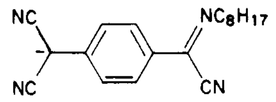
the TCNQ monosubstituted derivative was treated with other bases including butylamine, *N,N*-dimethyloctylamine, pyridine, and sodium hydroxide (the latter in acetonitrile). Since 7-(alkylamino)-7,8,8-tricyanoquinodimethanes are soluble in alkaline solutions from which they can be precipitated on acidification,[6,11] it is clear that what is being observed is simply the deprotonation of tautomer Ib to give the anion



which is not susceptible to nucleophilic attack.

A type I compound obtained from the reaction of TCNQ with a secondary amine cannot, however, exist in tautomeric forms, rendering a study of the required transformation feasible. Indeed, the deep blue 7-morpholino-7,8,8-tricyanoquinodimethane reacts smoothly with morpholine, producing the TCNQ 7,7-dimorpholino derivative as the only product (see Experimental Section). It also reacts with octylamine to give 7-morpholino-7-(octylamino)-8,8-dicyanoquinodimethane with a sharp isosbestic point at 475 nm (CH_3CN). That is, the reaction under consideration either occurs in one step or via an intermediate whose formation is rate limiting.[21] In view of what is known about the chemistry of substitution reactions of TCNQ[3,6] and TCNE[2,7,19] the second route is the plausible one.

The reaction of octylamine with 7-morpholino-7,8,8-tricyanoquinodimethane showed features similar to those observed for the octylamine–TCNQ reaction, except for lower rates. Thus whereas the latter reaction is very fast in acetonitrile, the former can be conveniently studied in this solvent, where it was found to be sluggish in dichloromethane. This is understandable in terms of the differences in reactivity (as Lewis acids) between the parent dye and its monosubstituted derivative, most probably coupled with some steric hiderance due to the substitution of the morpholine ring for the CN group. A kinetic study in acetonitrile yielded rate constant expression similar to eq 2 with $k_1 = 1.58\ M^{-2}\ s^{-1}$ and $k_{-1} = 0.0037\ M^{-1}\ s^{-1}$. Due to the intense absorption of the reactant and of the product, attempts to detect the formation of a charge-transfer complex were not sucessful; however, its exothermic formation accounts for the very small ΔH^* obtained, 1.4 kcal mol^{-1}.[40] The participation of a second amine molecule as a general base catalyst can be used to explain the highly negative ΔS^* value, −53 eu.[40] In summary, it seems that the second substitution reaction proceeds via the same mechanism suggested for substitution of the first CN group, the only differences is one of reactivity.

Acknowledgment. Support for this work from CNPq/PADCT and PRONAQ/CATÂLISE is gratefully acknowledged. We thank the Alexander von Humboldt Stiftung (O. A. El Seoud) the CNPq (P. P. Brotero) and Hoechst do Brasil (F. P. Ribeiro) for research fellowships.

Supplementary Material Available: Tables of observed rate constants of reaction of RNH_2 with TCNQ and dependence of k_{obsd} for reaction of octylamine and figure of $k_{obsd}/[RNH_2]$ vs. $[RNH_2]$ (4 pages). Ordering information is given on any current masthead page.

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(40) Calculated from the following k_{obsd} values obtained in the presence of 0.08 M octylamine: (7.9, 9.0, 10.1, and 10.6) × $10^{-3}\ s^{-1}$ at 15.1, 25.1, 35.7 and 40.4 °C, respectively. Since k_{-1} was negligible the values of k_1 were obtained from $k_1 = k_{obsd}/[C_8H_{17}NH_2]^2$. The error in ΔH^* is 0.2 kcal mol^{-1} and in ΔS^* is 0.5 eu.

Hydrogen Exchange between Methyl Viologen Cation and Basic Deuterium Oxide

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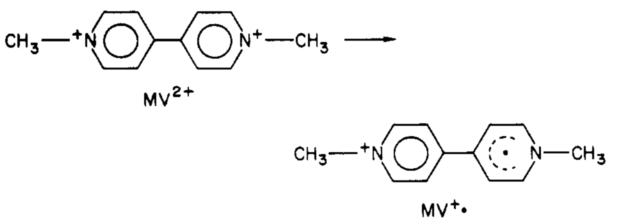
Received June 5, 1985

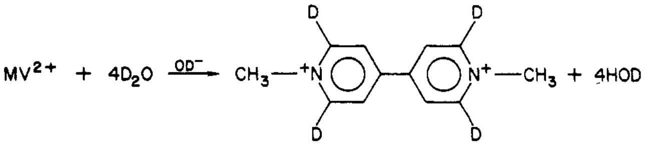
The methyl viologen cation has been found to exchange the 2,2′,6,6′-hydrogens with D_2O in basic solution. The rate, which can be conveniently followed by proton NMR at room temperature, is first order in both cation and hydroxide ion. The second-order rate constant at 24 °C and $\mu = 0.58$ is $1.7 \times 10^{-2}\ M^{-1}\ s^{-1}$. Activation parameters ΔH^* and ΔS^* have been found to be 80 kJ mol^{-1} and −8 J mol^{-1} K^{-1}, respectively. Benzyl viologen and diquat also exchange; however, multiple sites are involved so detailed studies have not been carried out.

The dipyridinium cation methyl viologen (MV^{2+}) is important as an electron-transfer reagent, and as the chloride salt (paraquat) it is used as a herbicide. The cation is known to undergo reduction in basic aqueous solution to give the radical–cation $MV^{+\cdot}$, eq 1). While investigating this reduction in alkaline D_2O by NMR, we found that the aromatic proton intensity of MV^{2+} decreased with time.



(1)

This was traced to exchange of the 2,6-set of hydrogens with D_2O (used as both solvent and NMR lock)–see eq 2; note that the numbering system used has the nitrogens at the 1- and 1′-positions on the ring.



(2)

Line-broadening of the proton NMR lines of MV^{2+} occurs when trace quantities of $MV^{+\cdot}$ are present.[1] Because

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(1) Johnson, C. S. *J. Chem. Phys.* **1963**, *39*, 2111.

Table I. Reactant Concentrations and Rate Constants[a]

$[MV^{2+}]$, M	[H], M[b]	$10^4 k_{obsd}$, s^{-1} [c]	RLE[d]
0.0316	0.127	1.93	±0.09
0.0271	0.108	2.11	±0.05
0.0105	0.0422	1.85	±0.04
0.00642	0.0253	1.92	±0.05
0.00316	0.0127	2.51	±0.12

[a] At 24.0 ± 0.5 °C, pD = 13.00, solutions not degassed, $\mu = 0.54$. [b] H means exchangeable hydrogens. [c] Average $k_{obsd} = 2.06 \times 10^{-4}$ s^{-1}. [d] Regression line error.

of the electron exchange broadening of the proton lines, the deuterium–hydrogen exchange can only be studied by NMR prior to the appearance of $MV^{+}\cdot$. Conditions of exchange and range of experiments were limited by the competitive formation of radical. The results of an exchange study are presented herein.

Exchange of hydrogens on quaternized pyridines has been investigated,[2] with particularly careful studies by Zoltewicz et al.[3]

There have been several inconclusive studies of the reaction of MV^{2+} with base to give $MV^{+}\cdot$, and these have been recently reviewed.[4] Our work on this reaction will be published elsewhere.

Results and Discussion

In order to study the proton–deuteron exchange in depth, sufficient enough that quantitative data could be obtained and analyzed, conditions had to be found where radical formation did not distort the proton NMR spectrum. It was observed that there were base concentrations sufficiently low that line broadening did not occur. The useable base range was extended by using nondegassed NMR samples. The reaction of radical with dissolved oxygen is rapid (eq 3). Before nondegassed solution were

$$O_2 + 4\ MV^{+}\cdot + 2H_2O \rightarrow 4MV^{2+} + 4\ HO^- \qquad (3)$$

used on a routine basis, it was ascertained that the hydrogen-exchange rate was unaffected by the presence or absence of small amounts of oxygen.

Also it was found important to limit or better to exclude methanol because radical formation was said to be enhanced by methanol; the redox process first postulated by Farrington et al.[5] apparently occurs (eq 4, see below). In

$$2MV^{2+} + CH_3O^- + HO^- \rightarrow 2MV^{+}\cdot + H_2O + CH_2O \qquad (4)$$

deuteromethanol with base, no MV^{2+} exchange was observed on our time scale; this is presumably due to the above fact concerning rapid radical formation in methanol.

Kinetics. The exchange of protons α to the nitrogen was followed by integration of the 2,6-line relative to the 3,5-line. No change in intensity was observed for either the 3,5-line or the methyl line of MV^{2+}. The 3,5-doublet collapsed to a singlet as the 2,6-line disappeared; this was expected to occur on substitution of deuterium for hydrogen at the 2,6-positions.

Plots of log concentration of unexchanged protons against time were linear, indicating that the reaction is first order in MV^{2+}. This order was confirmed by the observation that rate constants k_{obsd} are independent of initial MV^{2+} concentration, as may be seen in Table I.

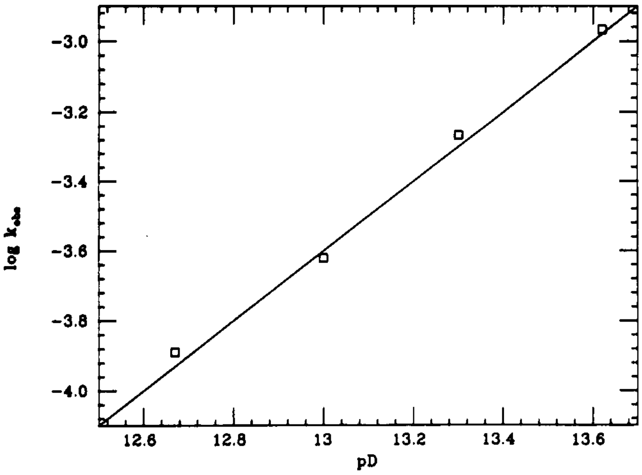

Figure 1. Plot showing dependence of base on deuteroxide ion concentration. Slope drawn is one. $T = 24.0$ °C and $\mu = 0.58$. Rate constant is 1.7×10^{-2} M^{-1} s^{-1}.

Table II. Methyl Viologen Exchange Rates[a]

$[MV^{2+}]$, M	pD	μ	$10^4 k_{obsd}$, s^{-1}	RLE[c]	remarks
0.0163	12.77	0.46	1.97	±.09	b
0.0163	13.00	0.47	2.43	±.11	b
0.0163	12.52	0.45	0.78	±.04	
0.0179	12.52	0.46	0.62	±.14	
0.0179	13.00	0.46	4.22	±.12	b
0.0179	12.70	0.45	1.41	±.04	
0.0179	13.14	0.47	7.95	±.22	
0.0164	13.14	0.47	7.51	±.46	
0.00895	13.14	0.45	4.16	±.21	
0.00383	13.14	0.42	7.34	±.39	b
0.0164	13.00	0.58	2.40	±.14	
0.0164	12.67	0.58	1.29	±.04	
0.0164	13.30	0.58	5.42	±.12	b
0.0164	13.62	0.58	10.8	±.07	
0.00819	13.30	0.55	3.64	±.15	
0.0316	13.02	0.61	2.13	±.03	
0.0215	13.02	0.58	2.10	±.02	
0.0106	13.02	0.52	2.21	±.06	
0.00527	13.02	0.49	2.06	±.04	
0.00263	13.02	0.47	2.18	±.15	
0.0316	13.20	0.61	4.34	±.13	
0.0106	13.20	0.52	4.45	±.17	
0.00316	13.20	0.48	3.42	±.20	
0.0147	13.20	1.04	1.87	±.17	
0.00723	13.20	1.03	1.43	±.06	

[a] All runs at 24.0 ± 0.5 °C in OD^-/CO_3^{2-} buffer. [b] Two runs (one degassed) combined; a single line was formed in the rate plot. [c] Regression line error.

The exchange rate is dependent on the first power of base concentration. A set of k_{obsd} values at different pD values is presented in Figure 1. The line drawn has the slope 1.00 showing the kinetic order in OD^-. Catalysis by the basic form of the carbonate buffer was not seen; absence of general base catalysis in pyridinium exchanges has been the usual report.[2,3]

Also expected was a negative salt effect, and this was observed. For example, k_{obsd} dropped by a factor of 2.5 on going from $\mu = 0.58$ to 1.04. Complicating the interpretation of ionic strength on rate is the fact that MV^{2+} has a tendency to form ion pairs.[6]

A summary of the kinetic runs that gave meaningful rate constants is presented in Table II. Suffice to say that all

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(2) For review, see: Elvidge, J. A.; Jones, J. R.; O'Brien, C.; Evans, E. A.; Sheppard, H. C. *Adv. Heterocycl. Chem.* **1974**, *16*, 1–31. See also: Koch, H. F. *Acc. Chem. Res.* **1984**, *17*, 137.

(3) (a) Zoltewicz, J. A.; Kauffman, G. M.; Smith, C. L. *J. Am. Chem. Soc.* **1968**, *90*, 5939. (b) Zoltewicz, J. A.; Helmick, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 7547. (c) Zoltewicz, J. A.; Cross, R. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1363; (d) *Ibid.* **1974**, 1368.

(4) Summers, L. A. In "The Bipyridinium Herbicides"; Academic Press: New York, 1980; pp 97–101.

(5) Farrington, J. A.; Ledwith, A.; Stam, M. F. *Chem. Commun.* **1969**, 259.

(6) C.f.: (a) Reference 3, pp 116–117. (b) Ebbesen, T. W.; Levey, G.; Patterson, L. K. *Nature (London)* **1982**, *298*, 545.

Table III. Dependence of Rate Constant on Temperature[a,b]

T, K	T, °C	$10^3 k_{obsd}$, s^{-1}	$10^2 k_2$, M^{-1} s^{-1}
		Series J	
292.7	19.6	0.217 ± 0.003	0.948
297.3	24.2	0.424 ± 0.008	1.85
307.2	34.0	1.45 ± 0.07	6.33
315.2	42.0	3.17 ± 0.10	13.8
317.4	44.2	4.08 ± 0.48	17.8
322.3	49.1	5.54 ± 0.97	24.2
329.1	55.9	9.88 ± 0.55	43.2
		Series K	
283.5	10.3	0.0638 ± 0.049	0.340
289.0	15.8	0.135 ± 0.005	0.718
297.5	24.3	0.484 ± 0.020	2.58
305.2	32.0	0.552 ± 0.142	2.94
307.0	33.8	0.822 ± 0.067	4.38
316.2	43.2	2.25 ± 0.15	12.0

[a] For series K, $[MV^{2+}]$ = 0.0345 M, pD = 13.14, and μ = 0.69. For series J, $[MV^{2+}]$ = 0.0358 M, pD = 13.23, and μ = 0.66. [b] The pD values were obtained from the reaction mixture at room temperature.

of the data therein are consistent with the kinetic information presented above.

From the four experiments of Figure 1, we have calculated the rate constant k_2 as defined by the law in eq 5 with $[OD^-]$ being calculated from eq 6. The value so obtained

$$k_{obsd} = k_2[OD^-] \tag{5}$$

$$pOD = pK_w^D - pD \tag{6}$$

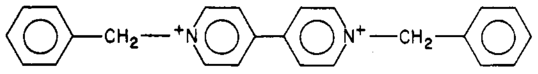
is 1.7 × 10^{-2} M^{-1} s^{-1} at 24 °C and μ = 0.58. This is comparable to the constant obtained for the 2-position of 3-chloro-1-methylpyridinium ion at 75 °C and 2 powers of 10 larger than that for the 6-position.[3c] Exchange in MV^{2+} is indeed rapid when compared to usual pyridinium ions.

The electronic effect of one quaternized ring of MV^{2+} on the other must be strongly electron withdrawing. This is also seen in the ease of radical $MV^{+}\cdot$ formation by one-electron reduction, for the potential is −0.46 V vs. the hydrogen electrode.

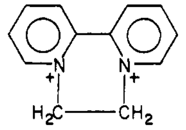
Two separate kinetic series for a total of 13 runs at temperatures from 10.3 to 55.9 °C were carried out in order to obtain activation parameters for the exchange process. To our knowledge no parameters have been obtained for any similar exchange. The data for our runs are given in Table III and lead to ΔH^* and ΔS^* values of 80 ± 0.06 kJ mol^{-1} and −8 ± 0.72 J mol^{-1} K^{-1}, respectively. The barrier to reaction is primarily enthalpic, for the activation entropy is near zero. At first sight a value of ΔS^* near zero for hydroxide abstracting a proton might be surprising; however, this is known for cases where hydroxide is a nucleophile in reactions at the carbon in carbon dioxide and cyanogen chloride,[7] and the small ΔS^* can be explained in these cases in terms of the need for desolvation of this strong base anion. Another instance of enthalpy-determined hydrogen exchanges where the entropy of activation values are near zero is the kinetic acidity of fluorinated bicycloalkanes.[8] With methanolic sodium methoxide, the five reported values of ΔS^* ranged from +17 to −33 J mol^{-1} K^{-1}.

Exchange of MV^{2+} hydrogens and formation of $MV^{+}\cdot$ appear to be independent reactions even though both are base catalyzed. Because of the line broadening, radical formation when rapid can hide the exchange. Nevertheless, exchange continues. If reaction mixtures in which radical builds up are allowed to stand for a few hours and then the radical is discharged by acid and air, the amount of exchanged hydrogen corresponds to that predicted by the rate constant.

The exchange with D_2O with cations benzyl viologen (BV^{2+}) and diquat (DQ^{2+}) has been investigated to a lesser extent. It was found that not only did the aromatic ring hydrogens in the expected positions exchange but so also did the aliphatic protons. This made kinetic studies impractical because of simultaneous multiple site exchanges.



BV^{2+}



DQ^{2+}

Experimental Section

Paraquat (K + K or ICN) was recrystallized from methanol/acetone and dried under vacuum at 100 °C to give a product shown to be free of water or methanol by NMR. Deuterium oxide was 99.8% (Stohler). Other chemicals were reagent grade. Stock buffers were prepared in D_2O from Na_2CO_3, NaOH, and NaCl (to keep ionic strength μ constant). When paraquat solutions of variable concentrations were prepared, NaCl was added to keep the chloride ion concentration constant; the variation of μ for any one set of runs because of this substitution was about ±0.03.

NMR measurements were recorded on a Bruker WM 250 spectrometer. Reaction was initiated by adding buffer with syringe to a solution of MV^{2+} in a 5-mm tube, which was then placed in the spectrometer. Spectra were recorded with a programmed sequence that collected a specified number of scans on the disk and repeated the process after a specified time. The interval between mixing and first point was recorded. Corrections were made for time needed to collect scans on the disk; these were small even for the fastest runs.

No new NMR peaks appeared during the course of a run, although on the longer term degradation of MV^{2+} (such as hydrolysis of the methyl group) is known to occur.

Glass electrode readings, taken on an Orion Model 801A meter, were made on a solution equivalent to that in the spectrometer. Based on the work of Bates et al.[9] coupled with measurements here, the value 0.40 was added to the measured pH in order to obtain pD. The pH was obtained from solutions identical with those used in the exchange runs, and the pH for each kinetic run solution was measured after the NMR data were complete; initial and final values did not differ by more than 0.01 unit.

The proton NMR spectrum (prior to exchange) matched that reported by Ross and Krieger,[10] and their assignments have been confirmed here.[11]

For the temperature-dependence study, solutions were prepared and pH measured at room temperature. The MV^{2+} solution was placed in an NMR tube in a water bath at the desired temperature, and a sample of buffer solution was also inserted in the bath. The NMR instrument was brought to the same temperature. The two solutions were then mixed and the tube inserted in the spectrometer. After the first few points, a good straight line was obtained for each run. A Bruker VT100 variable temperature unit with a calibrated thermocouple situated in the gas stream below the sample was employed to give control to ±0.1 °C.

Registry No. Methyl viologen, 1910-42-5; hydrogen, 1333-74-0.

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