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Kinetics of Reduction of Eight Viologens by Dithionite Ion

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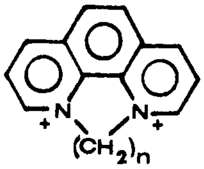
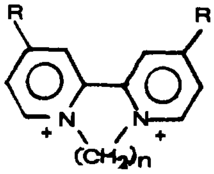
Abstract: The rate constants are reported for reduction by dithionite of methyl viologen, diquat, and six other diquaternary salts of 4,4′-bipyridine, 2,2′-bipyridine, and 1,10-phenanthroline. The active reductant is the SO_2^- radical, and rate constants vary from $>5 \times 10^8$ to 8.5×10^3 M^{-1} s^{-1} with increasing negative reduction potential of the viologen. It is concluded that self-exchange rate constants for the viologens ($X^{2+/+}$ couple) are $\sim 10^8$ M^{-1} s^{-1}, and this is supported by the results of a cross-reaction involving two viologens, the second-order rate constant being measured by pulse radiolytic techniques.

We have been interested in the reduction by dithionite of inorganic[1] and bioinorganic[2] compounds. In many of these systems the effective reducing agent is the SO_2^- radical which exists in small concentration in dithionite solutions. Recently, we have compared the rate constants for reduction by SO_2^- with the superoxide ion, O_2^-.[3]

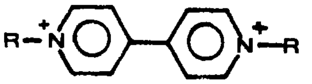
The viologens are diquaternary salts of 4,4′-bipyridine, 2,2′-bipyridine, and 1,10-phenanthroline. They undergo interesting one-electron reduction, to give strongly colored radical cations.[4,5] However, no kinetic studies of the reduction of viologens by dithionite, one of the most used reducing agents, have apparently been reported. We describe the kinetics of reduction of the eight viologens **1–3** which cover a range of structural types and reduction potentials. Two of prime interest are paraquat (1,1′-dimethyl-4,4′-bipyridylium ion **3a**) and diquat (1,1′-ethylene-2,2′-bipyridylium ion **2a**) which are effective herbicides,[6] redox indicators, and one-electron transfer agents, and mediators in photosensitive electron-transfer reactions (for solar energy conversion and storage).[7,8] We have also studied, by pulse radiolysis, the electron-transfer rate between MV^{2+} and $PDQ^{+}\cdot$ and $PDQ^{+}\cdot$ and between MV^{2+} and $BDQ^{+}\cdot$, to aid in our analysis of the dithionite reductions.



1a, n = 2 (EPQ^{2+})
1b, n = 3 (PPQ^{2+})



2a, R = H; n = 2 (DQ^{2+})
2b, R = CH_3; n = 2 (MDQ^{2+})
2c, R = H; n = 3 (PDQ^{2+})
2d, R = H; n = 4 (BDQ^{2+})



3a, R = CH_3 (MV^{2+})
3b, R = $C_6H_5CH_2$ (BV^{2+})

Table I. Electrochemical, Spectral, and Kinetic Characteristics of One-Electron Reduced Viologens

parent viologen	$E°$, V	spectral characteristics of radical: λ_{peak}, nm	spectral characteristics of radical: $\epsilon \times 10^{-3}$, M^{-1} cm^{-1}	k,[a] M^{-1} s^{-1}
1b (PPQ^{2+})	$-0.13^{b,c}$	570	$3.3^{d,e}$	$>5 \times 10^8$
		490	1.2^{e}	
		400	$6.3^{d,e}$	
1a (EPQ^{2+})	-0.25^{b}	520	$3.5^{d,e}$	$(1.4 \pm 0.2) \times 10^8$
		490	1.3^{e}	
		390	$5.7^{d,e}$	
2a (DQ^{2+})	-0.35^{f-h}	760	$2.7,^{e}$ 3.1^{i}	$(6.4 \pm 0.4) \times 10^7$
		370	$32,^{e}$ $38^{d,j}$	
3b (BV^{2+})	$-0.36^{g,h}$	603	$14,^{e}$ $15^{d,j,k}$	$(9.4 \pm 0.4) \times 10^7$
			$17^{l,m}$	$(9.0 \pm 0.6) \times 10^{7\,n}$
		386	$43^{d,j}$	
3a (MV^{2+})	$-0.45^{c,f-h}$	600	$13,^{e}$ $14,^{d,i}$ 14^{o}	$(9.0 \pm 0.2) \times 10^{6\,p}$
2b (MDQ^{2+})	$-0.49^{b,f}$	760	2.9^{e}	$(1.8 \pm 0.1) \times 10^6$
		370	32^{e}	
2c (PDQ^{2+})	$-0.55^{c,f-h,q}$	493	$2.0,^{e}$ $3.2^{d,j}$	$(3.0 \pm 0.1) \times 10^5$
		375	$15^{d,j}$	
2d (BDQ^{2+})	$-0.64^{b,f-h}$	520	$3.0^{d,j}$	$(8.5 \pm 3.1) \times 10^{3\,n}$
		500	$2.5^{d,e}$	6 ± 0.5^{r}
		460	0.6^{e}	
		390	$7.0^{d,e}$	
		383	$9.2^{d,j}$	

[a] Rate constant for reduction of viologen by SO_2^- at 25 °C, $I = 0.5$ M and pH 8.1. [b] Reference 11. [c] Reference 12. [d] Pulse radiolysis. [e] This work. [f] Reference 9. [g] Reference 13. [h] Reference 14. [i] Reference 17. [j] Estimated from the figure in ref 18. [k] Reference 19. [l] Reference 20. [m] In μM solution, the monomer of BV^+ predominates.[20] [n] pH 9.2. [o] Reference 21. [p] Independent of pH 7.2 to 9.2. [q] Reference 15. [r] For reaction with $S_2O_4^{2-}$ (k_5).

Experimental Section

Chemicals used were the purest commercial product. $MVCl_2$ (Sigma), $DQBr_2$ (Chemical Services, West Chester, PA), and $BVCl_2$ (K&K Lab., Inc.) were used as received. $PDQBr_2 \cdot H_2O$, $BDQBr_2 \cdot H_2O \cdot {}^1/_3 HBr$ and $MDQBr_2 \cdot H_2O$ (ref 9), and $EPQBr_2$ and $PPQBr_2$ (ref 10) were prepared as described in the literature.

Sodium dithionite (95% pure) was a gift from Dr. J. A. Peterson, who obtained it from Hardman-Holden, Manchester, England.

Kinetics. Low concentrations (5–10 μM) were used of the viologens whose radicals had high absorption coefficients (PDQ^{2+}, MV^{2+}, BV^{2+}, and DQ^{2+}). Higher concentrations (50–100 μM) of the other viologens were employed. For the very rapid reductions, 0.5–4.0 mM, and for the remainder 1–60 mM, dithionite concentrations were used. All the reactions were carried out in an argon atmosphere at 25 °C. Sodium dithionite was dissolved in argon-saturated buffer solutions and standardized by reacting with a slight excess of $Fe(CN)_6^{3-}$ ($\epsilon_{418nm} = 1.03 \times 10^3$

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M^{-1} cm^{-1}). The air-free solutions of dithionite and of the viologen in the appropriate buffer (usually 0.1 M Tris/H_2SO_4 at pH 8.1) and ionic strength (I = 0.5 M with Na_2SO_4) were transferred under argon pressure to the syringes of a Gibson-Dionex stopped-flow apparatus. This was linked to an OLIS data-collecting system. Great care was taken to exclude oxygen as far as possible in the manipulation of the solutions. Reactions were excellent first-order, monitored at radical peak (see Table I), always near 400 nm, and also at longer wavelengths, with no significant difference in rate constants. Spectra of the radicals were obtained by using a rapid-scan spectral stopped-flow apparatus (which employed a Harrick rapid scan monochromator) designed by Dr. DeSa (OLIS, Jefferson, GA). The spectra of the radicals derived from BDQ^{2+}, PPQ^{2+}, and EPQ^{2+} were also obtained by pulse radiolysis. An electron pulse of 100 ns duration was delivered to a deaerated solution of the sample (100 μM viologen at pH 7.6, I = 0.03 M with potassium phosphate and 5% t-BuOH) in a quartz cell with a 2.4 cm path length. Absorption by the radical was recorded 4 μs after the pulse, during which time the radical formed completely. The amount of radical generated was 4.1 μM.

In the pulse radiolysis kinetic experiments, mixtures of MV^{2+} (50–125 μM) with PDQ^{2+} or BDQ^{2+} (100 μM) at pH 7.6, I = 0.03 M, with a phosphate buffer and 5% *tert*-butyl alcohol in deaerated solution were electron pulsed. Production of MV^+ was monitored at 600 nm. A CN Van de Graaff electron accelerator at the Center for Fast Kinetics Research (The University of Texas, Austin) was utilized as an electron source. Electron pulses of 100-ns duration were delivered to samples in a quartz cell with a 2.4 cm optical path length. Spectral and signal changes were processed by computer.

Results and Discussion

The reduction potentials of the viologens **1**–**3** are taken from the literature (Table I).[9,11-15] There is a good consensus on the values except for that of PPQ^{2+}, which may arise from its poor electrochemical reversibility.[12] Fortunately, also, the potentials appear relatively insensitive to pH and ionic strength changes.[16] Addition of excess dithionite to these viologens at pH 7–9 produced intensely colored (green, red, or deep blue) solutions which are attributed to the one-electron reduced radical $X^{+}\cdot$. Absorbance peak positions and absorbance coefficients of the radicals produced by dithionite reduction are shown in Table I. They were obtained from the kinetic data and also by rapid scan spectrophotometry because, in some instances, of the instability of the radical (see below). Spectral characteristics of these radicals generated by pulse radiolysis (e_{aq}^-) and chemical and electrochemical means are also included in Table I.[17-21] For five of the radicals produced in this study, there is generally good agreement between ours and reported spectral characteristics. The radicals produced, however, by dithionite reduction of EPQ^{2+}, PPQ^{2+}, and BDQ^{2+} have absorbance peaks shifted markedly (30–80 nm to shorter wavelengths) from those shown by e_{aq}^- reduction of these viologens. The peak position and absorbance coefficient is unchanged when, for example, 500 or 10 μM EPQ^{2+} is reduced by dithionite in Tris or in phosphate buffer, so that the concentrations of radical and the medium conditions produced in the dithionite or e_{aq}^- reductions (4.1 μM) are comparable. If the dimerization constants were very large for $EPQ^{+}\cdot$, $PPQ^{+}\cdot$ and $BDQ^{+}\cdot$, the spectra obtained by dithionite reduction could be that for the dimer, whereas the immediate product of e_{aq}^- reduction would be monomer. This is unlikely, however, since the peak positions of the EPQ^{2+} and PPQ^{2+} electron adducts produced in pulse radiolysis do not shift in 130 μs, during which time dimerization would be expected to occur, unless the dimerization rate constants of the radicals were inordinately small.[22] We might have concluded that dithionite interaction with the radical occurs, modifying the radical spectra. However, the same species is produced whether dithionite or viologen^{2+} is in excess. We remain puzzled by the difference.

The stability of the first-formed radical in excess dithionite and in Tris buffer varied markedly. $MV^{+}\cdot$ only slowly discolored over hours,[23] whereas $PPQ^{+}\cdot$ and $EPQ^{+}\cdot$ transformed to other species within minutes. The kinetics of these decompositions were only briefly examined. The first-order rate constant for loss of radical was independent of dithionite concentration. Values were 50 ± 5 s^{-1} ($PPQ^{+}\cdot$), 0.5 ± 0.1 s^{-1} ($EPQ^{+}\cdot$), 0.02 ± 0.003 s^{-1} ($BV^{+}\cdot$), and (1.6 ± 0.4) × 10^{-4} s^{-1} ($MV^{+}\cdot$). This sequence parallels the increasing negative reduction potential for the $X^{2+}/X^{+}\cdot$ couple, although we doubt that this is significant. The chemical reduction of MV^{2+} is known to give a variety of products;[5] with dithionite, the two-electron-reduced MV^0 forms slowly.[23] The first reduction potential of MV^{2+} is independent of pH, and the second is pH dependent and markedly more negative.[5,24]

The rate law in (1) for the reduction of all viologens X^{2+}, except

$$d(X^{+}\cdot)/dt = k_{obsd}[X^{2+}] = k_1[X^{2+}][S_2O_4^{2-}]^{1/2} \qquad (1)$$

that for BDQ^{2+}, by dithionite contained a single term, which is consistent with a mechanism in which SO_2^- is the active reductant.

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^- \qquad K_2 \qquad (2)$$

$$SO_2^- + X^{2+} \rightarrow SO_2 + X^{+}\cdot \qquad k_3 \qquad (3)$$

With the viologens with large negative potentials (PDQ^{2+} and BDQ^{2+}), the reduction was forced to completion by using high concentrations of dithionite and raising the pH.[25] With MV^{2+}, the rate constant k_1 was shown to be independent of a change in pH from 7.2 to 9.2. For the reaction 2 and reaction 3 scheme the simple relationship in (4) holds. Using a value of K_2 = 1.4

$$k_1 = k_3K_2^{1/2} \qquad (4)$$

× 10^{-9} M,[26] k_3, the second-order rate constant for attack by SO_2^- can be estimated and values of k_3 are collected in Table I. For reduction of BDQ^{2+} an *additional* term to that in (1) was observed[27]

$$d(BDQ^{+}\cdot)/dt = k_{obsd}[BDQ^{2+}] = k_1[BDQ^{2+}][S_2O_4^{2-}]^{1/2} + 2k_5[BDQ^{2+}][S_2O_4^{2-}] \qquad (5)$$

indicating that direct reduction of BDQ^{2+} by $S_2O_4^{2-}$ as well as by SO_2^- could take place. Although direct reduction by $S_2O_4^{2-}$ is not common, it has been previously observed (sometimes along with SO_2^- reduction). Thus reduction by $S_2O_4^{2-}$ occurs, for example, with ferricytochrome c,[26] azurin,[3], plastocyanin,[26] $Fe(CN)_6^{3-}$ ion,[1b] some cobalt(III) complexes,[1a,3] nitro blue tetrazolium[3], and 2,6-dichlorophenol indophenol.[3] The value of k_5 for BDQ^{2+} (which is the rate constant for reaction of BDQ^{2+} with $S_2O_4^{2-}$ to give $S_2O_4^-$) is also shown in Table I.

We can apply the simple Marcus expression 6[28] to our data[29]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (6)$$

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(22) The dimerization constant for $BV^{+}\cdot$ is relatively large, 5 × 10^4 M^{-1} in 0.1 M potassium phosphate buffer at pH 7.5 and 25 °C.[20] When concentrations greater than 4 μM of $BV^{+}\cdot$ are produced by pulse radiolysis, subsequent dimerization is observed with $t_{1/2}$ = 25 μs.[19]

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(27) Plots of $k_{obsd}[S_2O_4^{2-}]^{-1/2}$ vs. $[S_2O_4^{2-}]^{1/2}$ are linear from (5). The value of the intercept is k_1, $M^{-1/2}$ s^{-1}. The slope is $2k_5$, M^{-1} s^{-1}.

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(29) We have omitted consideration of work terms[28] in applying expression 6. In view of their relatively small modifying effect, the difficulty in assessing them with this system and the ambiguity anyway in the final result (see below) we have chosen to ignore them.

Table II. Kinetic Data for the Reactions of MV^{2+} with $PDQ^{+}\cdot$ and $BDQ^{+}\cdot$ at 25 °C, I = 0.03 M and pH 7.6

$[MV^{2+}]_0$, μM	$[MV^{+}\cdot]$, μM	$[PDQ^{2+}]_0$, μM	$[PDQ^{+}\cdot]$, μM	$10^{-4}k$, s^{-1}	$10^{-8}k_8$, $M^{-1}\ s^{-1}$
50	1.7^a $(1.4)^b$	100	2.4^a	3.0	6.0
75	2.1^a $(2.0)^b$	100	2.0^a	4.3	5.7
100	2.4^a $(2.4)^b$	100	1.7^a	6.1	6.1
125	2.6^a $(2.6)^b$	100	1.5^a	7.3	5.8
				mean:	$(5.9 \pm 0.2) \times 10^8$

$[MV^{2+}]_0$, μM	$[MV^{+}\cdot]$, μM	$[BDQ^{2+}]_0$, μM	$[BDQ^{+}\cdot]$, μM	$10^{-4}k$, s^{-1}	$10^{-8}k_9$, $M^{-1}\ s^{-1}$
50	2.1^a $(1.8)^b$	100	2.0^a	3.1	6.2
75	2.5^a $(2.3)^b$	100	1.6^a	4.2	5.6
100	2.8^a $(2.5)^b$	100	1.3^a	6.5	6.5
125	3.0^a $(2.5)^b$	100	1.1^a	7.3	5.8
				mean:	$(6.0 \pm 0.5) \times 10^8$

[a] Calculated with the relationship $[MV^{+}\cdot]/[PDQ^{+}\cdot] = k_{MV^{2+}}[MV^{2+}]_0/k_{PDQ^{2+}}[PDQ^{2+}]_0$. $k_{MV^{2+}}$ (for reaction with e_{aq}^-) = $8.4 \times 10^{10}\ M^{-1}\ s^{-1}$; $k_{PDQ^{2+}} = 5.8 \times 10^{10}\ M^{-1}\ s^{-1}$; $k_{BDQ^{2+}} = 4.0 \times 10^{10}\ M^{-1}\ s^{-1}$ (ref 18). Total radical produced = 4.1 μM (concentration of e_{aq}^-). [b] Estimated from the initial absorbance change and $\epsilon_{600nm}(MV^{+}\cdot) = 1.4 \times 10^4\ M^{-1}\ cm^{-1}$.

where k_{12} is the rate constant for the "cross-reaction", k_{11} and k_{22} are the self-exchange rate constants for the $X^{2+}/X^{+}\cdot$ and $SO_2/SO_2^{-}\cdot$ couples, K_{12} is the equilibrium constant for the "cross-reaction", estimated from the potentials for the $X^{2+}/X^{+}\cdot$ couple (Table I) and the $SO_2/SO_2^{-}\cdot$ couple (−0.26 V[30]), and f_{12} is given by (7)

$$\ln f_{12} = \frac{(\ln K_{12})^2}{4 \ln (k_{11}k_{22}/10^{22})} \qquad (7)$$

Thus from (6) a plot of $\ln k_{12}$ vs. $\ln K_{12}f_{12}$ should be linear of slope 0.5.[31] Such a plot for the viologens is shown in Figure 1, which is reasonably linear with a slope shown of 0.53. When $\ln K_{12}f_{12} = 0$, $\ln k_{12} = 0.5 \ln k_{11}k_{22}$, and from Figure 1, $k_{11}k_{22} = 1.3 \times 10^{17}\ M^{-2}\ s^{-2}$. The product of the self-exchange rate constants for the $X^{2+}/X^{+}\cdot$ and $SO_2/SO_2^{-}\cdot$ couples is therefore $1.3 \times 10^{17}\ M^{-2}\ s^{-2}$ and the problem arises of assigning each couple a rate constant, and indeed in assuming that the self-exchange rate constant for each viologen is the same. An estimate of $8.4 \times 10^6\ M^{-1}\ s^{-1}$ has been made for the $MV^{2+/+}$ self-exchange in acetonitrile.[32] The calculation of this value has been reassessed and a value, $8 \times 10^5\ M^{-1}\ s^{-1}$, in water reached.[33] When this value was used, it was found[33] that there was good agreement between calculated (by Marcus reactive collision model) and experimental values for the Cr^{2+}–MV^{2+}, V^{2+}–MV^{2+}, and $*Ru(bpy)_3{}^{2+}$–MV^{2+} reactions, but not the $Ru(bpy)_3{}^{3+}$–$MV^{+}\cdot$ reaction. However, in our system, if a value of $10^6\ M^{-1}\ s^{-1}$ is used for the $X^{2+/+}$ self-exchange, that for $SO_2/SO_2^{-}\cdot$ is $10^{11}\ M^{-1}\ s^{-1}$, which is inordinately high. We decided therefore to obtain an estimate of the self-exchange rate constants for the viologens by measuring directly a "cross-reaction" involving them. We chose the following reactions

$$MV^{2+} + PDQ^{+}\cdot \rightarrow MV^{+}\cdot + PDQ^{2+} \qquad k_8 \qquad (8)$$

$$MV^{2+} + BDQ^{+}\cdot \rightarrow MV^{+}\cdot + BDQ^{2+} \qquad k_9 \qquad (9)$$

both of which will be unidirectional with $[MV^{2+}] > [PDQ^{+}\cdot]$ or $[BDQ^{+}\cdot]$. The reaction was too rapid to measure by stopped-flow, so a pulse-radiolysis approach was used. Mixtures of MV^{2+} (50–125 μM) and PDQ^{2+} or BDQ^{2+} (100 μM) were pulsed with e_{aq}^- (4.1 μM). Addition of 5% *t*-BuOH removed H and OH radicals. The radicals $MV^{+}\cdot$($k(MV^{2+} + e_{aq}^-) = 8.4 \times 10^{10}\ M^{-1}\ s^{-1}$)[18] and $PDQ^{+}\cdot$ ($k(PDQ^{2+} + e_{aq}^-) = 5.8 \times 10^{10}\ M^{-1}\ s^{-1}$)[18] or $BDQ^{+}\cdot$ ($k(BDQ^{2+} + e_{aq}^-) + e_{aq}^- = 4.0 \times 10^{10}\ M^{-1}\ s^{-1}$)[18] were produced in comparable amounts (see Table II). Only the production of $MV^{+}\cdot$ was monitored at 600 nm ($PDQ^{+}\cdot$ and $BDQ^{+}\cdot$ absorbing weakly here) and its rapid formation (<1 μs) by the MV^{2+}/e_{aq}^- reaction was followed by a slower first-order (k, Table II) production via reactions 8 or 9. The data are shown in Table II, which confirm the second-order character of these reactions. The similar rate constants for the two reactions, each involving a $MV^{2+/+}$ couple, suggest that the self-exchange rate constant for the $BDQ^{2+/+}$ couple is about 20 times less than that for the $PDQ^{2+/+}$ couple in view of the stronger driving force for reaction 9 than for reaction 8. This introduces a complication in the discussion, but overall the results strongly indicate that a value closer to $10^8\ M^{-1}\ s^{-1}$ than $10^6\ M^{-1}\ s^{-1}$ must apply to the self-exchange rate constant for the viologens. This requires that $k(SO_2/SO_2^-)$ is approximately 10^8–$10^9\ M^{-1}\ s^{-1}$, which still appears high. It is, however, relatively close to that estimated ($10^7\ M^{-1}\ s^{-1}$) from a comparison of the reactions of O_2^- and SO_2^- radicals.[3] Further work on the viologen cross reactions is contemplated.

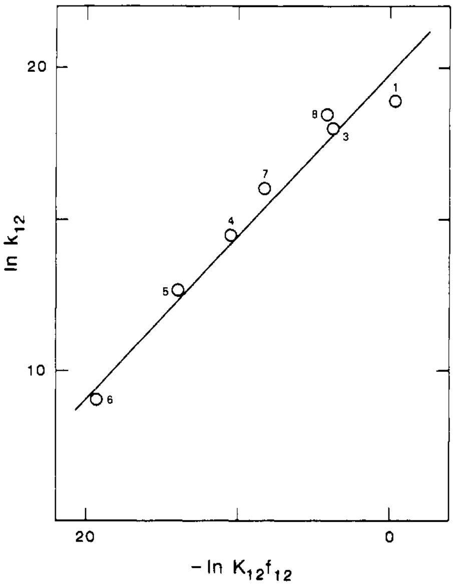

Figure 1. Plot of $\ln k_{12}$ vs. $\ln K_{12}f_{12}$ for reaction of viologens with SO_2^- radicals. The viologens indicated are EPQ^{2+} (1), DQ^{2+} (3), MDQ^{2+} (4), PDQ^{2+} (5), BDQ^{2+} (6), MV^{2+} (7), and BV^{2+} (8).

Finally, we can compare our data for the reduction of four viologens by SO_2^- with those estimated for reduction by O_2^-. The rate constants (k_{10}, $M^{-1}\ s^{-1}$) for reaction of $DQ^{+}\cdot$, $MV^{+}\cdot$, $PDQ^{+}\cdot$, and $BDQ^{+}\cdot$ with O_2 have been determined by a pulse radiolytic

$$X^{+}\cdot + O_2 \rightleftharpoons X^{2+} + O_2^- \qquad k_{10}, k_{-10}, K_{10} \qquad (10)$$

method and are 4.7×10^8, 8.0×10^8, 8.4×10^8, and 9.6×10^8, respectively.[18] Using the reduction potentials of these viologens, combined with that for the O_2/O_2^- couple (−0.16 V[34]), allows the calculation of the equilibrium constants K_{10} for (10). It is then

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(31) A sufficiently accurate value for $k_{11}k_{22}$ is obtained from the EPQ^{2+}/SO_2^- data ($K_{12}, f_{12} \sim 1$; $k_{11}k_{22} = k_{12}{}^2$). This can be used to estimate f_{12} for the reduction of the other viologens.

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easy to assess rate constants for O_2^- reactions with the viologens ($k_{-10} \equiv k_{O_2^-}$). These values ($M^{-1}\ s^{-1}$) and those for the ratio log $k_{SO_2^-}/k_{O_2^-}$ for the four viologens are as follows: DQ^{2+} 3.0×10^5, 2.3; MV^{2+} 1.0×10^4, 3.0; PDQ^{2+} 2.4×10^2, 3.1; and BDQ^{2+} 7.7, 3.0. The constant ratio (of approximately 10^3 for rate constants for reaction of SO_2^- and O_2^- with a common oxidant) is striking, and these can be added to a substantial list already compiled.[3]

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Registry No. 1a, 15302-80-4; **1a** (radical cation), 95617-21-3; **1b**, 15302-81-5; **1b** (radical cation), 95617-20-2; **2a**, 2764-72-9; **2a** (radical cation), 63406-50-8; **2b**, 16651-71-1; **2b** (radical cation), 94887-40-8; **2c**, 7325-63-5; **2c** (radical cation), 67509-62-0; **2d**, 16651-68-6; **2d** (radical cation), 67509-63-1; **3a** (radical cation), 25239-55-8; **3b**, 13096-46-3; **3b** (radical cation), 49765-27-7; sulfur dioxide radical anion, 12143-17-8; dithionite, 14844-07-6; sodium dithionite, 7775-14-6; methyl viologen, 1910-42-5.

Supplementary Material Available: Kinetic data for reduction of viologens with dithionite and obseration wavelengths (3 pages). Ordering information is given on any current masthead page.

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^{14}N and ^{15}N ENDOR Studies of Intrabridgehead Three-Electron σ-Bonded Radical Cations. Observation of Second-Order Splittings

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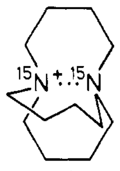
Abstract: EPR, ^1H, ^{14}N, and ^{15}N ENDOR and TRIPLE resonance measurements performed on intrabridgehead three-electron σ-bonded radical cations generated from 1,6-diazabicyclo[4.4.4]tetradecane and the doubly ^{15}N-labeled compound are reported. All evidence obtained supports the view that the N-N bond is truly symmetrical. Pronounced second-order splittings have been observed in the ^{14}N and ^{15}N ENDOR spectra owing to equivalent nuclei with large hyperfine coupling constants. It is shown that the measured second-order effects are in full agreement with theory. Relative signs of the hyperfine couplings have been determined by TRIPLE resonance and by the interpretation of cross-relaxation effects. The influence of the negative sign of the gyromagnetic ratio of the ^{15}N nucleus on the second-order shifts and the cross-relaxation effects is demonstrated.

Bicyclic diamines built from medium-sized rings and containing bridgehead nitrogen atoms show unusual physical and chemical properties due to the enforced interaction of the nitrogen lone pairs imposed by the ring systems.[2-4] In this paper we report on ^1H, ^{14}N, and ^{15}N ENDOR studies of the radical cation of 1,6-diazabicyclo [4.4.4]tetradecane (**1**) and of the doubly ^{15}N labeled species (**2**).

1



2

These propellane-type radical cations are interesting for their bonding properties and their structures. The N-N bond in **1** is probably best described as a three-electron σ bond, and the σ* character of the spin-bearing orbital gives rise to a large ^{14}N hyperfine coupling ($a_{^{14}N} = 96.4$ MHz).[3] In particular, it is a challenge to find out whether these species are truly symmetrical. The two nitrogen atoms in **1** should be equivalent either if the radical cation has a symmetrical equilibrium structure or if the radical cation is rapidly interconverting between two unsymmetrical structures.

Whereas the EPR spectrum of **1** indicates that the two nitrogen atoms are indeed equivalent,[3] the ENDOR spectrum should provide a much more accurate test of this assumption owing to the higher resolving power of ENDOR spectroscopy. However, in view of the extraordinarily large value of the ^{14}N hyperfine coupling constant, it may be expected that the ENDOR spectrum will be complicated by significant second-order effects. It has long been recognized that ENDOR signals belonging to sets of equivalent nuclei with large coupling constants should exhibit splittings due to second-order effects.[5] Whereas the appearance of second-order frequency *shifts* of ENDOR signals has been observed occasionally,[6] experimental evidence for second-order *splittings* in ENDOR-in-solution spectra was lacking hitherto.[7]

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