

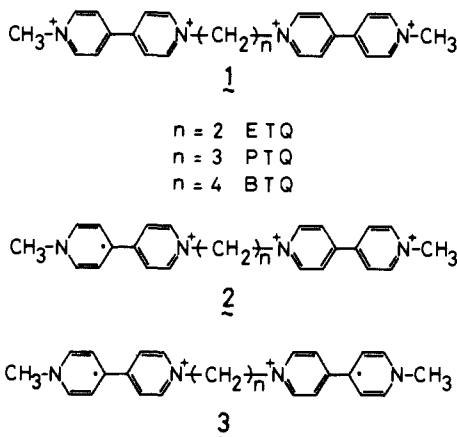
Reactions of Three Bis(viologen) Tetraquateryary Salts and Their Reduced Radicals

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Abstract: Monoradical trications X^{3+} and diradical dication X^{2+} were produced by reduction of three bis(viologen) X^{4+} (1,1'-alkanediylbis(1'-alkyl-4,4'-bipyridinium)) tetraquateryary salts. The spectral properties of X^{3+} and its disproportionation kinetics were examined by e_{aq}^-/CO_2^- reduction of X^{4+} . Reduction potentials of the X^{4+}/X^{3+} and X^{3+}/X^{2+} couples were determined by cyclic voltammetry and spectral examination of equilibrated mixtures of X^{4+} and X^{2+} radicals. These potentials were used to apply successfully the Marcus theory to reduction of X^{4+} by SO_2^- and oxidation of X^{3+} and of X^{2+} by O_2 and cobalt(III) complexes. The reactivity toward O_2 and the comproportionation of X^{2+} (with X^{4+}) is believed to be influenced by the tendency of X^{2+} to form an intramolecularly associated conformation.

The viologens are diquateryary salts of 2,2'-bipyridine, 4,4'-bipyridine, and 1,10-phenanthroline. They undergo reversible one-electron reduction to colored radical cations.² This property is utilized in mediation of electron-transfer processes, for example, in biochemical redox systems, and in catalytic photolysis of water where light is converted into chemical energy²⁻⁷ and as the main components of electrochromic display devices.^{2,8-10} In addition, the 1,1'-dimethyl-4,4'-bipyridinium ion known as paraquat or methylviologen is used extensively as a herbicide.¹¹ It is no wonder therefore that the viologens have been the object of extensive investigations. The poly(viologens) are highly conducting redox polymers which have been examined recently for their redox characteristics.¹² The simplest poly(viologens) are the bis(viologen) compounds **1** which are tetraquateryary salts which contain two viologen units, joined by a varying number of methylene groups. Spectral and electrochemical characteristics



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Table I. Spectral Data for Bis(viologens) and Reduced Species

species	λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)
ETQ ⁴⁺	264 (4.2×10^4), ^a 263 (4.4×10^4), ^b 265 (4.4×10^4) ^c
PTQ ⁴⁺	261 (4.4×10^4), ^a 260 (4.4×10^4), ^b 262 (4.4×10^4) ^c
BTQ ⁴⁺	260 (4.3×10^4), ^a 259 (3.9×10^4), ^b 262 (4.5×10^4) ^c
ETQ ³⁺	560 sh (7.2×10^3), ^a 600 (1.1×10^4) ^a
PTQ ³⁺	560 sh (6.8×10^3), ^a 620 (1.1×10^4) ^a
BTQ ³⁺	560 sh (7.5×10^3), ^a 600 (1.0×10^4) ^a
ETQ ²⁺	600 (2.2×10^4), ^{a,d} 595 (2.0×10^4) ^b
PTQ ²⁺	534 (2.3×10^4), ^{a,e} 533 (2.4×10^4) ^b
BTQ ²⁺	536 (2.3×10^4), ^a 536 (2.4×10^4) ^b

^aThis work. ^bReference 14. ^cReference 17. ^dObeys Beer's law at $\lambda = 530$ and 600 nm, 10–50 μM , and pH 7.2. At >200 μM , violet-blue solid precipitates. ^eObeys Beer's law at $\lambda = 470$, 534, and 560 nm, 6–200 μM , and pH 7.2.

of **1** and of one- and two-electron reduced species **2** and **3** have been recently reported.^{9,13-17} In continuation of our examination of the kinetics of reaction of viologen species,^{18,19} we report on the electrochemical, spectral, and equilibria characteristics of the bis(viologens) **1**–**3**, generally designated X^{4+} , X^{3+} , and X^{2+} and on the kinetics of a variety of reactions of these species involving reduction, oxidation, and disproportionation.

Experimental Section

Chemicals used were the purest commercial product. The three bis(viologens) were prepared by a slight modification of the method described by Furue and Nozakura.¹⁴ The 1,1'-poly(methylene)bis(4,4'-bipyridinium) dibromide compounds were converted to the corresponding 1,1'-poly(methylene)bis(1'-methyl-4,4'-bipyridinium) salts by using a large excess of methyl iodide in DMF at 90 °C for 24 h. After recrystallizing from water, the iodide salts were converted to the chloride salts using a Dowex 1X-8 (Cl⁻ form) column, and then the perchlorate salt was precipitated by adding NaClO₄ to a concentrated solution of the chloride. The absorption spectral data for ETQ(ClO₄)₄, PTQ(ClO₄)₄, and BTQ(ClO₄)₄ were in good agreement with those reported in the literature (Table I).

Cyclic voltammetry was carried out in an argon atmosphere in an aqueous Tris/H₂SO₄ buffer (pH 7.2) with a BAS Model CV-1B instrument. A three-electrode system was used with a Pt auxiliary electrode and a Pt working electrode against a Ag/AgCl (3 M NaCl) reference electrode. Voltammograms were recorded on a Houston Instruments Omnigraphic 100 X-Y recorder at scan rates from 20 to 200 mV s⁻¹. The instrument was checked using methylviologen which showed a reversible wave ($E^0 = -0.45$ V and $\Delta E_p = 60$ mV).¹⁸

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The comproportionation constants were determined by treating various concentrations of PTQ⁴⁺ (0.1–3.0 mM) or BTQ⁴⁺ (0.5–1.0 mM) with variable amounts of dithionite solution (final concentrations, 5–30 μM). Some of this dithionite was invariably consumed by traces of O₂ (~5–10 μM). The amounts of bis(viologens) reduced could be estimated from the absorptions at the isosbestic points for disproportionation of PTQ³⁺ to PTQ^{2+•} (560 nm, ε_{PTQ³⁺} = 6.8 × 10³ M⁻¹ cm⁻¹) or BTQ³⁺ to BTQ^{2+•} (564 nm, ε_{BTQ³⁺} = 7.5 × 10³ M⁻¹ cm⁻¹). The amounts of PTQ³⁺ and PTQ^{2+•} or BTQ³⁺ and BTQ^{2+•} could then be estimated from absorbances at other wavelengths, knowing ε values for the mono- and diradicals obtained from the pulse radiolysis and dithionite reduction work. In a few experiments, reduced radicals of PTQ were produced by light irradiation of PTQ⁴⁺ (8 mM) for 5–15 s in a mixture of 3,10-dimethyl-5-deazaalloxazine (~5 μM) and Na₂H₂edta (~0.5 mM).²⁰ The equilibrium constant for reaction of PTQ⁴⁺ with DQ^{•+} was determined by adding 26.9 μM dithionite to mixtures of DQ²⁺ and BTQ⁴⁺ ((a) 40 and 40 μM, (b) 50 and 30 μM, respectively). The concentration of BTQ^{2+•} was determined at 536 nm (ε_{BTQ^{2+•}} = 2.3 × 10⁴, ε_{DQ^{•+}} = 300 M⁻¹ cm⁻¹). The equilibrium constant for reaction of PTQ⁴⁺ with ETQ^{2+•} was determined by adding 30 μM dithionite to mixtures of PTQ⁴⁺ and ETQ^{2+•} (total concentration 50 μM). The total reduced species was determined at 550 nm (ε_{ETQ^{2+•}} = ε_{PTQ^{2+•}} = 1.9 × 10⁴ M⁻¹ cm⁻¹). The concentrations of ETQ^{2+•} and PTQ^{2+•} were determined at 500 nm (ε_{ETQ^{2+•}} = 6.7 × 10³, ε_{PTQ^{2+•}} = 1.9 × 10⁴ M⁻¹ cm⁻¹), 534 nm (ε_{ETQ^{2+•}} = 1.4 × 10⁴, ε_{PTQ^{2+•}} = 2.3 × 10⁴ M⁻¹ cm⁻¹), and 600 nm (ε_{ETQ^{2+•}} = 2.2 × 10⁴, ε_{PTQ^{2+•}} = 2.7 × 10³ M⁻¹ cm⁻¹). The equilibrium constant for reaction of ETQ⁴⁺ with DQ^{•+} was determined by electron-pulsing mixtures of ETQ⁴⁺ (10–50 μM), DQ²⁺ (50–200 μM), NaHCO₂ (0.1 M), and N₂O (saturated). The reaction was studied at 600 nm where absorbance of ETQ³⁺ greatly exceeds that of DQ^{•+}, and production of ETQ³⁺ can be monitored as it is produced in the reduction of ETQ⁴⁺ by DQ^{•+}.

In the stopped-flow kinetic experiments, the following conditions were used: 10–20 μM X⁴⁺ mixed with 2–20 mM dithionite; 5–10 μM X^{2+•} mixed with 5–15 mM Co(en)₃³⁺, 20–60 μM Co(edta)⁻, or Fe(CN)₆³⁻; 1–5 μM X^{2+•} mixed with ~5 (degassed buffer)—130 μM O₂. The reaction between PTQ^{2+•} (13–25 μM) and PTQ⁴⁺ (~500 μM) was studied in the presence of ~5–25 μM O₂. In the pulse-radiolysis experiments, ~5 μM e_{aq}⁻ or CO₂⁻ was reacted with 50–100 μM X⁴⁺ to determine reduction rates. The concentration of e_{aq}⁻ was determined from the absorbance change associated with its loss at 650 nm (ε = 1.6 × 10⁴ M⁻¹ cm⁻¹). In the disproportionation experiments, ~10 μM X³⁺ generated by CO₂⁻ or e_{aq}⁻/CO₂⁻ reduction of 50–250 μM X⁴⁺ was monitored spectrally for about 4 ms (light instability prevented longer time observations). In the study of other reactions, 10–15 μM X³⁺ in the presence of 0.25–1.5 mM X⁴⁺ reacted with 0.26–1.3 mM O₂ or 1–2 mM Co(edta)⁻ present in the pulsed solution. All reactions of X³⁺ with added oxidant were much faster than disproportionation of X³⁺. Most of the reactions were monitored at the absorption peaks of the radicals (Table I). Excellent first-order kinetic traces were obtained. A Gibson-Dionex stopped-flow apparatus interfaced with an OLIS data-collecting system was used. A CN Van de Graaf electron accelerator at the Center for Fast Kinetics Research (The University of Texas, Austin) was used as an electron source. Pulses of 100-ns duration are delivered to samples in a quartz cell with a 1-cm optical path length. When the only reducing radical was e_{aq}⁻, irradiation was carried out in 5% (CH₃)₂COH which removes OH and H radicals, also generated in the pulse (OH(H) + RH → R + H₂O(H₂)). When CO₂⁻ alone was used, the irradiated solution contained N₂O and 0.1 M HCO₂⁻ (e_{aq}⁻ + N₂O + H₂O → N₂ + OH + OH⁻; OH(H) + HCO₂⁻ → CO₂⁻ + H₂O(H₂)). For a reducing mixture of e_{aq}⁻ and CO₂⁻, 0.1 M HCO₂⁻ and an inert atmosphere of N₂ were used.²¹ All manipulations involving radicals were carried out with scrupulous exclusion of O₂. A variety of conditions (ionic strength, buffer constituents) were used at 25 °C dictated by the type of experiment. Different conditions had little effect on the rates.

Results

It was found that 5–10 μM O₂ was always present in freshly prepared buffer solutions. This did not interfere in the equilibrium measurements since the concentrations of radicals were determined spectrally. The traces of O₂ showed up as a rapid loss of X^{2+•} (with a small absorbance change) when it was mixed with the oxidant or the buffer system alone in the stopped-flow apparatus. It was usually separable from the reaction under investigation. In the pulse radiolysis experiments, traces of O₂ were sometimes removed by reduction to O₂⁻ in the first pulse.

Table II. Equilibria Data for Reactions Involving Bis(viologens)

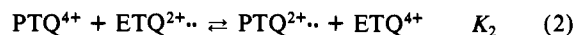
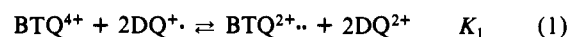
reaction	E ₁ ^o , V	E ₂ ^o , V	E ₁₂ ^o , V	K
ETQ ⁴⁺ + 2e ⁻ → ETQ ^{2+•}	-0.28 ^a	-0.28 ^b	-0.30, ^c -0.28, ^d -0.31 ^e	
PTQ ⁴⁺ + 2e ⁻ → PTQ ^{2+•}	-0.33 ^f	-0.19 ^f	-0.26, ^c -0.28 ^e	
BTQ ⁴⁺ + 2e ⁻ → BTQ ^{2+•}	-0.39 ^f	-0.29 ^f	-0.34, ^c -0.35, ^g -0.37 ^e	
2ETQ ³⁺ ⇌ ETQ ⁴⁺ + ETQ ^{2+•}				~1 ^b
2PTQ ³⁺ ⇌ PTQ ⁴⁺ + PTQ ^{2+•}				260 ± 60 ^b
2BTQ ³⁺ ⇌ BTQ ⁴⁺ + BTQ ^{2+•}				220 ± 30/ 49 ± 18 ^h
PTQ ⁴⁺ + ETQ ^{2+•} ⇌ PTQ ^{2+•} + ETQ ⁴⁺				11 ± 5 ^j
BTQ ⁴⁺ + 2DQ ^{•+} ⇌ BTQ ^{2+•} + 2DQ ²⁺				0.8 ± 0.2 ^j
ETQ ⁴⁺ + DQ ^{•+} ⇌ ETQ ³⁺ + DQ ²⁺				13 ± 6 ^k
				11 ± 3 ^l

^a Pulse radiolysis, from ETQ⁴⁺, DQ^{•+} cross reaction using E^o(DQ^{2+•}) = -0.35 V at I = 0.1 M (NaHCO₂), pH 7.3. ^b Estimated from E₁^o and E₁₂^o values. ^c This work; cyclic voltammetry at I = 0.01 M, 10 mM Tris, pH 7.2. ^d From PTQ⁴⁺, ETQ^{2+•} cross reaction and E₁₂^o for PTQ^{4+•}/2+ system. ^e Reference 16, cyclic voltammetry at I = 0.1 M (KCl). ^f Estimated from E₁₂^o and K_{dis} values. ^g From BTQ⁴⁺, DQ^{•+} cross reaction using E^o(DQ^{2+•}) = -0.35 V, ref 18. ^h I = 0.04 M, pH 8.2. ⁱ Reduced species generated by ~5–15-s irradiation of 5 μM 3,10-dimethyl-5-deazaalloxazine and 0.1 mM EDTA solutions containing PTQ⁴⁺ at I = 0.09 M and pH 8.2. ^j I = 0.1 M, pH 7.2. ^k K_s, from spectral analysis of equilibrated solution, I = 0.1 M (NaHCO₂), pH 7.3. ^l K_s, from kinetics (k₅/k₋₅) by pulse radiolysis. I = 0.1 M (NaHCO₂).

Spectra. The three bis(viologen) species X⁴⁺ are reduced by the pulse radiolytically generated radicals e_{aq}⁻ and CO₂⁻ to the radical trications X³⁺. The same spectra are obtained with both reductants. The concentration of the X³⁺ radical was equated to that of the e_{aq}⁻ used in generating the radical and knowing this value, the molar absorptivity of X³⁺ could be determined. These are recorded in Table I. PTQ³⁺ is produced in methanol by short-time white-light irradiation (500-W lamp) of a mixture of PTQ⁴⁺Cl₄ (8 mM), 3,10-dimethyl-5-deazaalloxazine (5 μM), and Na₂H₂edta (0.1 mM).²⁰ The absorbance ratio A₆₀₅/A₅₃₇ decreases with increasing irradiation time (increasing radical production). With 15-s irradiation, ~90% PTQ³⁺ is produced. When 50 μM PTQ⁴⁺ is irradiated for even short times (10 s), substantial amounts of PTQ^{2+•} are formed.

Dithionite reduction produced the diradical dication X^{2+•}, shown by spectral titration at 534 and 560 nm (2.2 ± 0.2 electrons per mole of X⁴⁺). The fully reduced X^{2+•} could also be produced by 15-s white-light irradiation (500-W lamp) of a mixture of X⁴⁺ (20 μM), 3,10-dimethyl-5-deazaalloxazine (5 μM), and Na₂H₂edta (0.1 mM).²⁰ The spectral characteristics of X⁴⁺, X³⁺, and X^{2+•} are shown in Table I. Those of ETQ^{2+•} and PTQ^{2+•} were concentration-independent over 10–50 and 6–200 μM, respectively.

Reduction Potentials. Overall potentials E₁₂^o for the X⁴⁺ + 2e⁻ ⇌ X^{2+•} couple were determined by cyclic voltammetry. The results are shown in Table II. With X = PTQ, a reversible two-electron reduction wave was obtained (ΔE_p = 37 mV at a scan rate of 25 mV s⁻¹). With X = ETQ and BTQ, adsorption of the reduced radicals on the electrodes occurred and the overall reduction potential was estimated from the cathodic wave at a slow scan rate. The constants for the equilibria (1) and (2) were determined spectrally (DQ²⁺ = 1,1'-ethylene-2,2'-bipyridinium ion). Isosbestic points were observed at 404 and 452 nm for (1)



and at 440 and 550 nm for (2). The reduction potential for DQ^{2+•} is well characterized with our conditions (E^o = -0.35 V)¹⁸

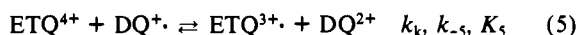
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and combined with K_1 leads to a value for E_{12}° for PTQ^{4+} similar to that estimated by cyclic voltammetry (Table II). The value of K_2 was likewise consistent with the E_{12}° values for the $\text{PTQ}^{4+/2+}$ and $\text{ETQ}^{4+/2+}$ couples (Table II). Production of small concentrations of X^{2+} (by dithionite or photochemically) in the presence of large concentrations of X^{4+} leads to a series of spectra, with an isosbestic point near 560 nm, which can be quantitatively related to the establishment of equilibria (3) and (4). Although

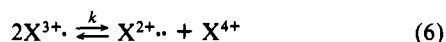


the equilibria lie to the left, 3 mM BTQ^{4+} reduced with 10 μM $\text{S}_2\text{O}_4^{2-}$ produces $\geq 90\%$ BTQ^{3+} . Values of disproportionation constants K_{disp} ($=K_3^{-1}$ and K_4^{-1}) are shown in Table II. These are, within a fairly large experimental error, independent of wavelength of observation and concentration of radical. Combination of E_{12}° with K_3 (K_4) leads to values for E_1° and E_2° (for $\text{X}^{4+} + e^- \rightleftharpoons \text{X}^{3+}$; $\text{X}^{3+} + e^- \rightleftharpoons \text{X}^{2+}$, respectively, $\text{X} = \text{PTQ}$ and BTQ) shown in Table II. The same procedure could not be used with ETQ^{4+} since the absorbance coefficients of ETQ^{3+} were half those of ETQ^{2+} at all wavelengths, and comproportionation would be unaccompanied by spectral change. Instead the equilibrium (5) was examined spectrally by a pulse radiolysis method. A



mixture of ETQ^{4+} and DQ^{2+} was reacted with a small concentration of $\text{CO}_2^{\cdot-}$ radicals. The very rapid absorbance increase at 600 nm due to generation of ETQ^{3+} and DQ^{\cdot} was followed by a further absorbance increase at 600 nm as DQ^{\cdot} ($\epsilon_{600} = 1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) is replaced by ETQ^{3+} ($\epsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) as reaction 5 ensues. Spectral analysis of the equilibrated solution allows determination of K_5 and combined with E° for $\text{DQ}^{2+}/\text{DQ}^{\cdot}$ leads to an E_1° value for $\text{ETQ}^{4+}/\text{ETQ}^{3+}$. Values of E_1° and E_2° ($2E_{12}^\circ - E_1^\circ$) and K_{disp} are shown in Table II.

Kinetics. One-Electron Reduction of X^{4+} . The strongly reducing radicals e_{aq}^- and $\text{CO}_2^{\cdot-}$ produced by pulse radiolysis in micromolar concentrations effect only one-electron reduction of X^{4+} , when the latter is used in excess. The observed rate constant k_{obsd} is directly dependent on $[\text{X}^{4+}]$, and the second-order rate constants $k_{\text{obsd}}/[\text{X}^{4+}]$ are given in Table III. The kinetics of (5) reduce to those for a first-order reversible reaction (rate constant $= k_{\text{obsd}}$) since both ETQ^{4+} and DQ^{2+} are both present in excess over ETQ^{3+} and DQ^{\cdot} . The plot of $k_{\text{obsd}}/[\text{DQ}^{2+}]_0$ vs. $[\text{ETQ}^{4+}]_0/[\text{DQ}^{2+}]_0$ was linear with a slope value k_5 and an intercept k_{-5} . The values are shown in Table III. The singly reduced species react with $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ radicals also produced when $(\text{C}-\text{H}_3)_3\text{COH}$ was included in the solution (to scavenge H and OH). This former reaction occupied several hundred microseconds and interfered with the observation of disproportionation. The problem was avoided when $(\text{CH}_3)_3\text{COH}$ was excluded and the trication radicals generated by $\text{CO}_2^{\cdot-}$ or by a mixture of $\text{CO}_2^{\cdot-}$ and e_{aq}^- . With these conditions, PTQ^{3+} and BTQ^{3+} underwent spectral changes with isosbestic points at 460 and 560 nm (PTQ^{3+}) and 370, 440, and 560 nm (BTQ^{3+}). ETQ^{3+} did not show any spectral changes. Those with PTQ^{3+} and BTQ^{3+} corresponded to 100% and $\sim 90\%$ disproportionation, and data on the time-dependent absorbance changes (Figure 1) allow calculation of k_3 and k_4 . In terms of the general equilibrium (6), eq 7 and 8 come about.



$$-\frac{1}{2} \frac{d[\text{X}^{3+}]_t}{dt} = \frac{d[\text{X}^{2+}]_t}{dt} = k[\text{X}^{3+}]_t^2 \quad (7)$$

$$\frac{1}{[\text{X}^{3+}]_t} - \frac{1}{[\text{X}^{3+}]_0} = 2kt \quad (8)$$

The absorbances (1-cm cell; $\epsilon_{\text{X}^{4+}} = 0$) at zero time, t , and equilibrium (subscripts 0, t , and e) are given by (9)–(11), respectively. In conjunction with (12), the simple expression (13) results.

Table III. Rate Constants for Reactions of Bis(viologen) Species at 25 $^\circ\text{C}$

bis(viologen) ⁿ⁺ - (ClO ₄) _n	reactant	k_{obsd} , M ⁻¹ s ⁻¹	k_{calcd} , ^a M ⁻¹ s ⁻¹
ETQ ⁴⁺	e_{aq}^-	$(5.8 \pm 0.5) \times 10^{10b}$	
	$\text{SO}_2^{\cdot-}$	$(1.4 \pm 0.1) \times 10^{8c}$	2.1×10^{8d}
	DQ^{\cdot}	$(3.4 \pm 0.3) \times 10^{8e}$	3.4×10^{8a}
ETQ ³⁺	O_2	$(2.5 \pm 0.2) \times 10^{8e}$	3.1×10^{7f}
	DQ^{2+}	$(3.2 \pm 0.3) \times 10^{7e}$	3×10^{7a}
ETQ ²⁺	O_2	$\geq 8 \times 10^{7c}$	3.1×10^{7f}
	Co(en)_3^{3+}	61 ± 4^c	$4.1 \times 10^{2g,k}$
PTQ ⁴⁺	e_{aq}^-	$(5.9 \pm 0.5) \times 10^{10b}$	
	$\text{SO}_2^{\cdot-}$	$(6.3 \pm 0.4) \times 10^{7h}$	7.5×10^{7d}
PTQ ³⁺	PTQ^{3+}	$(7.0 \pm 0.6) \times 10^{7c}$	
	O_2	$(1.2 \pm 0.2) \times 10^{8e,i}$	6.6×10^{7f}
	O_2	$(1.4 \pm 0.2) \times 10^{8e,i}$	
	O_2	$(1.6 \pm 0.1) \times 10^{8b}$	
PTQ ²⁺	Co(edta)^-	$(3.2 \pm 0.2) \times 10^{7e}$	7.7×10^{5j}
	PTQ^{4+}	$(7 \pm 3) \times 10^{5c}$	4.6×10^{5l}
	O_2	$(1.9 \pm 0.2) \times 10^{6c}$	5.6×10^{6f}
BTQ ⁴⁺	O_2	$(1.8 \pm 0.2) \times 10^{6e}$	
	Co(edta)^-	$(7.8 \pm 0.8) \times 10^{6b}$	1.0×10^{5j}
	Co(en)_3^{3+}	15.4 ± 0.8^c	1.0×10^{6k}
	Fe(CN)_6^{3-}	$> 5 \times 10^{7c}$	$63^{g,k}$
BTQ ³⁺	$\text{CO}_2^{\cdot-}$	$(1.5 \pm 0.2) \times 10^{10e}$	4.8×10^{9m}
	$\text{SO}_2^{\cdot-}$	$(5.1 \pm 0.5) \times 10^{7c}$	1.7×10^{10n}
BTQ ²⁺	BTQ^{3+}	$(2.5 \pm 0.6) \times 10^{8e,i}$	1.9×10^{7d}
	O_2	$(3.7 \pm 0.3) \times 10^{8e}$	1.7 ± 10^{8f}
BTQ ²⁺	O_2	$\sim 4 \times 10^{7c}$	3.4×10^{7f}
	Co(en)_3^{3+}	$(1.3 \pm 0.1) \times 10^{2c}$	$4.2 \times 10^{2g,k}$

^aOn the basis of $k_{12} = (k_{11}k_{22}K_{12}/I_2)^{1/2}$ using $k_{11} = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for self-exchange of DQ^{2+} and all bis(viologens) and radii 12 Å for monoradical and 6 Å for PTQ^{2+} and BTQ^{2+} "closed" diradical conformation. ^b $I = 0.03 \text{ M}$ (10 mM phosphate), pH 7.2. ^c $I = 0.50 \text{ M}$ (Na_2SO_4), pH 8.2. ^dUsing $k_{22} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $E^\circ = -0.26 \text{ V}$, ref 34 for $\text{SO}_2/\text{SO}_2^{\cdot-}$ couple. ^e $I = 0.1 \text{ M}$ (NaHCO_3), pH 7.3. ^fUsing $k_{22} = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (best fit), $E^\circ = -0.16 \text{ V}$, ref 35 for $\text{O}_2/\text{O}_2^{\cdot-}$ couple. ^gUsing $k_{22} = 4.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, $E^\circ = -0.20 \text{ V}$, ref 36 and 37 for $\text{Co(en)}_3^{3+/2+}$ couple. ^hUsing tetrachloride salt at $I = 0.50 \text{ M}$ ($\text{Na}_2\text{S}_2\text{O}_4$), pH 7.2. ⁱDisproportionation. ^jUsing $k_{22} = 3.5 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, $E^\circ = 0.38 \text{ V}$, $r = 4.5 \text{ \AA}$, ref 38 and 39 for Co(edta)^{-2-} couple. ^kIncludes work term. This is negligible in all other systems. ^lEstimated from $k(\text{PTQ}^{3+} + \text{PTQ}^{3+})/K(\text{disproportionation})$. ^mUsing $k_{22} = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $E^\circ = 0.36 \text{ V}$, ref 40 and 41 for $\text{Fe(CN)}_6^{3-/4-}$ couple. ⁿUsing $k_{22} = 1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, $E^\circ = -2.0 \text{ V}$, ref 21 and 31 for $\text{CO}_2/\text{CO}_2^{\cdot-}$ couple.

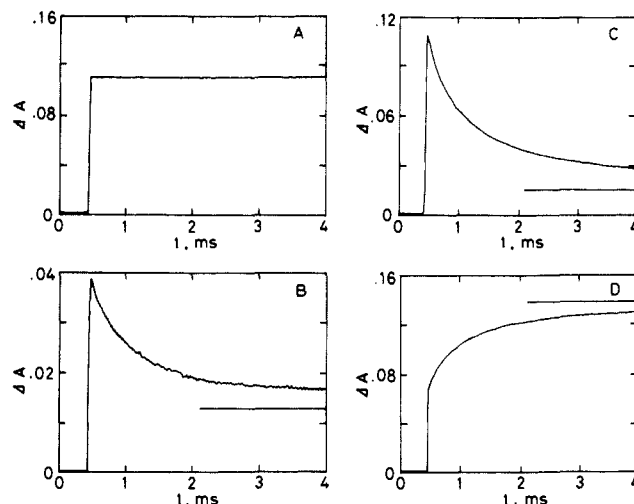


Figure 1. Absorbance changes following production of X^{3+} by irradiation of X^{4+} (50 μM) with $\text{CO}_2^{\cdot-}$ or $\text{CO}_2^{\cdot-}/e_{\text{aq}}^-$. The rapid production of the radical (vertical line) is followed by disproportionation. (A) ETQ^{3+} , (10 μM) at 600 nm, (B) BTQ^{3+} , (3.8 μM) at 600 nm, (C) PTQ^{3+} , (10 μM) at 600 nm, (D) PTQ^{3+} , (10 μM) at 510 nm. The solid lines for (B)–(D) are coincidental with the experimental trace and represent the theoretical curves on the basis of eq 13, rate constants in Table III, and known absorbance coefficients. The value of A_e is indicated on the figures.

$$A_0 = \epsilon_{X^{3+}}[X^{3+}]_0 \quad (9)$$

$$A_t = \epsilon_{X^{3+}}[X^{3+}]_t + \epsilon_{X^{2+}}[X^{2+}]_t \quad (10)$$

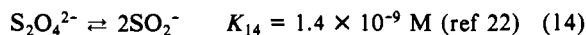
$$A_e = \frac{1}{2}\epsilon_{X^{2+}}[X^{3+}]_0 \quad (11)$$

$$[X^{3+}]_0 = [X^{3+}]_t + 2[X^{2+}]_t \quad (12)$$

$$\frac{1}{A_t - A_e} = \frac{2kt}{\epsilon_{X^{3+}} - \frac{1}{2}\epsilon_{X^{2+}}} + \frac{1}{\epsilon_{X^{3+}} - \frac{1}{2}\epsilon_{X^{2+}}} \frac{1}{[X^{3+}]_0} \quad (13)$$

The disproportionation of PTQ^{3+} and BTQ^{3+} conforms very well to expression (13); see Figure 1. The derived values of $(\Delta A)^{-1}t^{-1} [=S]$ are given in the supplementary tables, and the resulting values of $k(=1/2S[\epsilon_{X^{3+}} - 1/2\epsilon_{X^{2+}}])$ are shown in Table III. The latter are independent of the wavelength of observation and the concentration of the radical.

Two-Electron Reduction of X^{4+} . Dithionite in excess reduces the oxidized species X^{4+} to X^{2+} by a single first-order process. Rapid-scan stopped-flow examination of the systems shows no signs of the singly reduced X^{3+} . Decay of X^{2+} or further reaction with dithionite is slow (e.g., <10% in 200 s). The pseudo-first-order rate constant k_{obsd} is exactly dependent on $[S_2O_4^{2-}]^{1/2}$ such that SO_2^- is the sole effective reducing species (14) and (15). The second-order rate constants $k_{15}(k_{\text{obsd}}K_{14}^{-1/2}[S_2O_4^{2-}]^{-1/2})$ are recorded in Table III.

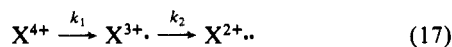


$$\text{rate} = k_{15}K_{14}^{1/2}[S_2O_4^{2-}]^{1/2}[X^{4+}] = k_{\text{obsd}}[X^{4+}] \quad (16)$$

Oxidation Reactions. The reactions of X^{3+} and X^{2+} with excess oxidant were studied from time-dependent loss of radical absorbance. Oxidant concentrations were chosen to make the loss of X^{3+} by disproportionation negligible. The reducing radicals produced by pulse radiolysis will effect reduction of some of the oxidant present also. However, the rates $k[X^{4+}][e_{\text{aq}}^-]$ and $k[\text{oxid}][e_{\text{aq}}^-]$, being comparable, will ensure some production of X^{3+} . In all cases, first-order rate constants k_{obsd} were linearly dependent on oxidant concentrations, with zero intercepts for the k_{obsd} vs. [oxidant] plots. All kinetic data are given in supplementary tables, and the second-order rate constants are collected in Table III.

Discussion

By selecting reducing agents and conditions it is possible to produce either X^{3+} or X^{2+} from X^{4+} . The pulse radiolytically produced radicals e_{aq}^- and CO_2^- , generated in small concentrations (μM), effect one-electron reduction of the (excess) oxidized bis(viologen) X^{4+} . This is a very useful and general technique for producing only the one-electron reduced product, when further reduction is possible. This arises because in the sequence (17) $k_1[X^{4+}] \gg k_2[X^{3+}]$ at all times, since k_1 is diffusion-controlled (Table III), and therefore k_2 cannot exceed k_1 . Further, the



amount of X^{3+} generated is small (μM) compared with the amount of X^{4+} , mostly unused. The spectra of ETQ^{3+} , PTQ^{3+} , and BTQ^{3+} are similar with a maximum near 600 nm and absorbance coefficient = $1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Table I). They thus resemble closely the spectrum of MV^{3+} which has a peak at 600 nm ($\epsilon = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁸ Reduction in methanol of a high concentration of PTQ^{4+} by 15-s irradiation with white light in the presence of 3,10-dimethyl-5-deazaalloxazine and EDTA produces PTQ^{3+} with spectral characteristics close to those produced by reduction of PTQ^{4+} by hydroxydiphenylmethyl radicals in methanol at 60 °C.¹⁴

Two-electron reduction of X^{4+} can be effected by using dithionite or by irradiation with white light in the presence of

3,10-dimethyl-5-deazaalloxazine and EDTA.²⁰ The spectra of the products ETQ^{2+} , PTQ^{2+} , and BTQ^{2+} resemble closely those reported by Furue and Nozakura,¹⁴ produced by dithionite reduction, and by Deronzier et al.,¹⁶ from electrochemical spectroscopy. The similarity in the characteristics of ETQ^{3+} and ETQ^{2+} indicates that there is no interaction between the two reduced centers in ETQ^{2+} . The shift in the absorption maxima from ~600 nm in PTQ^{3+} and BTQ^{3+} to 534 nm with PTQ^{2+} and BTQ^{2+} , however, indicates association of the two viologen units, such as occurs in the transformation of monomer to dimer forms of MV^{+} (monomer $\epsilon_{605}^{\text{max}} = 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; dimer $\epsilon_{545}^{\text{max}} = 9.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)²³⁻²⁵ and BV^{+} (monomer $\epsilon_{604}^{\text{max}} = 1.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; dimer $\epsilon_{540}^{\text{max}} = 2.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).²⁶ The adherence to Beer's law of PTQ^{2+} over a wide range of concentrations shows, however, that the association is *intramolecular*. It has been suggested that the doubly reduced species PTQ^{2+} and BTQ^{2+} adopt an intramolecular associated form ("closed" conformation) which is not possible sterically with ETQ^{2+} which has an open structure.^{14,15} Similar proposals for open and closed forms of dimer diradicals had been made much earlier for 4-(carbomethoxy)pyridinyl dimer diradicals. These are more complex in their behavior and form covalent bonds in the dimer structure.²⁷ Finally, similar behavior of the poly(viologens), poly(propylviologen) (PPrV) dibromide, and poly(butylviologen) (PBuV) dibromide is noted. Poly(viologen) (1 mM) reduced by e_{aq}^- (11 μM) shows maxima at 595 nm ($\epsilon = 1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 595 ($\epsilon = 1.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) for PPrV and PBuV, respectively. Further reduction promotes an absorbance maximum shift to 545 nm and eventually 526 nm.¹²

Equilibria. The values of the overall potentials for $X^{4+} \rightarrow X^{2+}$, determined by cyclic voltametry are close to those reported.¹⁶ Voltammograms for ETQ^{4+} and BTQ^{4+} (but not PTQ^{4+}) showed slight peculiarities ascribed to electrode deposition. The overall potentials were therefore checked by spectral examination of reactions 1 and 2. The equilibria constants for (1) and (2), combined with the well-established reduction potentials for the $PTQ^{4+/2+}$ and $DQ^{2+/+}$ couples, lead to reduction potentials for the $ETQ^{4+/2+}$ and $BTQ^{4+/2+}$ couples which are in good agreement with those deduced from cyclic voltametry (Table II). Addition of a large excess of PTQ^{4+} to PTQ^{2+} or of BTQ^{4+} to BTQ^{2+} shifts the absorbance peak to ~600 nm, indicating the production of PTQ^{3+} or BTQ^{3+} . Spectral examination of the systems allowed determination of disproportionation constants, and combined with overall potentials, reduction potentials for the discrete 4+/3+ and 3+/2+ couples could be calculated (Table II). No spectral changes accompany the disproportionation of ETQ^{3+} , and the value of E_1^0 was determined from the value of K_3 and the known $DQ^{2+/+}$ reduction potential. The disproportionation constant for ETQ^{3+} could thus be estimated (Table II). The trend for disproportionation $PTQ^{3+} > BTQ^{3+} > ETQ^{3+}$ resembles that observed in DMF solution, estimated from cyclic voltametry data,¹⁵ although the differences are more pronounced in water. Disproportionation occurs most readily with PTQ^{3+} , suggesting greater stability for the closed form of PTQ^{2+} compared with the other diradicals. The value of the disproportionation constant for ETQ^{3+} (≈ 1) is consistent with that expected (0.25) for two noninteracting reducing centers in the ETQ^{2+} product. On the basis of polarography at a dropping mercury electrode, half-wave potentials of -0.20 and -0.35 V for PTQ^{4+} and -0.18 and -0.35 V for BTQ^{4+} have been reported.¹⁷ We feel that these values are incorrect since they would indicate considerable stability for PTQ^{3+} and BTQ^{3+} , and our results do not support this. With ETQ^{4+} , however, our results are in agreement since only a single two-electron reduction wave was observed at a half-wave potential of -0.27 V due to the formation of the diradical dication.¹⁷

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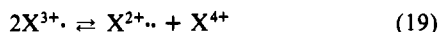
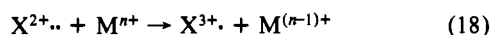
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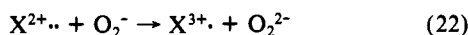
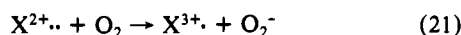
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Kinetic Aspects. Tertiary butanol was avoided in the study of disproportionation of PTQ^{3+} and BTQ^{3+} since these reacted with tertiary butanol radicals (see also ref 28). The radicals PTQ^{3+} and BTQ^{3+} disproportionate ($\geq 90\%$ completely), (3) and (4), with similar second-order rate constants. The second-order rate constants for comproportionation of PTQ and BTQ systems can be estimated (e.g., $k_3 = k_{-3}K_3$) as $(4.6 \pm 2.0) \times 10^5$ and $(5.1 \pm 2.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively, showing that comproportionation is mainly controlled by the comproportionation rate constant, the slower rate constant for PTQ^{2+} (with PTQ^{4+}) arising perhaps from its very stable closed structure. The estimated rate constant for the reaction of PTQ^{2+} with PTQ^{4+} was confirmed experimentally. The kinetic data for the reactions of the radical trications are helpful in interpreting the kinetic data for oxidations of X^{2+} and reductions of X^{4+} . Consider the oxidation of X^{2+} by M^{n+} . The first-step (eq 18) is a one-electron oxidation, and this is followed by either (19) or (20). Both combinations lead

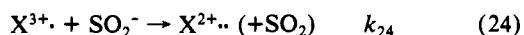
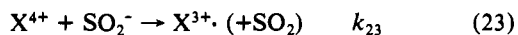


to the same overall stoichiometry and rate law. For $\text{M}^{n+} = \text{Co}(\text{en})_3^{3+}$, second-order rate constants for (18) and (20) are relatively small, and disproportionation reaction (19) will be much faster than (20). For $\text{M}^{n+} = \text{Co}(\text{edta})^-$ or $\text{Fe}(\text{CN})_6^{3-}$ which are much more reactive, $k_{20}[\text{M}^{n+}][\text{X}^{3+}] \approx k_{19}[\text{X}^{3+}]^2$, and both paths will account for loss of X^{3+} . For $\text{M}^{n+} = \text{Co}(\text{edta})^-$, for example, with our conditions ($20\text{--}60 \mu\text{M Co}(\text{edta})^-$), the disproportionation of PTQ^{3+} ($t_{1/2} = 1\text{--}2 \text{ ms}$) will compete with the reaction of $\text{Co}(\text{edta})^-$ with PTQ^{3+} ($t_{1/2} \sim 2\text{--}5 \text{ ms}$). In oxidation by O_2 , additional steps are possible involving O_2^- , e.g., eq 21 and 22, and corresponding steps involving X^{3+} . The rate constants for reaction



of O_2 and O_2^- with X^{2+} or X^{3+} are likely to be comparable.^{29,30} With our conditions, therefore, $[\text{O}_2]_0 \gg [\text{X}^{2+}]_0$ or $[\text{O}_2]_0 \gg [\text{X}^{3+}]_0$, and step (22) is negligible. The large rate constants for X^{3+} with O_2 suggests that this reaction should be now faster than disproportionation, when $[\text{O}_2] \gg [\text{radical}]_0$.

In the reduction of X^{4+} by SO_2^- , the first step (eq 23) is followed by reduction of X^{3+} by SO_2^- (eq 24) and/or disproportionation of X^{3+} (eq 19). It can be estimated that $k_{24} \approx k_{23}$, since the



rate constant for reaction of X^{3+} with O_2^- can be calculated as $10^5\text{--}10^6 \text{ M}^{-1} \text{ s}^{-1}$ and rate constants for $\text{SO}_2^-/\text{O}_2^-$ are $\sim 10^2$ (see below). The uniphase character of the reduction of X^{4+} arises then from very rapid disproportionation of X^{3+} as it is formed in (23).

We have recently shown^{18,19} that both reduction by dithionite (SO_2^- radical) and oxidation by a wide range of cobalt(III) complexes of a number of viologen species conform quite well to Marcus theory.³¹ The same conclusion is reached when redox reactions of the bis(viologens) with a number of types of oxidants and reductants shown in Table III are considered. This includes CO_2^- , a self-exchange rate constant for which has been assessed recently.³¹ Self-exchange rate constants for the viologens^{18,19,32,33}

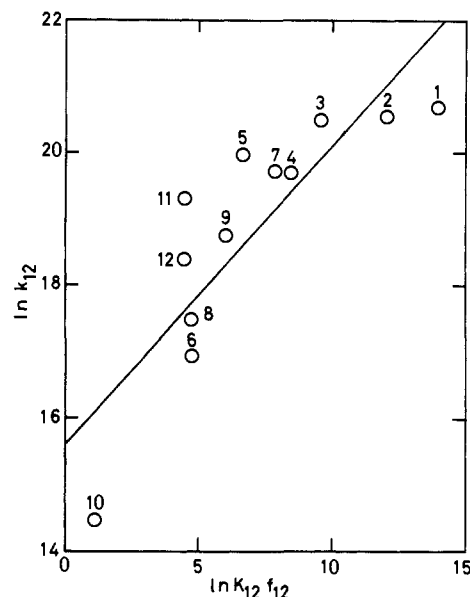


Figure 2. Plot of $\ln k_{12}$ vs. $\ln K_{12}f_{12}$ for reaction of monoviologens and bis(viologens) with O_2 . The viologens indicated are radical cations 1,1'-tetramethylene-2,2'-bipyridinium (1), 1,1'-trimethylene-2,2'-bipyridinium (2), 1,1'-dimethyl-4,4'-bipyridinium (3), 1,1'-bis(2-(hydroxyethyl)-4,4'-bipyridinium) (4), 1,1'-ethylene-2,2'-bipyridinium (5), 1,1'-diphenyl-4,4'-bipyridinium (6), BTQ^{3+} (7), BTQ^{2+} (8), PTQ^{3+} (9), PTQ^{2+} (10), ETQ^{3+} (11), and ETQ^{2+} (12). The data for the monoviologens are from ref 30.

($1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) are also used for the $\text{X}^{4+}/\text{X}^{3+}$ and $\text{X}^{3+}/\text{X}^{2+}$ couples. Other data for the calculations are taken from the literature.³⁴⁻⁴¹ The reactions of viologens³⁰ and bis(viologen) radicals with O_2 make an interesting group for analysis. The plot of $\ln k_{12}$ ($\ln k_{\text{obs}}$) vs. $\ln K_{12}f_{12}$ is shown in Figure 2. Within some scatter, resulting from a small range of rate constants difficult to measure accurately, there is a reasonable agreement between the experimental (0.45) and the theoretical slopes (0.5). The resulting product of self-exchange rate constants for viologens and O_2 is $3.5 \times 10^{13} \text{ M}^{-2} \text{ s}^{-2}$ and can be considered as arising from $\text{X}^{n+}/(\text{n}-1)^+$ ($10^8 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{O}_2^{0/-}$ ($3.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$). The obvious lowered rate constant for reaction of PTQ^{2+} (10 in Figure 2) with O_2 probably arises from the closed conformation of PTQ^{2+} being either less reactive or unreactive, with reaction occurring through a small percentage ($\sim 1\%$) of the open form in equilibrium with the closed conformation.

Finally, we can continue our comparison of the rate constants of reductions by SO_2^- and O_2^- .^{18,42} The rate constants for reaction of O_2^- with ETQ^{4+} , PTQ^{4+} , and BTQ^{4+} ($k_{\text{O}_2^-}$) can be calculated as 2.3×10^6 , 1.9×10^5 , and $4.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively (from the calculated equilibrium constants for the X^{3+}/O_2 reactions (1.1×10^2 , 7.4×10^2 , and 7.6×10^3 , respectively) and the $\text{O}_2/\text{ETQ}^{3+}$, $\text{O}_2/\text{PTQ}^{3+}$, and $\text{O}_2/\text{BTQ}^{3+}$ rate constants (Table III)). The ratios $k_{\text{SO}_2^-}/k_{\text{O}_2^-}$ are thus 0.6×10^2 , 3.3×10^2 , and 1×10^3 for ETQ^{4+} , PTQ^{4+} , and BTQ^{4+} , close to $10^2\text{--}10^3$ values found previously with a large number of oxidants.^{18,42}

Acknowledgment. We are grateful to the National Science Foundation for a grant to support this work. The pulse radiolysis

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experiments were carried out at the Center for Fast Kinetics Research, The University of Texas, Austin, 78712. The Center is supported jointly by the Biotechnology Branch of the Division of Research Resources of NIH (RR 00886) and by the University of Texas, Austin.

Supplementary Material Available: Kinetic data for reactions of bis(viologens) and spectral equilibria data for disproportionation of PTQ^{3+} and BTQ^{3+} and reactions of ETQ^{4+} with DQ^+ , BTQ^{4+} with DQ^+ , and PTQ^{4+} with ETQ^{2+} (8 pages). Ordering information is given on any current masthead page.

Regiochemical Control in Intramolecular Photochemical Reactions of 1,6-Heptadienes: Carbonyl-Substituted 1-(4-Alkenyl)-1-cyclopentenes

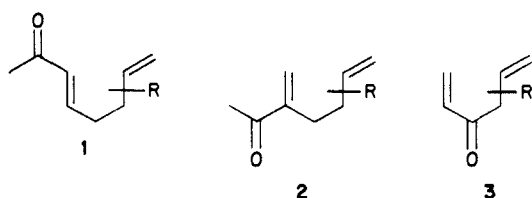
Albert R. Matlin,[†] Clifford F. George,[‡] Steven Wolff,*[†] and William C. Agosta*[†]

Contribution from the Laboratories of The Rockefeller University,

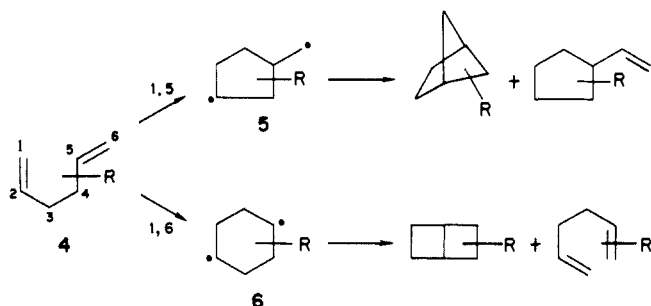
New York, New York 10021-6399, and Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375-5000. Received September 23, 1985

Abstract: The regiochemistry of intramolecular photochemical reaction has been studied in three series of ketones of types 10-12, with particular attention to the effect of alkyl substitution on the side-chain double bond [C(6) and C(7)]. Results for 13 ketones are summarized in Tables I-III and permit these generalizations: (1) ketones 10 follow the "rule of five" and always give straight closure, (2) ketones 11 respond to substitution at C(6) with crossed closure, and (3) ketones 12 respond to substitution at C(6) with reduced crossed closure. Several anomalies would be clarified if initial 1,7 bonding can occur, and this possibility is discussed.

In previous studies we have investigated the role of structural features in control of the regiochemistry of the intramolecular photochemical reactions of carbonyl-substituted 1,5-hexadienes of the general structures 1-3.¹⁻⁴ There is a well-known generalization,⁵ the "rule of five", that irradiation of hexadienes (4)



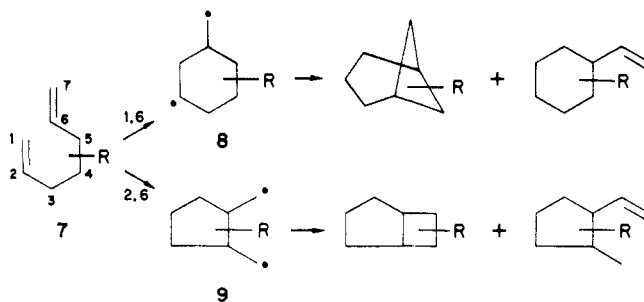
leads preferentially to 1,5 (crossed) closure, with intermediate formation of biradical 5 that then leads to products through collapse or disproportionation. All indication of the alternative



1,6 (straight) closure to 6 is frequently completely absent. We found, however, that in 1-acyl-1,5-hexadienes (1) and 1,5-hexadien-3-ones (3) incorporation of the conjugated double bond into a five- or six-membered ring or substitution of the diene with an alkyl group at C(5) causes 1,6 closure to become competitive.^{1,3} These effects are additive, and in molecules containing both features highly regioselective 1,6 closure can occur. Interestingly,

neither effect influences the regiochemistry of the third class of hexadienes, 2-acyl-1,5-hexadienes (2), and all representatives of this group that were studied close in the crossed fashion.² More recently we have found that substitution of a trimethylsilyl, but not a *tert*-butyl, group at C(1) in series 3 also favors 1,6 closure.⁴

We wished to pursue a similar investigation of regiochemical effects in 1,6-heptadienes (7), particularly since these compounds have seen much more use as intermediates in the synthesis of natural products than have their lower homologues.⁶ In 7 the



rule of five predicts straight closure by way of 9 to be favored over crossed closure to 8.⁵ It was attractive to examine the three types of carbonyl-substituted heptadienes homologous to 1-3, but for these new studies we chose to focus our effort specifically on compounds in which the conjugated double bond was incorporated

(1) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1292. This paper contains references to reviews and discussions pertinent to the general topics of the present report.

(2) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1299.

(3) Matlin, A. R.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1983**, *24*, 2961.

(4) Wilson, P.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1985**, *26*, 5883.

(5) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936. A theoretical treatment has recently appeared: Gleiter, R.; Sander, W. *Angew. Chem.* **1985**, *97*, 575; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 566.

(6) See for example: Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.

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