

Table V. Effect of Concentration of Perchlorate Ions on the Rate Constant for the Reduction of $\text{Co}(\text{en})_3^{3+}$ by Vanadium(II) and Chromium(II) in Aqueous *N,N*-Dimethylformamide

HCONMe ₂ , mol fraction	$[\text{ClO}_4^-]$, M	Rate constant, ^a $\text{M}^{-1} \text{s}^{-1}$
0 ^b	0.50	4.9×10^{-4}
	1.00	5.6×10^{-4}
	1.50	6.7×10^{-4}
0.26 ^b	0.50	2.6×10^{-2}
	1.00	6.2×10^{-2}
	1.50	1.1×10^{-1}
0 ^c	0.50	3.9×10^{-5}
	1.00	4.4×10^{-5}
	1.50	5.3×10^{-5}
0.35 ^c	0.50	8.4×10^{-3}
	1.00	3.5×10^{-2}
	1.50	4.7×10^{-2}

^a Each value is the average of at least two determinations. ^b Vanadium(II) reductions, $[\text{H}^+] 0.38 \text{ M}$, $[\text{V}^{2+}] 6.0 \times 10^{-2} \text{ M}$; $25.0 \pm 0.2^\circ \text{C}$. ^c Chromium(II) reductions, $[\text{H}^+] 0.38 \text{ M}$, $[\text{Cr}^{2+}] 6.0 \times 10^{-2} \text{ M}$; $25.0 \pm 0.2^\circ \text{C}$.

Table VI. Effect of Concentration of Perchlorate Ions on the Rate Constant for the Reduction of $\text{Co}(\text{Cl})(\text{NH}_3)_5^{2+}$ by Vanadium(II) in Aqueous *N,N*-Dimethylformamide

$[\text{ClO}_4^-]$, M	Rate constant, ^a $\text{M}^{-1} \text{s}^{-1}$
0.92	7.2^b
1.42	8.1^b
1.90	9.8^b
0.92	5.3×10^c
1.42	8.0×10^c
1.90	9.2×10^c

^a Each value is the average of at least three determinations. ^b In aqueous solution. ^c *N,N*-Dimethylformamide 0.13 mol fraction, $[\text{V}^{2+}] 6.0 \times 10^{-2} \text{ M}$, $[\text{H}^+] 0.60 \text{ M}$; $25.0 \pm 0.2^\circ \text{C}$.

of *N,N*-dimethylformamide. The rates of reduction increase with the increase in the concentration of perchlorate in both media, but the enhancement by perchlorate of the reduction in aqueous *N,N*-dimethylformamide solution is larger than that in a pure aqueous solution.

Though Tanaka demonstrated that the ion-pair formation constant between $\text{Co}(\text{en})_3^{3+}$ and perchlorate ions in *N,N*-dimethylformamide is larger than that in a pure aqueous solution,¹⁵ it is not clear whether the effect of perchlorate on the reduction rates is attributed to the simple salt effect or the ion-pair formation between $\text{Co}(\text{en})_3^{3+}$ and perchlorate.

Mechanism. The reduction of $\text{Co}(\text{en})_3^{3+}$ by vanadium(II) in aqueous solutions of *N,N*-dimethylformamide must proceed via an outer-sphere mechanism as well as in the case of in aqueous solution.¹⁶ It is noteworthy that the outer-sphere electron-transfer reaction between $\text{Co}(\text{en})_3^{3+}$ and vanadium(II) is accelerated upon addition of *N,N*-dimethylformamide, whereas the rate of electron-transfer between $\text{Co}(\text{phen})_3^{2+}$ and $\text{Co}(\text{phen})_3^{3+}$ in aqueous acetone decreases with the increase in the content of acetone.¹⁷

For the reduction of $\text{Co}(\text{Cl})(\text{NH}_3)_5^{2+}$ by vanadium(II), an outer-sphere mechanism was proposed by Taube,¹⁸ Linck,¹³ and Sykes.¹⁹ It was found that the rate of reduction of $\text{Co}(\text{Cl})(\text{NH}_3)_5^{2+}$ by vanadium(II) increases with the increase in the mole fraction of *N,N*-dimethylformamide (Table IV). The difference between the effect of *N,N*-dimethylformamide in the reductions of $\text{Co}(\text{Cl})(\text{NH}_3)_5^{2+}$ and $\text{Co}(\text{N}_3)(\text{NH}_3)_5^{2+}$ may be related to a difference of mechanism. The inner-sphere electron-transfer mechanism and the formation of the precursor complex as the rate-determining step have been proposed for the reduction of $\text{Co}(\text{N}_3)(\text{NH}_3)_5^{2+}$ by vanadium(II) in aqueous solution.²⁰

Watts et al.⁴ suggested that the reductions of $\text{Co}(\text{X})(\text{NH}_3)_5^{2+}$ ($\text{X} = \text{F}^-$, Cl^- , and Br^-) by iron(II) in dimethyl sulfoxide and *N,N*-dimethylformamide proceed through the inner-sphere mechanism, as is the case in a pure aqueous solution. We favor the inner-sphere mechanism for the reduction of *cis*- $\text{Co}(\text{Cl})(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})(\text{en})_2^{2+}$ by iron(II) based on the effect of the alcohols such as methanol, ethanol, 2-propanol, and 2-methyl-2-propanol (Table I).

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Registry No. *cis*- $\text{Co}(\text{Cl})(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})(\text{en})_2^{2+}$, 17631-57-1; Fe(II), 15438-31-0; *cis*(*N*)- $\text{Co}(\text{ox})(\beta\text{-ala})_2^-$, 64281-54-5; $\text{Co}(\text{en})_3^{3+}$, 14878-41-2; V(II), 15121-26-3; Cr(II), 22541-79-3; $\text{Co}(\text{Cl})(\text{NH}_3)_5^{2+}$, 14970-14-0.

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Chemically Catalyzed Disproportionation of $\text{Ru}(\text{bpy})_3^{2+*}$

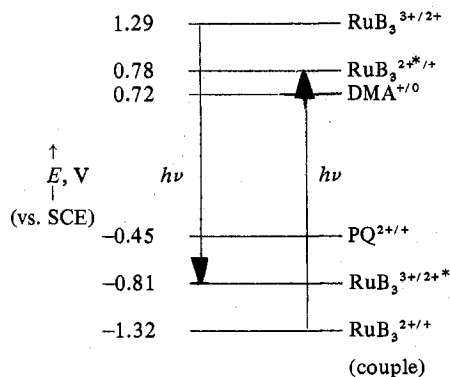
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Received April 26, 1977

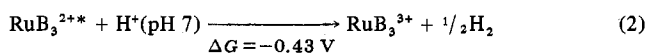
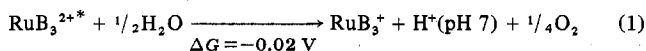
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The complex $\text{Ru}(\text{bpy})_3^{2+}$ (bpy is 2,2'-bipyridine) absorbs light strongly in the visible region to give the relatively long-lived charge-transfer excited state $\text{Ru}(\text{bpy})_3^{2+*}$.¹ The excited state is known to undergo oxidative quenching to give $\text{Ru}(\text{bpy})_3^{3+}$ and reductive quenching to give $\text{Ru}(\text{bpy})_3^{+}$.²⁻¹⁵ The formal reduction potential for the excited-state couple $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+*}$ has been estimated in a quenching study using a series of nitroaromatics as quenchers.¹⁴ The value obtained in the quenching study and the potentials for the ground-state couples $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{+}$ have been used to construct the reduction potential diagram in Scheme I (DMA = dimethylaniline). In the reduced ion $\text{Ru}(\text{bpy})_3^{+}$, the added electron appears to be in a $\pi^*(\text{bpy})$ level, as expected.^{11,12}

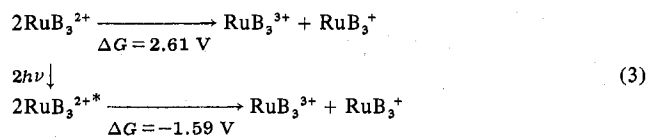
Scheme I. Formal Reduction Potentials in Acetonitrile ($I = 0.1 \text{ M}$; $22 \pm 2^\circ \text{C}$)



As shown by the excitation arrows in the scheme, both the oxidizing and reducing properties of the complex are enhanced in the excited state by the excited-state energy of 2.10 V.¹⁴ Formal reduction potentials in water are similar to those in acetonitrile^{9,17} and the potentials are remarkable in that they show that the excited state is capable of both oxidizing and reducing water at pH 7 (eq 1, 2).^{17,18}



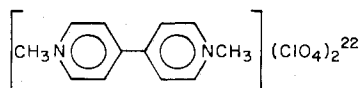
The excited state by itself has not been found to either oxidize or reduce water. An alternate approach to its exploitation involves initial disproportionation into $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$. Optical excitation increases both the oxidizing and reducing strengths of the excited state sufficiently that disproportionation is highly favored even though the ground state is stable with respect to disproportionation (eq 3). Initial



disproportionation offers the potential mechanistic advantage that oxidizing (RuB_3^{3+}) and reducing (RuB_3^+) agents are created which are both stronger as redox reagents than is $\text{Ru}(\text{bpy})_3^{2+*}$ (Scheme I). The excited state is short-lived ($\tau_0 = 580 \text{ ns}$ in water),¹⁹ and attempts to observe disproportionation to give $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ by a direct bimolecular reaction involving $\text{Ru}(\text{bpy})_3^{2+*}$ have been unsuccessful.²⁰ However, using flash photolysis, it can be shown that the disproportionation reaction can be catalyzed chemically and that $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ can be generated simultaneously using visible photolysis.

Experimental Section

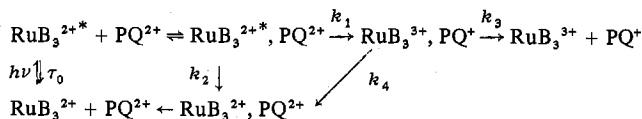
The salts $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$ ²¹ and



($\text{PQ}(\text{ClO}_4)_2$; $\text{PQ}^{2+} = \text{paraquat}$) were prepared and purified as described previously.^{21,22} *N,N*-Dimethylaniline (DMA) (Allied Chemical Co.) was vacuum distilled and tetra-*n*-butylammonium perchlorate (TBAP) (G. F. Smith) recrystallized from ethanol before use. Spectroquality acetonitrile (MCB) was used without further purification. In all of the flash photolysis experiments, the concentration of $\text{Ru}(\text{bpy})_3^{2+}$ was $1.0 \times 10^{-5} \text{ M}$ and the ionic strength was held at 0.1 M using TBAP.

For the flash photolysis experiments, 2.5-cm optical cells were used. Solutions were freeze-pump-thaw degassed to $\leq 10^{-4}$ Torr for ex-

Scheme II

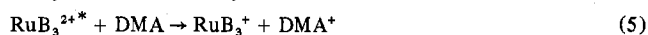
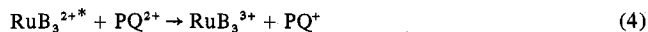


periments which involved DMA as quencher. In experiments where DMA⁺ was produced during the flash, a series of successive flashes gave rise to noticeable formation of the DMA⁺ dimer as shown by an enhancement in the transient absorbance at $\lambda_{\text{max}} 470 \text{ nm}$ ^{22,23} which occurs because of a nearly tenfold increase in the extinction coefficient of the dimer *N,N,N',N'*-tetramethylbenzidine cation (TMBZ⁺) compared to DMA⁺.^{23b} In such experiments data were obtained only for the first few flashes in order to avoid any complications arising from dimer formation. Air-saturated solutions were used for experiments in which O₂ was used to scavenge $\text{Ru}(\text{bpy})_3^+$. In experiments where only PQ^{2+} was used as quencher, the solutions were bubble degassed with either purified nitrogen or argon.

The flash photolysis apparatus has been described.^{22,24} Flash photolysis was limited to visible excitation ($\lambda > 400 \text{ nm}$) using Corning 3-73 glass filters. A 10- μF capacitor and a voltage of 4.0 kV were used in all experiments. The flash pulse time was $\sim 30 \mu\text{s}$. Transient spectral changes which occurred after the flash were followed at a series of wavelengths in the visible region. For the determination of difference spectra, ΔI values were measured at 100 μs as a function of wavelength in the visible region and converted into absorbance differences, ΔA , using the Beer's law equation $\Delta A = \log(1 + \Delta I/I_0)$. ΔI refers to the differences in I values at the end of the flash (100 μs) and at the end of the transient spectral changes. Under the conditions of the experiments, excitation of $\text{Ru}(\text{bpy})_3^{2+}$ and quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ occur during the flash and the transient spectral changes arise from back-electron-transfer reactions which occur after the flash, e.g., $\text{Ru}(\text{bpy})_3^{3+} + \text{PQ}^{\cdot+} \rightarrow \text{Ru}(\text{bpy})_3^{2+} + \text{PQ}^{2+}$. The concentrations of redox products formed during the flash were calculated from ΔA values where $\Delta A = \Delta \epsilon bc$. $\Delta \epsilon$ is the difference in molar extinction coefficients between products and reactants and b is the cell path length. DMA and PQ^{2+} are transparent in the visible region and known ϵ values for DMA⁺,^{22,23a} $\text{PQ}^{\cdot+}$,²⁵ $\text{Ru}(\text{bpy})_3^{3+}$, and $\text{Ru}(\text{bpy})_3^{2+}$ ²² were used. The output of the flash lamp was constant to within $\pm 20\%$. In order to minimize fluctuations from experiment to experiment, the results of several flashes monitored at a series of wavelengths were used to calculate c .

Results and Discussion

Oxidative and Reductive Quenching of $\text{Ru}(\text{bpy})_3^{2+}$. It has been shown previously that visible flash photolysis of acetonitrile solutions containing $\text{Ru}(\text{bpy})_3^{2+}$ and paraquat (PQ^{2+})^{3,13} or $\text{Ru}(\text{bpy})_3^{2+}$ and *N,N*-dimethylaniline (DMA)¹² leads to oxidative or reductive quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ (eq 4, 5).



From the reduction potentials in Scheme I it is clear that both the reduction of RuB_3^{2+*} by DMA and its oxidation by PQ^{2+} are thermodynamically allowed. The experiments were carried out at fairly high quencher concentrations so that excitation to $\text{Ru}(\text{bpy})_3^{2+}$ and quenching occur during the flash, and the expected redox products (eq 4, 5) are observed following the flash.

Flash photolysis of a $\text{Ru}(\text{bpy})_3^{2+}$ solution containing both PQ^{2+} and DMA must lead to simultaneous oxidation and reduction of the excited state. Quenching rate constants in 0.1 M $[\text{N}(\text{n-C}_4\text{H}_9)_4](\text{ClO}_4)$ -acetonitrile at $22 \pm 2^\circ \text{C}$ are known for the two quenchers: $k(\text{PQ}^{2+}) = 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,^{13,22} and $k(\text{DMA}) = 7.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.^{12,22}

The quenching rate constants are not an accurate measure of the amounts of redox products formed per flash. The extent of production of *separated* redox products in solution depends on the relative efficiencies of ionic separation (k_3) and back electron transfer (k_4) within the ion pair following quenching (Scheme II; τ_0 is the excited-state lifetime). The overall

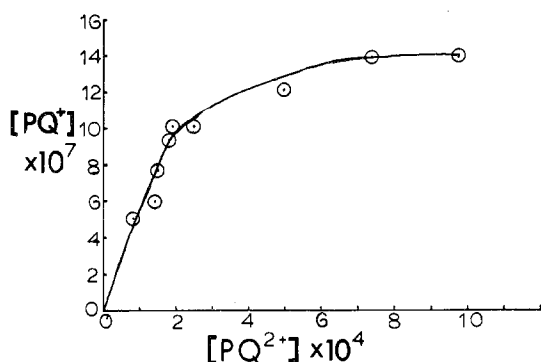


Figure 1. Plot of concentration of redox intermediates formed after 100 μ s in the quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ by PQ^{2+} vs. quencher concentration (in 0.1 M $[\text{N}(\text{n-C}_4\text{H}_9)_4](\text{ClO}_4)$ -acetonitrile at $22 \pm 2^\circ\text{C}$). The concentrations are averaged values determined by measuring absorbance changes at several wavelengths.

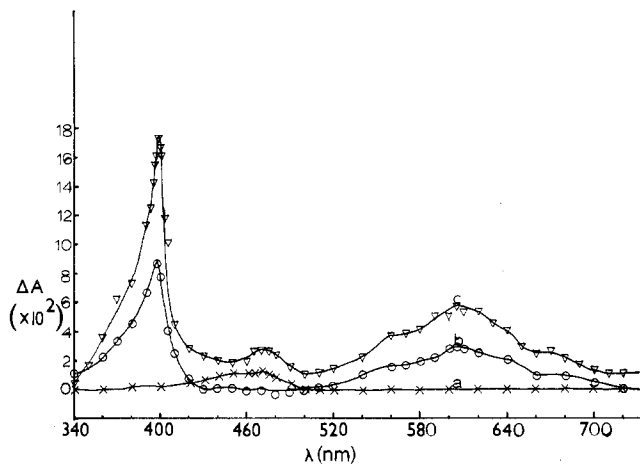


Figure 2. Difference spectra in 0.1 M TBAP- CH_3CN at $22 \pm 2^\circ\text{C}$ following visible flash photolysis of the following solutions: (a) $\text{Ru}(\text{bpy})_3^{2+}$ (1.0×10^{-5} M), DMA (1.8×10^{-3} M), air saturated; (b) $\text{Ru}(\text{bpy})_3^{2+}$ (1.0×10^{-5} M), PQ^2 (7.5×10^{-4} M) (the spectrum has been corrected for the $\text{Ru}(\text{bpy})_3^{3+} \rightarrow \text{Ru}(\text{bpy})_3^{2+}$ absorbance change; (c) $\text{Ru}(\text{bpy})_3^{2+}$ (1.0×10^{-5} M), DMA (1.8×10^{-3} M), PQ^{2+} (7.5×10^{-4} M). The spectra were obtained by drawing smooth curves through absorbance points determined at a series of wavelengths as shown in the figure.

efficiency will also be determined by competitive energy transfer or quencher-induced collisional deactivation (k_2) if such processes are important. The separation step depends on charge type and on the properties of the medium²⁶ and back electron transfer on the activation barrier to electron transfer. The measured quenching rate constants will also include the effects of the preequilibrium between $\text{Ru}(\text{bpy})_3^{2+*}$ and DMA and of diffusional effects for the reaction between $\text{Ru}(\text{bpy})_3^{2+*}$ and PQ^{2+} , and these effects are expected to be different for the two cases.

By use of the apparatus and conditions described here, visible flash photolysis of a 0.1 M TBAP- CH_3CN solution containing 1.8×10^{-3} M DMA and 1.0×10^{-5} M $\text{Ru}(\text{bpy})_3^{2+}$ gave redox products ($\text{Ru}(\text{bpy})_3^+$ and DMA^+ or DMA^+ and O_2^- in aerated solutions)¹² at a level of 1.4×10^{-6} M. In order to determine the amount of PQ^{2+} needed to produce the same concentrations of $\text{Ru}(\text{bpy})_3^{3+}$ and PQ^+ by oxidative quenching the concentration of redox products was observed following flash photolysis as a function of quencher concentration. The data are shown plotted in Figure 1. From the figure, it can be seen that $\text{Ru}(\text{bpy})_3^{3+}$ and PQ^+ are formed at 1.4×10^{-6} M when $[\text{PQ}^{2+}] \approx 7.5 \times 10^{-4}$ M.

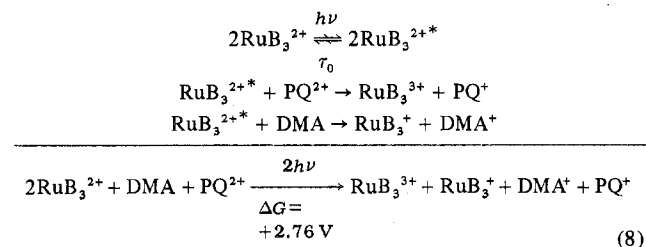
Chemically Catalyzed Disproportionation. In Figure 2 are shown three difference spectra obtained by flash photolysis

of 0.1 M TBAP- CH_3CN solutions containing 1.0×10^{-5} M $\text{Ru}(\text{bpy})_3^{2+}$ and differing combinations of the two quenchers. For Figure 2a, $[\text{PQ}^{2+}] = 7.5 \times 10^{-4}$ M, the quenching reaction is eq 4, and the difference spectrum is for the back-reaction $\text{Ru}(\text{bpy})_3^{3+} + \text{PQ}^+ \rightarrow \text{Ru}(\text{bpy})_3^{2+} + \text{PQ}^{2+}$. The spectrum has been corrected for the contributions from $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ using known extinction coefficients. Since PQ^{2+} is transparent in the visible region, the spectrum in Figure 2a is the absorption spectrum of PQ^+ .²⁵ Figure 2b shows the difference spectrum obtained following flash photolysis of an air-saturated solution containing 1.8×10^{-3} M DMA. Under these conditions reductive quenching occurs (eq 5) followed by rapid scavenging of $\text{Ru}(\text{bpy})_3^+$ to give $\text{Ru}(\text{bpy})_3^{2+}$ and O_2^- (eq 6).¹² The difference spectrum observed is for the reaction



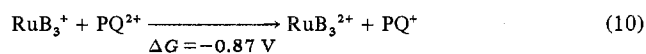
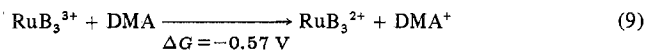
between O_2^- and DMA^+ (eq 7). O_2^- is transparent in the visible region²⁷ and Figure 2b is the absorption spectrum of DMA^+ .¹²

Scheme III



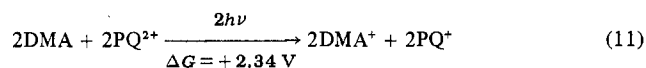
In Figure 2c is shown the difference spectrum following flash photolysis of a deaerated solution containing 1.8×10^{-3} M DMA and 7.5×10^{-4} M PQ^{2+} . The spectrum clearly shows the presence of both PQ^+ and DMA^+ following the flash, and the two ions are present in equal amounts as expected. With both quenchers present, simultaneous oxidation and reduction have led to the chemically catalyzed disproportionation of $\text{Ru}(\text{bpy})_3^{2+*}$ (Scheme III).

$\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ do not appear in the difference spectrum in Figure 2c. Under the conditions of the experiment, $\text{Ru}(\text{bpy})_3^{3+}$, $\text{Ru}(\text{bpy})_3^+$, DMA^+ , and PQ^+ are produced during the flash. In the presence of relatively high concentrations of DMA and PQ^{2+} , $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ disappear rapidly by eq 9 and 10. The presence of the disproportionation products as transients is signaled by the near-doubling in the DMA^+ and PQ^+ concentrations (eq 8 followed by eq 9 and 10) which can be seen when Figure 2c is compared to Figure



2a and b.²⁸

By addition of eq 8, 9, and 10, the net effect of the photolysis is to drive the reaction between DMA and PQ^{2+} in the nonspontaneous direction using visible light (eq 11). Following



the flash, transient spectral changes are observed for the back-electron-transfer reaction between DMA^+ and PQ^+ (eq 12). The transient spectral data followed second-order, $\text{DMA}^+ + \text{PQ}^+ \rightarrow \text{DMA} + \text{PQ}^{2+}$ (12)

equal-concentration kinetics in that plots of $1/\Delta A$ vs. t were linear for 2–3 half-times where ΔA is the absorbance change

at time t . The observation of second-order, equal-concentration kinetics shows that reactions 8, 9, and 10 are all stoichiometric as written and that $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ were formed in equal amounts in the separate redox quenching steps. For eq 12, $k(22 \pm 2^\circ\text{C}) = (2.2 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($I = 0.1 \text{ M}$).²⁹

Conclusions

The flash photolysis experiment shows that the disproportionation of $\text{Ru}(\text{bpy})_3^{2+*}$ can be catalyzed in the presence of two different one-electron redox couples. In the experiment, DMA and PQ^{2+} act both as quenchers and, by the enhanced production of DMA^+ and PQ^+ , as analytical reagents for the determination of $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Ru}(\text{bpy})_3^+$ once formed. From the potential diagram in Scheme I, it is clear that thermodynamically, the catalyzed disproportionation of $\text{Ru}(\text{bpy})_3^{2+*}$ can be achieved by a combination of two one-electron couples or by both oxidized and reduced forms of a single couple. This will be so as long as the reduction potentials involved fall within the disproportionation energy gap (-0.81 to $+0.78 \text{ V}$) between the $\text{Ru}(\text{bpy})_3^{2+*/+}$ and $\text{Ru}(\text{bpy})_3^{3+/2+*}$ potentials.

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Registry No. $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; PQ^{2+} , 4685-14-7; DMA, 121-69-7.

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- In solutions containing both quenchers in high concentration and the excited state as a limiting reagent, competition between quenchers for the excited state would decrease the enhanced production of DMA^+ and PQ^+ below 2. Such a competition is not important here as evidenced by conversion of only $\sim 30\%$ of the $\text{Ru}(\text{bpy})_3^{2+}$ ($1 \times 10^{-5} \text{ M}$) present initially to redox products ($2.4 \times 10^{-6} \text{ M}$; Figure 2) during the whole flash. The quencher concentrations used were relatively low, and the efficiencies of redox product formation for both quenchers are well below 1. A quenching act which leads back to $\text{Ru}(\text{bpy})_3^{2+}$ (Scheme II) also

- leads to $\text{Ru}(\text{bpy})_3^{2+*}$ because of the pumping action of the flash.
 (29) k was calculated from the slopes of plots of $1/\Delta A$ vs. t where slope = $k/b\Delta\epsilon$, b is the cell path length, and $\Delta\epsilon$ was calculated from $\Delta\epsilon = 1.006 \times 10^4$ at 605 nm.

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Preparation of Decacarbonyl[bis(diphenylphosphino)methane]triruthenium and the Elucidation of Its Structure by Dynamic Carbon-13 NMR Spectroscopy

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Metal carbonyl clusters containing three or more metal atoms have been proposed as models for covered metal surfaces.¹ The mobility of adsorbed carbon monoxide on a metal surface is a phenomenon which is not readily studied by direct experimentation.² Carbon monoxide mobility in cluster compounds is well known³ and easily studied by carbon-13 NMR. Thus, the study of the fluxionality of carbonyl clusters, in addition to its fundamental interest, is worthwhile because it may lead to a better understanding of CO mobility on metal surfaces.

At the present time, however, no study of a metal cluster has revealed a carbonyl exchange process that could be directly applicable to a metal surface. In metal clusters there are exchange processes occurring in the same plane as the metal atoms or involving more than one terminal CO per metal atom, but these can have no direct analogues on metallic surfaces.

We have prepared a derivative of $\text{Ru}_3(\text{CO})_{12}$ in which the bidentate ligand, bis(diphenylphosphino)methane, bridges two ruthenium atoms in the equatorial plane. $(\text{dppm})\text{Ru}_3(\text{CO})_{10}$ (1) executes a CO exchange process that may be regarded as a model for CO migration on a metal surface.

Experimental Section

All operations were performed under argon using standard techniques. THF was distilled prior to use from Na-K benzophenone. Bis(diphenylphosphino)methane and $\text{Ru}_3(\text{CO})_{12}$ were purchased from Strem Chemical Co. and used without further purification. Toluene- d_8 was stored over 4-Å molecular sieves and freeze-thaw degassed before use; Freons 12 and 21 were used directly from the lecture bottles.

Synthesis of $(\text{dppm})\text{Ru}_3(\text{CO})_{10}$. Triruthenium dodecacarbonyl (160 mg, 0.25 mmol) and dppm (105 mg, 0.27 mmol) were placed in a 100-mL side arm flask and degassed. THF, 50 mL, was added and the resulting solution warmed to 50°C for 36 h. The solution was then reduced in volume and chromatographed on Florisil, eluting with a 50/50 mixture of THF and hexane. After the removal of a small amount of $\text{Ru}_3(\text{CO})_{12}$ a red-orange band was collected. No other bands developed on the column. The fraction collected was reduced in volume and cooled, yielding red-orange crystals of $(\text{dppm})\text{Ru}_3(\text{CO})_{10}$. The infrared spectrum in CH_2Cl_2 shows carbonyl stretches at 2080 (m), 2040 (w), 2010 (s), 1988 (sh), and 1960 (m) cm^{-1} . Anal. Calcd for $\text{C}_{35}\text{H}_{22}\text{O}_{10}\text{P}_2\text{Ru}$: C, 43.4; H, 2.3. Found: C, 43.7; H, 2.5.

The sample used for the carbon-13 NMR measurements was prepared as above using $\text{Ru}_3(\text{CO})_{12}$ enriched to ca. 60% in ^{13}C .

Carbon-13 NMR Spectra. The spectra were recorded on a JEOL PS100/Nicolet 1080 Fourier transform NMR spectrometer operating at 25.0355 MHz. A tilt angle of 30° and a repetition rate of 1.2 s were employed to collect 500–4000 scans/spectrum.

Above 33°C toluene- d_8 containing 5% THF was the solvent used; from 33 to -83°C , 30% toluene- d_8 and 70% THF was used; below -83°C , 15% toluene- d_8 , 5% THF, 40% CF_2Cl_2 , and 40% CFHCl_2 was used. Chemical shifts were referenced to the downfield peak of THF and converted to the Me_4Si scale using $\delta_{\text{Me}_4\text{Si}} = \delta_{\text{THF}} + 68.0$ ppm. No $\text{Cr}(\text{acac})_3$ was added to the sample.