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Stable Free Radicals. II. The Reduction of 1-Methyl-4-cyanopyridinium Ion to Methylviologen Cation Radical

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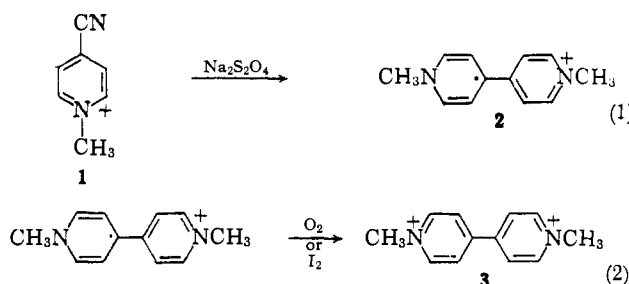
Treatment of 1-methyl-4-cyanopyridinium iodide with aqueous sodium dithionite at pH 10.5 in the absence of oxygen yields methylviologen cation radical iodide (the cation radical formed by one-electron reduction of 1,1'-dimethyl-4,4'-dipyridinium diiodide). The structure of the cation radical is shown by spectroscopic, titrimetric, and electron spin resonance methods. The mechanism of the reaction is outlined, some aspects of pyridinyl radical dimer chemistry are discussed, and complexes of the methylviologen cation radical are described.

The reaction of sodium dithionite with 1-methyl-4-carbamidopyridinium ion in alkaline aqueous solution yields an orange sulfoxylate-pyridinium ion complex.⁴ It was predicted from the positions of the charge-transfer bands observed for iodide-pyridinium ion complexes that replacement of the 4-carbamido group with a 4-cyano group would result in an orange-red sulfoxylate-pyridinium ion complex ($\text{SO}_2^{-2} \rightarrow \text{Py}^+$).⁵⁻⁷ To our surprise, the reaction of sodium dithionite with 1-methyl-4-cyanopyridinium ion forms a deep purple-blue solution, from which a stable free radical may be extracted with methylene chloride. We report here the nature of the stable free radical, a probable mechanism of its formation, and a few of its properties.

Results

The reaction of 1-methyl-4-cyanopyridinium iodide (1) with sodium dithionite in water at pH 10.5 produces a dark blue crystalline precipitate in addition to a dark purple-blue or reddish purple solution. In a vacuum system (see Experimental), the precipitate may be filtered off and recrystallized from acetonitrile. It could be demonstrated that iodide ion was present in the product but that sulfur and cyanide ion were absent. Oxidation of the product with iodine, followed by removal of iodide and triiodide ions, yields a solution with an absorption spectrum identical with that observed for 1,1'-dimethyl-4,4'-dipyridinium (methylviologen) ion (3) and quite different from that expected for 1-methyl-4-cyanopyridinium ion. An acetonitrile solution of the recrystallized dark blue product has an e.s.r. spectrum identical with that found for the methylviologen radical cation (2)⁸ (Fig. 1). These reactions may be formulated as shown in eq. 1 and 2.

Further confirmation of the structure of 2 came from an examination of the visible and ultraviolet absorption spectrum. The spectrum of 2 was identical in almost all respects with that of the reduction product of 3, obtained with sodium dithionite. A difference in the spectra was readily shown to be attributed to the



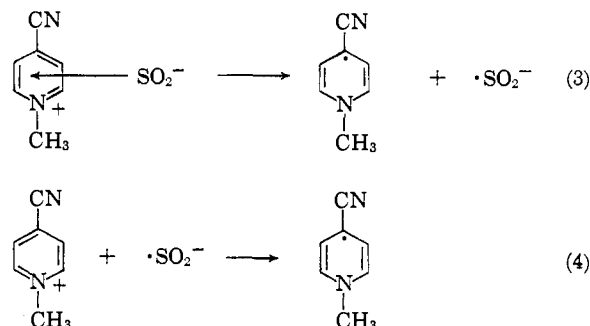
presence of iodide ion, which has a maximum at 2475 Å. in acetonitrile,⁹ in the solution of 2. The absorption coefficient for 2 at 6050 Å. was 10,060 by titration with iodine in comparison with a value of 10,700 for methylviologen radical cation obtained by electrochemical reduction of 3.¹⁰ A complete spectrum of 2 is shown in Fig. 2.

Methylviologen radical cation reacts rapidly with both tetrachloro- and tetrabromomethane, but only very slowly with dichloromethane. In fact, the e.s.r. spectrum of a solution of 2 in dichloromethane has been measured. Thus, as one might expect, radical 2 is less reactive than 1-ethyl-4-carbomethoxy-pyridinyl toward halocarbons.¹¹

Discussion

The most probable mechanism for the formation of methylviologen cation radical (2) from the 1-methyl-4-cyanopyridinium ion (1) is shown in Fig. 3.

The pathway for the formation of 1-methyl-4-cyanopyridinyl radical from the pyridinium ion is not clear, but is so rapid that one of two possible electron-transfer reactions are reasonable choices. These are intramolecular electron transfer within the sulfoxylate-1-methyl-4-cyanopyridinium ion complex (eq. 3) or reaction between the SO_2^- anion radical (which is present



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(2) The first paper in this series is E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **86**, 5515 (1964).

(3) Support of the Air Force Office of Scientific Research through Contract AF 49(638)-282 is gratefully acknowledged.

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(5) E. M. Kosower, J. A. Skorcz, W. M. Schwarz, Jr., and J. W. Patton, *ibid.*, **82**, 2188 (1960).

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(8) C. S. Johnson, Jr., and H. S. Gutowsky, *J. Chem. Phys.*, **39**, 58 (1963).

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(11) E. M. Kosower and I. Schwager, *J. Am. Chem. Soc.*, **86**, 5528 (1964).

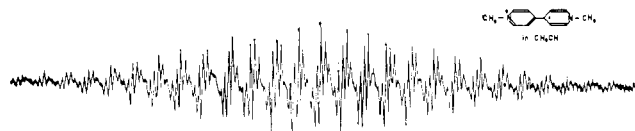


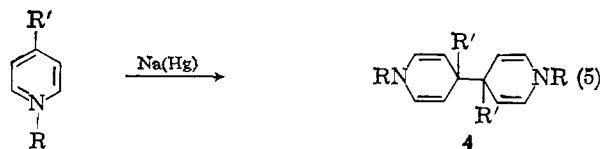
Fig. 1.—The e.s.r. spectrum of methylviologen cation radical in acetonitrile.

in equilibrium with dithionite ion¹²) and the pyridinium ion (eq. 4).

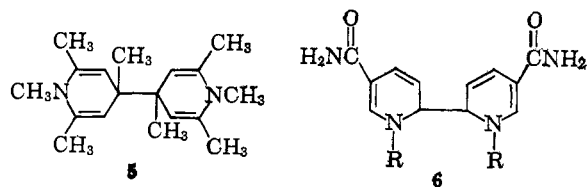
The 1-ethyl-4-cyanopyridinyl radical has been detected by triangular wave cyclic voltammetry both in water and in acetonitrile.¹³ An unstable solution of the radical in *n*-heptane has been prepared by the "thermal" reduction of 1-ethyl-4-cyanopyridinium iodide with magnesium.¹⁴

Subsequent formation of ethylviologen cation radical from the pyridinyl radical proceeds in water¹⁰ at a rate of *ca.* 20 l. mole⁻¹ sec.⁻¹, more slowly in acetonitrile,¹⁰ and is slowest in the least polar solvent, *n*-heptane.¹⁴ The high sensitivity of the reaction rate to solvent polarity suggests that an ionization reaction is rate determining. Either of the two steps shown in Fig. 3 in which cyanide ion is lost fits the description of the slow step. The reduction of 3 to 2 is presumed to be very fast either electrochemically^{10,13} or with sodium dithionite.

The first dimer of a pyridinyl radical was prepared in 1881 by sodium amalgam reduction of 1-methylpyridinium and 1-benzylpyridinium ions¹⁵ (eq. 5, R' = H, R = CH₃ or C₆H₅CH₂). A number of other



dimers derived from pyridinium ions have been prepared; for example, 1,1',2,2',4,4',6,6'-octamethyltetrahydro-4,4'-dipyridyl (5),¹⁶ 1,1'-diacetyltetrahydro-4,4'-dipyridyl (4, R' = H, R = COCH₃),^{17,18} 1,1'-dicarboxytetrahydro-4,4'-dipyridyl (4, R' = H, R = COOC₂H₅),¹⁹ and the compounds derived from the reduction of 1-alkyl-3-carbamidopyridinium ions (6).^{20,21}



In most cases, the structure assigned is through analogy with those dimers which give rise to 4,4'-dipyridyl on oxidation (and hydrolysis, as in the case of the diacetyl derivative). A spectroscopic criterion was applied in the case of 6. In none of these cases is it certain

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(13) W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Am. Chem. Soc.*, **83**, 3164 (1961).

(14) E. J. Poziomek, unpublished results.

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(16) B. Emmert and O. Werb, *ibid.*, **55**, 1352 (1922).

(17) O. Dimroth and R. Heene, *ibid.*, **54**, 2934 (1921).

(18) O. Dimroth and F. Frister, *ibid.*, **55**, 1223 (1922).

(19) D. A. van Dorp and J. F. Arens, *Rec. trav. chim.*, **66**, 189 (1947).

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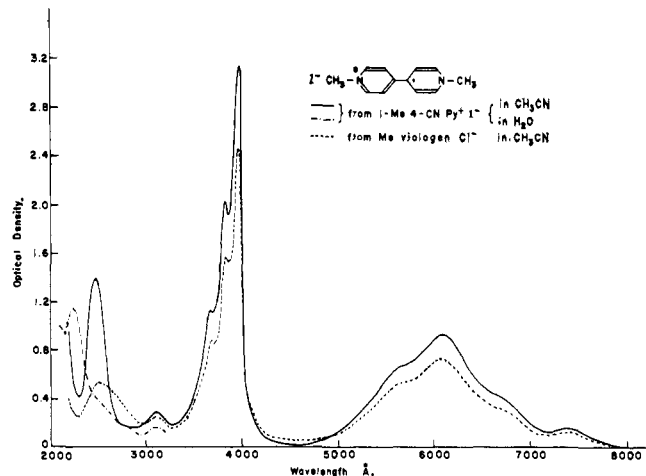


Fig. 2.—The ultraviolet and visible absorption spectrum of methylviologen cation radical iodide (acetonitrile and water) and chloride (acetonitrile).

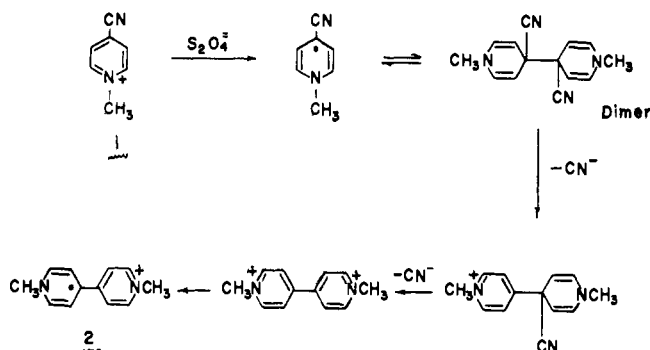


Fig. 3.—The mechanism of the formation of methylviologen cation radical from 1-methyl-4-cyanopyridinium ion and sodium dithionite.

that *free* pyridinyl radicals were intermediates, rather than complexes of a pyridinyl radical and the reducing agent, with dimer formation occurring through combination of the complexes. Even in the case of sodium amalgam, pyridinyl radical-mercury surface complexation is a distinct possibility since Schwarz¹⁰ has shown that methylviologen cation radical complexes with a mercury surface and that such complexation is associated with the occurrence of an adsorption wave in the polarographic reduction of 3. Emmert tried to detect 2,2'-dipyridyl with ferrous ion in the decomposition products of 1,1'-dibenzyltetrahydro-4,4'-dipyridyl pyrolysis in the presence of zinc dust and found only 4,4'-dipyridyl.²²

We may conclude from the foregoing that the formulation of the dimer of 1-methyl-4-cyanopyridinyl as shown in Fig. 3 is reasonable even if it does not represent the whole of the dimeric material.

It might be added that the tendency of some pyridinyl radicals to dimerize is so great that sodium pyridine radical anion has only been reported once,²³ the usual product of the treatment of pyridine with sodium or potassium being the anion or dianion of 4,4'-dipyridyl.²⁴⁻²⁶

The evidence for the dissociation of pyridinyl radical dimers into pyridinyl radicals is circumstantial, based

(22) B. Emmert, *Ber.*, **52**, 1351 (1919).

(23) J. W. Dodd, F. J. Hopton, and N. S. Hush, *Proc. Chem. Soc.*, 61 (1962).

(24) B. Emmert, *Ber.*, **47**, 2598 (1914); **50**, 31 (1917).

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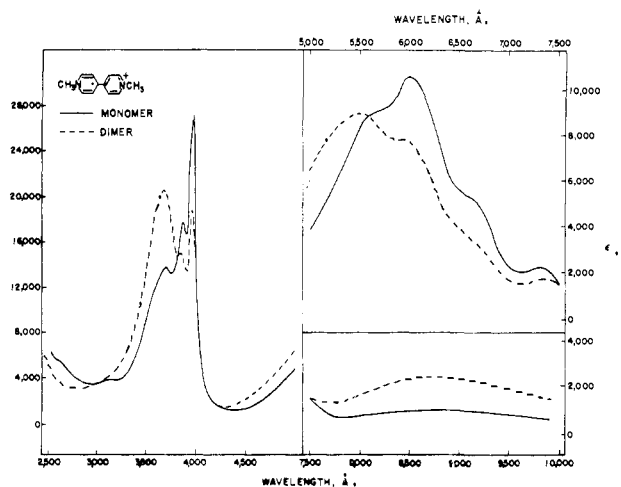
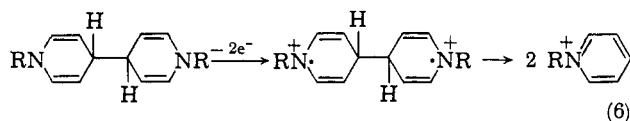
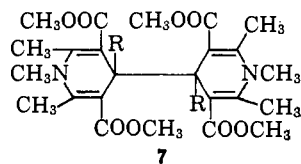


Fig. 4.—A comparison of the absorption curves for methylviologen radical monomer and dimer in water (adapted from ref. 10).

on the detection or isolation of pyridinium ion derivatives related to the pyridinyl radicals by the loss of one electron. Thus, dimer **5** reduces benzylviologen dication (**3**, with $C_6H_5CH_2$ instead of CH_3) to the corresponding benzylviologen cation radical (**2**, $C_6H_5CH_2$ in place of CH_3), with the simultaneous formation of 1,2,4,6-tetramethylpyridinium ion (isolated as the perchlorate).²⁷ Although it is known that free pyridinyl radicals can reduce viologen dications to viologen cation radicals,² it is also possible that the dimer itself loses two electrons and then dissociates directly to the pyridinium ion (eq. 6). However, it seems likely that the last two of the series of dimers **7** ($R = H, CH_3, CH_3CH_2, (CH_3)_2CHCH_2$) do dissociate into pyridinyl



radicals since the stability of the dimers are influenced so markedly by the size of the 4-alkyl group, and disproportionation products are obtained after decomposition.²⁸ Silver ion²⁷ and iodine²⁹ are other reagents from which the formation of monocyclic pyridinium ion derivatives suggests the possibility of dissociation.



If the dimers possess 4- and 4'-hydrogens, reaction with a limited amount of oxygen produces the corresponding viologen cation radical. After some initial confusion about the origin of the colors present in such reaction mixtures, including the incorrect proposal that 1-benzoylpyridinyl³⁰ and 1-benzylpyridinyl³¹ had been isolated, the presently accepted structures for the viologen cation radicals were formulated.³² The

(27) B. Emmert and O. Varenkamp, *Ber.*, **56**, 491 (1923).

(28) O. Mumm and H. Ludwig, *ibid.*, **59**, 1805 (1926).

(29) E. Weitz and T. König, *ibid.*, **55**, 2864 (1964).

(30) E. Weitz, A. Roth, and A. Nelken, *Ann.*, **425**, 161 (1921).

(31) E. Weitz and A. Nelken, *ibid.*, **425**, 187 (1921).

(32) E. Weitz and R. Ludwig, *Ber.*, **55**, 395 (1922).

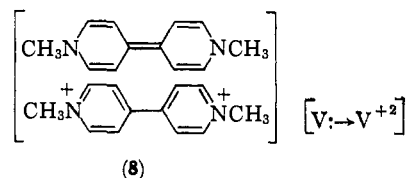
reduction of methylviologen dication (**3**) to a highly colored cation radical led Michaelis³³ to propose its use, as an oxidation-reduction indicator and the name, viologen.

The formation of cyanide adducts from the reaction of pyridinium ions and cyanide ion is a well-known phenomenon.³⁴ Thus, each of the steps and intermediates in the mechanism for the formation of methylviologen radical cation from 1-methyl-4-cyanopyridinium ion (Fig. 3) has a good or reasonable precedent: formation of a pyridinyl radical, reversible dimerization of the pyridinyl radical, ionization of cyanide ion from the dimer, presumably in two discrete steps, and, finally, reduction of the dication to the monocation radical.

Several properties of the methylviologen radical cation are worthy of special attention. In aqueous solution, the color of the viologen solutions range from blue to purple depending upon concentration. A monomer-dimer equilibrium was proposed to explain the related observation that cold benzylviologen cation radical solutions of a certain concentration are violet but become blue on warming. The color change is reversible.^{35,36} Schwarz¹⁰ has examined the spectra of solutions of **2** produced electrochemically over the concentration range in which an obvious color change occurs and has confirmed the idea that a monomer-dimer equilibrium is involved, with $K_{diss} = 2.6 \times 10^{-3} M$ (at 1 M salt concentration). The spectroscopic changes are striking and are reproduced in Fig. 4. The equilibrium is expressed as in eq. 7, with $V^{\cdot+}$ = methylviologen cation radical



The differences between the absorption spectrum of the dimer and the monomer include a new band at 8700 Å. (ϵ 2400), a shift in the visible absorption to shorter wave lengths, and a shift of the near ultraviolet absorption to shorter wave lengths with some loss in fine structure. The gross appearance of the spectrum suggests that the transitions responsible for absorption in the 4000 and 6000 Å. regions are the same in the dimer as in the monomer, excluding a gross difference in structure between the monomer and dimer. The dimer is thus *not* a complex of the oxidized and reduced forms of the viologen cation radical **8**. The dimer is *presumably* a diradical and the 8700 Å. band is probably best regarded as an allowed transition in the



dimer according to the tentative energy-level scheme shown in Fig. 5, and *not as a charge-transfer transition*, which would be forbidden. We have observed the color changes associated with dimerization only in water and not in acetonitrile. It is likely that ion-pair formation in acetonitrile precludes dimerization.³⁷

(33) L. Michaelis, *Biochem. Z.*, **250**, 564 (1932).

(34) Cf. discussion in E. M. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 173.

(35) E. Weitz, *Ber.*, **75**, 1927 (1942).

(36) E. Müller and K. A. Bruhn, *Chem. Ber.*, **86**, 1122 (1953)!

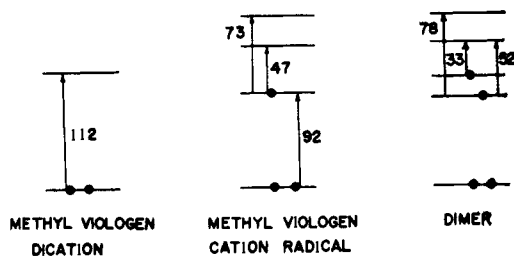


Fig. 5.—Energy level scheme for methylviologen dication, methylviologen cation radical monomer, and methylviologen cation radical dimer.

A solid complex which apparently consists of two methylviologen cation radical iodides and one methylviologen dication diiodide has been isolated and analyzed.³⁸ The complex is dark and said to be stable in dry air. Signs of such complexes have not been noted by us in the course of our work, but seem worth a specific search, especially in light of the relatively low rates observed for electron exchange (*ca.* 10^6 l. mole⁻¹ sec.⁻¹ at 0°) between 4,4'-dipyridyl and the potassium salt of the anion of 4,4'-dipyridyl.³⁹

Experimental

Materials.—1-Methyl-4-cyanopyridinium iodide,⁴⁰ m.p. 198°; equiv. wt. 246.7, calcd. 246.1. The perchlorate salt was prepared from the iodide and silver perchlorate; m.p. 166.2–170.0°.⁴¹ Methylviologen chloride (3 Cl⁻; British Drug Houses) was recrystallized three times from cold methanol by the addition of acetone. Sodium dithionite (hydrosulfite) was a technical product. Acetonitrile, methanol, isooctane, and dichloromethane (Matheson Coleman and Bell) were Spectro grade solvents and were used without further purification except for degassing when used in oxygen-free systems.

Spectra.—Cary Model 11 or Model 14 recording spectrophotometers were used for all measurements.

Preparation of Radical.—All work described below was carried out in oxygen-free all-glass systems carrying appropriate break-off seals. Evacuation with a good oil pump (usual pressure 0.01 mm.), filling with nitrogen, and re-evacuation was carried out three or four times to ensure an oxygen-free system. All solvents and solutions were degassed before use unless otherwise specified.

The apparatus shown in Fig. 6 was used in the preparation. Sodium dithionite (*ca.* 0.6 g.) in sodium bicarbonate–sodium carbonate buffer (pH 10.5) was placed in A. 1-Methyl-4-cyanopyridinium iodide (*ca.* 0.4 g.) was added through B which was then sealed off. After pumping the system down (as above), the constriction at X was sealed. The reducing agent was mixed with the pyridinium iodide, resulting in a vigorous effervescence and the formation of a dark precipitate suspended in a reddish blue solution. The apparatus was inverted, the precipitate collected on the sintered glass disk C, the filtrate in D, constriction Y was sealed, the precipitate dried by cooling A in liquid nitrogen, and constriction Z sealed off. A connection to another apparatus was made through break-off seal H, the precipitate dissolved in degassed acetonitrile, the solution filtered, then concentrated by

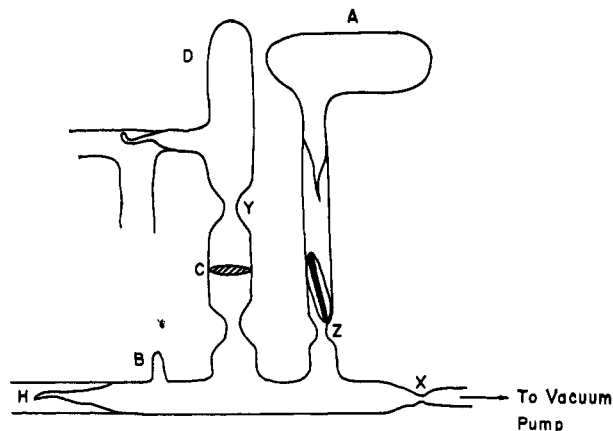


Fig. 6.—Apparatus for the preparation of methylviologen cation radical iodide under oxygen-free conditions.

removal of the solvent until crystals appeared. The container holding the suspension was warmed until clear, then cooled until small, well-defined needles appeared. The solid was filtered off and utilized for further work as recrystallized radical. Solutions were prepared by connecting the container to an apparatus carrying a tube of solvent. When appropriate, quartz cells bearing a graded seal to Pyrex and quartz e.s.r. tubes with graded seals were attached.

Titration.—An accurate titration of the radical with iodine in acetonitrile was possible by breaking a fine tip attached to a buret holding the titrant and allowing it to flow into a magnetically stirred solution of the radical. The end point was sharp, the beautiful royal blue color of the radical being replaced by a pale yellow color. Decolorization of 27.8 cc. of radical solution (optical density 0.72 at 6050 Å. in a 0.5-cm. cell) required 1.81 cc. of 1.10×10^{-3} M iodine solution. Assuming that 1 equiv. of iodine was required for each mole of radical, the ϵ_{605} was 10,060. The oxidized solution contained material with an absorption maximum at 2550 Å., after passage through an iodide ion-exchange column (to remove triiodide) and a perchlorate ion-exchange column (to remove iodide).

The oxidation product expected from 1-methyl-4-cyanopyridinyl, *i.e.*, 1-methyl-4-cyanopyridinium ion, has an absorption maximum at 2775 Å., but methylviologen chloride has a maximum at 2550 Å. (ϵ 21,000). Reduction of methylviologen chloride gave radical which was identical in all respects with that prepared from the 1-methyl-4-cyanopyridinium iodide except for an absorption maximum at 2475 Å. (Fig. 2). Iodides in acetonitrile have an absorption maximum at 2475 Å.,⁹ and it could readily be shown that the radical made from the cyanopyridinium iodide contained iodide by treatment with CCl₄ and chlorine water. The iodide ion is responsible for the fact that the equivalence of given radical solution against silver nitrate or perchlorate in acetonitrile was twice that of the solution against iodine. The spectrum of the radical iodide in water resembles that in acetonitrile except for the maximum attributed to iodide which is found, as expected, at 2250 Å.⁵ The radical contained neither sulfur nor cyanide ion.

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(37) Monomer–dimer equilibria have been examined for a number of metal ketyls and the dimers found to be diradicals in certain solvents; N. Hirota and S. Weissman, *J. Am. Chem. Soc.*, **86**, 2538 (1964).

(38) B. Emmert, G. Jungck, and H. Haffner, *Ber.*, **57**, 1792 (1924).

(39) W. L. Reynolds, *J. Phys. Chem.*, **67**, 2866 (1963).

(40) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(41) J. W. Patton, Ph.D. Thesis, University of Wisconsin, 1961.