_{405} = 2.6 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$) was reported [11, 12]. For the protolytic equilibrium of these two species a $\text{pK} = 5.1$ was determined [14]. By the flash photolysis investigations also dye decomposition has been observed [11]. No rate constants for the formation and decay of semiquinone have been reported yet.

It might be mentioned that the electron donor used for the quenching of the triplet dye is converted into an equivalent amount of the corresponding radical cation. The absorption spectrum of this species is in most cases at least partly superimposed

with that of semiquinone, and therefore the concentration of the last one can only be estimated. Hence, the spectroscopic data obtained by means of flash or laser photolysis techniques are of insufficient accuracy. The pulse radiolysis method, on the other side, offers the possibility for a direct formation of dye semiquinone by reaction of H-atoms or solvated electrons (e_{aq}^-) with acridine orange in aqueous solutions. In addition to this one can resolve superimposed transient spectra as well as obtain correct kinetic data of eventually simultaneous reaction processes by using simulation computations. This kind of combined studies has been already applied successfully in the case of thionine and methylene blue [15–17]. Hence, pulse radiolysis investigations combined with a simulation computation procedure on acridine orange in acid aqueous solutions were performed and the results are presented in this paper.

2. Experimental

2.1. Preparation of Solutions

Acridine orange (EGA Chemie, FRG) was purified by the method previously described [18, 19]. As a final step of purification it was sublimated under low pressure before reconverting it into $\text{AO} \cdot \text{HCl}^+$. All other chemicals (reagent grade, LOBA Chemie, Austria) were used without further purification. The solutions were prepared with four times freshly distilled water and contained 5×10^{-6} to $2 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ AOH^+ and $2 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

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t-butanol acting as OH-scavenger ($k(\text{OH} + t\text{-C}_4\text{H}_9\text{OH}) = 5.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [20]). The formation of dimers has been taken into account [18, 19]. For adjusting $\text{pH}=1$ to 3 of the solutions sulfuric acid was used. Thereby e_{aq}^- were converted into H-atoms ($k(\text{e}_{\text{aq}}^- + \text{H}^+) = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [21]), and the total H-yield amounted to $G(\text{H}) = 3.55$ at $\text{pH}=1$, and 3.3 at $\text{pH}=3$ respectively [22]. A number of experiments were also performed in the pH -range from 0.8 to 4 in order to determine the pK_1 -value of dye semiquinone.

2.2. Pulse Radiolysis Facility

A 3 MeV Van de Graaff accelerator (Type K High Voltage Eng., Burlington, USA) provided electron pulses of $0.4 \mu\text{s}$ duration**. The solutions were irradiated in a suprasil quartz cell (6 cm light path) at room temperature and were exchanged after each electron pulse by means of a remote-controlled valve. The analysing light (XBO 450 W Xenon lamp OSRAM, equipped for flashing operation) was combined with a double-monochromator with quartz prism (Zeiss MM 12), photomultiplier (Hamamatsu R 955) and on-line computer (PDP 11), which made it possible to achieve a strong reduction of the noise by sampling. Further details

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of the pulse radiolysis equipment and dosimetry were reported previously [23, 24]. The applied dose amounted 1 to $5 \text{ J} \cdot \text{kg}^{-1}$ (100 to 500 rad) per pulse, but the transient absorption spectra were normalized or a dose of $10 \text{ J} \cdot \text{kg}^{-1}$ (1 krad).

2.3. Simulation Computations

The simulation computations were performed on the CDC-computer of the Vienna University, applying a special computer programm [25].

3. Results and Discussion

3.1. Pulse Radiolysis Results

The total transient absorption spectrum was measured in the range from 250 to 600 nm at $\text{pH}=1$, 1.8 and 2.8, using 5×10^{-6} to $2 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ AOH^+ in the presence of $2 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ t-butanol in argon saturated aqueous solutions. The absorption spectra measured at $15 \mu\text{s}$ and $60 \mu\text{s}$ after the pulse end ($\text{pH} 1$) are presented in Figure 1. Although they are showing practically the same absorption maxima (360, 410 and 560 nm) and bleaching minima (260, 290 and 480 nm), their lapses are different. So, in the range of 410 nm spectrum A ($15 \mu\text{s}$) possesses a higher optical density than spectrum B ($60 \mu\text{s}$). The absorption spectrum of acridine orange at $\text{pH} 2.6$ is shown for comparison as insert in Figure 1.

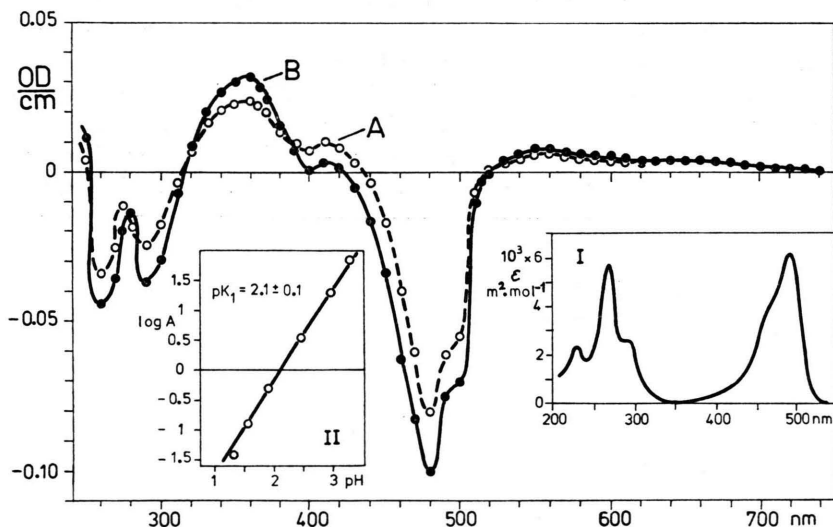


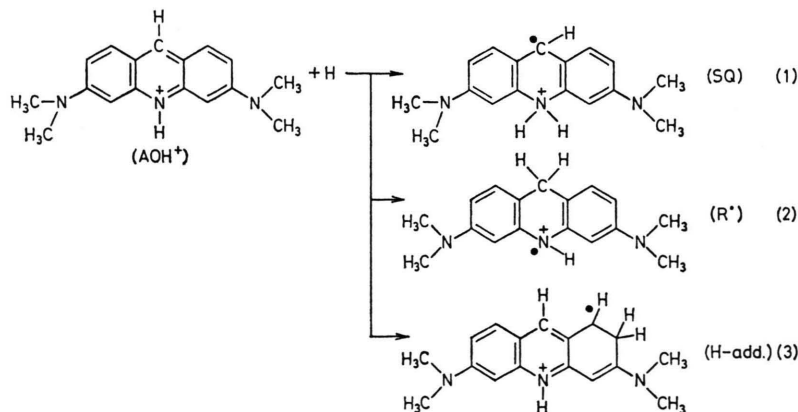
Fig. 1. Total absorption spectrum of transients produced by the attack of H-atoms on acridine orange (A) $15 \mu\text{s}$ and (B) $60 \mu\text{s}$ after pulse end. (Solution: $10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ AOH^+ , $2 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ t-butanol, saturated with argon, $\text{pH}=1$. OD/cm-values were normalized to $10 \text{ J} \cdot \text{kg}^{-1}$). Insert I: Absorption spectrum of AOH^+ in aqueous solution at $\text{pH}=2.6$. Insert II: Determination of pK_1 -value for semiquinone of AOH^+ at 360 nm.

Further, the rate constants for the reaction of H-atoms with AOH^+ were determined by following the pseudo-first order build-up of the transient absorption at 360, 410 and 560 nm (solution: $5 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ AOH^+ , $2 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ t-butanol, airfree, $\text{pH} = 1$). Following mean values were obtained: $k'_{360} = 5.0 \times 10^4 \text{ s}^{-1}$, $k'_{410} = 1 \times 10^5 \text{ s}^{-1}$ and $k'_{560} = 6.0 \times 10^4 \text{ s}^{-1}$. It was established that the k'_{360} -value is also valid for the range between 330 and 365 nm (AOH^+ does not absorb significantly in this field, see insert I, Fig. 1) and the k'_{560} -value is practically the same for the region 550 to 660 nm. The different curve lapses of spectrum A and B (Fig. 1) indicate clearly that the reaction of H-atoms with AOH^+ leads to the formation of more than one transient.

Some preliminary pulse radiolysis experiments were also carried out with 10^{-5} M AOH^+ in neutral solution (saturated with N_2O), in order to determine the reactivity of AOH^+ with the OH-radicals. An approximate overall rate constant $k(\text{OH} + \text{AOH}^+) = 9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was obtained. This value, as well as $k(\text{e}_{\text{aq}}^- + \text{AOH}^+) = 3.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [26] was required for the computer simulation procedure.

3.2. Computer Simulation

In analogy to previous studies with methylene blue and thionine [15–17], it is postulated that the H-atoms can attack the acridine orange on three different positions: 1) on the N-atom of the chromophore ring, leading to the formation of semi-quinone (SQ, reaction 1) [12], 2) on the meso-C-atom, leading to the formation of R'-species (reaction 2) and 3) on the aromatic ring carbons, forming H-adducts (reaction 3):



Simultaneously to these processes a number of further reactions take place, which are summarized in Table 1, together with the corresponding rate constants. Assuming a homogeneous distribution of H-atoms in the diluted acridine orange solutions (AOH^+), the reaction mechanism can now be expressed by a system of differential equations, presented in Table 2.

The unknown parameters (k_1 to k_3 , k_6 to k_8' and the ϵ -values of SQ, R' and H-adduct on ring carbon) were determined by applying a non-linear least-squares fitting treatment in such a manner, that the computed OD-values approximate best the experimental data, obtained by pulse radiolysis. In such an optimisation procedure the unknown parameters were varied until the sum of squared deviations between computed and experimental OD-values become a minimum [29, 30]. Thereby the squared deviations for every set of data at each wavelength were weighted, according to their different absorption intensities [25]. By applying a fourth order Runge-Kutta method, in the version by Gill [17, 31] for solving the non-linear differential equations in Table 2, a high sensitivity was achieved with regard to the time interval used in the calculations. Large differences in the sensitivities always appear in those systems of differential equations, in which the rate of production and consumption of the various species differ by orders of magnitude; such systems are called "stiff". Correct results can be only obtained by setting the time step size extremely small, because numerical errors introduced by excessive step size in the initial period of the reactions are propagated also in regions of higher conversions. But, the computer time required to cover high conversions of reactions by very small time increments

| No. | Reaction | Rate constant ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) * |
|-----|--|--|
| 1 | $\text{AOH}^+ + \text{H} \rightarrow \text{SQ}$ | $k_1 = ?$ |
| 2 | $\rightarrow \text{R}^{\cdot}$ | $k_2 = ?$ |
| 3 | $\rightarrow \text{H-add.}$ | $k_3 = ?$ |
| 4 | $\text{AOH}^+ + \text{OH} \rightarrow \text{AOH}^+ \cdot \text{OH} (\text{OH-add.})$ | $k_4 = 9 \times 10^9$ |
| 5 | $\text{AOH}^+ + e_{\text{aq}}^- \rightarrow \text{SQ}$ | $k_5 = 3.2 \times 10^{10}$ |
| 6 | $2\text{SQ} \rightarrow \text{Products}$ | $2k_6 = ?$ |
| 7 | $\text{R}^{\cdot} \rightarrow \text{Products}$ | $k'_7 = ?$ |
| 8 | $\text{H-add.} \rightarrow \text{Products}$ | $k'_8 = ?$ |
| 9 | $\text{H} + \text{H} \rightarrow \text{H}_2$ | $2k_9 = 2.3 \times 10^{10}$ |
| 10 | $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$ | $2k_{10} = 1.2 \times 10^{10}$ |
| 11 | $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ | $k_{11} = 2 \times 10^{10}$ |
| 12 | $e_{\text{aq}}^- + \text{OH} \rightarrow \text{OH}^-$ | $k_{12} = 3 \times 10^{10}$ |
| 13 | $e_{\text{aq}}^- + e_{\text{aq}}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ | $2k_{13} = 1.2 \times 10^{10}$ |
| 14 | $e_{\text{aq}}^- + \text{H} \rightarrow \text{H}_2 + \text{OH}^-$ | $k_{14} = 2.5 \times 10^{10}$ |
| 15 | $\text{H}^+ + e_{\text{aq}}^- \rightarrow \text{H}$ | $k_{15} = 2.3 \times 10^{10}$ |
| 16 | $\text{t-C}_4\text{H}_9\text{OH} + \text{H} \rightarrow \text{t-C}_4\text{H}_8\text{OH} + \text{H}_2$ | $k_{16} = 3 \times 10^5$ |
| 17 | $\text{t-C}_4\text{H}_9\text{OH} + \text{OH} \rightarrow \text{t-C}_4\text{H}_8\text{OH} + \text{H}_2\text{O}$ | $k_{17} = 5.5 \times 10^8$ |
| 18 | $2\text{t-C}_4\text{H}_8\text{OH} \rightarrow (\text{C}_4\text{H}_8\text{OH})_2$ | $2k_{18} = 1.4 \times 10^9$ |
| 19 | $\text{t-C}_4\text{H}_8\text{OH} + \text{AOH}^+ \rightarrow \text{SQ} + \text{Products}$ | $k_{19} = 5 \times 10^6$ |
| 20 | $\text{AOH}^+ \cdot \text{OH} \rightarrow \text{Products}$ | $k'_{20} = 5 \times 10^2$ |

* k' is given in s^{-1} . The rate constants were taken from [27, 28].

Table 1. Reactions and rate constants taking place by pulse radiolysis of acridine orange in the presence of t-butanol in aqueous solutions.

Table 2. System of differential equations applied for solutions of the simultaneous proceeding reactions, given in Table 1 for the acridine orange/t- $\text{C}_4\text{H}_9\text{OH}$ system.

| No. | Equations |
|-----|--|
| 1 | $\frac{d[\text{AOH}^+]}{dt} = -\{(k_1 + k_2 + k_3)[\text{H}] + k_4[\text{OH}] + k_5[e_{\text{aq}}^-] + k_{19}[\text{t-C}_4\text{H}_8\text{OH}]\}[\text{AOH}^+]$ |
| 2 | $\frac{d[\text{H}]}{dt} = k_{15}[\text{H}^+][e_{\text{aq}}^-] - \{(k_1 + k_2 + k_3)[\text{AOH}^+] + 2k_9[\text{H}] + k_{11}[\text{OH}] + k_{14}[e_{\text{aq}}^-] + k_{16}[\text{t-C}_4\text{H}_9\text{OH}]\}[\text{H}]$ |
| 3 | $\frac{d[\text{SQ}]}{dt} = \{k_1[\text{H}] + k_5[e_{\text{aq}}^-] + k_{19}[\text{t-C}_4\text{H}_8\text{OH}]\}[\text{AOH}^+] - 2k_6[\text{SQ}]^2$ |
| 4 | $\frac{d[\text{R}^{\cdot}]}{dt} = k_2[\text{H}^+][\text{AOH}^+] - k'_7[\text{R}^{\cdot}]$ |
| 5 | $\frac{d[\text{H-add}]}{dt} = k_3[\text{H}][\text{AOH}^+] - k'_8[\text{H-add}]$ |
| 6 | $\frac{d[\text{AOH}^+ \cdot \text{OH}]}{dt} = k_4[\text{OH}][\text{AOH}^+] - k'_{20}[\text{AOH}^+ \cdot \text{OH}]$ |
| 7 | $\frac{d[\text{OH}]}{dt} = -\{k_4[\text{AOH}^+] + 2k_{10}[\text{OH}] + k_{11}[\text{H}] + k_{12}[e_{\text{aq}}^-] + k_{17}[\text{t-C}_4\text{H}_9\text{OH}]\}[\text{OH}]$ |
| 8 | $\frac{d[e_{\text{aq}}^-]}{dt} = -\{k_5[\text{AOH}^+] + k_{12}[\text{OH}] + 2k_{13}[e_{\text{aq}}^-] + k_{14}[\text{H}] + k_{15}[\text{H}^+]\}[e_{\text{aq}}^-]$ |
| 9 | $\frac{d(\text{t-C}_4\text{H}_9\text{OH})}{dt} = -\{k_{16}[\text{H}] + k_{17}[\text{OH}]\}[\text{t-C}_4\text{H}_9\text{OH}]$ |
| 10 | $\frac{d(\text{t-C}_4\text{H}_8\text{OH})}{dt} = \{k_{16}[\text{H}] + k_{17}[\text{OH}]\}[\text{t-C}_4\text{H}_9\text{OH}] - 2k_{18}[\text{t-C}_4\text{H}_8\text{OH}]^2 - k_{19}[\text{t-C}_4\text{H}_8\text{OH}][\text{AOH}^+]$ |
| 11 | $\frac{d[\text{OH}^-]}{dt} = \{2k_{13}[e_{\text{aq}}^-] + k_{14}[\text{H}] + k_{12}[\text{OH}]\}[e_{\text{aq}}^-]$ |
| 12 | $\frac{d[\text{H}^+]}{dt} = -k_{15}[\text{H}^+][e_{\text{aq}}^-]$ |

is then extremely long. Therefore, the computer program [17] was modified by applying Gear's method [32] for the solution of "stiff" differential equations. This fast numerical algorithm contains an efficient self adjusting optimum step size control, which allows rapid variations in concentrations by small step sizes and, vice versa, low variations permit large step sizes. In this way the applied algorithm prevents the accumulation of computational errors.

In order to obtain a numerical solution of the differential equation systems, approximate starting values for the unknown rate constants (k_1 , k_2 , k_3 and k_6 , k_7' , k_8') are needed. The first three are estimated from the pseudo-first order build-up of the intermediates at different wavelengths. The corresponding decay rates (k_6 to k_8') of the species have been approximated by plotting $1/\text{OD}$ and $\ln \Delta \text{OD}$ values as a function of time up to $2000 \mu\text{s}$ at 360, 410 and 560 nm. The initial values for the spectroscopic data in the iterative optimisation procedure were estimated in the following way: for SQ $\epsilon_{360} = 1000 \text{ m}^2 \text{ mol}^{-1}$ [11, 12] and for R' and H-adduct in analogy to methylene blue [15].

The experiments and the computer simulations were carried out for 5×10^{-6} , 10^{-5} and $2 \times 10^{-5} \text{ mol dm}^{-3}$ AOH⁺ in the presence of $2 \times 10^{-2} \text{ mol dm}^{-3}$ t-butanol at pH=1, 1.8 and 2.8 in airfree aqueous solutions. All measured OD-changes as a function of time from $2 \mu\text{s}$ upto $2000 \mu\text{s}$ in the range of 250 to 600 nm in steps of 10 nm were analysed together in one single step by an optimisation procedure, which yielded one set of rate constants and extinction coefficients for each individual wavelength. For all experimental conditions used, a satisfactory consistency between the experimental and the calculated OD-values was obtained. It was possible to resolve the composite absorption spectrum (Fig. 1), even in that ranges, where a strong dye bleaching occurs.

Some of the kinetic courses for the formation and decay of the various transients and the bleaching of AOH⁺ are presented as typical examples for illustration of the computation method. In Fig. 2 the computed changes of the OD-values as a function of time are shown for semiquinone (CSQ), R'-species (CR') and the dye bleaching (CDB) at 300 nm. The measured (MTA) and computed total absorption (CTA) show a satisfactory consistency.

The ability of the applied procedure is especially evident in Fig. 3, where the absorption of SQ, R' and H-adduct are superimposed with the strong dye

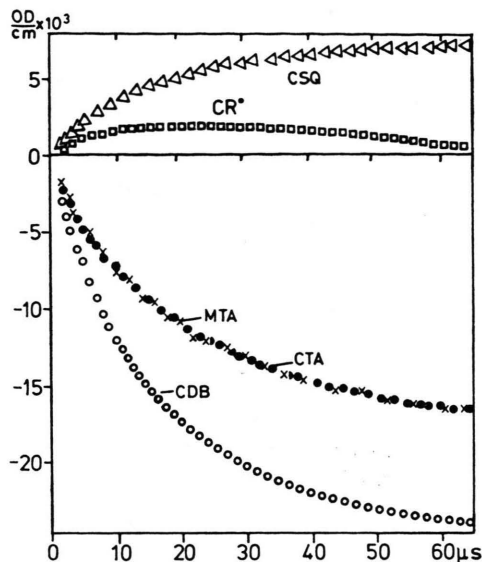


Fig. 2. Optical density (OD/cm) as a function of time (μs) at 300 nm for computed formation of semiquinone (CSQ, Δ) and CR' (\square) as well as for dye bleaching (CDB, \circ), measured (MTA, \times) and computed total absorption (CTA, \bullet). (Solution: $5 \times 10^{-6} \text{ mol dm}^{-3}$ AOH⁺, $2 \times 10^{-2} \text{ mol dm}^{-3}$ t-butanol, pH=1.8, saturated with Argon; $3.2 \text{ J kg}^{-1}/0.4 \mu\text{s}$ pulse.)

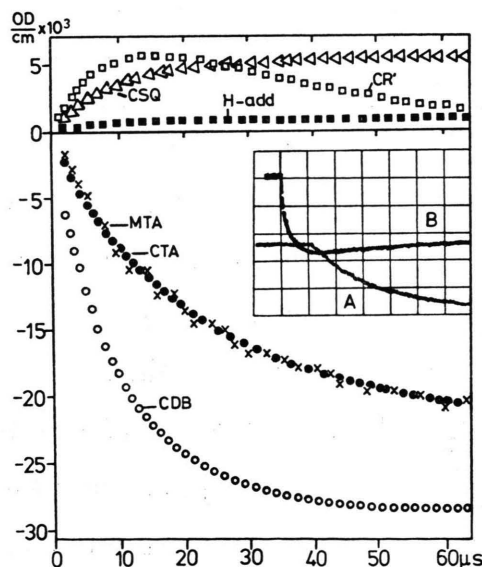


Fig. 3. Optical density (OD/cm) as a function of time (μs) at 460 nm for computed formation of semiquinone (CSQ, Δ), CR' species (\square) and H-adducts (\blacksquare) as well as for dye bleaching (CDB, \circ), measured (MTA, \times) and computed total absorption (CTA, \bullet). (Solution: $10^{-5} \text{ mol dm}^{-3}$ AOH⁺, $2 \times 10^{-2} \text{ mol dm}^{-3}$ t-butanol, pH=1.8, saturated with Argon; $3 \text{ J kg}^{-1}/0.4 \mu\text{s}$ pulse.) Oscilloscope traces at 460 nm for the total formation (A, $10 \mu\text{s}/\text{div.}$) and decay (B, $200 \mu\text{s}/\text{div.}$, sensitivity $200 \text{ mV}/\text{div.}$) of SQ R' and H-adduct, superimposed with dye bleaching.

bleaching at 460 nm. It can be seen, that the R'-formation reaches its maximum 15 μ s a.p.e. (compare with the spectrum in Fig. 1), whereas the SQ and H-adduct need about 60 μ s. The course of the absorption change as a function of time is illustrated by the oscilloscope traces given in the insert of Figure 3.

An other example is shown in Fig. 4, which represents the formation of SQ, superimposed with dye bleaching, and a negligible contribution of R'-species at 500 nm. For simplicity the presentation of R' is omitted, however, its fraction is considered in the CTA-values. The very good agreement be-

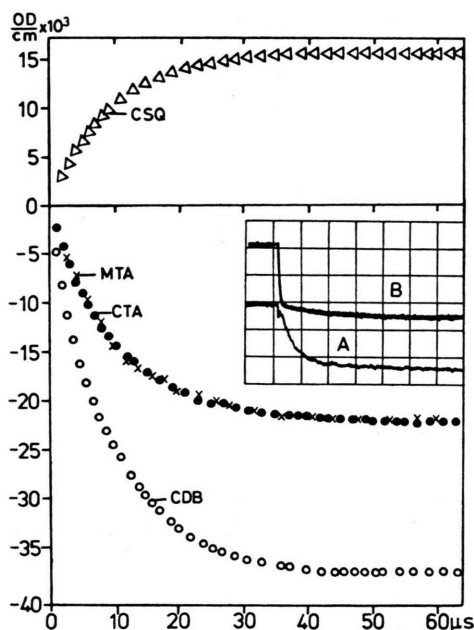


Fig. 4. Optical density (OD/cm) as a function of time (μ s) at 500 nm for computed formation of semiquinone (CSQ, Δ) as well as for dye bleaching (CDB, \circ), measured (MTA, \times) and computed total absorption (CTA, \bullet). (Solution: 10^{-5} mol \cdot dm $^{-3}$ AOH $^{+}$, 2×10^{-2} t-butanol, pH=2, saturated with Argon; 3.2 J \cdot kg $^{-1}$ /0.4 μ s pulse.) Insert: Oscilloscope traces at 500 nm for formation of SQ and dye bleaching (A, 20 μ s/div.) and decay (B, 200 μ s/div, sensitivity: 50 mV/div.).

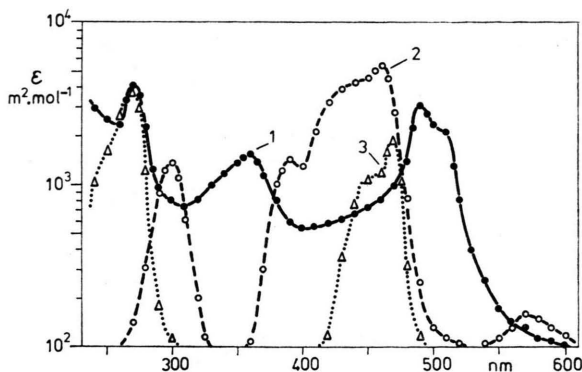


Fig. 5. Absorption spectra of transients produced by reaction of H-atoms with acridine orange in aqueous solution at pH=1.8. (1) semiquinone, (2) R' species and (3) H-adducts (for details see text).

tween MTA- and CTA-values is obvious. For comparison the registered oscilloscope traces for the absorption changes are given as insert.

By combination of the pulse radiolysis with computer simulation procedure it was possible to obtain the extinction coefficients for every individual specie (SQ, R' and H-adduct) in the range of 240 to 600 nm. These computed absorption spectra are presented in Figure 5. It is obvious that there is a strong superimposition of their absorption bands, with exception of the second absorption band of SQ (330 to about 370 nm). SQ possesses three absorption maxima and their ϵ -values are given in Table 3 for three pH values. The R'-species show two main absorptions, namely for pH=1.8 at 460 nm ($\epsilon_{460} = 5.4 \times 10^3$ m 2 mol $^{-1}$) and 300 nm ($\epsilon_{300} = 1.35 \times 10^3$ m 2 mol $^{-1}$). The absorption maxima and ϵ -values (at pH=1.8) of the H-adduct on ring carbon are: 470 nm ($\epsilon_{470} = 1.8 \times 10^3$ m 2 mol $^{-1}$) and 270 nm ($\epsilon_{270} = 3.7 \times 10^3$ m 2 mol $^{-1}$).

Simultaneously with the spectroscopic data of the three dye transients also their individual formation and decay kinetics were computed for pH=1.1, 1.8 and 2.8 and are compiled in Table 4. In addition to the dismutation of SQ the formation of dimers is

| Absorption bands of SQ | pH = 1.1 | | pH = 1.8 | | pH = 2.8 | |
|------------------------|-----------------------|---|-----------------------|---|-----------------------|---|
| | λ_{\max} (nm) | ϵ_{\max} (m 2 \cdot mol $^{-1}$) | λ_{\max} (nm) | ϵ_{\max} (m 2 \cdot mol $^{-1}$) | λ_{\max} (nm) | ϵ_{\max} (m 2 \cdot mol $^{-1}$) |
| 1st | 495 | 2500 | 490 | 3000 | 480 | 3900 |
| 2nd | 350 | 1470 | 360 | 1500 | 370 | 1680 |
| 3rd | 270 | 4100 | 270 | 4120 | 270 | 4200 |

Table 3. Absorption maxima (λ_{\max}) and molar extinction coefficients (ϵ) for dye semiquinone (SQ) at different pH's.

Table 4. Formation and decay kinetics of transients formed by pulse radiolysis of aqueous 5×10^{-6} to 2×10^{-5} mol · dm⁻³ acridine orange, 2×10^{-2} mol · dm⁻³ t-butanol, saturated with argon.

| Transient | Formation kinetics (pH 1 to 3) k in (dm ³ · mol ⁻¹ · s ⁻¹) | Decay kinetics ($2k$ in dm ³ · mol ⁻¹ · s ⁻¹ and k' in s ⁻¹) * at: | | |
|-----------|--|--|------------------------------------|----------------------------------|
| | | pH = 1.1 | pH = 1.8 | pH = 2.8 |
| SQ | $(7.0 \pm 0.5) \times 10^9$ | $2k = (0.69 \pm 0.05) \times 10^9$ | $2k = (0.84 \pm 0.05) \times 10^9$ | $2k = (1.4 \pm 0.1) \times 10^9$ |
| R' | $(2.0 \pm 0.3) \times 10^9$ | $k' = (3.5 \pm 0.5) \times 10^4$ | $k' = (3.5 \pm 0.5) \times 10^4$ | $k' = (3.5 \pm 0.5) \times 10^4$ |
| H-adduct | $(1.0 \pm 0.2) \times 10^9$ | $k' = (0.3 \pm 0.1) \times 10^4$ | $k' = (0.4 \pm 0.1) \times 10^4$ | $k' = (0.6 \pm 0.2) \times 10^4$ |

* k' = rate constant for pseudo first order decay.

also possible. In this case the reported $2k$ -value for disappearance of SQ species should be taken as a total rate constant for both reactions. It was not possible to resolve these processes yet, but further work in this respect is in progress.

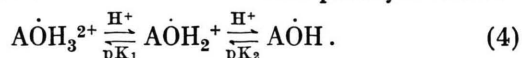
No significant difference could be observed for the formation kinetics of the three species in the pH-range 1–3. The rate of disappearance of SQ and H-adduct show a significant increase with pH, whereas this of the R'-species remains unchanged. This effect could be explained by the differences in the solvation shell of the various protonated forms of the species. Similar observations have been previously made on amines [33].

Based on the formation kinetics it has been calculated, that 70% of the H-atoms reacting with AOH⁺ result in the formation of SQ, 20% H produce R'-species and the remaining 10% H give H-adduct on ring carbon.

Finally it should be mentioned that Zanker et al. [34] have observed a neutral N-radical (absorption band 580 nm) and a N-radicalcation (650 nm) in addition to an "orange" radical by photolysis of 9-substituted acridanes in alcohol at very low temperatures. Applying flash photolysis technique Kira and Koizumi [35] established the formation only of a C-radical (SQ; absorption bands at 350 and 520 nm) by photolysis of biacridane in dimethylsulfoxide solutions. Using acridine and acridane in methanol or benzene they produced additionally a N-radical (R' species; absorption at 350 and 560 nm). The authors didn't present any molar extinction coefficients and kinetic data for further characterisation of these species.

pK-determination

Depending on the pH of the solution the produced SQ of AOH⁺ can exist in various protolytic forms:



The pK₂-value has been already determined by flash photolysis to be 5.1 [14]. By measuring the optical density at 350 nm as a function of pH in the range from 0.8 to 4 it was possible to determine pK₁ by using the Hammett's relation (5) [36]:

$$pK = pH - \log \frac{OD_b - OD}{OD - OD_a} \quad (5)$$

OD_a and OD_b are the optical densities of the pure acid and basic form of SQ. Plotting the logarithmic expression from Eq. (5) as log A in dependence of pH a pK₁ = 2.1 ± 0.1 was obtained (insert II in Figure 1).

Conclusion

The combination of both, pulse radiolysis and computer simulation, is proved to be a powerful method for precise elucidation of complicated reaction mechanisms like the multisite radical attack on a solute. By the reaction of H-atoms with acridine orange in aqueous solutions three transients were formed, SQ, R' and H-adduct on ring carbon. It was possible to resolve their superimposed spectra and to obtain the corresponding spectroscopic and kinetic data. These results could explain, at least partly, the decomposition of acridine orange, used as sensitizer, in the photoelectrochemical cells applied for solar energy utilization.

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