

(XVI) and the methylmalonic ester. Heating at 50 °C and 1 mm removed the diethyl methylmalonate and, on distilling the residual liquid at 146–148 °C (1 mm), 0.32 g (72% recovery) of colorless cumyl phenyl sulfide was obtained. Its NMR spectrum was identical with that of the starting material.

(b) **With the Lithium Salt of 2-Nitropropane.** Under argon,¹⁹ 850 mg (9 mmol) of the lithium salt of 2-nitropropane and 500 mg (1.8 mmol) of *p*-nitrocumyl phenyl sulfide were dissolved in 15 mL of HMPA. The red solution was stirred for 72 h⁷ and then worked up as usual. This gave 0.6 g of an orange-brown crude product, which was digested with warm absolute ethanol, cooled, filtered, and washed with cold ethanol. The almost white, ethanol insoluble solid is the carbon alkylate III: 0.11 g (27% yield); mp 204–206 °C (lit.³ mp 206–208 °C).

Evaporation of the ethanol left 0.48 g of a residue, which was loaded onto a silica gel column and eluted with hexane and then with hexane–benzene (1:1). In this way an additional 30 mg of III was obtained, for a total yield of 0.14 g (28%). In addition, 245 mg (50%) of the starting *p*-nitrocumyl phenyl sulfide (VII), mp 50–52 °C, was recovered.

A duplicate of this experiment was carried out by using 0.469 g (2 mmol) of cumyl phenyl sulfide (XVI), 0.95 g (10 mmol) of the lithium salt of 2-nitropropane and 20 mL of HMPA. After 5 days the usual workup gave 0.4 g of a crude material, which, by NMR, was devoid of any product. On distillation at 145–148 °C (1 mm) 0.33 g (70% recovery) was obtained; the NMR spectrum of this colorless liquid was identical with that of the starting cumyl phenyl sulfide.

(c) **With the Sodium Salt of *p*-tert-Butylthiophenol.** Under argon,¹⁹ sodium *p*-tert-butylphenyl sulfide (3.3 g, 18 mmol) and 0.5 g (1.8 mmol) of *p*-nitrocumyl phenyl sulfide (VII) were placed in 35 mL of HMPA. The deep purple solution was stirred for 1 h⁷ and then poured into ice–water, which was extracted with benzene, and the benzene phase, after washing with water, 10% NaOH, and water, was dried (Na₂SO₄). Removal of the solvent left a yellow solid (0.64 g), which by NMR and TLC was free of VII. Recrystallization from absolute ethanol gave colorless crystals of *p*-nitrocumyl *p*-tert-butylphenyl sulfide (0.48 g, 81% yield),

mp 81–82 °C: NMR (CDCl₃) δ 1.28 (s, 9 H), 1.72 (s, 6 H), 7.1–7.3 (m, 4 H), 7.55 (d, 2 H), 8.15 (d, 2 H). Anal. Calcd for C₁₉H₂₃NO₂S: C, 69.26; H, 7.03; N, 4.25. Found: C, 69.21; H, 6.89; N, 4.16.

(d) **With the Sodium Salt of *p*-Thiocresol.** In DMF (20 mL) 2.6 g (18 mmol) of the sodium salt of *p*-thiocresol reacted with *p*-nitrocumyl phenyl sulfide (0.5 g, 1.8 mmol) in 6 h⁷ when the procedure of the preceding experiment was followed. Workup in the usual way gave 0.42 g (79% yield) of *p*-nitrocumyl *p*-tolyl sulfide, mp 47–48 °C. The analytical sample (vide supra) has mp 47–48 °C, and the NMR spectra of the two samples are identical.

Acknowledgment. These studies were supported by grants from The National Science Foundation, the donors of the Petroleum Research Fund, administered by The American Chemical Society, Eli Lilly and Company, and the Hoffmann-La Roche Foundation.

Registry No. Ib, 3276-35-5; I (X = SC₆H₄-*p*-CH₃), 113109-56-1; I (X = OC₆H₅), 113109-58-3; I (X = H), 1817-47-6; I (X = OH), 22357-57-9; I (X = SCH₃), 113109-61-8; II, 105639-48-3; III, 14851-03-7; III⁺, 113109-62-9; IV, 53439-66-0; V, 70951-74-5; VI, 75506-57-9; VII, 15013-24-8; VIII-Na⁺, 18424-77-6; IX, 113109-57-2; X, 14851-08-2; XI, 113109-64-1; XII, 14851-05-9; XIII, 105639-51-8; XIV, 105639-50-7; XV, 113109-59-4; XVI, 4148-93-0; XVII, 113109-60-7; XVIII, 65253-42-1; (CH₃)₂C⁻NO₂Li⁺, 3958-63-2; C₆H₅SO₂Na, 873-55-2; C₆H₅SNa, 930-69-8; Na⁺CH(COOEt)₂, 996-82-7; NaN₃, 26628-22-8; NaNO₂, 7632-00-0; NaOC₆H₅, 139-02-6; C₆H₅COOLi, 553-54-8; CH₃SNa, 5188-07-8; C₆H₅SH, 108-98-5; cumyl azide, 32366-26-0; sodium *p*-thiocresolate, 10486-08-5; sodium *p*-toluenesulfinate, 824-79-3; sodium 1-methyl-2-naphtholate, 14851-07-1; β-naphthol, 135-19-3; α-methyl-*p*-nitrostyrene, 1830-68-8; sodium *p*-tert-butylthiophenoxide, 54166-35-7; *p*-nitrocumyl radical, 80866-17-7; *p*-benzoylcumyl methyl sulfide, 69719-15-9; *p*-benzoylcumene, 18864-76-1; *p*-benzoyl-α-methylstyrene, 103384-71-0; α-methylstyrene, 98-83-9; cumyl chloride, 934-53-2; *p*-aminocumyl phenyl sulfone, 113109-63-0.

Methyl Viologen Reactions. 5. Rates and Mechanism of Cation-Radical Formation in Aqueous Base¹

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Initial rates for methyl viologen cation-radical (MV^{•+}) formation from methyl viologen (MV²⁺) in aqueous base have been obtained by spectrophotometry at 604 nm and 24 °C. From rate runs at various reactant concentrations, the order in MV²⁺ was found to be 2 and the order in base was 1 (or in a few sets of runs somewhat larger). The rate constant *k*₀ based on the third-order rate law is 1.46 × 10⁻⁴ M⁻² s⁻¹ in H₂O; in D₂O the constant is 2.48 × 10⁻³ M⁻² s⁻¹.

Introduction

Methyl viologen ion MV²⁺ (also known as Paraquat)² has been the focus of numerous studies. (For list of symbols used, see Glossary at the beginning of the Results Section.) In recent years it has been used as a herbicide;³ there has been widespread interest in its potential in solar

energy collection and storage systems,⁴ and it serves as a biological redox indicator in photosynthetic research.⁵ Several comprehensive reviews of the chemistry of MV²⁺ and related compounds are available.⁶

(1) Previous articles: (a) Levey, G.; Rieger, A. L.; Edwards, J. O. *J. Org. Chem.* 1981, 46, 1255. (b) Rieger, A. L.; Edwards, J. O.; Levey, G. *Photochem. Photobiol.* 1983, 38, 123. (c) Rieger, A. L.; Rieger, P. H. *J. Phys. Chem.* 1984, 88, 5845. (d) Rieger, A. L.; Edwards, J. O. *J. Org. Chem.* 1985, 50, 5102.

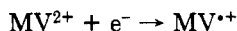
(2) Paraquat is the trade name for the dichloride salt of MV²⁺.

(3) (a) Boon, W. R. *Chem. Ind. (London)* 1965, 782. (b) Akhavein, A. A.; Linscott, D. L. *Residue Rev.* 1968, 23, 97.

(4) (a) Graetzel, A. *Acc. Chem. Res.* 1981, 14, 376. (b) Harriman, A., West, M. A., Eds.; *Photogeneration of Hydrogen*: Academic Press: New York, 1982. (c) Willner, E.; Laane, C.; Oros, J.; Calvin, M.; *Adv. Chem. Ser.* 1982, 177, 71. (d) Whitten, D. G.; Russel, J. C.; Schnell, R. H. *Tetrahedron* 1982, 38, 2455. (e) Whitten, D. G. *Acc. Chem. Res.* 1980, 13, 83.

(5) (a) Darwent, J. R.; Kalyanasundaram, K.; Porter, G. *Proc. R. Soc. (London)*, Ser. A 1980, 373, 179. (b) Kalyanasundaram, K.; Porter, G. *Ibid.* 1978, 364, 29. (c) Ford, W. E.; Tollin, G. *Photochem. Photobiol.* 1982, 35, 809. (d) Lever, A. B. P.; Ramaswamy, B. S.; Liccoccia, S. J. *Photochem.* 1982, 19, 173.

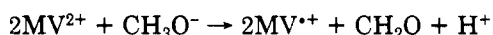
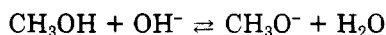
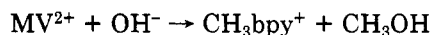
Treatment of MV^{2+} with a strongly basic aqueous solution gives a deep blue color.⁷ The color, which can be discharged with air (oxygen),⁸ has been shown to be due to the cation-radical derived from the reduction of MV^{2+} .



Some results bearing on the stoichiometry and the mechanism have been published.⁹⁻¹¹ We have reinvestigated the kinetics of radical formation in aqueous solution and have obtained new results which help to delineate the mechanism of this reaction.

Corwin et al.⁹ investigated the action of nitrogen and oxygen bases on MV^{2+} and on BV^{2+} in the absence of air. The products (other than $BV^{\bullet+}$) from the aqueous reaction of BV^{2+} and hydroxide ion were reported to include benzaldehyde and 4,4'-bipyridine (pbpy). Formaldehyde and pbpy were reported to be the products from the analogous reaction of MV^{2+} . A stoichiometry and mechanism with a complex series of steps were proposed.

Later it was suggested¹⁰ that the reagent causing reduction of MV^{2+} in anaerobic aqueous base was methoxide from the monodequaternization of MV^{2+} . Identified products after aeration were CH_3bpy^+ and formaldehyde plus a small amount of formic acid. About 66% yield of $MV^{\bullet+}$ was reported at 90 °C after 20 min. The proposed mechanism was



Consistent with this mechanism was the observation¹⁰ that change of solvent to methanol brought about an increased yield of $MV^{\bullet+}$.

Simultaneously with the first submission of our manuscript, the related article by Novakovic and Hoffman¹¹ appeared. Several differences between their work and ours are mentioned below.

Two-electron reduction of MV^{2+} has also been reported,¹² but this reaction requires a stronger reducing agent than methoxide. It further appears that certain oxidants including oxygen and hydrogen peroxide when present along with the reductant will bring about formation of pyridones.¹³ However, neither of these unusual reactions need be considered as relevant to our conditions.

The present study of the kinetics of MV^{2+} reduction suggests an interesting new mechanism involving an imine as reductant.

Experimental Section

Methyl viologen chloride (K&K or Aldrich) was crystallized from methanol/acetone and dried under vacuum at 100 °C to a

product free of OH protons (i.e., water and methanol) by NMR. Deuterium oxide was 99.8% (Stohler). Methanol- d_4 was 99.5% (Stohler). Deuterium chloride 38% v/v in D_2O was from Merck. Methanol (Analytical) was treated with $LiAlH_4$ and then distilled. Stock solutions of Na_2CO_3 and NaOH were prepared in deionized water with NaCl added to maintain ionic strength (μ). In addition, phosphate buffers (with chloride) and carbonate buffers (with no added chloride) were prepared.

The rate of $MV^{\bullet+}$ formation from MV^{2+} in aqueous buffer was followed by using the absorbance at 604 nm with a Gilford 250 spectrophotometer equipped with a dwell timer and automatic positioner allowing the measurement and recording of absorbances from three samples plus a blank (used as stability check). After rapid weighing of MV^{2+} chloride, stock solutions were prepared by normal procedures; buffers were similarly prepared. Buffer was introduced into cuvettes (10 mm, type 21 cells) with bottle necks; the necks were capped with serum stoppers, and the buffer was deoxygenated by using syringe techniques with solvent presaturated argon. Flasks containing MV^{2+} solutions were similarly deoxygenated. Gas tight syringes swept thoroughly with argon were used to transfer MV^{2+} solutions to cuvettes, and mixing was accomplished with a vortex mixer. Solutions were prepared and mixed under low light levels as UV and short wavelength visible light promotes radical formation. Absorbances were converted to concentrations using the value $\epsilon = 13700$.¹⁴

Rate plots of absorbance against time (taking into account the programmed dwell time and the switching from sample to sample) were prepared. The first 10 to 15 points (about 2% conversion) for each run normally gave a straight line, and from the slope of this line as initial rate R_i was calculated. Since $MV^{\bullet+}$ at concentrations higher than 10^{-4} M in water does not obey Beer's law,⁹ determination of final radical concentrations was not attempted for the kinetic runs. Orders were obtained from $\log R_i$ against \log concentration plots, and k_0 values were calculated by standard procedures. All rate runs were carried out at $T = 24$ °C.

Spectra were taken on a Perkin-Elmer 552A spectrophotometer with a PE 561 recorder. NMR data (1H and ^{13}C) were obtained with a Bruker WM 250 spectrometer on degassed samples. With tubes containing CD_3OD proton assignments on MV^{2+} , etc., were made relative to the $DOCD_2H$ peak. Assignments in D_2O were made by locating the 3,5-protons (using a shift reported by Ross and Krieger¹⁵). In the case of ^{13}C NMR spectra in D_2O a sample spectrum of MV^{2+} was run with *tert*-butyl alcohol as internal standard plus primary assignment of the 3,5-protons.

As will be seen below, it became necessary to run the reaction in D_2O as well as H_2O in order to make a rate comparison of the radical formation reaction and hydrogen exchange (between the methyl groups and the solvent) reaction. These two related reactions of different rate law and stoichiometry had been found to have similar rates. A quantitative comparison was needed in order to find out which one is faster because they were postulated to proceed through the same intermediate—the methyl imine (see below). An important aspect of this comparison was the evaluation of base concentration in D_2O as well as H_2O . The base concentration was evaluated by using two methods: analytical NaOH (NaOD) and measured pH (pD). The kinetic order in base was determined by using both methods; the conclusion as to order was independent of the method but the value of the specific rate constant differed by a factor of 2, presumably because of the activity coefficient inherent in pH measurement.

The range of concentration of added base was from 0.0055 M up to 1.78 M, and the range of $[MV^{2+}]$ was from 8.21×10^{-3} to 6.61×10^{-2} M. pH readings were taken on either an Orion 801A or a Corning 130 meter. In D_2O it was also necessary to correct the readings for solvent change; this was carried out as before.¹⁴ The correction value 0.50 was added to the measured pH in order to obtain pD.

Absolute concentrations of $MV^{\bullet+}$ were measured by ESR on a Bruker ER22 Ob spectrometer equipped with a Systron-Donover 646A microwave frequency counter, Aspect 2000 computer, and IBM software. A quartz flat cell was deoxygenated with argon; the contents of an attached reaction vessel could be introduced into or withdrawn from the flat cell by valves and argon pressure.

(6) (a) Bard, A. J.; Ledwith, A.; Shine, J. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 55-278. (b) Summers, L. A. *Adv. Heterocycl. Chem.* **1984**, *35*, 281-374. (c) Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49-82. (d) Hanson, B. P. *Adv. Heterocycl. Chem.* **1979**, *25*, 257-265. (e) Summers, L. A. *The Bipyridinium Herbicides*; Academic Press: London 1980.

(7) Weidel, H.; Russo, M. *Monatsh. Chem.* **1982**, *3*, 830.

(8) (a) Emmert, B.; Dollein, V. *Ber.* **1923**, *56B*, 2068. (b) Emmert, B.; Parr, P. *Ber.* **1921**, *54B*, 3168.

(9) Corwin, A. H.; Arellano, R. R.; Chivvis, A. B. *Biochem. Biophys. Acta* **1968**, *162*, 533.

(10) (a) Farrington, J. A.; Ledwith, A.; Stam, M. F. *J. Chem. Soc. D* **1969**, 259. (b) Stam, M. F. Ph.D. Thesis, Univ. Liverpool, 1969.

(11) Novakovic, Y.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1987**, *109*, 2341.

(12) Carey, J. G.; Cairns, J. F.; Colechester, J. E. *J. Chem. Soc. D* **1969**, 1280.

(13) Calderbank, A.; Charlton, D. F.; Farrington, J. A.; James, R. J. *Chem. Soc., Perkin Trans. 1* **1972**, 138 (1972).

(14) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(15) Ross, J. H.; Krieger, R. I. *J. Agric. Food Chem.* **1980**, *28*, 1026.

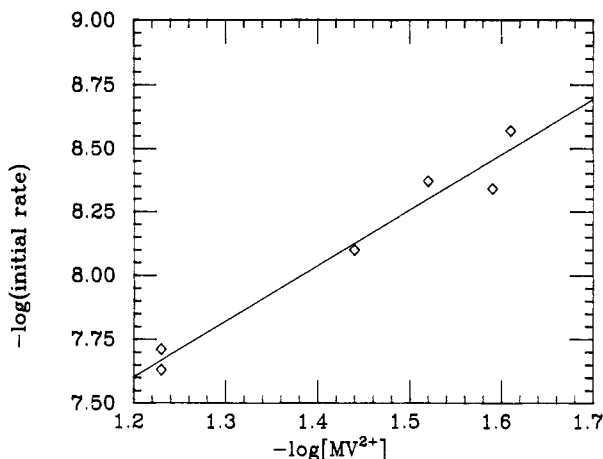


Figure 1. Plot of $-\log R_i$ against $-\log [MV^{2+}]$ for data used to evaluate order in MV^{2+} . Slope is 2.18 ± 0.21 . Concentration of base was 0.0309 ± 0.0009 M, at a temperature of 24°C .

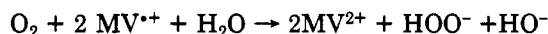
Signal intensity of a reaction mixture could be compared to a solution of known radical (di-*tert*-butyl nitroxide) concentrations in water. Reproducibility of integrations for standards was 1%.

Analysis by HPLC was carried out with a Perkin-Elmer 400 instrument with ISCO variable wavelength detector and reverse phase column; eluant was 0.1 M ammonium phosphate (pH 4) in 40/60 methanol (v/v).

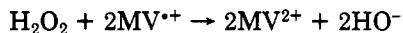
Results

Glossary. The following symbols are used: MV^{2+} , methyl viologen ion; $MV^{\bullet+}$, methyl viologen radical-cation; BV^{2+} , benzyl viologen ion; $BV^{\bullet+}$, benzyl viologen radical-cation; nm, nanometer; R_i , initial rate of $MV^{\bullet+}$ appearance; pbpy, 4,4'-bipyridine; CH_3bpy^+ , methyl-4,4'-bipyridinium ion; $R_2NCH_2^+$, methyl imine of MV^{2+} ; $R_2NCH_2^{\bullet+}$, radical derived from the methyl imine intermediate.

Effect of Oxygen. In order to obtain a quantitative measure of the rate of appearance of $MV^{\bullet+}$, it is necessary that O_2 be excluded from the reaction mixture as rigorously as possible. Oxygen is known¹⁶ to react very rapidly ($k = 7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) with $MV^{\bullet+}$ by the reaction



which is followed^{1a} by the slower ($k = 2.0 \text{ M}^{-1} \text{ s}^{-1}$) process



Because the rate of radical formation was followed by the growth of absorption at 604 nm ($\epsilon = 13700^{14}$) due to the radical, an induction period was seen when trace quantities of O_2 were present. In the essential absence of O_2 , little or no induction period was seen. When a significant amount of O_2 is present in aqueous solution or when the solvent contains more than 10% methanol, a longer induction period is followed by an erratic rate of radical appearance. The latter effect is ascribed to the presence of peroxide generated by O_2 reduction. The induction period and erratic rate behavior may be more serious in methanol than in water because of the greater solubility of O_2 in methanol and a consequent more difficult task of deoxygenation. When the initial rate was erratic and/or nonlinear, the rate data were excluded from the tables and from calculations.

Kinetics. The rate of $MV^{\bullet+}$ formation in aqueous solutions has been found to depend on the concentrations

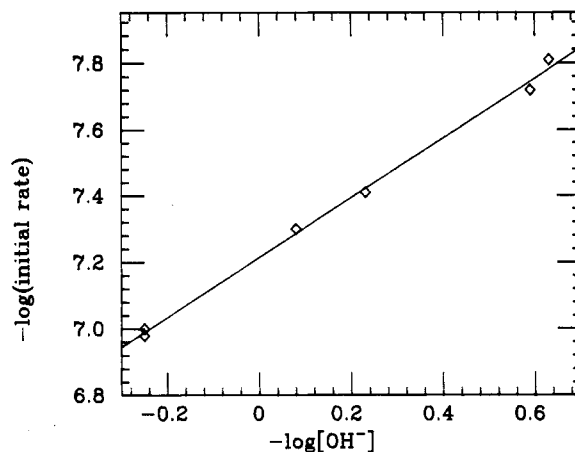


Figure 2. Plot of $-\log R_i$ against $-\log [OH^-]$ for data used to evaluate order in base. Slope is 0.90 ± 0.03 . Concentration of MV^{2+} was 0.0240 M, at a temperature of 24°C .

Table I. Summary of Third-Order Rate Constants

rate constant ^a	std dev	no. of runs	solvent	buffer ^b
1.65×10^{-4}	0.34×10^{-4}	5	H ₂ O	C ^c
1.46×10^{-4}	0.56×10^{-4}	34	H ₂ O	C ^d
1.92×10^{-4}	0.20×10^{-4}	7	H ₂ O	P ^c
2.48×10^{-3}	0.50×10^{-3}	23	D ₂ O	C ^c
1.51×10^{-4}	0.43×10^{-4}	7	4.8% MeOH	C ^d
5.6×10^{-4}	1.5×10^{-4}	8	9.1% MeOH	C ^d

^a Average rate constant k_0 ; units are $\text{M}^{-2} \text{ s}^{-1}$ 24°C . ^b Type of buffer amon: C = carbonate and P = phosphate. ^c With no added chloride. ^d With added chloride. ^e In water solution.

of MV^{2+} and base. About 80 kinetic runs have been carried out here and conclusions about the kinetic orders have been reached. A summary of the results is presented in Table I and order plots given in Figures 1 and 2. The tables containing the data from the individual runs are obtainable in the supplementary material (see paragraph at end of paper).

In Figure 1, a log rate against log concentration of MV^{2+} is given. The slope is 2.18 and it is concluded that the order in MV^{2+} is 2. This agrees with the results of Novakovic and Hoffman.¹¹

The results for base dependence are complicated. As seen in Figure 2, the order in base appeared to be one in some of our experiments. In other experiments, the change in rate with base concentration suggested a somewhat higher order—up to 1.4. The rate results are not sufficiently precise to indicate that there are two independent paths, one of which is first order and one which is second order. Calculations for all the runs using the rate law (1)

$$\frac{d[MV^{\bullet+}]}{dt} = k_0[MV^{2+}]^2[OH^-] \quad (1)$$

showed no consistent trend toward higher values at higher base concentration. Rate constants based on the above rate law gave an average of $1.46 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$ with a standard deviation of 0.56×10^{-4} .

At these necessarily high ionic strengths, the influence of ionic strength was small. Neither added chloride ion nor change in buffer from carbonate to phosphate had a noticeable change on the observed rate constant. The small influence of concentration and nature of ion additives on rate constant is consistent with the observations that activity coefficients of many ionic salts go through a minimum and others show a little change between $\mu = 0.1$ and 1.0 .¹⁷

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Because of the relationship between imine formation and radical formation (see Discussion below), rates in D₂O were investigated. What is striking is the large increase in rate constant k_0 when D₂O is the solvent. As seen in the summary table, the value of k_0 is 17-fold larger in heavy water. A study of kinetic orders indicated that the same rate law as in H₂O held.

Because of the Farrington¹⁰ dequaternization proposal, it is important to consider the effect of small amounts of methanol on the rate of radical formation. When the solvent contains 5% methanol, neither the rate law nor the rate constant was changed (see table). The influence on rate of 9% methanol is barely detectable.

Product Identification. One aromatic product (other than MV^{•+}) derived from MV²⁺ was detected by NMR and HPLC. The ¹H NMR of reaction mixtures were examined, usually under degassed conditions. When a small amount of MV^{•+} is present, fast electron exchange between MV^{•+} and MV²⁺ broadens out the lines of these two ions.^{1c} The remaining proton spectrum gave chemical shifts which agree for CH₃bpy^{•+} with those reported by Ross and Krieger¹⁵ provided a small correction is made for ionic strength. Examination of ¹³C NMR provided further evidence for CH₃bpy^{•+} as new peaks were found in the aromatic region. No further aromatic compound peak (other than that attributed to CH₃bpy^{•+}) was detected by HPLC and in particular no pbpy was present as indicated by the absence of a peak at the appropriate retention time for pbpy. Trace amounts of visibly absorbing products were observed.

Two additional peaks were observed in the carbon NMR spectra. One each at 172 and 83 ppm, which are assigned to formate ion and formaldehyde, respectively. As mentioned, Farrington et al.¹⁰ had reported these two products from oxidation of the methyl group. The formaldehyde derived from a methyl group of MV²⁺ shows that the methyl group is the reducing site for the reaction.

Methyl-Hydrogen Exchange. If the small amount of radical MV^{•+} is discharged with oxygen, MV²⁺ is reformed. This regenerated MV²⁺ and the material that had not formed radical can then be inspected for exchange by NMR. Exchange of the 2,6-hydrogens was expected^{1d} and was essentially complete in a matter of an hour; in this time period, little methyl-hydrogen exchange was observed under the conditions used before.^{1d}

Because the methyl imine is a probable intermediate on the reaction path (see below), it became important to obtain an estimate of the rate of methyl-hydrogen exchange in base. This exchange is presumed to have imine formation as the rate-determining step. It was found possible to obtain the appropriate rate data for methyl exchange by carefully adjusting conditions; at constant pD, acceptable plots of log fraction exchange against time were obtained. At pD 12.88 and 24 °C with $\mu = 0.43$, the average first-order constant is $3(\pm 1) \times 10^{-4} \text{ s}^{-1}$ from four runs. We shall use this in the Discussion to compare rates for the three reactions of MV²⁺ that occur in basic solution.

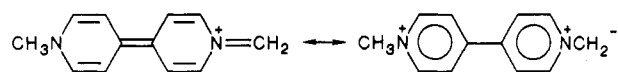
ESR of Radical. Under our kinetics conditions the amount of radical formed during a run was usually about 2% of the initial MV²⁺ concentration. Using ESR several radical determinations were carried out. For example, at a MV²⁺ concentration of $2.41 \times 10^{-2} \text{ M}$ in 0.2 M base, comparison of MV^{•+} and standard signals showed a conversion of 1.5% at the end of 9 hours. Under more forcing conditions (1.0 M base and $[\text{MV}^{2+}] = 1.85 \times 10^{-2} \text{ M}$), a radical yield of 41% was found at 6.5 h. No attempt was

made to achieve the extent of reaction previously reported.¹⁰

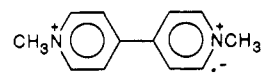
Discussion

Proposed Mechanism. An appropriate method for discussing this redox reaction is to present a postulated mechanism and then to detail the supporting evidence, after which a brief comparison with other proposals is made. The experimental rate law is important because the order in MV²⁺ severely limits the possible mechanisms.¹⁸ The order of 2 reflects the need for one MV²⁺ (specifically one of its methyl groups) to be a reducing agent toward a second MV²⁺. The first MV²⁺ is converted to a reducing agent when it reacts with a hydroxide ion to form a conjugate base.

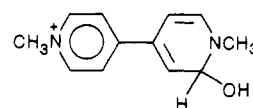
There are three choices for conjugate base structure of MV²⁺; one of these is the imine whose chemical properties



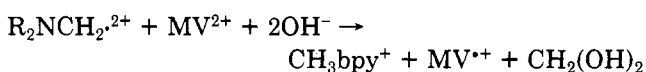
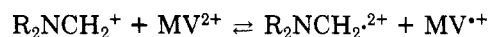
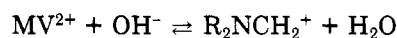
would reflect to some extent an ylide type of behavior,¹⁹ the ortho ylide is a second,



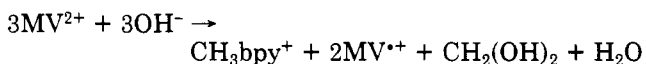
and the third is the so-called pseudobase²⁰



The isolation of formaldehyde indicates that a methyl group on MV²⁺ is the reducing function; because of this, it would appear that the imine is the most reasonable choice for reducing conjugate base. Therefore the postulated steps in the mechanism are



and this gives the stoichiometry



which predicts that the maximum yield of MV^{•+} (in the absence of any other reductant) will be 67% of the initial MV²⁺. Also the yields of CH₃bpy^{•+} and CH₂(OH)₂ should be roughly half the amount of MV^{•+}. (A small amount of reduction of MV²⁺ by formaldehyde or its conjugate base is conceivable.) Evidence in support of this stoichiometry is available. Farrington et al.¹⁰ report under forcing conditions a maximum yield of 66% MV^{•+} in aqueous solution; they also reported that formaldehyde was a product

(18) After our kinetic studies were almost finished, we obtained a copy of the Stam thesis.^{10b} In the thesis he suggests that the order in MV²⁺ is 2 even though the publication^{10a} implies first order. We recalculated some of Stam's thesis data on the basis of 2nd order in MV²⁺ and find that his and our rate constants are the same within a factor of 2. This level of agreement is well inside the combined experimental errors.

(19) Ratts, K. W.; Howe, R. K.; Phillips, W. G. *J. Am. Chem. Soc.* 1969, 91, 6115.

(20) For data on formation and NMR spectra of pyridones, see: (a) Rodig, O. R. In *Heterocyclic Compounds, Pyridine and its Derivatives*, Vol. 14, Suppl. Part 1, John Wiley & Sons: New York, 1974; pp 309-430. (b) Kavalič, J.; Lycka, A.; Machacek, V.; Sterba, V. *Collect. Czech. Chem. Commun.* 1975, 40, 1166. (c) Batterham, T. *NMR Spectra of Simple Heterocycles*; R. E. Krieger Pub. Co.: Malabar, FL, 1982; pp 69-71 and 47-62.

(17) C. f. Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959, pp 491-508.

along with small amounts of formate. We also have found evidence for formaldehyde and CH_3bpy^+ . There was no evidence found for the formation of pseudobase and none for the mono- and dipyrindones which are expected oxidation products if oxygen is present in the reaction mixture.

When the steady-state approximation is applied to the imine in the proposed intermediate, is obtained. This can

$$\frac{d[\text{R}_2\text{NCH}_2^+]}{dt} = k_1[\text{MV}^{2+}][\text{OH}^-] - k_2[\text{R}_2\text{NCH}_2^+][\text{H}_2\text{O}] - k_3[\text{R}_2\text{NCH}_2^+][\text{MV}^{2+}] = 0 \quad (2)$$

be rearranged to give

$$[\text{R}_2\text{NCH}_2^+] = \frac{k_1[\text{MV}^{2+}][\text{OH}^-]}{k_2[\text{H}_2\text{O}] + k_3[\text{MV}^{2+}]} \quad (3)$$

Substitution of this into the k_3 step differential equation gives

$$d[\text{MV}^{\bullet+}] = \frac{2k_1k_3[\text{MV}^{2+}]^2[\text{OH}^-]}{k_2[\text{H}_2\text{O}] + k_3[\text{MV}^{2+}]} \quad (4)$$

Provided $k_2[\text{H}_2\text{O}] \gg k_3[\text{MV}^{2+}]$, this law reduces to

$$\frac{d[\text{MV}^{\bullet+}]}{dt} = \left(\frac{2k_1k_3}{k_2'} \right) [\text{MV}^{2+}]^2[\text{OH}^-] \quad (5)$$

where $k_2' = k_2[\text{H}_2\text{O}]$.

Solvent Isotope Effect. A strong piece of evidence for the mechanism is the fact that the rate of radical formation is 17 times as rapid in D_2O as in H_2O . In large measure this can be ascribed to the k_2 step which involves transfer of a solvent hydrogen to the imine. This should proceed more rapidly in H_2O than in D_2O and k_2' will be larger in H_2O than in D_2O . Therefore it is predicted that the complex constant $2k_1k_3/k_2'$ will be larger in D_2O as observed.

Comparison of Rates. There are three reactions of MV^{2+} in basic solution, namely (1) formation of $\text{MV}^{\bullet+}$, (2) hydrogen exchange between the ortho positions of MV^{2+} with water, and (3) hydrogen exchange between the methyl group and water. Exchange for the ortho hydrogens, which have been studied and presumably has the ortho ylide as an intermediate, should be and is faster than the methyl exchange.^{12,19}

The methyl exchange which is presumed to proceed with the imine as intermediate is predicted to be faster than the reduction by the postulated mechanism and is consistent with the observed solvent isotope effect. A brief investigation of the methyl exchange rate by a proton NMR analysis has been carried out. After oxidation of the small amount of radical, the intensities of the methyl peak and of the 3,5,3',5' peak (which reports nonexchanging hydrogens) can be used to determine the fraction exchanged of methyl hydrogens. Four exchange runs were carried out and the average rate constant assuming the rate law

$$R = k[\text{MV}^{2+}][\text{OH}^-] \quad (6)$$

was $2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Under comparable concentrations and statistical correction, the calculated exchange rate is 15-fold faster than radical formation in D_2O . The con-

dition $k_2[\text{D}_2\text{O}] > k_3[\text{MV}^{2+}]$ is therefore confirmed for our system.

The observations here that 2,6-hydrogen exchange is faster than methyl-hydrogen exchange and that the methyl imine (which is related to a methyl ylide) reacts with a carbon substrate faster than the ortho ylide are not unprecedented. Ratts et al.¹⁹ who studied the condensation of ylides from *N*-methylpyridinium salts with aldehydes found methyl exchange to be about 2 powers of ten slower than 2,6-exchange and the methyl ylide to be much more reactive in condensations with carbon substrates.

Other Possible Mechanisms. The mechanism of Farrington et al.¹⁰ can be eliminated on the basis that the rate-determining step would have to be first order in MV^{2+} and that small amounts of methanol would enhance the rate of radical formation. As seen from the data found here and by Novakovic and Hoffman,¹¹ neither in the case.

The qualitative data of Corwin et al.⁹ on base-induced radical formation from BV^{2+} led them to postulate a series of steps which involved a benzyl imine intermediate. They reported $\text{BV}^{\bullet+}$ and pbpy as products. (Their experiments on MV^{2+} were limited.) If one accepts their reaction sequence as it might apply to MV^{2+} , then their second step can be considered as an analogue of the present rate-determining step. No pbpy was found in the present study.

As seen above, there are the two other ways by which hydroxide ion can interact with MV^{2+} , and the consequent intermediates as possible reductants for a second MV^{2+} can be considered. One of these is the ortho ylide where in a proton is abstracted from the 2-position on the ring. This would of course favor reduction by the ring part of MV^{2+} instead of the methyl group. Although we can not exclude on any factual basis a mechanism involving as ortho ylide interaction with another MV^{2+} , that of the methyl imine seems the more likely in view of the fact that the methyl group is the site of the reducing electrons. Further any mechanism invoking the ortho ylide would be quite cumbersome.

Finally the pseudobase intermediate can be considered as the possible reductant. The objections to this are the same as to the ortho ylide intermediate. Further the probability is that from a pseudobase one would expect a pyridone as a major oxidized product; we found no pyridone under our oxygen-free conditions.

The mechanisms of Novakovic and Hoffman¹¹ invoke pseudobase intermediates. After the postulated rapidly formed double pseudobase, no details were given and the crucial role of the methyl group was not addressed.

Acknowledgment. We are pleased to express our thanks to Dr. J. Van Epp for assistance with NMR work, to Professor D. T. Sawyer for several helpful conversations, and to a referee and Professor F. D. Greene for useful suggestions.

Registry No. MV^+ , 25239-55-8; D_2 , 7782-39-0; methyl viologen chloride, 1910-42-5.

Supplementary Material Available: Table A containing conditions, rates, and rate constants for $\text{MV}^{\bullet+}$ formation in water, Table B with similar data for reaction in D_2O , and Table C with data for reaction in water with added methanol (4 pages). Ordering information is given on any current masthead page.