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PROBES OF NONREACTIVE ENVIRONMENT

II. MOLECULAR ASSOCIATION EFFECTS WITH METHYLVIOLOGEN

by

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November 1971

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13. ABSTRACT

The purpose of this investigation was to learn more about the discovery that the epr (electron paramagnetic resonance) spectra of methylviologen cation radical chloride vary markedly depending on the environment in which the radical was produced. Methylviologen cation radical chloride was formed by allowing 0.5, 2.5 X 10^{-2}, and 1.35 X 10^{-3} *M* aqueous solutions of 1,1'-dimethyl-4,4'-bipyridinium dichloride to react with either zinc or diethylamine. The radical formed in the presence of the highest concentration of the bipyridinium dichloride exhibited a single epr line, whereas that formed at the lower concentrations showed a multiline pattern. The single epr line is attributed to a molecular association between methylviologen cation radical chloride and 1,1'-dimethyl-4,4'-bipyridinium dichloride (methylviologen dication dichloride). Rapid exchange in the complex explains the loss of hyperfine structure in the epr spectra. This finding may be useful in designing studies involving electron transfer in many chemical and biochemical systems. Viologen complexes may be helpful as chain carriers of electrons between molecular sites, thus acting as a probe for what normally would be a nonreactive system.

14. KEYWORDS

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by

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DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
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FOREWORD

The work described in this report was authorized under Task 1B662710AD2901, Chemical Detection and Identification Technology, Detection and Identification Concepts. The work was performed in January 1971. The results are recorded in notebook 7554.

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DIGEST

The purpose of this investigation was to learn more about the discovery that the epr (electron paramagnetic resonance) spectra of methylviologen cation radical chloride vary markedly depending on the environment in which the radical was produced. Methylviologen cation radical chloride was formed by allowing 0.5, 2.5 × 10^{-2}, and 1.35 × 10^{-3} *M* aqueous solutions of 1,1'-dimethyl-4,4'-bipyridinium dichloride to react with either zinc or diethylamine. The radical formed in the presence of the highest concentration of the bipyridinium dichloride exhibited a single epr line, whereas that formed at the lower concentrations showed a multiline pattern. The single epr line is attributed to a molecular association between methylviologen cation radical chloride and 1,1'-dimethyl-4,4'bipyridinium dichloride (methylviologen dication dichloride). Rapid exchange in the complex explains the loss of hyperfine structure in the epr spectra. This finding may be useful in designing studies involving electron transfer in many chemical and biochemical systems. Viologen complexes may be helpful as chain carriers of electrons between molecular sites, thus acting as a probe for what normally would be a nonreactive system.

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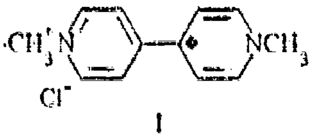
I. INTRODUCTION.

We have been interested in viologen radicals in connection with chemical detection mechanisms involving electron transfer.[1,2] During the course of these studies, it was discovered that the epr (electron paramagnetic resonance) spectra of methylviologen cation radical chloride (I) varied markedly, depending on the environment in which the radical was produced. It was of



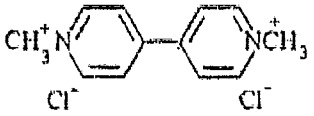
I

interest to learn more about this effect because it appeared to provide a new method of probing molecular environment. Viologens have been used as herbicides, oxidation-reduction indicators, inhibitors of electron transfer in both the cytochrome chain of chloroplasts and the cytochrome chain of mitochondria, and electron carriers in enzyme systems, to mention a few things.

II. EXPERIMENTATION.

A. Reduction With Zinc.

About 700 ml of distilled water (prepared using a Corning AG-3 distillation apparatus) were placed in a 1-liter Erlenmeyer flask. The water was allowed to boil for 10 minutes; the flask was placed in a glove bag (containing nitrogen gas) and allowed to cool while nitrogen was bubbled through the solution. The water was used to fill a 250-ml volumetric flask containing 0.0876 gram methylviologen dichloride (1,1'-dimethyl-4,4'-bipyridinium dichloride, II) giving a 1.35 × $10^{-3}M$



II

solution. One piece of zinc shot (previously washed with dilute HCl) was placed in the flask. The solution was stirred magnetically. Samples were withdrawn over a 3-hour period into epr and spectrophotometric absorption cells. Epr measurements were performed using a Varian E-3 spectrometer; visible and ultraviolet absorption curves were obtained with a Cary 14 spectrophotometer. Typical results are shown in figures 1 and 2. Time of sampling made little difference except for absorption intensity.

In another experiment, 1.25 grams of II was used to prepare 10 ml of 0.49 *M* solution. One zinc shot was added. Samples of solution were withdrawn at 3 and 45 minutes. Epr spectra are given in figure 3. A visible absorption spectrum appears in figure 4.

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[1] Poziomek, E. J. CRDLR 3295. Perspectives in Detection. August 1965. UNCLASSIFIED Report.

[2] Poziomek, E. J. Cyclic Catalytic Reactions as Amplifiers in Chemical Detection. Army Res. Develop. News Mag. *11*, 40 (1970).

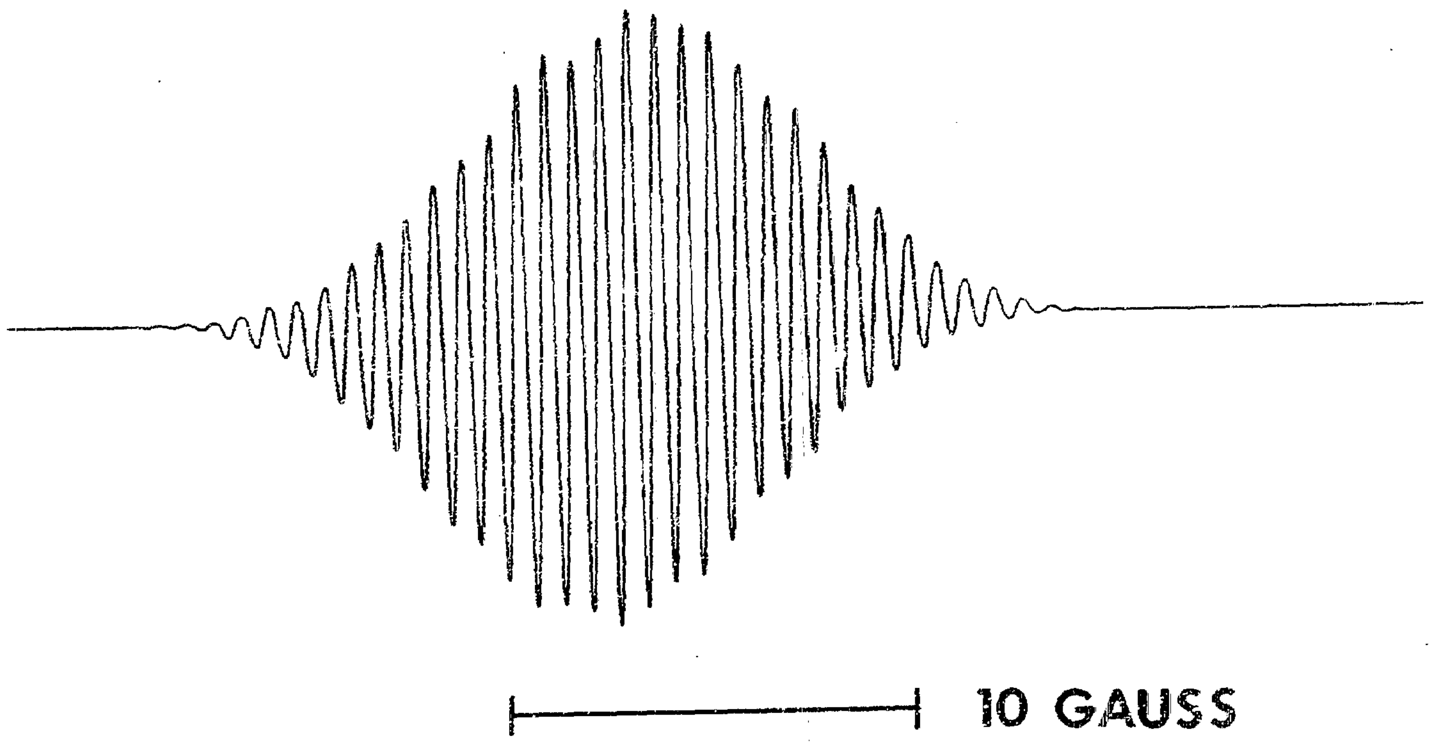


Figure 1. Epr Spectrum of Methylviologen Cation Radical Chloride (I) Obtained During a Reduction With Zinc of a 1.35×10^{-3} *M* Aqueous Solution of 1,1'-Dimethyl-4,4'-Bipyridinium Dichloride (II)

$g = 2.00$.

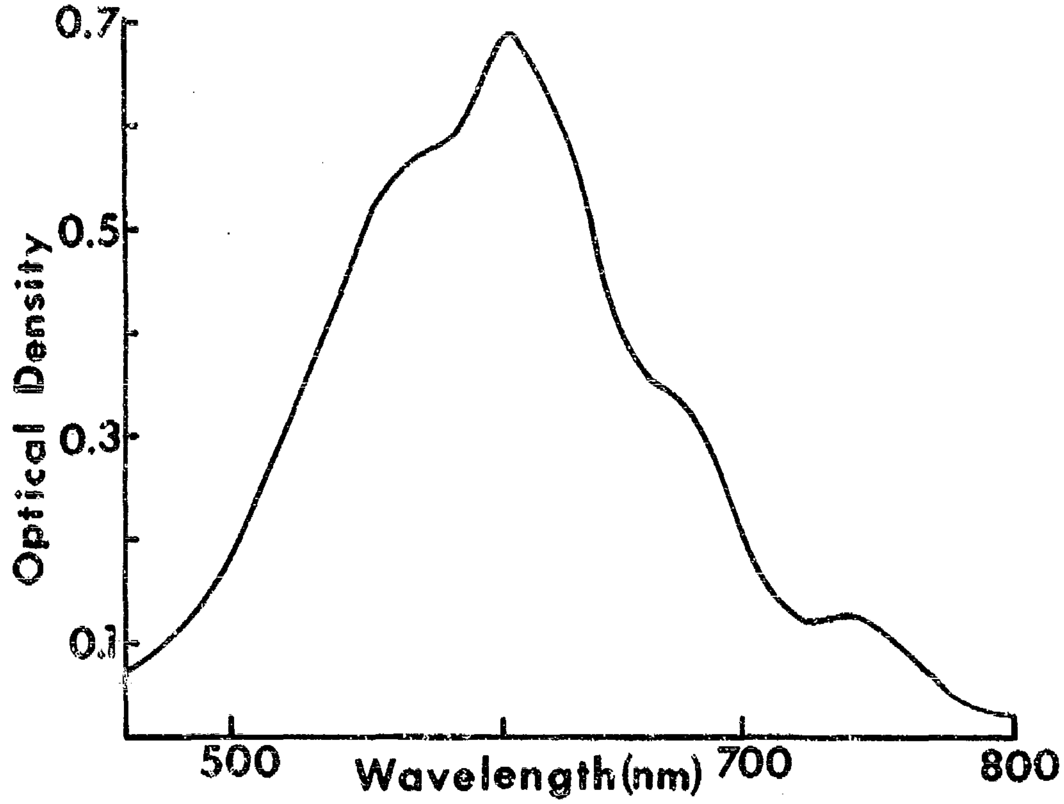


Figure 2. Visible Absorption Spectrum of Methylviologen Cation Radical Chloride (I) Obtained During a Reduction With Zinc of a 1.35 X 10^{-3} *M* Aqueous Solution of 1,1'-Dimethyl-4,4'-Bipyridinium Dichloride (II)

λ_{max} = 603 nm.

All the operations described above (with exception of the spectral measurements) were performed in a nitrogen-filled glove bag with nitrogen purged solutions. However, similar results were obtained without taking precautions to exclude air. For example, 25 mg of zinc dust were added to 5 ml of 2.5 X 10^{-2} *M* aqueous II. The resulting blue-purple mixture was filtered immediately. The epr spectrum is given in figure 5. Spectra similar to that shown in figure 1 were obtained when the reaction was allowed to proceed longer. When 4.2 mg of zinc dust was added to 1 ml of 0.39 *M* II and the mixture placed directly into an epr cell, spectra similar to the more intense one shown in figure 3 were obtained.

B. Reduction With Diethylamine.

To 1 ml of a nitrogen purged solution of 0.5 *M* aqueous II was added 2 μl diethylamine. (This gave a solution approximately 2 X 10^{-2} *M* in diethylamine.) The solution turned dark immediately and was transferred in air to an epr cell. The first spectrum, which was obtained at 5 minutes after preparing the solution, showed a single line. The intensity at 65 minutes was about five times that observed in the beginning.

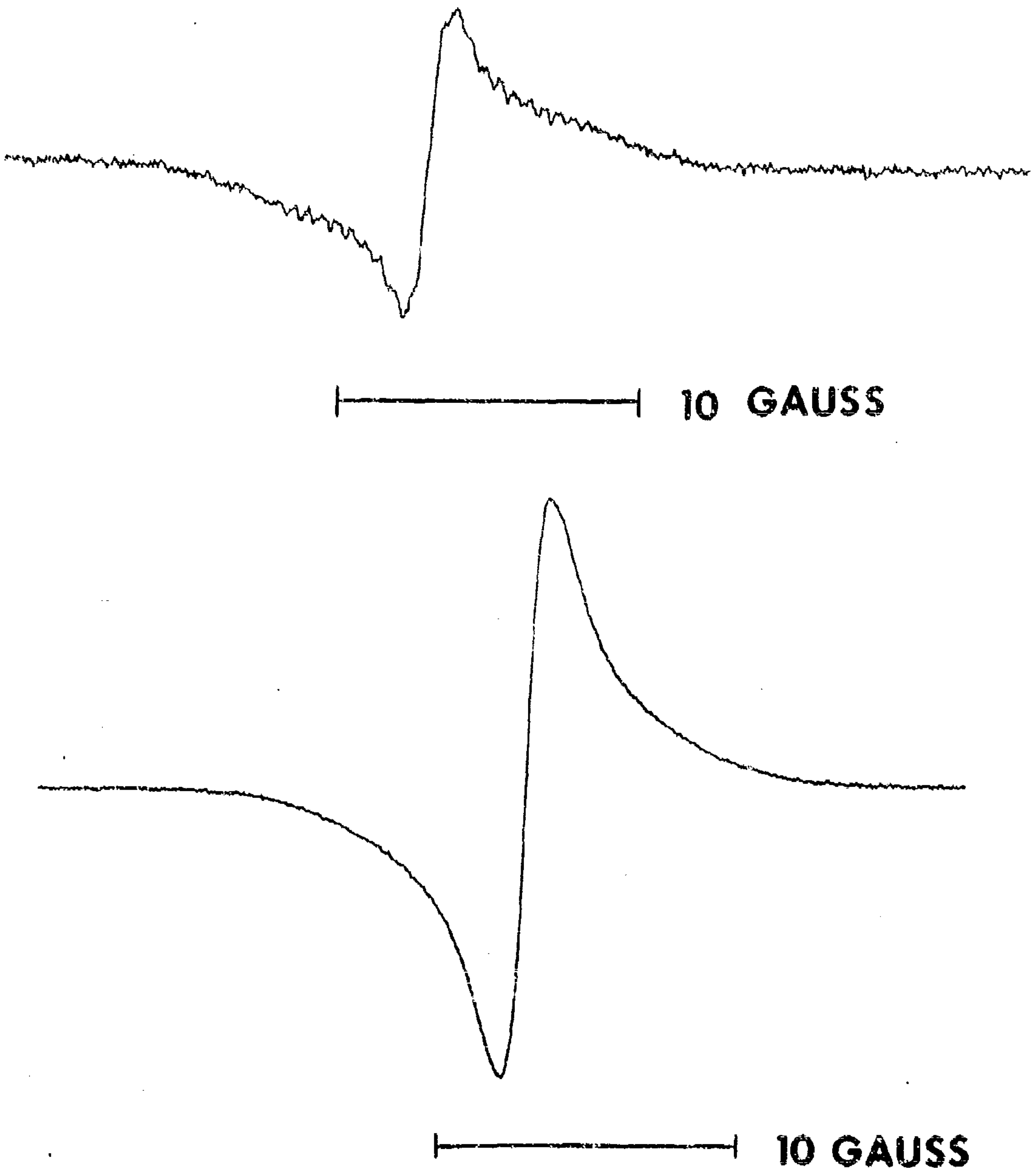


Figure 3. EPR Spectra of Methylviologen Cation Radical Chloride (I) Obtained During an Initial (A) and a Later (B) Stage of the Reduction With Zinc of a 0.60 *M* Aqueous Solution of 1,1'-Dimethyl-4,4'-Bipyridinium Dichloride (II)

$g = 2.00$.

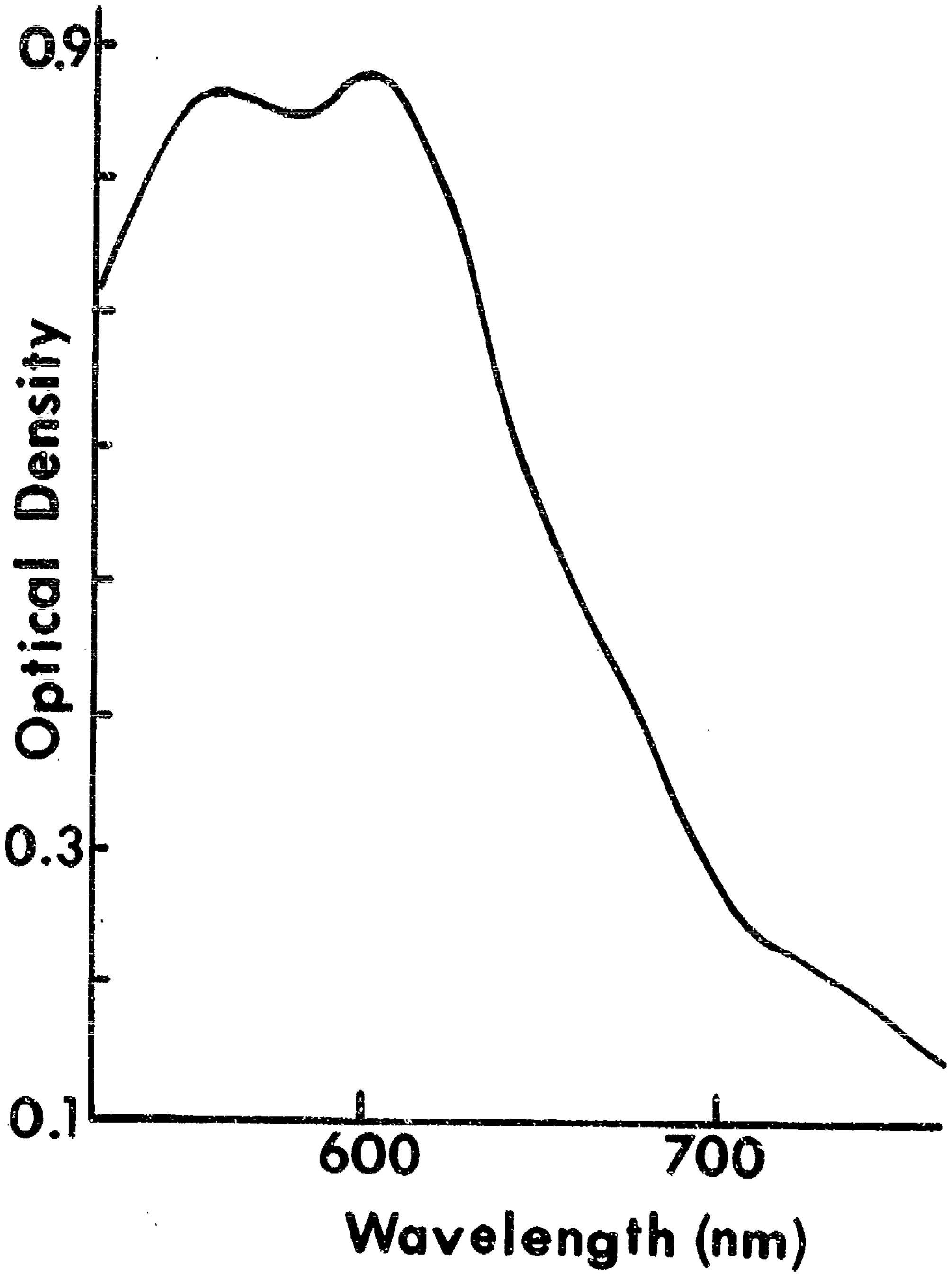


Figure 4. Visible Absorption Spectrum of Methylviologen Cation Radical Chloride (I) Obtained During an Initial Stage of the Reduction With Zinc of a 0.60*M* Aqueous Solution of 1,1'-Dimethyl-4,4'-Bipyridinium Dichloride (II)

λ_{max} = 558, 601 nm.

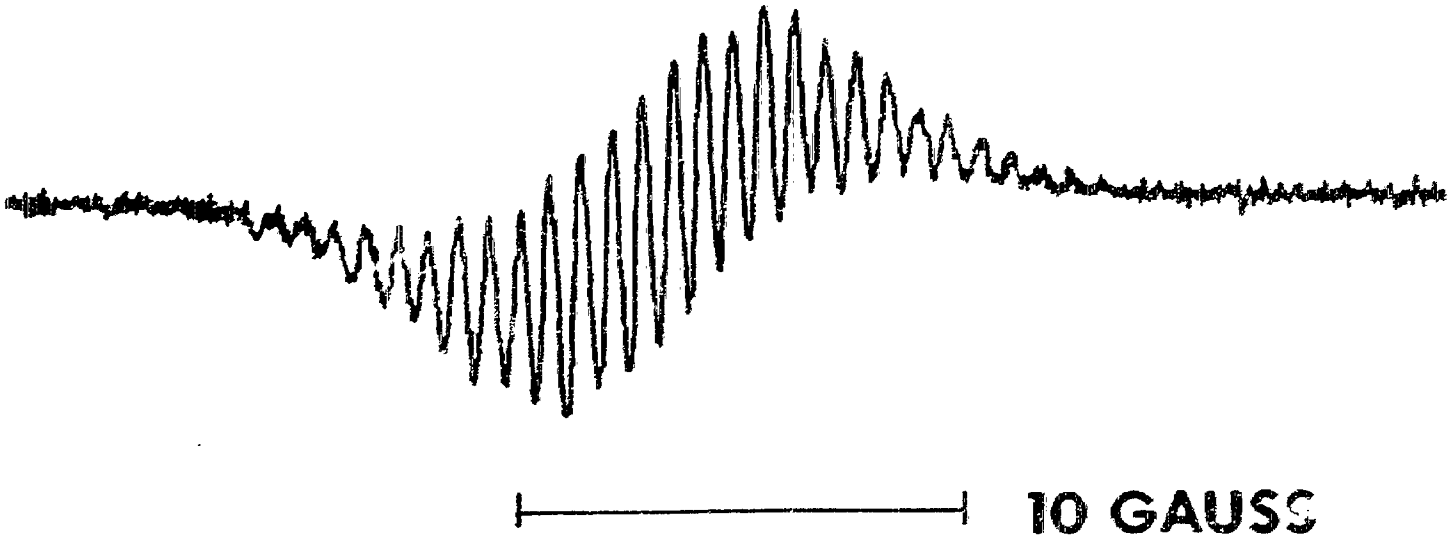


Figure 5. Epr Spectrum of Methylviologen Cation Radical Chloride (I) Obtained During a Reduction With Zinc of a 2.5 X 10^{-2} *M* Aqueous Solution of 1,1'-Dimethyl-4,4'-Bipyridinium Dichloride

$g = 2.00$.

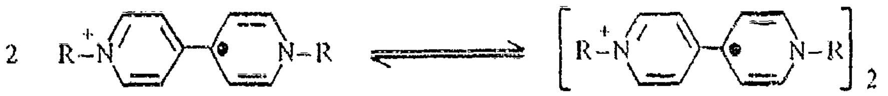
In another experiment it was found that a solution 2.5 × 10^{-2} M in II and 0.5 M in diethylamine gave a multiline epr pattern.

C. Methylviologen Dication Dichloride (II).

Compound II was obtained from Gallard Schlesinger Chemical Manufacturing Corporation. The sample was part of lot 2906210 with a listed redox potential (E_0') at pH 7.0 of −0.511 volts. It was used as received for the diethylamine experiments and recrystallized from methanol-acetone for the zinc runs.

III. DISCUSSION.

A monomer-dimer equilibrium of viologen cation radical (equation 1)



has been the subject of special attention during the last decade.[3-6] Concentration dependence of spectra together with previous reports on the reversibility of the absorption changes with temperature have been used to substantiate the presence of this equilibrium.[3,4] The dimer has been presumed to be a diradical composed of two molecules. The possibility that it might be a complex of viologen dication and a 1,1'-dihydro-4,4'-bipyridine was eliminated because gross differences do not exist between spectra of monomer and dimer.

The relative strength of the epr signal from methylviologen radical in water was reported to *decrease* with increasing concentration.[6] (This is in accord with the formation of a diamagnetic dimer.) The decrease in paramagnetism was much greater than that predicted for a simple monomer-dimer equilibrium and was ascribed to clustering. Also, it has been reported that the multiline pattern of methylviologen radical in water changes to a single line at 77°K. An excellent summary of the early history of viologen chemistry is available.[4]

As mentioned in the introduction, we have been interested in viologen radicals in connection with chemical detection mechanisms involving electron transfer.[1,2] During the course of these studies, it was discovered that the concentration of II has marked effects on the epr spectra of I. When I is generated in the presence of appreciable amounts of II in water (in our experiments about 0.5 M), the epr signal appears as a single line (figure 3). Multiline spectra at room temperature have been reported by others[4,5,7] and were found by us when the radical was prepared in aqueous

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[3] Schwarz, W. M., Jr. Investigation of Stable Free Radicals Formed by Electroreduction of N-Alkylpyridinium Salts. Ph.D. Thesis. University of Wisconsin. June 1961.

[4] Kosower, E. M., and Cotter, J. L. The Reduction of 1-Methyl-4-cyanopyridinium Ion to Methylviologen Cation Radical. J. Amer. Chem. Soc. *86*, 5524-5527 (1964).

[5] Blandamer, M. J., Symons, M. C. R., and Verma, G. S. P. Ion-pair and Ion-cluster Formation Induced by Water Structure. Chem. Commun. 629-630 (1965).

[6] Blandamer, M. J., Brivati, J. A., Fox, M. F., Symons, M. C. R., and Verma. G. S. P. Solvation Spectra. Part 17. Water-Induced Dimerization of Various Dye and Related Paramagnetic Ions Studied by Optical and Electron Spin Resonance Spectroscopy. Trans. Faraday Soc. *63*, 1850-1857 (1967).

[7] Johnson, C. S., Jr., and Gutowsky, H. S. High-Resolution ESR Spectra of Photochemically Generated Free Radicals: The Viologens. J. Chem. Phys. *39*, 58-62 (1963).

solutions containing 2.5×10^{-2} *M* or less of II (figures 1 and 5). The same general results were obtained regardless of the method of reduction (i.e., use of zinc or diethylamine). Discussions of the reaction of viologens with amines and other bases are available.[8,9]

We attribute the single epr line found in the present investigation to molecular association between methylviologen cation radical I and methylviologen dication II. Rapid exchange in the molecular complex explains the loss of hyperfine structure. Epr evidence for such viologen complexation has not been noted before. However, there is an earlier report of the isolation and analysis of a solid complex formulated as two methylviologen diiodides and one 1,1'-dimethyl-1,1'-dihydro-4,4'-bipyridine.[10] This complex apparently consists of two methylviologen cation radical iodides and one methylviologen cation diiodide. Also, a complex of II with $CuCl_2$ has been prepared that in the solid state contains some viologen cation radical.[11]

The visible spectrum of I obtained concurrently with multiline epr curves corresponds to that reported previously by others and attributed to viologen cation radical monomer.[3,4] The visible spectrum of I in the presence of high concentrations of II is explained easily on the basis of a complex of I with II. However, the absorption curve also corresponds to that reported[3] for a mixture of viologen radical monomer and dimer. Without additional experimentation, the presence of some radical dimer cannot be ruled out unequivocally. The dimer though, is diamagnetic and would not be expected to contribute to the epr signal from remaining monomer.

IV. CONCLUSIONS.

Methylviologen cation radical chloride and its parent compound, 1,1'-dimethyl-4,4'-bipyridinium dichloride, form complexes exhibiting rapid intermolecular exchange of electrons.

This finding may be useful in designing studies involving electron transfer in many chemical and biochemical systems. Viologen complexes may be helpful as chain carriers of electrons between molecular sites, thus acting as a probe for what normally would be a nonreactive system.

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[8] Corwin, A. H., Arellano, R. R., and Chivis, A. B. Anomalies of Viologens in Bases and Water. Biochim. Biophys. Acta *162*, 533-538 (1968).

[9] Farrington, J. A., Ledwith, A., and Stam, M. F. Cation-Radicals: Oxidation of Methoxide Ion with 1,1'-Dimethyl-4,4'-bipyridinium Dichloride (Paraquat Dichloride). Chem Commun. 259-260 (1969).

[10] Emmert, B., Jungck, G., and Haffner, H. Über chinhydron-artig Verbindungen des Dihydro-γ,γ'-dipyridyls. Chem. Ber. 57, 1792-1797 (1924).

[11] Prout, C. K., and Murray-Rust, P. Crystal and Molecular Structures of the N,N'-Dimethyl-4,4'bipyridinium (Paraquat) Salts with the Chlorometallate anions $CoCl_4^{-2}$, $[CuCl_2]_n^{-n}$ and $PdCl_4^{-2}$. J. Chem. Soc. (A) 1520-1525 (1969).

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8. Corwin, A. H., Arellano, R. R., and Chivis, A. B. Anomalies of Viologens in Bases and Water. Biochim. Biophys. Acta *162*, 533-538 (1968).

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