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Pulse Radiolysis of Methyl Viologen in Aqueous Solutions

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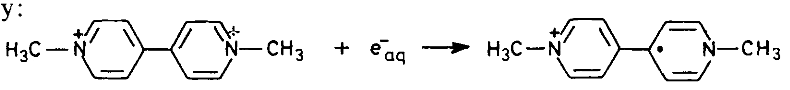
Pulse radiolysis of air-free aqueous methyl viologen (MV^{2+}) solutions was carried out at various pH. The attack of e^-_{aq} on MV^{2+}, with $k(e^-_{aq}+MV^{2+}) = 7.5\times10^{10}$ dm^3 mol^{-1} s^{-1}, leads to the formation of the long-lived radical cation ($MV^{\cdot+}$), which possesses two absorption maxima at 392.5 nm ($\varepsilon_{392.5} = 4200$ m^2 mol^{-1}) and 600 nm ($\varepsilon_{600} = 1450$ m^2 mol^{-1}). The H-atoms react with MV^{2+} at pH 1 forming two species, which have superimposed absorption bands. By means of a computer simulation they are resolved in the absorptions belonging to: (1) a protonated form of the radical cation ($MV^{\cdot+}H^+$), which is produced with $k(H+MV^{2+}) = (3.5\pm0.2)\times10^8$ dm^3 mol^{-1} s^{-1}, has 2 absorption maxima at 390 nm ($\varepsilon_{390} = 1700$ m^2 mol^{-1}) and 595 nm ($\varepsilon_{595} = 760$ m^2 mol^{-1}) and decays by second-order kinetics with $k = 3.5\times10^9$ dm^3 mol^{-1} s^{-1}; (2) an H-adduct ($MV^{\cdot2+}H$) on the ring carbon, which is formed with $k(H+MV^{2+}) = 2.5\times10^8$ dm^3 mol^{-1} s^{-1}, absorbs at 310 nm ($\varepsilon_{310} = 900$ m^2 mol^{-1}) and 470 nm ($\varepsilon_{470} = 630$ m^2 mol^{-1}) and decays by conversion into $MV^{\cdot+}H^+$ in a first-order process with $k = 6\times10^3$ s^{-1}. For the equilibrium

$$MV^{\cdot+}H^+ \rightleftharpoons MV^{\cdot+} + H^+$$

$pK = 2.9\pm0.1$ was determined. The presented data explain, at least partly, the instability of MV^{2+} when used as an electron acceptor in various devices for the utilization of solar energy.

Methyl viologen [(also called paraquat) 1,1′-dimethyl-4,4′-bipyridinium dihalide; MV^{2+}] has previously been studied because of its herbicidal and toxicological activity.[1-3] Owing to its ability to act as a strong electron acceptor it is also an important component in various photochemical and photoelectrochemical cells for the utilization of solar energy.[4, 5] The formation and reactivity of its reduced form ($MV^{\cdot+}$, radical cation), produced by a one-electron reduction, is of particular interest for both types of study:



MV^{2+} $MV^{\cdot+}$ (1)

The rate constant of reaction (1) determined by pulse radiolysis is very high: 7×10^{10} dm^3 mol^{-1} s^{-1} [ref. (6)] or 8.4×10^{10} dm^3 mol^{-1} s^{-1} [ref. (7) and (8)]. Two absorption maxima of $MV^{\cdot+}$ at 600 and 395 nm were reported, but the reported values of the corresponding molar extinction coefficients differ widely, ε_{600} from 1010[9] to *ca.* 1370 m^2 mol^{-1}[10] and ε_{395} from 3300[6] to 4500 m^2 mol^{-1}.[10]

A relatively strong consumption of MV^{2+} is established when it is used as an electron acceptor in various devices for hydrogen production by solar energy in aqueous solutions. In such systems, $MV^{\cdot+}$ appears as an intermediate, and is usually assumed to be regenerated in the presence of a suitable catalyst (*e.g.* PtO_2[11]). This regeneration is in most cases not quantitative.[12, 13] The reason for that is not precisely known. Since in such devices the precursors of H_2 are the H-atoms, which can partly diffuse away from the catalyst's surface, these could be involved in the decomposition of MV^{2+}. To elucidate this problem, the intermediates produced by the attack of H-atoms on MV^{2+} in acidic aqueous solutions were studied by pulse radiolysis. Some experiments were also performed at pH 7-9.8 in air-free aqueous solutions in order to verify the previous spectroscopic and kinetic data concerning $MV^{\cdot +}$.

EXPERIMENTAL

IRRADIATION FACILITIES*

Two sets of pulse radiolysis equipment were used.

(1) The 10 MeV LINAC at RISÖ (Haimson Research Corp., HRC-712; pulse duration variable from 10 ns to 1 μs, equipped for optical detection of transients[14] was combined with Nicolet Explorer III digital storage oscilloscope, where the data were stored on disks. Further treatment of the data was performed using an on-line PDP 8 computer.

(2) A 3 MeV Van de Graaff accelerator (type K, High Voltage Engineering Co., Burlington, USA) provided 0.4 μs pulses.[15, 16] The kinetic spectroscopy measurements of the short-lived species were performed in combination with an on-line PDP 11 computer. The applied dose in both cases was 2.5-6 J kg^{-1} (0.25-0.6 krad) per pulse.

PREPARATION OF SOLUTIONS

The aqueous solutions were prepared using triply distilled water. Methyl viologen dichloride (p.a. quality, B.D.H. Chemicals Ltd, Poole) and all other chemicals [NaCl, t-butyl alcohol, $HClO_4$, NaOH and $Ba(OH)_2$; E. Merck, p.a. grade] were used without further purification. Before irradiation the solutions were purged with high-purity argon for *ca.* 1 h in order to remove oxygen. As appropriate OH scavengers, one series of experiments used Cl^- ions [$k(OH+Cl^-) = 4.3\times 10^9\ dm^3\ mol^{-1}\ s^{-1}$][17] and a second t-butyl alcohol [$k(OH)+t\text{-}C_4H_9OH) = 5.5\times 10^8\ dm^3\ mol^{-1}\ s^{-1}$].[18]

COMPUTER SIMULATIONS

Because of the complexity of the kinetics, computer simulations of the experimental data for the attack of H-atoms on MV^{2+} were performed. For this purpose the CDC-computer of the Vienna University was used.

RESULTS AND DISCUSSION

REACTIVITY OF MV^{2+} WITH e^-_{aq}

The rate constant for the attack of e^-_{aq} on MV^{2+} [reaction (1)] was determined using airfree solutions of 10^{-5} mol dm^{-3} $MV^{2+}$with 5×10^{-3} mol dm^{-3} t-butyl alcohol at pH 8.2. The pH of the solutions was adjusted with a NaOH + $Ba(OH)_2$ mixture in order to remove bicarbonate. The measurements were performed at 720 nm, following the first-order decay of e^-_{aq} (dose: 2-4 J kg^{-1} per 0.4 μs pulse). After matrix corrections a mean value of several determinations was obtained:

$$k(e^-_{aq}+MV^{2+}) = (8.3\pm 1.0)\times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}.$$

In a second series of experiments (air-free solutions of 10^{-5} mol dm^{-3} MV^{2+} with 10^{-2} mol dm^{-3} t-butyl alcohol at pH 9.7; dose: 1.5-2 J kg^{-1} per 1 μs pulse) the rate

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constant was determined by the transient build-up at 392.5 nm (absorption maximum of $MV^{\cdot +}$). The mean value of several experiments is:

$$k(e^-_{aq}+MV^{2+}) = (6.7 \pm 1.0) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The mean value for the rate constant, determined by both methods is therefore:

$$k(e^-_{aq}+MV^{2+}) = 7.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

This value agrees with previous data.[6-8]

The absorption spectrum of the methyl viologen radical cation ($MV^{\cdot +}$), produced by the reaction of MV^{2+} with e^-_{aq}, was measured in air-free solutions [(2-4) × 10^{-4} mol dm^{-3} MV^{2+}, *ca.* pH 9] in the range 300-700 nm. Two maxima were found, at 392.5 nm ($\varepsilon_{392.5} = 4200$ m^2 mol^{-1}) and at 600 nm ($\varepsilon_{600} = 1450$ m^2 mol^{-1}), in agreement with the previously published spectrum.[10]

REACTIVITY OF MV^{2+} WITH H-ATOMS

Two series of experiments were performed, one using Cl^- ions and a second using t-butyl alcohol as OH-scavengers.

THE MV^{2+}/Cl^- SYSTEM

In acidic aqueous solutions the Cl^- ions (present in the original compound) act as efficient scavengers for OH radicals:[17]

$$Cl^- + OH \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \dot{C}lOH^- \tag{2}$$

$$k_2 = 4.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
$$k_2' = 6.1 \times 10^9 \text{ s}^{-1}$$

$$\dot{C}lOH^- + H^+ \xrightarrow{k_3} Cl^{\cdot} + H_2O \tag{3}$$

$$k_3 = 2.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$Cl^- + Cl^{\cdot} \xrightarrow{k_4} Cl_2^{\cdot -} \tag{4}$$

$$k_4 = 2.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$Cl_2^{\cdot -} + Cl_2^{\cdot -} \xrightarrow{k_5} Cl_3^- + Cl^- \tag{5}$$

$$2k_5 = 7.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The absorption maximum of $Cl_2^{\cdot -}$, at 340 nm ($\varepsilon_{340} = 880$ m^2 mol^{-1}), and of $\dot{C}lOH^-$, at 350 nm ($\varepsilon_{350} = 370$ m^2 mol^{-1}), and also their formation and decay kinetics are taken into account in the subsequent studies.

The total value for the reactivity of H-atoms with MV^{2+} was determined by following the formation of the transient absorption at 390 nm, which is the absorption maximum of $MV^{\cdot +}H^+$ species (the protonated form of $MV^{\cdot +}$; see later). The air-free solution at pH 1 used contained 2×10^{-2} mol dm^{-3} MV^{2+} and 5×10^{-3} mol dm^{-3} Cl^- as OH scavenger (dose rate: 5 J kg^{-1} per 0.4 μs). The apparent rate constant resulting from several determinations, after correction for the chlorine radical, was found to be:

$$k(H+MV^{2+})_{total} = (6 \pm 0.5) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

Similar rate constants were obtained under the same experimental conditions at 470 and 595 nm. They have been used as the starting parameters in the subsequent computer simulations.

In order to determine the reactivity of MV^{2+} with OH-radicals, needed for completion of the reaction mechanism, preliminary pulse-radiolysis studies were carried out with 2×10^{-4} mol dm^{-3} MV^{2+} saturated with N_2O (pH 6.3). In this case e^-_{aq} is converted into OH (total $G_{OH} = 5.5$) and the transient spectrum showed absorption maxima at 395, 470 and 570 nm. Following the build-up of the transients at 470 and 570 nm, and after appropriate corrections for the species resulting from the reaction of H with MV^{2+}, a rate constant for the reaction of OH with MV^{2+} was obtained:

$$k(\mathrm{OH}+\mathrm{MV}^{2+}) = 4 \times 10^8 \ \mathrm{dm^3\ mol^{-1}\ s^{-1}}.$$

Note that in neutral solution Cl^- does not act as OH scavenger, because reaction (3) does not take place. A detailed report on this subject will be published later.[19]

The absorption spectrum of the methyl viologen transients, formed by the attack of H-atoms, was measured in air-free acid solutions (pH 1) using $(1\text{-}4) \times 10^4$ mol dm^{-3} MV^{2+} and 5.8×10^{-3} mol dm^{-3} Cl^- (dose: 3-6 J kg^{-1} per 0.4 μs pulse) and is presented

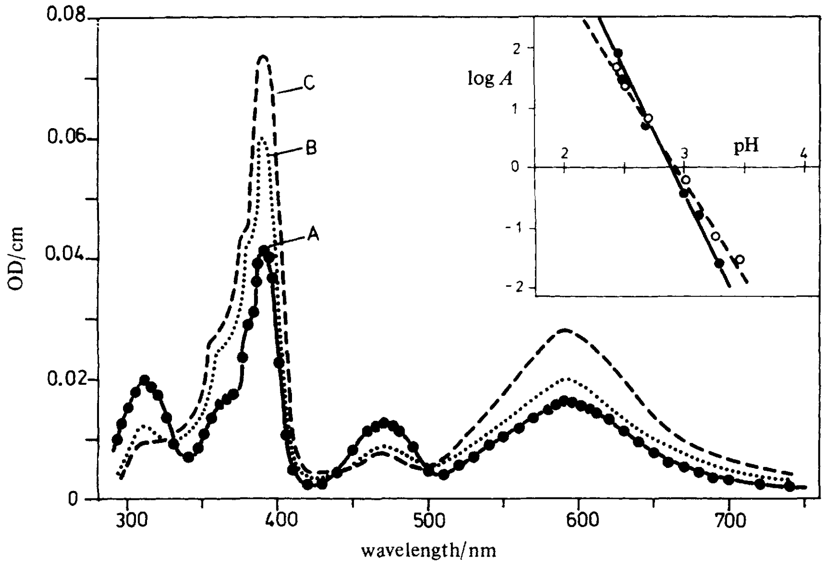
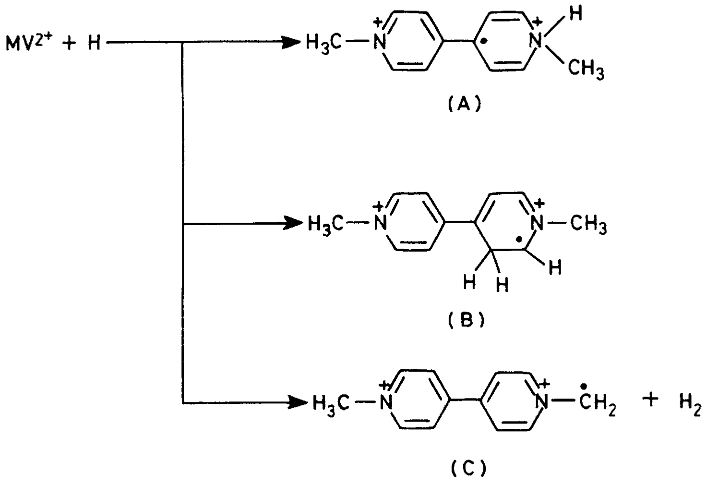


FIG. 1.—Absorption spectra of transients produced by attack of H-atoms on methyl viologen in air-free solution at pH 1. A: 4×10^{-4} mol dm^{-3} MV^{2+}, 5.8×10^{-3} mol dm^{-3} Cl^-, corrected for $Cl_2^{\cdot-}$ absorption. B: 2×10^{-4} mol dm^{-3} MV^{2+}, 0.1 mol dm^{-3} t-C_4H_9OH. C: 4×10^{-4} mol dm^{-3} MV^{2+}, 0.5 mol dm^{-3} t-C_4H_9OH. Insert: Determination of pK for the equilibrium $MV^{\cdot+} + H^+ \rightleftharpoons MV^{\cdot+}H^+$ (see text): ○, 600 and ●, 392.5 nm.

in fig. 1, spectrum A. The spectrum is corrected for $Cl_2^{\cdot-}$ and shows absorption maxima at 310, 390, 470 and 595 nm. The kinetics of the disappearance of the transient at these wavelengths were quite different. At 390 and 595 nm the decay is pure second order ($k \approx 2.6 \times 10^9$ dm^3 mol^{-1} s^{-1}), whereas at 310 nm it is mixed and at 470 nm predominantly first order ($k \approx 4 \times 10^3$ s^{-1}). This requires the assumption that the measured absorption belongs to more than one species. Theoretically, the H-atoms can attack the MV^{2+} molecules at different positions. Hence the formation of the following intermediates is assumed:



(6)

(7)

(8)

Radical (A), $(MV^{\cdot +}H^{+})$, is denoted as the protonated form of the radical cation $(MV^{\cdot +})$, whereas radical (B) represents one type of the various H-adducts $(MV^{\cdot 2+}H)$ on the ring carbon. The transient (C), resulting as a third possibility from the attack of H-atoms on MV^{2+} by abstraction of an H-atom from the $—CH_3$ group, seems to be less probable, since reactions of this type usually proceed with a rate constant of the order of 10^6 dm^3 mol^{-1} s^{-1}.[20-22]

COMPUTER SIMULATION OF THE MV^{2+}/Cl^- SYSTEM

The composite spectrum (fig. 1A) and the reaction kinetics resulting from the multisite attack of H-atoms on MV^{2+} can be resolved by a computer simulation.[23] This has previously been applied to the elucidation of the pulse-radiolysis data of aqueous methylene blue, thionine and acridine orange.[24-27] In the present case the observed rate constants for formation and decay of the methyl viologen species (given above) and the measured molar extinction coefficients, calculated from fig. 1A (which are approximate values), have been taken likewise as starting conditions for the computations. All reactions, together with the corresponding rate constants which can influence the reaction mechanism, are summarized in table 1. Assuming a homogenous distribution of H-atoms in the solution, the corresponding differential equations expressing the kinetic course of the reaction mechanism were set up. By applying a non-linear least-squares fitting procedure, the unknown parameters (k_6, k_7, k_{10}, k'_{11} as well as ε^{A}_{310}, ε^{A}_{390}, ε^{A}_{470}, ε^{A}_{595}, ε^{B}_{310} and ε^{B}_{470}) have been computed, so that OD/cm values calculated for the reaction scheme (table 1) best reflect the experimental OD/cm data from the pulse-radiolysis experiments for all given wavelengths. In this optimisation procedure the unknown parameters were varied until the sum of the squared deviations between calculated and experimental OD/cm values reached a minimum.[28, 29] The squared deviations for every set of data at each desired wavelength were weighted according to their different absorption intensities.[23] For solving the stiff differential equation system based on the reaction mechanism (table 1), Gear's[30] numerical algorithm was applied. This method contains an efficient self-adjusting optimum step-size control, which is necessary in this case because of the large differences in the rates of production and consumption of the various radical species.

TABLE 1.—REACTIONS AND RATE CONSTANTS IN PULSE RADIOLYSIS OF THE MV^{2+}/Cl^- SYSTEM

no.	reaction	rate constants $/dm^3\ mol^{-1}\ s^{-1}$ [a]
1	$MV^{2+} + e^-_{aq} \rightarrow MV^{\cdot +}$	$k_1 = 7.5 \times 10^{10}$
2	$Cl^- + OH^\cdot \rightarrow \dot{C}lOH^-$	$k_2 = 4.3 \times 10^9$
2*a*	$\dot{C}lOH^- \rightarrow Cl^- + OH^\cdot$	$k'_{2a} = 6.1 \times 10^9$
3	$\dot{C}lOH^- + H^+ \rightarrow Cl^\cdot + H_2O$	$k_3 = 2.1 \times 10^{10}$
4	$Cl^\cdot + Cl^- \rightarrow Cl_2^{\cdot -}$	$k_4 = 2.1 \times 10^{10}$
5	$Cl_2^{\cdot -} + Cl_2^{\cdot -} \rightarrow Cl_3^- + Cl^-$	$2k_5 = 7.8 \times 10^9$
6	$MV^{2+} + H^\cdot \rightarrow MV^{\cdot +}H^+$ (A)	$k_6 = ?$
7	$\rightarrow MV^{\cdot 2+}H$ (B)	$k_7 = ?$
8	$\rightarrow$ (C)	$k_8 = 10^6$
9	$MV^{2+} + OH^\cdot \rightarrow MV^{\cdot + 2}OH$	$k_9 = 4 \times 10^8$
10	$2MV^{\cdot +}H^+$ (A) $\rightarrow$ products	$2k_{10} = ?$
11	$MV^{\cdot 2+}H$ (B) $\rightarrow MV^{\cdot +}H^+$ (A)	$k'_{11} = ?$
12	$H^\cdot + H^\cdot \rightarrow H_2$	$2k_{12} = 2.3 \times 10^{10}$
13	$OH^\cdot + OH^\cdot \rightarrow H_2O_2$	$2k_{13} = 1.2 \times 10^{10}$
14	$H^\cdot + OH^\cdot \rightarrow H_2O$	$k_{14} = 2 \times 10^{10}$
15	$e^-_{aq} + OH^\cdot \rightarrow OH^-$	$k_{15} = 3 \times 10^{10}$
16	$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-$	$2k_{16} = 1.2 \times 10^{10}$
17	$e^-_{aq} + H^\cdot + H_2O \rightarrow H_2 + OH^-$	$k_{17} = 2.5 \times 10^{10}$
18	$H^+ + e^-_{aq} \rightarrow H^\cdot$	$k_{18} = 2.3 \times 10^{10}$
19	$MV^{\cdot +}OH \rightarrow$ products	$k'_{19} = 4 \times 10^2$

[a] k' is given in s^{-1}. The rate constants are taken from ref. (17), (31) and (32).

The computations were performed for three MV^{2+} concentrations (10^{-4}, 2×10^{-4} and 4×10^{-4} mol dm^{-3}) in the presence of (1-5) $\times 10^{-3}$ mol dm^{-3} Cl^- at pH 1. Based on the similarity of the kinetics, the absorption bands at 390 and 595 nm were assigned to species (A) (the protonated form of the radical cation, $MV^{\cdot +}H^+$). The absorption at 310 and 470 nm belongs predominantly to the H-adducts (B) ($MV^{\cdot 2+}H$). The kinetic course of the various species absorbing at 310 nm, which was resolved by the described computation method, is presented in fig. 2. It can be seen that the measured total absorption (MTA) and computed total absorption (CTA) are in agreement, indicating the correctness of the applied reaction mechanism. This is also the case at 390 nm, as shown in fig. 3, where only two species are superimposed, $MV^{\cdot +}H^+$ and $Cl_2^{\cdot -}$. The $MV^{\cdot 2+}H$ species are not absorbing at this wavelength.

The absorption band at 470 nm (fig. 4) is caused by both methyl viologen transients, $MV^{\cdot +}H^+$ (the protonated form of the radical cation), and, predominantly, $MV^{\cdot 2+}H$ (H-adduct of MV^{2+}). At 595 nm only one transient, ($MV^{\cdot +}H^+$), is absorbing, hence its kinetics is not presented in detail. The final results of the computer simulations are shown in table 2.

Based on the formation kinetics (table 2) it has been calculated that at pH 1 *ca.* 60% of the H-atoms produce the protonated form of the radical cation ($MV^{\cdot +}H^+$) and *ca.* 40% form H-adducts.

It was established that the observed first-order decay of the $MV^{\cdot 2+}H$ species ($k = 6 \times 10^3\ s^{-1}$) was independent of solute concentration and dose rate up to 10 J kg^{-1} per 0.4 μs pulse. Above a dose of 25 J kg^{-1} the decay follows second-order kinetics. On this basis one can conclude that at low dose rate, where first-order reactions are

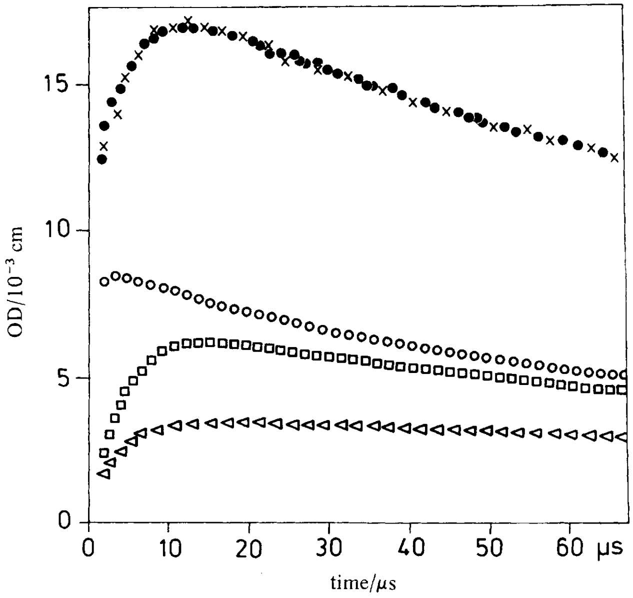


FIG. 2.—Plot of optical density as a function of time at 310 nm for computed formation of $MV^{\cdot+}H^+$ (△), $MV^{\cdot 2+}H$ (□) and $Cl_2^{\cdot -}$ (○) as well as measured (MTA, ×) and computed (CTA, ●) total absorption. Solution: 10^{-4} mol dm^{-3} MV^{2+}, 5.1×10^{-3} mol dm^{-3} Cl^-, pH 1, saturated with argon.

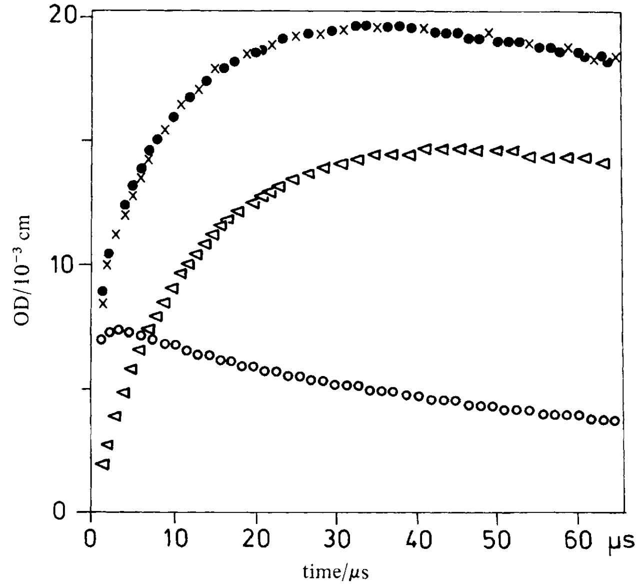


FIG. 3.—Plot of optical density as a function of time at 390 nm for the formation of $MV^{\cdot+}H^+$ (△) and of $Cl_2^{\cdot -}$ (○), as well as for the measured (MTA, ×) and computed (CTA, ●) total absorption. Solution: 10^{-4} mol dm^{-3} MV^{2+}, 5.1×10^{-4} mol dm^{-3} Cl^-, pH 1, saturated with argon.

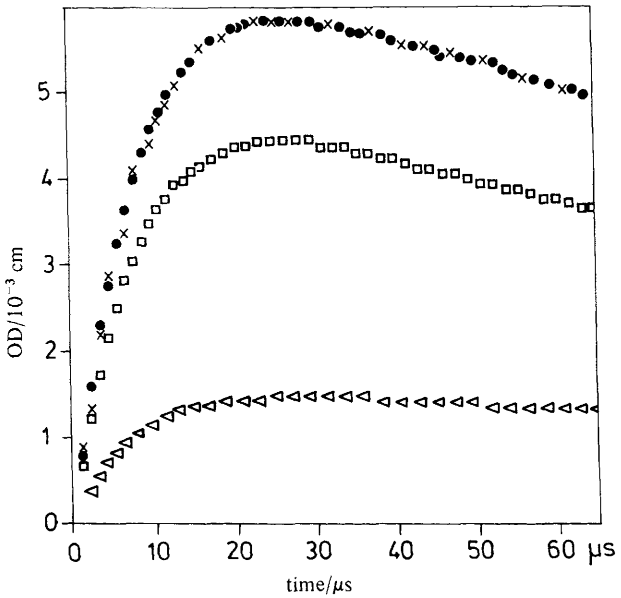


FIG. 4.—Plot of optical density as a function of time at 470 nm for the formation of $MV^{\cdot +}H^+$ (△) and of $MV^{\cdot 2+}H$ (□), as well as for the measured (MTA, ×) and computed (CTA, ●) total absorption.

TABLE 2.—KINETIC AND SPECTROSCOPIC DATA FOR TRANSIENTS FORMED BY ATTACK OF H-ATOMS ON METHYL VIOLOGEN IN AIR-FREE AQUEOUS SOLUTIONS AT pH 1, OBTAINED BY THE OPTIMIZATION PROCEDURE

	rate constant, k /dm^3 mol^{-1} s^{-1}		molar extinction coefficient /m^2 mol^{-1}			
transient	formation	decay	310 nm	390 nm	470 nm	595 nm
$MV^{\cdot +}H^+$ (A)	$(3.5 \pm 0.2) \times 10^8$	$(3.5 \pm 0.3) \times 10^9$	350 ± 10	1700 ± 30	140 ± 10	760 ± 10
$MV^{\cdot 2+}H$ (B)	$(2.5 \pm 0.2) \times 10^8$	$(6 \pm 0.5) \times 10^{3}$[a]	900 ± 20	—	630 ± 20	—

[a] First-order reaction (k' in s^{-1}).

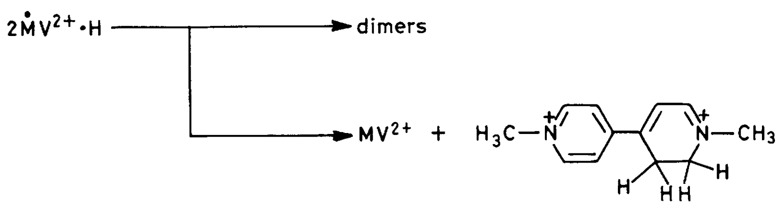
more easily observable, the adducts (half-life $\tau/2 \approx 100$ µs) at pH 1 are converted into protonated radical cations ($MV^{\cdot +}H^+$):

$$\underset{(B)}{MV^{\cdot 2+}H} \rightarrow \underset{(A)}{MV^{\cdot +}H^+}. \tag{11}$$

However, at higher concentrations of $MV^{\cdot 2+}H$, in addition to the conversion process (11) two further reactions become important, namely: (*a*) reaction of $MV^{\cdot 2+}H$ with $Cl_2^{\cdot -}$ radicals by charge-transfer regeneration of MV^{2+}:

$$MV^{\cdot 2+}H + Cl_2^{\cdot -} \rightarrow MV^{2+} + 2Cl^- + H^+ \tag{20}$$

and (*b*) dimerisation or/and disproportionation:



(21)

(22)

The second-order decay of the protonated radical cations ($MV^{\cdot +}H^+$) might also be due to dimerisation or/and disproportionation, as shown for $MV^{\cdot 2+}H$ species in reactions (21) and (22). The possibility of reaction of $MV^{\cdot +}H^+$ with $Cl_2^{\cdot -}$ was examined by a set of simulation computations. It was established that such a process, if possible, does not play an essential role under the experimental conditions.

DETERMINATION OF p*K*

By measuring the optical density at 390 and 595 nm as a function of pH in the range from 0.5 to 5.6 it was possible to determine p*K* for the equilibrium

$$MV^{\cdot +} + H^+ \rightleftharpoons MV^{\cdot +}H^+ \qquad (23)$$

using the Hammett[33] relationship:

$$pK = pH - \log\frac{OD_b - OD}{OD - OD_a} \qquad (24)$$

where OD_a and OD_b are the optical densities of the pure acid and base forms. Plotting the logarithmic expression from eqn (24), log *A*, as function of pH, $pK = 2.9 \pm 0.1$ was obtained (insert, fig. 1).

THE MV^{2+}/t-BUTYL ALCOHOL SYSTEM

In these series of experiments the solutions contained $(1\text{-}8) \times 10^{-4}$ mol dm^{-3} MV^{2+} and 5×10^{-2} to 0.5 mol dm^{-3} t-butyl alcohol (as OH scavenger; pH 1) and were purged with high-purity argon before use. 5×10^{-2} mol dm^{-3} t-butyl alcohol was sufficient to scavenge all OH radicals, so no $Cl_2^{\cdot -}$ radicals were formed.

The formation of methyl viologen transients was rapid in the first 30 μs after the end of the pulse, and was followed by an additional slow component. The reaction was not completed before 120-150 μs. This indicates that not only the H-atoms but also the t-butyl alcohol radicals are involved in the reduction of MV^{2+}, by analogy with the methyl alcohol radical:[6]

$$MV^{2+} + t\text{-}\dot{C}_4H_8OH \rightarrow MV^{\cdot +}H^+ + C_4H_8O. \qquad (25)$$

The effect of t-butyl alcohol is illustrated by two examples, using: (*a*) 2×10^{-4} mol dm^{-3} MV^{2+} with 0.1 mol dm^{-3} t-C_4H_9OH (fig. 1 B) and (*b*) 4×10^{-4} mol dm^{-3} MV^{2+} with 0.5 mol dm^{-3} t-C_4H_9OH (fig. 1 C). Both solutions were air-free at pH 1. As can be seen from the fig. 1 the transient absorption is enhanced at 390 and 595 nm and diminished at 310 and 470 nm, when the t-butyl alcohol concentration is increased. Using a concentration $> 5 \times 10^{-2}$ mol dm^{-3} t-C_4H_9OH in the presence of 10^{-4} mol dm^{-3} MV^{2+}, some of the H-atoms are scavenged by the alcohol.

In order to verify the role of reaction (25), a computer simulation was carried out for $(1\text{-}4) \times 10^{-4}$ mol dm^{-3} MV^{2+} in the presence of $(4\text{-}16) \times 10^{-2}$ mol dm^{-3} t-butyl alcohol. The reactions taking place in this system, together with the corresponding rate constants, are shown in table 3. The kinetic and spectroscopic data from table 2 were used as input parameters for the computer simulation. It was established that the computed values for this system are consistent with experiment, assuming a rate constant for reaction (25) of $k = (1 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}.

TABLE 3.—REACTIONS AND RATE CONSTANTS INVOLVED IN THE PULSE RADIOLYSIS OF THE MV^{2+}/t-BUTYL ALCOHOL SYSTEM

no.	reaction	rate constants used /dm^3 mol^{-1} s^{-1} [a]
1	$MV^{2+} + e^-_{aq} \rightarrow MV^{\cdot +}$	$k_1 = 7.5 \times 10^{10}$
6	$MV^{2+} + H^{\cdot} \rightarrow MV^{\cdot +}H^+$ (A)	$k_6 = ?$
7	$\rightarrow MV^{\cdot 2+}H$ (B)	$k_7 = ?$
8	$\rightarrow$ (C)	$k_8 = 10^6$
9	$MV^{2+} + OH^{\cdot} \rightarrow MV^{\cdot 2+}OH$	$k_9 = 4 \times 10^8$
10	$2MV^{\cdot +}H^+$ (A) $\rightarrow$ products	$2k_{10} = ?$
11	$MV^{\cdot 2+}H$ (B) $\rightarrow MV^{\cdot +}H^+$ (A)	$k'_{11} = ?$
12	$H^{\cdot} + H^{\cdot} \rightarrow H_2$	$2k_{12} = 2.3 \times 10^{10}$
13	$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$	$2k_{13} = 1.2 \times 10^{10}$
14	$H^{\cdot} + OH^{\cdot} \rightarrow H_2O$	$k_{14} = 2 \times 10^{10}$
15	$e^-_{aq} + OH^{\cdot} \rightarrow OH^-$	$k_{15} = 3 \times 10^{10}$
16	$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-$	$2k_{16} = 1.2 \times 10^{10}$
17	$e^-_{aq} + H^{\cdot} + H_2O \rightarrow H_2 + OH^-$	$k_{17} = 2.5 \times 10^{10}$
18	$H^+ + e^-_{aq} \rightarrow H^{\cdot}$	$k_{18} = 2.3 \times 10^{10}$
19	$MV^{\cdot 2+}OH \rightarrow$ products	$k'_{19} = 4 \times 10^2$
26	$t\text{-}C_4H_8OH + H^{\cdot} \rightarrow H_2 + t\text{-}\dot{C}_4H_8OH$	$k_{26} = 3 \times 10^5$
27	$t\text{-}C_4H_8OH + OH^{\cdot} \rightarrow H_2O + t\text{-}\dot{C}_4H_8OH$	$k_{27} = 5.5 \times 10^8$
25	$t\text{-}\dot{C}_4H_8OH + MV^{2+} \rightarrow MV^{\cdot +}H^+$ (A) $+ C_4H_8O$	$k_{28} = ?$
28	$2t\text{-}\dot{C}_4H_8OH \rightarrow (t\text{-}\dot{C}_4H_8OH)_2$	$2k_{29} = 1.4 \times 10^9$

[a] k' is given in s^{-1}. The rate constants are taken from ref. (17), (31) and (32).

Any further enhancement of [t-butyl alcohol] ($> 2 \times 10^{-1}$ mol dm^{-3}), however, leads to an additional increase in the absorption at 390 and 595 nm (fig. 1). This indicates that the yield of the t-butyl alcohol radicals is enhanced accordingly, probably due to the influence of spur reactions and the beginning of the direct alcohol radiolysis.

CONCLUSIONS

Methyl viologen (MV^{2+}) in aqueous solutions is very reactive towards e^-_{aq}, H-atoms and OH radicals. Reaction (1) of MV^{2+} with e^-_{aq} leads to the formation of just one transient ($MV^{\cdot +}$) and the measured rate constant as well as its absorption spectrum are in good agreement with previously reported data.[6-8] The determined molar extinction coefficients of the first ($\varepsilon_{600} = 1450$ m^2 dm^{-3}) and second ($\varepsilon_{392.5} = 4200$ m^2 dm^{-3}) absorption bands of the radical cation ($MV^{\cdot +}$) partially agree with published data.[10]

Using the pulse-radiolysis technique in combination with a computer simulation method[23] it was possible to resolve the composite transient spectrum obtained by the reaction of H-atoms with MV^{2+} (fig. 1). Two intermediates were observed: the protonated form of the radical cation ($MV^{\cdot +}H^+$) and the H-adducts on the ring carbon ($MV^{\cdot 2+}H$). Their kinetic and spectroscopic characteristics are summarized in table 2.

When t-butyl alcohol is used as OH-scavenger, the t-$\dot{C}_4H_8OH$ radicals are involved in the reaction mechanism, leading to the $MV^{\cdot+}H^+$ transients. This is demonstrated by the decrease of the transient absorption at 310 and 470 nm in the presence of the alcohol, whereas the absorption at 390 and 595 nm increases strongly. The computed rate constant, $k(MV^{2+} + t\text{-}\dot{C}_4H_8OH) = (1 \pm 0.4) \times 10^7$ dm^3 mol^{-1} s^{-1}, is less than the corresponding value for methyl alcohol radicals, $k(MV^{2+} + \dot{C}H_2OH) = 3 \times 10^8$ dm^3 mol^{-1} s^{-1}.[6]

Based on the present experimental results it can be concluded that the primary products of water radiolysis (e^-_{aq}, H, OH), which also appear during photoelectrochemical processes, can initiate the decomposition of MV^{2+} [see reactions (21) and (22)] in devices for the utilization of solar energy.

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