Detection and Analysis of Two Fluorescing Products

Detlef W. Bahnemann,*† Christian-Herbert Fischer, Eberhard Janata and Arnim Henglein

Bereich Strahlenchemie, Hahn-Meitner Institut GmbH, Glienicker Strasse 100, D 1000 Berlin 39, Federal Republic of Germany

The oxidation of methyl viologen, 1,1'-dimethyl-4,4'-bipyridylium chloride (MV^{2+}) , in aqueous solution has been carried out y-radiolytically and photocatalytically (in the presence of colloidal titanium dioxide). Two strongly fluorescing products have been observed, separated and identified: the 1',2'-dihydro-1,1'-dimethyl-2'-oxo-4,4'-bipyridylium cation ['2-one', $\lambda_{\text{max}}^{\text{fl}}(\text{H}_2\text{O}) = 516 \text{ nm}$] and the 3,4-dihydro-1,1'-dimethyl-3-oxo-4,4'-bipyridylium cation ['3-one', $\lambda_{max}^{f1}(H_2O) = 528$ nm]. Both compounds exhibit characteristic u.v.-visible absorption spectra in aqueous solution with maxima 222, 260 and 347 nm $(\varepsilon = 14800,$ 20200 and at 2400 dm³ mol⁻¹ cm⁻¹) or 236, 260 (shoulder) and 390 nm ($\varepsilon = 12000, 5800$ and 3700 dm³ mol⁻¹ cm⁻¹) for the 2-one or 3-one, respectively. Their relative abundance in the radiolysis experiments is strongly dependent on the absence or presence of secondary oxidants, e.g. dioxygen and ferric ions. The overall low G-values in the radiation chemical studies $[G_{max}(2-one) = 0.04]$ $G_{\text{max}}(3\text{-one}) = 0.11$ indicates the formation of other as yet unidentified oxidation products. Comparatively high quantum yields are observed for both products upon ultra-bandgap irradiation of aqueous colloidal suspensions of TiO₂[ϕ (2-one) = 0.032, ϕ (3-one) = 0.01], suggesting a simultaneous or consecutive two-hole transfer mechanism rather than a homogeneous free radical pathway is involved. Probable mechanisms of the 'OH-induced oxidation of methyl viologen are discussed as well as the possible implication of these results on the use of MV²⁺ as an electron relay in solar energy devices.

The one- and two-electron reduction of methyl viologen or paraquat (MV^{2+} , 1,1'dimethyl-4,4'-bipyridylium chloride) has been extensively studied during the last 15 years. Impressive research activity was mainly caused by the unique properties of the reduction products MV^{++} and MV^{0} . While aqueous solutions of MV^{2+} do not absorb light to an appreciable extent above 350 nm, both MV^{++} and MV^{0} exhibit wellcharacterized u.v.-visible spectra with maxima at 396 ($\varepsilon = 42\,100\,dm^3\,mol^{-1}\,cm^{-1}$) and 606 nm ($\varepsilon = 13\,700\,dm^3\,mol^{-1}\,cm^{-1}$) for MV^{++} and at 370 ($\varepsilon = 34\,500\,dm^3\,mol^{-1}\,cm^{-1}$) and 390 nm ($\varepsilon = 42\,500\,dm^3\,mol^{-1}\,cm^{-1}$) for $MV^{0,1-4}$ Since both species are very long-lived in the absence of electron acceptors^{5, 6} they constitute ideal reference standards for dosimetry and actinometry purposes in radiation chemistry and photochemistry, respectively.⁷⁻⁹ Furthermore, both reduction steps are completely reversible with well known pH-independent one-electron redox potentials of $E_7^1(MV^{+}/MV^{2+}) = -0.45 V$ vs. NHE and $E_7^2(MV^0/MV^{++}) = -0.80 V vs$. NHE.^{4, 10} One-electron redox potentials of various chemicals¹¹ as well as of conduction-band electrons (e_{CB}) in semiconductors¹²⁻¹⁴ have therefore been determined using the MV^{++}/MV^{2+} couple as a standard. The kinetics

[†] Present address: W. M. Keck Laboratories, California Institute of Technology, Pasadena, California 91125, U.S.A.

of the electron transfer to methyl viologen have been extensively studied in an attempt to characterize complex microheterogeneous systems like micelles^{15, 16} or colloidal semiconductor suspensions.¹⁷⁻²¹ Charge-injection from MV⁺⁺ into the conduction band of $Fe_2O_3^{22}$ and TiO_2^{23} has also been observed, thus establishing the reversibility of this redox step. Furthermore, it has been shown that the methyl viologen radical cation is capable of reducing water to dihydrogen in the presence of suitable catalysts, e.g. colloidal platinum and palladium.²⁴⁻³¹ These observations led to the incorporation of paraquat into water photoelectrolysis systems as an electron relay for the reductive cycle.³²⁻³⁴ Hydrogenation of MV²⁺, which appeared to be the only problematic sidereaction in these experiments (leading to a net loss of the relay compound^{35a}), could seemingly be avoided by the proper choice of reaction conditions.^{35b} However, a possible irreversible attack of MV^{2+} by valence-band holes, h_{VB}^+ , which together with e_{CB}^- are generated upon bandgap irradiation of semiconductor particles and possess an extremely high oxidation potential,³⁶ has not been reported or discussed in the literature. Moreover, even though Calderbank et al. 37 synthesized and characterized some keto-derivatives of methyl viologen, its free-radical-induced oxidation has so far only been studied kinetically by Solar et al.³⁸ using pulse radiolysis. We first encountered the oxidation of MV^{2+} as a side-reaction when we studied its photocatalysed reduction in alkaline colloidal suspensions of TiO₂ in the absence of colloid stabilizers, e.g. poly(vinylalcohol) (PVA), and observed a pronounced fluorescence around 520 nm upon steady-state illumination at 366 nm.³⁹ Similar fluorescences have been observed for mono- and di-keto derivatives of methyl viologen³⁷ and seem to be typical for pyridones.⁴⁰ In a recent publication Sasse and coworkers observed fluorescing compounds in concentrated aqueous solutions of MV^{2+} and identified one of them as the 2-keto derivative present as an impurity.⁴¹ This led to a reinterpretation of earlier data,^{42, 43} where fluorescence effects had been explained by ion-pair formation in solutions containing paraquat. However, no attempt was made to identify another detected 'green' fluorescence.⁴¹ Considering the apparent lack of data in this area, we decided to study the 'OH-induced oxidation of MV^{2+} in homogeneous aqueous solution by means of γ -radiolysis combined with end-product analysis. The apprehension of the foregoing is thus required as a prerequisite for the qualitative and quantitative analysis of the observed methyl viologen photo-oxidation on TiO₂.

Experimental

All chemicals were of the highest available grade and used without further purification. 1,1'-dimethyl-4,4'-bipyridyl-2,2'-dione and 1',2'-dihydro-1,1'-dimethyl-2'-oxo-4,4'-bipyridylium ('2-one') iodide were synthesized following the methods of Calderbank *et al.*³⁷ Ion exchange using a Lewatit ion-exchange resin (Cl⁻-form) yielded the respective chloride salt of the latter compound. The absorption spectrum of an aqueous solution of this pyridone (6.8×10^{-5} mol dm⁻³) is shown in fig. 1(*a*). The yellow compound has three absorption maxima at 222, 260 and 347 nm ($\varepsilon = 14800$, 20200 and 2400 dm³ mol⁻¹ cm⁻¹). These values are in good agreement with those reported by Sasse and coworkers⁴¹ and by Calderbank *et al.*³⁷ The latter, however, measured a higher absorption in the u.v. [ε (225 nm) = 22000 dm³ mol⁻¹ cm⁻¹].³⁷ The 2-one fluoresces strongly in the visible ($\lambda_{max}^{rl} = 516$ nm) with an excitation spectrum that closely resembles the absorption spectrum [fig. 1(*b*)]. As anticipated, the fluorescence spectrum is independent of the excitation wavelength.

The preparation of aqueous colloidal suspensions of titanium dioxide, TiO_2 , has been described in detail elsewhere.^{39, 44} All corresponding experiments were performed with alkaline solutions (6.3×10^{-3} mol dm⁻³ TiO₂) at pH 11.5, which did not coagulate for several days in the absence of colloid stabilizers.

Steady-state illuminations were executed using monochromatic light (366 nm) from



2561



Fig. 1. (a) Absorption spectrum of an aqueous solution containing 6.8×10^{-5} mol dm⁻³ 1',2'dihydro-1',1'-dimethyl-2'-oxo-4,4'-bipyridylium chloride at pH 6. (b) Fluorescence emission and excitation spectra of an aqueous solution containing 5×10^{-6} mol dm⁻³ 1',2'-dihydro-1,1'dimethyl-2'-oxo-4,4'-bipyridylium chloride at pH 6.

a 450 W Hg–Xe lamp (Osram HB0). Details of this set-up and the employed actinometry have been published;^{39, 44} the incident photon flux was found to be 10^{-6} ein dm⁻³ s⁻¹.†. γ -Radiolysis experiments were conducted with a ⁶⁰Co-source at 5.3×10^5 rad h⁻¹. Prep-

 $\dagger 1 \operatorname{ein} = 1 \operatorname{mol}.$

arative irradiations were carried out using 5 μ s pulses of a 4 MeV van de Graaff electron accelerator (beam current 0.8 A, pulse frequency 10 Hz).

Product separation was achieved by thin-layer chromatography (t.l.c.) with cellulose as the stationary phase and a mixture of n-butanol, water and acetic acid (8:2:1) as the eluent. A newly developed technique to measure the fluorescence intensity of the individual t.l.c. spots was employed for quantitative analysis. A 2 m column packed with cellulose was used for preparative separations using the abovementioned eluent. All separations were carried out in the absence of room light to prevent photoreactions of the products.

A 90 MHz ¹H n.m.r. spectrometer [Varian EM 390, solvent [²H₄]methanol, tetramethylsilane (TMS) as external standard] and a mass spectrometer (Varian MAT 44) with EI (electron impact) ionization technique was used for structural assays. Absorption spectra were measured with an MPS 2000 (Shimadzu) spectrophotometer, fluorescence spectra with an RF 540 (Shimadzu) spectrofluorometer. All experiments were performed at room temperature (*ca.* 22 °C).

Results

Two stable fluorescing products are formed upon γ -irradiation of an aerated aqueous solution containing 5×10^{-3} mol dm⁻³ methyl viologen at pH 4. They can be separated from one another and from the non-fluorescing parent molecule by t.l.c. (fig. 2). Qualitative and quantitative analysis of the chromatogram shown in fig. 2 requires the use of suitable reference standards. However, the synthesis of oxidation products of methyl viologen other than the 1',2'-dihydro-1,1'-dimethyl-2'-oxo-4,4'-bipyridylium salt and 1,1'-dimethyl-4,4'-bipyridyl-2,2'-dione³⁷ has not been described in the literature. Comparison with these compounds indicates that the second peak in fig. 2 (labelled 'yellow') is attributable to the 2-one species. No bipyridone is detected with less than 10% conversion of MV²⁺. Preparative radiolysis appeared to be a reasonable way to obtain product concentrations high enough to identify the green compound and to verify the above assignment. An aerated aqueous solution of 2×10^{-2} mol dm⁻³ MV²⁺ has therefore been irradiated with an electron pulse sequence for 1 h in the presence of 5×10^{-3} mol dm⁻³ FeCl₃ (pH 4), leading to the almost complete turnover of the parent compound. Addition of ferric ions results in a higher yield of the green relative to the yellow product (cf. later part of Results section). Since under the given experimental conditions Fe³⁺ elutes concurrently with the green compound, the former is precipitated (as $FePO_4$) prior to the preparative separation. A few hundred mg each of the two fluorescing products are finally obtained via this process and are recrystallized from aqueous ethanol. Comparison of their spectroscopic features indeed identifies the yellow compound as the 2-one species, thus verifying the original assignment.

The ¹H n.m.r. spectrum of the green species is shown in fig. 3. Besides the two singlets of N-methyl groups 4 signals due to 7 unsaturated ring protons are observed. This indicates one substitution as compared with MV^{2+} , most probably by an oxygen function. In neutral solution the two doublets of the unsubstituted ring are found at $\delta = 8.8$ and $\delta = 9.0$, unusually close together for methyl viologens. However, upon acidification with trifluoroacetic acid these doublets exhibit chemical shifts of 8.8 and 9.3, which are typical for intact pyridinium structures. At the same time the position of the broad singlet, which can be assigned to the proton at C-2, changes from $\delta = 7.9$ (see fig. 3) to 8.8, which is just 0.4 ppm higher than in MV^{2+} , evincing the presence of an *ortho*-hydroxy group. All the above observations comply with a keto-substitution of MV^{2+} in the 3-position (for neutral solution). This exchange ensues in a chinoidal coupling of the pyridine rings (see lower left in scheme 1). However, in acidic solution the enol form is favoured, thereby reconstituting the original bipyridinium structure.

The following peaks are observed in the mass spectrum of the green compound under

D. W. Bahnemann et al.



Fig. 2. T.l.c. chromatogram of the fluorescing products formed upon γ -irradiation (1.5 Mrad) of an aerated aqueous solution containing 5×10^{-3} mol dm⁻³ methyl viologen at pH 4 (10⁻² mol dm⁻³ phosphate buffer), chromatographic conditions: cellulose n-butanol-H₂O-acetic acid 8:2:1, migration distance 5.7 cm.



Fig. 3. ¹H n.m.r. spectrum of the green product formed upon MV^{2+} radiolysis (see text for conditions) taken at pH 7 in [²H₄]methanol (* = solvent peaks).

mild conditions (fast atom bombardment, f.a.b.): m/z 201 (M⁺, 100%), 202 (85), 187 (33) and 173 (39). Surprisingly, m/z 201, *i.e.* the molecular weight of a monoketo derivative of methyl viologen, is not detected in the EI/m.s., which exhibits the following pattern: m/z 214 (19%), 200 (46), 199 (57), 186 (57), 185 (89), 63 (73) and 51 (100).

The absorption spectrum of an aqueous solution of the purified green product is shown in fig. 4(a). It has two maxima at 236 ($\varepsilon = 12000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 390 nm



Scheme 1. Possible resonance structures of the 1',2'-dihydro-1,1'-dimethyl-2'-oxo-4,4'-bipyridylium cation (upper part) and the 3,4-dihydro-1,1'-dimethyl-3-oxo-4,4'-bipyridylium cation (lower part).



Fig. 4. (a) Absorption spectrum of an aqueous solution containing 8×10^{-5} mol dm⁻³ 3,4dihydro-1,1'-dimethyl-4,4'-bipyridylium chloride at pH 6. (b) Fluorescence emission and excitation spectra of an aqueous solution containing 5×10^{-6} mol dm⁻³ 3,4-dihydro-1,1'-dimethyl-4,4'bipyridylium chloride at pH 6.

D. W. Bahnemann et al.



Fig. 5. Absorption spectra taken before and after y-irradiation (1.5 Mrad) of aerated aqueous solutions containing 5×10⁻³ mol dm⁻³ methyl viologen at pH 4 (10⁻² mol dm⁻³ phosphate buffer): (a) in the absence of additives, (b) in the presence of 10⁻³ mol dm⁻³ FeCl_a.

 $(\varepsilon = 3700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ and a shoulder around 260 nm ($\varepsilon = 5800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The fluorescence spectrum depicts a maximum at 528 nm [fig. 4(b)] the position of which does not depend on the excitation wavelength. The excitation spectrum reveals the same qualitative features as the u.v.-visible spectrum, indicating that the separation process yielded a comparatively clean compound. Since the output of the Xe light source of the spectrofluorometer decreases significantly towards shorter wavelengths, rhodamine B has been used as a standard to correct the excitation spectrum.⁴⁵ A fluorescence yield of 24.5% has been determined with fluorescein as the reference ($\lambda_{ex} = 321 \text{ nm}$).⁴⁶

The characterization of the two fluorescing products which are formed upon oxidation of MV^{2+} appears to be well accomplished at this point, thus permitting the execution of quantitative irradiations. Fig. 5 shows the absorption spectra of aerated aqueous solutions of paraquat $(5 \times 10^{-3} \text{ mol dm}^{-3})$ before and after γ -irradiation (absorbed dose 1.5 Mrad). The pronounced increase of absorption between 300 and 400 nm together with the concomitant formation of a strong fluorescence around 520 nm reveals the production of the keto derivatives of MV^{2+} . Since the spectra of these species are distinctively different from one another, a mathematical treatment of the results in fig. 5 should quantitatively yield the composition of the reaction mixture. However, the spectral augmentation above 500 nm, which is especially obvious in the presence of 10^{-3} mol dm⁻³ FeCl₃, reveals the formation of other as yet unidentified products. Even though the contribution of the latter seems to be calculable [see 'calc.' in fig. 5(b)] we relied on the chromatographic analysis, *cf.* fig. 2, for quantitative data. It should be noted that very good agreement of the results from both methods was generally observed.

The yields of the two products for a number of different conditions are given in fig. 6(a). As mentioned before, the green 3-one is preferentially formed when γ -radiolysis is performed in the presence of ferric ions. Furthermore, molecular oxygen also favours its formation. The yellow 2-one, on the other hand, is produced in rather similar quantities irrespective of the absence or presence of O_2 and/or Fe³⁺. No fluorescing products are detected when irradiations are performed in the presence of 0.1 mol dm⁻³ t-butanol. The quantum yields for the photocatalytic conversion of MV²⁺ into its two keto derivatives upon bandgap illumination of aerated aqueous colloidal suspensions of TiO₂ (at pH 11.5) are shown in fig. 6(b). While the 2-one always represents the major product, the yield of both species drops significantly in the presence of FeCl₃. Addition of poly(vinylalcohol) (PVA), which is often employed as a colloid stabilizer but is also known to be an efficient hole scavenger,^{44a} has a similar effect.



Fig. 6. (a) G values [see ref. (43) for definition] for the formation of the fluorescing oxidation products detected upon y-irradiation (0.5 and 1.5 Mrad) of aqueous solutions containing 5×10^{-3} mol dm⁻³ methyl viologen at pH 4 (10^{-2} mol dm⁻³ phosphate buffer). (----) Air, (----) N₂O. (b) Quantum yield for the formation of the fluorescing oxidation products detected upon illumination ($\lambda_{ex} = 366$ nm for 3 h) of aerated aqueous colloidal suspensions containing 0.5 g dm⁻³ TiO₂ and 5×10^{-3} mol dm⁻³ methyl viologen at pH 11.5.

Discussion

Two strongly fluorescing products, i.e. the 1',2'-dihydro-1,1'-dimethyl-2'-oxo-4,4'bipyridylium cation (2-one) and the 3,4-dihydro-1,1'-dimethyl-3-oxo-4,4'-bipyridylium cation (3-one), are produced upon the free-radical-induced irreversible oxidation of methyl viologen. Both products can be separated via t.l.c. on cellulose and can be determined quantitatively by measurement of the integral fluorescence intensity of chromatographic spots. However, the independent preparation of the compounds constitutes a necessity for the calibration of the analytical method. While the 2-one could be synthesized according to a recipe of Calderbank $et al.^{37}$ the other fluorescent material had to be prepared radiolytically followed by a tedious work-up of the complex reaction mixture. The resulting green product is hence identified to be the 3-one derivative of MV^{2+} by ¹H n.m.r., including the latter's marked pH-dependence and f.a.b./m.s. (with the following peak assignment: m/z = 201, parent ion; 202, protonated form; 187, $-CH_2$; 173, $-2CH_2$). Scheme 2 presents our explanation for the (at first sight) surprising fragment pattern observed in EI-m.s. The methoxy derivative (m/z = 214) should thus stem from a gas-phase reaction in the mass spectrometer facilitated by the more rigorous ionization conditions of EI. The observed shift of the visible absorption maximum from 347 nm for the 2-one to 390 nm for the 3-one [cf. fig. 1(a) and 4(a)] is also explained well by the chinoidal structure of the latter, which leads to a higher conjugation of double bonds (scheme 1). The above discussion indeed shows that the green product is the 3-oxo derivative of paraquat.

The following mechanism is proposed to account for the radiation chemical results [fig. 6(a)]. Water radiolysis with γ -rays or high-energy electrons leads to the formation of extremely reactive radicals:⁴⁷

$$H_2O \xrightarrow{\gamma} OH, H^{\cdot}, e_{aq}^{-}$$
 (1)



Scheme 2. Interpretation of the fragments observed upon EI/m.s. of 3,4-dihydro-1,1'-dimethyl-3-oxo-4,4'-bipyridylium chloride.

The reduction of methyl viologen by e_{aq}^- and H[•] is very fast,^{5, 6, 48, 49} yielding MV⁺ or its protonated form, MV⁺H⁺, respectively:

$$e_{a\alpha}^{-} + MV^{2+} \to MV^{+}$$
⁽²⁾

$$H^{*} + MV^{2+} \rightarrow MV^{*+}H^{+} \rightleftharpoons MV^{*+} + H^{+}_{aq} \quad pK_{a} = 2.9.5$$
(3)

In the presence of dioxygen, superoxide is subsequently formed

$$MV^{+} + O_2 \rightarrow MV^{2+} + O_2^{-}$$
⁽⁴⁾

restoring the parent molecule:

$$\mathbf{H}_{\mathrm{aq}}^{+} + \mathbf{O}_{2}^{-} \rightleftharpoons \mathbf{HO}_{2}^{\cdot}. \tag{5}$$

Neither HO₂ nor O₂⁻ [reaction (5)]⁵⁰ reacts with MV²⁺;⁴⁸ the disproportionation of superoxide⁵⁰ should therefore terminate the reductive route, yielding H₂O₂. The hydroxyl radical, on the other hand, also reacts rapidly with paraquat.³⁸ We visualize the initial addition of 'OH to the 2- or 3-position of the pyridylium ring to result in the formation of a nitrogen- or carbon-centred radical, respectively (scheme 3). Further oxidation of the latter by Fe³⁺ and/or O₂ appears to be a favourable process and leads to the 3-one compound. The extremely low yield of the green product in the absence of additional oxidants also supports this mechanism. The presence of dioxygen or ferric ions hardly affects the yield of the 2-one product, suggesting that other reactions, *e.g.* radical-radical disproportionations, might be operational in this route. Nitrous oxide, N₂O, which leads to the formation of additional hydroxyl radicals *via*

$$e_{aq}^{-} + N_2 O + H_2 O \rightarrow OH + OH^{-} + N_2$$
(6)

does not significantly increase the yield of the yellow product. Moreover, the almost complete inhibition of the 3-one formation in N₂O-saturated solutions again indicates the necessity of sacrificial electron acceptors. The fact that hydroxyl radicals are indeed essential for the initial attack of MV^{2+} is unambiguously proven by the absence of products when irradiations are performed in the presence of t-butanol. This alcohol is



Scheme 3. Proposed reaction mechanism for the formation of the green and yellow products upon γ-radiolysis of aqueous solutions containing methyl viologen.

known to be an efficient 'OH-scavenger [reaction (7)], yielding a very unreactive β -hydroxy radical:⁴⁷

$$OH + (CH_3)_3 COH \rightarrow CH_2 (CH_3)_2 COH + H_2 O.$$
(7)

At this point we wish to emphasize that the sum of the observed G-values of the two fluorescing oxidation products of MV^{2+} never exceeds 0.13, *i.e.* <5% of the initially formed 'OH [G('OH) = 2.8 for reaction (1)] led to the formation of these species. The presence of other compounds after γ -irradiation of aqueous MV^{2+} solutions has already been indicated (*e.g.* fig. 5). Their identification and quantification, which is, however, far beyond the scope of this paper, is required to understand the complete mechanism of the free-radical-induced oxidation of methyl viologen.

The photocatalytic oxidation of MV^{2+} in the presence of TiO₂, on the other hand, appears to be a rather efficient process, with the sum of the quantum yields, ϕ , of the yellow and green product being 0.042 in the absence of Fe³⁺ [fig. 6(b)]. It is well established^{12-14, 17-21, 32-36, 39, 44} that the photocatalytic activity of semiconductor materials like titanium dioxide is based on the formation of an electron-hole pair upon bandgap illumination:

$$\operatorname{TiO}_{2} \frac{h_{\nu}}{\lambda_{ex} \leqslant 380 \, \mathrm{nm}} e_{\mathrm{CB}}^{-} + h_{\mathrm{VB}}^{+}.$$
(8)

 MV^{2+} is strongly adsorbed on the oxide's negatively charged surface at pH 11.5^{12, 39} and can thus effectively interfere with the e⁻/h⁺ recombination.⁵¹ The reaction of MV^{2+} with conduction-band electrons, e⁻_{CB} [reaction (9)], has been extensively studied and was found to proceed with a quantum yield of unity:¹²

$$e_{\rm CB}^- + MV^{2+} \to MV^{+}.$$
 (9)

In the presence of dioxygen, reactions (4) and (5) and the subsequent disproportionation of the superoxide radical should then terminate the reductive cycle, closely matching the radiation chemical experiments. Oxidation of methyl viologen can thus be initiated by the remaining valence-band holes, h_{VB}^+ , which are extremely good oxidants.³⁶ Based on the high yields of oxo-products and in analogy to results observed when halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) reacted with h_{VB}^+ ,^{44b} we propose the initial formation of surface 'OH radicals

$$h_{VB}^{+} + OH_{surface}^{-} \rightarrow OH_{surface}$$
(10)

which afterwards attack MV^{2+} to form radicals similar to those proposed in scheme 3:

$$^{\circ}OH_{surface} + MV^{2+} \rightarrow MV(-H)OH^{+} + H_{aq}^{+}.$$
 (11)

As in the case of halothane, the high yield of the oxidation products can only be understood when the intermediate $MV(-H)OH^{+}$ radical is stabilized on the TiO₂ surface awaiting another h_{VB}^+ :

$$MV(-H)OH^{+} + h_{VB}^{+} \rightarrow MV(-H_{2})O^{+} + H_{ag}^{+}.$$
 (12)

The pronounced inhibitory effect of ferric ions [fig. 6(b)] can be rationalized in terms of a 'short-circuiting' of the catalyst *via* the reactions

$$e_{CB}^{-} + Fe_{surface}^{3+} \rightarrow Fe_{surface}^{2+}$$
(13)

$$h_{VB}^+ + Fe_{surface}^{2+} \rightarrow Fe_{surface}^{3+}$$
 (14)

Furthermore, this result supports the proposed mechanism [reactions (10)–(12)], as it stands in clear contrast to the behaviour that is observed during γ -radiolysis when homogeneous free-radical reactions are involved.

The decreased yield of oxidation products which is encountered in the presence of poly(vinylalcohol) (PVA) can be explained by a competition of reactions (10) and (11) with the reaction

$$h_{VB}^+ + PVA \rightarrow PVA(-H)^+ + H_{aq}^+$$
 (15)

The resulting PVA(-H) radical possesses reducing properties,³⁹ thus leading to an efficient blockage of the oxidative route.

In conclusion, we have for the first time observed the formation of two strongly fluorescing products upon the two-electron oxidation of methyl viologen initiated by homogeneously distributed or surface-adsorbed hydroxyl radicals. The successful separation and unambiguous characterization of these mono-keto derivatives of MV^{2+} permitted quantitative radiation and photochemical studies. However, a mechanism which has been proposed to account for the γ -radiolytic results bears the uncertainty that the majority of reaction products have not yet been identified. The photocatalytic oxidation of methyl viologen, on the other hand, proceeds with high quantum yields in the presence of colloidal TiO₂. Since two valence-band holes are required for the formation of one product molecule [reactions (10)–(12)] 8.4% of all absorbed photons participate in these processes. This astonishing selectivity is explained by the stabilizing effect of the TiO₂ surface towards free-radical intermediates.

The observed oxidation irreversibly removes methyl viologen from the reaction mixture, thus suggesting that the applicability of MV^{2+} as an electron relay which has been extensively discussed in recent years²⁴⁻³⁵ should be limited to systems that do not involve intermediates like 'OH. Explicitly, we strongly disagree that methyl viologen can be used in realistic water-splitting experiments.

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D. W. Bahnemann et al.

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