(reaction 3).[38] Reaction 4 describes this reduction process, while reaction 5 represents a competing pathway involving combination of two solvent radicals. According to this

$$trans\text{-}Cr(tfa)_3 + (CH_3)_2\dot{C}OH \xrightarrow{k_r} \mathbf{2} + \text{products} \quad (4)$$

$$2(CH_3)_2\dot{C}OH \xrightarrow{k_d} \text{products} \quad (5)$$

mechanism, the slow formation of the Cr(II) product can be described by the integrated rate law in eq 6, where $[Cr(II)]_{50}$

$$[Cr(II)] = [Cr(II)]_{50} + \frac{k_r[Cr(III)]}{2k_d} \times \ln\left(\frac{k_r[Cr(III)] + 4k_d[Cr(II)]_{50}}{k_r[Cr(III)] + 2k_d[Cr(II)]_{50}(1 + e^{-k_r[Cr(III)]t})}\right) \quad (6)$$

(measured 50 μs after the flash) is taken to be the initial concentration of this species, [Cr(III)] denotes the concentration of *trans*-Cr(tfa)$_3$, and *t* is time. The ratio of the Cr(II) concentrations at infinite time (>1 ms) and at 50 μs is given by eq 7.

$$\frac{[Cr(II)]_\infty}{[Cr(II)]_{50}} = 1 + \frac{k_r[Cr(III)]}{2k_d[Cr(II)]_{50}} \times \ln\left(1 + \frac{2k_d[Cr(II)]_{50}}{(k_r[Cr(III)] + 2k_d[Cr(II)]_{50})}\right) \quad (7)$$

Values of $[Cr(II)]_\infty \approx 4.0 \times 10^{-6}$ M and $[Cr(II)]_{50} \approx 2.0 \times 10^{-6}$ M result from flash photolysis (250 J/pulse) of a 2×10^{-4} M solution of *trans*-Cr(tfa)$_3$ in 2-propanol. Substituting these concentrations into eq 7 establishes the ratio between k_r and k_d shown in eq 8.

$$k_r/2k_d \approx 0.4 \quad (8)$$

Finally, substitution of this ratio into eq 6 leads to the rate expression given by eq 9.

$$[Cr(II)] = [Cr(II)]_{50} + 0.4[Cr(III)] \times \ln\left(\frac{0.4[Cr(III)] + 2[Cr(II)]_{50}}{0.4[Cr(III)] + [Cr(II)]_{50}(1 + e^{-k_r[Cr(III)]t})}\right) \quad (9)$$

An excellent nonlinear least-squares fit of the experimental concentrations of [Cr(II)] is obtained by using eq 9 with $k_r = (5\text{–}6) \times 10^8$ M^{-1} s^{-1}.

Registry No. *trans*-Cr(tfa)$_3$, 21496-96-8.

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Photoinduced Reduction of $Ru(bpy)_3^{2+}$ by Some Dithio Anions

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The luminescing excited state $Ru(bpy)_3^{2+*}$ (bpy is 2,2′-bipyridine) is quenched in acetonitrile by a series of dithio anions like diethyldithiocarbamate (dtc$^-$). The quenching reaction involves reduction of the excited state giving $Ru(bpy)_3^+$ and the disulfide (dtc)$_2$, and its generality has been shown by using dtc$^-$ to quench a series of MLCT excited states. In the $Ru(bpy)_3^{2+*}$–dtc$^-$ system, complications in the quenching step exist because of static-quenching and specific-ion effects. It has not proven possible to build up $Ru(bpy)_3^+$ or the other reduced complexes following quenching because of slow back electron transfer between the reduced forms of the complexes and the disulfide which returns the system to its initial state. However, in multicomponent systems containing $Ru(bpy)_3^{2+}$, dtc$^-$, and a weak electron acceptor like anthraquinone or a dinitrobenzene, it is possible to build up the radical anions of the added third component which provides a powerful technique for obtaining the spectroscopic properties of the radical anions. The overall pattern of reactions also provides a conceptual basis for the design of light to chemical energy conversion schemes based on an initial excited-state reduction step.

Introduction

It has been well established that the complex $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine) absorbs visible light to give a charge-transfer excited state $Ru(bpy)_3^{2+*}$ which is able to react as an electron-transfer reagent.[2] Oxidative quenching of $Ru(bpy)_3^{2+*}$ gives $Ru(bpy)_3^{3+}$ which is a strong oxidant ($E°(Ru(bpy)^{3+/2+}) = 1.3$ V vs. the saturated calomel electrode (SCE)) capable of oxidizing water to O$_2$; reductive quenching gives $Ru(bpy)_3^+$ which is a strong reductant ($E°(Ru(bpy)_3^{2+/+}) = -1.3$ V vs. SCE) capable of reducing water to H$_2$.[3] However, in most photosystems the utilization of the redox properties of photogenerated $Ru(bpy)_3^{3+}$ or $Ru(bpy)_3^+$ is prevented because of electron-transfer back-reactions which return the system to the ground state, e.g.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*}$$

$$Ru(bpy)_3^{2+*} + Me_2NPh \xrightarrow{k_q} Ru(bpy)_3^{+} + Me_2NPh^{+\cdot}$$

$$Ru(bpy)_3^{+} + Me_2NPh^{+\cdot} \xrightarrow{k_b} Ru(bpy)_3^{2+} + Me_2NPh$$

In an attempt to circumvent the back-reaction and build up $Ru(bpy)_3^+$ in solution, we have studied the utilization of some dithio anions, which are irreversible reductants, as quenchers. In particular, we have studied the series of anions I–IV, and most of our emphasis has been with the diethyldithiocarbamate anion which gave the most significant results.

Experimental Section

Materials. Spectroquality acetonitrile (MCB) was either heated at reflux for 4 h, distilled over P$_2$O$_5$, and stored over molecular sieves or used without purification from a freshly opened bottle. The photochemical properties of the systems studied did not present any differences in purified or spectroscopic solvents, except in the experiments where water was deliberately added in known concentrations in which case the dried solvent was used. Water was distilled twice from alkaline potassium permanganate.

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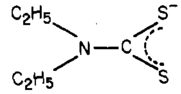
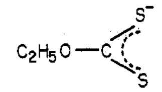
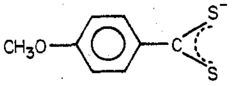


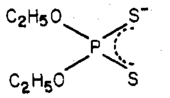
diethyldithiocarbamate anion
dtc⁻
I



ethyl xanthate anion
xan⁻
II



p-methoxydithiobenzoate anion
dtb⁻
III

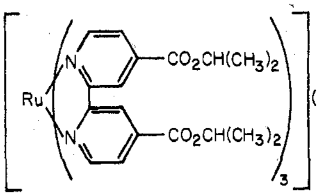


O,O'-diethyl dithiophosphate anion
dtp⁻
IV

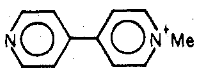
Tetra-*n*-butylammonium and tetraethylammonium perchlorates (Eastman) were recrystallized from ethanol and dried under vacuum. Lithium and sodium perchlorate, anhydrous (G.S.F.), were dried in vacuum.

Sodium diethyldithiocarbamate trihydrate (Eastman) was recrystallized twice from ethanol/ether and washed under nitrogen. The dehydrated salt was obtained by drying in an oven at 80 °C under vacuum for 48 h. Bis(diethylthiocarbamyl) disulfide, $(dtc)_2$, was prepared by oxidation of dtc⁻ with iodine and recrystallized twice from methanol. Xanthate was prepared[4a] and purified as described previously.[4b] The preparation and purification of the monohydrate of sodium *p*-methoxydithiobenzoate was described by one of us elsewhere[5] and sodium *O,O'*-diethyl dithiophosphate was prepared and purified according to an established method.[6] *N,N,N',N'*-Tetramethyl-*o*-phenylenediamine (Aldrich) was recrystallized from deoxygenated aqueous ethanol. Anthraquinone (Eastman) was recrystallized twice from toluene and *o*-dinitrobenzene (Aldrich) and purified by recrystallization from ethanol.

The preparation and purification of the complexes $[Ru(bpy)_3](BF_4)_2$, $[Ru(bpy)_2(CN)_2]$, and $[Ru(bpy)_2(4,4'\text{-}bpyMe^+)_2](BF_4)_4$ were described elsewhere,[7] and the ester complex salt (V) was kindly provided by P. J. Delaive.



V



4,4'-bpyMe⁺

Quenching Measurements. Samples for quenching measurements in acetonitrile and in water contained the ruthenium complexes (5×10^{-5}–10^{-4} M) with the appropriate concentration of added dithio quencher. Solvents were bubble degassed with N_2 before use, and the solutions were made up under a nitrogen atmosphere. Otherwise the spectrophotometric and general experimental techniques were the same as those described previously.[8]

Flash Photolysis. For the flash photolysis experiments a 10-cm optical cell was used. Solutions were freeze–pump–thaw degassed to $\leq 10^{-5}$ torr five times. The solutions were made up containing the complexes of ruthenium ($(1.0\text{–}3.6) \times 10^{-5}$ M) and appropriate amounts of quencher: 10^{-3} M in the case of the dtc⁻ flash experiments with each ruthenium(II) complex, 5×10^{-3} M for xan⁻ and dtb⁻, and 5×10^{-2} M for dtp⁻ in the flash experiments using $Ru(bpy)_3^{2+}$. The technique for the determination of the difference spectra and rate constants and the flash photolysis spectrophotometer used have been described previously.[7,8]

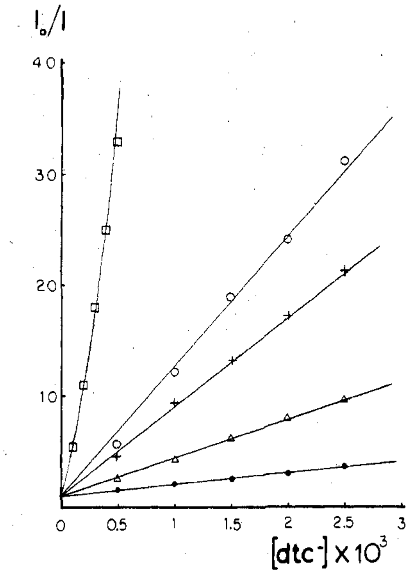
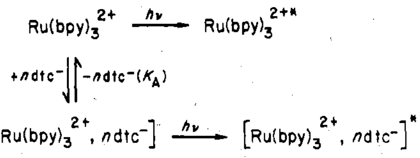


Figure 1. Stern–Volmer quenching plots of $Ru(bpy)_3^{2+*}$ by dtc⁻ in CH_3CN: (□) no added electrolyte, (○) 0.1 M $(n\text{-}Bu)_4NClO_4$, (+) 0.1 M Et_4NClO_4, (△) 0.1 M $NaClO_4$, (•) 0.1 M $LiClO_4$.

Lifetime Measurements. The measurements were made by using an apparatus based on excitation by a Molectron (UV-400) nitrogen laser; the apparatus has been described in detail elsewhere.[7] Solutions were made in an identical manner as for quenching measurements. All data were obtained at room temperature (23 ± 1 °C).

Results and Discussion

Quenching. In acetonitrile solution the emission from $Ru(bpy)_3^{2+*}$ is quenched by dtc⁻, and the quenching was studied as a function of quencher concentration. A slight concave curvature in Stern–Volmer plots of the data (I_0/I vs. concentration of quencher added) was observed (Figure 1; I_0/I is the ratio of the luminescence intensity in the absence and presence of quencher at the wavelength of maximum luminescence for each complex). By analogy with the case of the quenching of $Ru(bpy)_3^{2+*}$ by anionic metallic complexes in water and in DMF,[9] the curvature suggests that both static and dynamic quenchings are occurring simultaneously under the conditions of the experiment. The static component arises because of ground-state ion-pair formation (eq 1).



(1)

To check for the existence of this equilibrium, we monitored the absorption spectrum of a solution containing $Ru(bpy)_3^{2+}$ and dtc⁻, but the modification in the visible absorption band for $Ru(bpy)_3^{2+}$ was not significant enough to demonstrate ion-pair formation. However, the following observation strongly supports the existence of ground-state ion pairing. In a laser lifetime experiment, plots of (τ_0/τ) vs. the concentration of the quencher (τ_0 is the lifetime of $Ru(bpy)_3^{2+*}$ without quencher and τ is the lifetime with different concentrations of quencher) were linear under the same conditions which led to a slight curvature for the luminescence quenching experiments. Since static quenching should have no influence on

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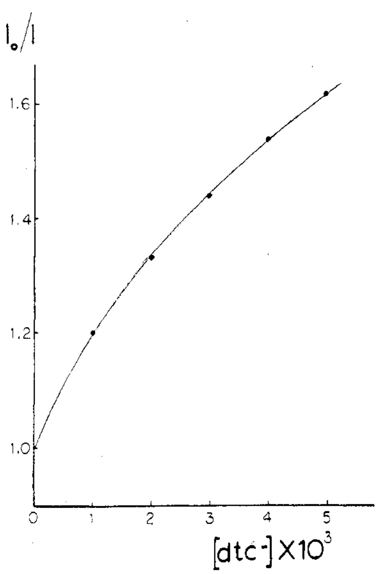

Figure 2. Stern–Volmer quenching plots of $Ru(bpy)_2(CN)_2$* by dtc^- in CH_3CN without added electrolyte.

Table I. Dependence of the Quenching Rate Constant, k_q, for Quenching of $Ru(bpy)_3{}^{2+}$* by dtc^- in CH_3CN with 0.1 M Electrolyte (23 ± 1 °C)

0.1 M electrolyte	$n\text{-}Bu_4NClO_4$	Et_4NClO_4	$NaClO_4$	$LiClO_4$
k_q, $M^{-1}\ s^{-1}$	1.3×10^{10}	9.6×10^9	4.0×10^9	1.3×10^9

the lifetime decay measurement, variations in τ_0/τ with quencher concentration are due only to the dynamic quenching of $Ru(bpy)_3{}^{2+}$*.[9] The value of the quenching rate constant obtained by lifetime quenching, $k_q = 2.9 \times 10^{10}\ M^{-1}\ s^{-1}$, is significantly lower than the value obtained by luminescence quenching, $5.8 \times 10^{10}\ M^{-1}\ s^{-1}$. Although the lifetime technique is less precise than the luminescence technique, the difference in rate constants is too large to be due only to an experimental error and can probably be attributed to static quenching.[10]

An additional, complicating feature of the system involves the effect of the association of dtc^- with its counterion to form an ion pair (eq 2). This type of association in acetonitrile

$$Na^+ + dtc^- \rightleftarrows Na^+,dtc^- \qquad (2)$$

has been shown previously for the Na^+,dtb^- ion pair.[5] Indeed, for quenching of the excited state of the neutral complex $Ru(bpy)_2(CN)_2$ by dtc^-, Stern–Volmer plots have a convex curvature (Figure 2). The origin of the effect apparently lies in the fact that Na^+,dtc^- is not completely dissociated in acetonitrile under the conditions of the experiments (eq 2) and free, unassociated dtc^- appears to be the reactive quencher. As a consequence, an increase in the concentration of the Na^+,dtc^- added (10^{-3}–5×10^{-3} M) does not result in the extent of quenching expected. For the same reason, with a less strongly reducing quencher such as dtp^-, plots of I_0/I vs. concentration of quencher for the quenching of $Ru(bpy)_3{}^{2+}$* also show a convex curvature. Apparently, at the high concentrations needed to get quenching ((0.25–1.25) × 10^{-1} M), the role of inhibition by ion pairing is playing a more important role than static quenching. In the presence of 0.1 M added electrolyte, Stern–Volmer plots of luminescence quenching of $Ru(bpy)_3{}^{2+}$* by dtc^- are straight lines (Figure 1) apparently because ground-state ion-pair formation (eq 1) is inhibited.

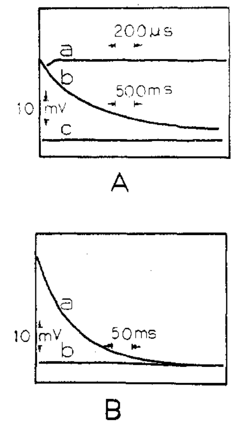

Figure 3. Oscillographic trace obtained following flash photolysis of $Ru(bpy)_3{}^{2+}$ (10^{-5} M) in the presence of dtc^- (10^{-3} M) in CH_3CN at 510 nm. A: a, scale = 200 μs/division; b, scale = 500 ms/division; c, base line. B: a, scale = 50 ms/division; b, base line.

The quenching rate constants in the presence of added electrolyte are lower than the value obtained in the lifetime experiment in the absence of added electrolyte. With added electrolyte, the k_q values decrease as the size of the cation decreases (see Figure 1 (○, +, △, and ● curves) and Table I). The existence of specific ion effects suggests that with added electrolyte ion pairing is also important (eq 3) but with the cation of the added electrolyte, M^+.

$$M^+ + dtc^- \rightleftarrows M^+,dtc^- \qquad (3)$$

In water without added electrolyte, the sodium salt of diethyldithiocarbamate is nearly completely dissociated[11] and the Stern–Volmer plots for quenching of $Ru(bpy)_3{}^{2+}$* by dtc^- are also straight lines ($k_q = 2.2 \times 10^9\ M^{-1}\ s^{-1}$) over the concentration range used. The result also suggests that in this solvent there is no significant ground-state association between the quencher and $Ru(bpy)_3{}^{2+}$ and therefore that static quenching is negligible. The k_q value in water is lower than the k_q value in acetonitrile which is also true for oxidative quenching of $Ru(bpy)_3{}^{2+}$* by paraquat in both solvents[12] and is expected for reactions near the diffusion-controlled limit.

Obviously, the quenching power of the dithio anions should depend on their ability to be oxidized and is no doubt reflected in the k_q values in Table II. However, there is no obvious correlation between k_q and $E_{1/2}$ values for oxidation of the sulfides (Table II), but that is not unexpected. The oxidations are electrochemically irreversible, and the $E_{1/2}$ values are not the desired thermodynamic potentials for the $RS\cdot/RS^-$ couples.

Flash Photolysis. Flash photolysis experiments on vacuum-degassed solutions containing the quencher dtc^- (10^{-3} M) and $Ru(bpy)_3{}^{2+}$ (10^{-5} M) in acetonitrile show that following the quenching step (eq 4), $Ru(bpy)_3{}^+$ has appeared in solution

$$Ru(bpy)_3{}^{2+*} + dtc^- \rightarrow Ru(bpy)_3{}^+ + dtc\cdot \qquad (4)$$

and is identifiable by its spectrum (λ_{max} = 495 nm)[15] obtained from difference spectra obtained before and 2 ms after the

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(10) The diffusion-controlled rate constant for the association

$$Ru(bpy)_3{}^{2+} + dtc^- \overset{K_A}{\rightleftarrows} [Ru(bpy)_3{}^{2+},dtc^-]$$

was calculated by using the Debye–Smoluchowsky equation $k_D = 4\pi N(D_A + D_B)(r_A + r_B)F/1000$ to be $k_D = 6.0 \times 10^{10}\ M^{-1}\ s^{-1}$ at $I = 6 \times 10^{-4}$ M. D_A and D_B are the diffusion coeffficients for the two components and r_A and r_B are their molecular radii. F is the electrostatic contribution from the charges on the components (note ref 8). K_A = 40.4 is calculated for ion-pair formation at the same ionic strength by using the Eigen–Fuoss equation (note ref 8).

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Table II. Dependence of the Quenching Rate Constant for Quenching of $Ru(bpy)_3^{2+*}$ (k_q) and of Electron-Transfer Back-Reaction between $Ru(bpy)_3^+$ and the Disulfides (k_2) in CH_3CN (23 ± 1 °C)

	quencher			
	dtc^-	xan^-	dtb^-	dtp^-
k_q, $M^{-1}\ s^{-1}$ (0.1 M CH_3CN-$NaClO_4$)	4.0×10^9	3.6×10^9	5.0×10^9 [a]	$<1.3 \times 10^7$ [b]
$E_{1/2}$ (V. vs. SCE) for the irreversible oxidation of RS_2^- in 0.1 M CH_3CN-Et_4NClO_4 [c]	0.05 (13)	0.21 (11)	0.19 (5)	0.71 (11)
k_2, $M^{-1}\ s^{-1}$	$(6.2 \pm 0.5) \times 10^5$	$(8.7 \pm 0.4) \times 10^8$	$(9.0 \pm 0.5) \times 10^9$	$(7.1 \pm 0.4) \times 10^9$
$E_{1/2}$ (V vs. SCE) of the reduction of the corresponding disulfide in 0.1 M CH_3CN-Et_4NClO_4 [c]	−1.85 (13)	−1.50 (11)	∼−0.85 (5)	∼−0.9 (11)

[a] I_0/I was corrected because of light absorption by the quencher dtb^- according to ref 14. [b] The Stern–Volmer plot is curved. [c] Literature references are indicated in parentheses following the data.

Table III. Rate Constants for Reduction of $(dtc)_2$ by Following Reductive Quenching at 23 ± 1 °C in CH_3CN

	$Ru(bpy)_2(CN)_2^-$	$Ru(bpy)_3^+$	$Ru(bpyR_2)_3^+$ [a]	$Ru(bpy)_2$-$(4,4'\text{-}bpyMe^+)_2^{3+}$ [b]
wavelength at which the decay was analyzed, nm	540	510	510	595
k_2, $M^{-1}\ s^{-1}$	$(7.2 \pm 1.6) \times 10^5$	$(6.5 \pm 1.5) \times 10^5$	$(3.25 \pm 0.15) \times 10^3$	$(1.15 \pm 0.25) \times 10^3$
$E_{1/2}$ (V vs. SCE) of the Ru^{2+}/Ru^+ couple in 0.1 M CH_3CN-Et_4NClO_4 [b]	−1.53 (17)	−1.32 (15)	−0.9 (18)	−0.76 (19)

[a] R = $-COOCH(CH_3)_2$ on the 4,4′ positions of the pyridyl groups. [b] Literature references are noted in parentheses following the data.

flash. In $Ru(bpy)_3^+$ an electron has been added to a π^*(bpy) level. The only species that absorb after the flash are $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^+$; the dtc· radical has no obvious strong absorption bands in the visible region. There is no evidence for an electron-transfer back-reaction between dtc· and $Ru(bpy)_3^+$ from flash photolysis experiments in the time range 0–2 ms (Figure 3A, curve a) whereas the electron-transfer back-reaction following reductive quenching by reagents like *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) is clearly observable.[15] Apparently, radical coupling to give the corresponding disulfide $(dtc)_2$ (eq 5a)[16] is more rapid than electron-transfer back-reaction (eq 5b). However, on a longer

$$2dtc\cdot \rightarrow (dtc)_2 \qquad (5a)$$

$$Ru(bpy)_3^+ + dtc\cdot \rightarrow Ru(bpy)_3^{2+} + dtc^- \qquad (5b)$$

time scale (∼5 s) $Ru(bpy)_3^+$ disappears from the solution with a second-order rate constant of $k_2 = (6.2 \pm 0.5) \times 10^5\ M^{-1}\ s^{-1}$ (Figure 3A, curve b). The system is completely photochromic 20 s after photolysis. The slow reaction appears to be the reduction by $Ru(bpy)_3^+$ ($E_{1/2}$ = −1.32 V)[15] of the disulfide $(dtc)_2$ ($E_{1/2}$ = −1.85 V)[13] which is formed during the flash (eq 6). On the basis of $E_{1/2}$ values, the reduction of the disulfide appears to be thermodynamically unfavorable but it should be recalled that the reduction of $(dtc)_2$ to give dtc^- is electrochemically irreversible.

$$Ru(bpy)_3^+ + {}^1/_2(dtc)_2 \rightarrow Ru(bpy)_3^{2+} + dtc^- \qquad (6)$$

If great care is not taken to exclude oxygen during the purification of dtc^- and preparation of the solutions, dtc^- is oxidized to the disulfide and the reaction following flash photolysis obeys first- rather than second-order kinetics (Figure 3B, curve a). First-order kinetics are observed because only small amounts of $(dtc)_2$ are sufficient to change the second-order kinetics into pseudo-first-order kinetics with respect to the disulfide. The suggested role of the disulfide was corroborated by a series of experiments in the presence of increasing amounts of $(dtc)_2$; $(dtc)_2$ does not quench the excited state directly. The solution contained dtc^- (10^{-3} M) and $Ru(bpy)_3^{2+}$ (3.6×10^{-5} M) in acetonitrile and varying amounts of $(dtc)_2$ (Figure 4). The results of the experiments showed that following flash photolysis, the reaction observed is indeed first order in $(dtc)_2$ and that for eq 6, $k_2 = (6.5 \pm 1.2) \times 10^5\ M^{-1}\ s^{-1}$.

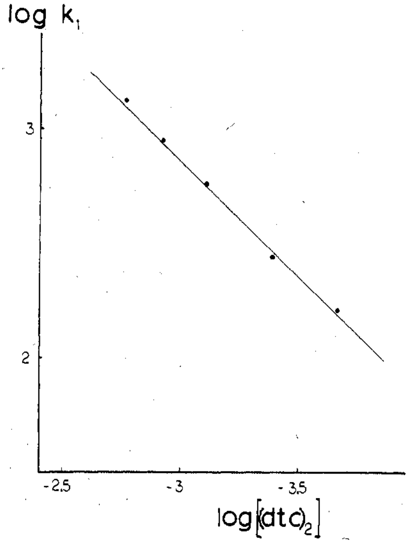

Figure 4. Plot of log of the pseudo-first-order rate constant k_1 (eq 6) vs. log of the concentration of the disulfide $(dtc)_2$ in CH_3CN.

Additional evidence supporting the absence of a competitive back-reaction (eq 5b) between dtc· and $Ru(bpy)_3^+$ was provided by the results of a flash photolysis experiment on a solution containing $Ru(bpy)_3^{2+}$ (10^{-5} M) and the reversible, reductive quencher TMPD (*N,N,N′,N′*-tetramethyl-*p*-phenylenediamine) in the presence of the disulfide $(dtc)_2$. During the flash, $Ru(bpy)_3^{2+}$ was quenched by TMPD with an efficiency qualitatively similar to that observed with dtc^- (eq 7) and the back-reaction (eq 8) in this case is rapid, $k = 5.2 \times 10^9\ M^{-1}\ s^{-1}$.[15] For the range of concentrations of TMPD used ($(1\text{–}5) \times 10^{-5}$ M) the back-reaction was not prevented by the presence of $(dtc)_2$ and the slow reduction of $Ru(bpy)_3^+$ by $(dtc)_2$ was not observed.

$$Ru(bpy)_3^{2+*} + TMPD \rightarrow Ru(bpy)_3^+ + TMPD^{+\cdot} \qquad (7)$$

$$Ru(bpy)_3^+ + TMPD^{+\cdot} \rightarrow Ru(bpy)_3^{2+} + TMPD \qquad (8)$$

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(16) Cauquis, G.; Lachenal, D. *J. Electroanal. Chem.* **1973**, *43*, 205. These authors gave a rate constant for the dimerization of $2 \times 10^5\ M^{-1}\ s^{-1}$ determined by an electrochemical method.

(17) Matsumura-Inoue, T.; Morimoto, T.; Nakayama, T. *Nara Kyoiku Daigaku Kiyo, Shizen Kagaku* **1977**, *26*, 83.

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Rate constants following reductive quenching of a series of related CT excited states for the electron-transfer back-reaction with $(dtc)_2$ are strongly dependent on the reduction potentials for the relevant Ru(II)/Ru(I) couples as shown by the data in Table III. The experiments summarized in Table III were conducted by using the same concentration of Ru(II) complex, the same sample of dtc^-, and the same solvent. The quantity of ligand-reduced complex, called Ru(I) here for convenience, built up after the flash was nearly independent of the nature of the complex used ($\sim 3.0 \times 10^{-6}$ M as determined from difference spectra) except for $Ru(bpy)_2(CN)_2^-$. The smaller amount of the reduced dicyano complex is consistent with the lower reduction potential for the Ru(II)/Ru(I) couple, the relatively short lifetime of the Ru(II) complex compared to $Ru(bpy)_3^{2+}$ (255 ns against 860 ns),[20] and the fact that there is no ground-state association between the complex and dtc^-. The k_2 values were estimated by flash photolysis. The transient absorbance changes following the flash obeyed first-order kinetics and k_2 values were calculated from $k_2 = k_{obsd}/[(dtc)_2]$. The $(dtc)_2$ concentration in the dtc^- stock solution was calculated by using k_{obsd} for the reaction between $Ru(bpy)_3^+$ and $(dtc)_2$ (eq 6) and the known k_2 value for the reaction with $Ru(bpy)_3^+$.

Attempts to build up $Ru(bpy)_3^+$ in solutions of $Ru(bpy)_3^{2+}$ (10^{-4} M) in the presence of dtc^- (5×10^{-3} M) in acetonitrile by extended photolysis were unsuccessful. The back-reaction with the disulfide (eq 6) is apparently sufficiently rapid that the steady-state concentration of $Ru(bpy)_3^+$ is too low to detect. The addition of a small amount of water (10^{-3}–5×10^{-1} M) does not significantly modify the rate of back-reaction with $(dtc)_2$. However, with a larger concentration of water (20%) the quantity of $Ru(bpy)_3^+$ produced by the flash decreases. Part of the $Ru(bpy)_3^+$ produced during the flash disappears by a process different from the reaction with the disulfide. In pure water the decay of $Ru(bpy)_3^+$ is very rapid with poorly defined kinetics, but the system is still photochromic. The reaction of $Ru(bpy)_3^+$ with H_2O is currently under investigation.[21]

Induced Electron Transfer. If a convenient electron acceptor, A, like anthraquinone ($E_{1/2} = -0.94$ V)[22] or *o*-dinitrobenzene ($E_{1/2} = -0.8$ V)[23] (at 5×10^{-4} M) is added to a solution in acetonitrile containing $Ru(bpy)_3^{2+}$ (10^{-5} M) and dtc^- (10^{-3} M), the formation of the radical anion $A^{-}\cdot$ is observed after the flash.[24] The overall scheme involved is eq 4 and 5 followed by electron transfer between $Ru(bpy)_3^+$ and the electron acceptor, A (eq 9), which is very rapid.[25]

$$Ru(bpy)_3^+ + A \rightarrow Ru(bpy)_3^{2+} + A^{-}\cdot \qquad (9)$$

There is a good agreement between the spectrum of the anthraquinone radical anion $A^{-}\cdot$ described in the literature in CH_3CN (0.1 M in Et_4NClO_4)[26] and the spectrum obtained by the flash experiment in the same medium (see Figure 5, for our spectrum). An important point to be noted in the type of scheme involved here (eq 4, 5, 9) is that the change of the absorption after the flash gives *directly* the *real* absorption of the species $A^{-}\cdot$ because the reaction in eq 9 is very rapid and A does not absorb up to 450 nm. The system is photochromic but only after waiting several minutes (see below), and with only one solution it was possible to characterize the total spectrum of $A^{-}\cdot$. The utilization of the system $Ru(bpy)_3^{2+}$–dtc^- in a flash experiment is potentially an excellent method for characterizing the spectra of transiently reduced species formed from any compound able to be reduced at a potential higher than ~ -1.3 V (~ -1.5 V using $Ru(bpy)_2(CN)_2$; note Table II) and any compound which does not give a charge-transfer complex with dtc^-. Without electrolyte the maximum of the absorption is slightly displaced toward longer wavelengths (535 nm against 545 nm; Figure 5) apparently because there is no longer an association of $A^{-}\cdot$ with the cation of the electrolyte.

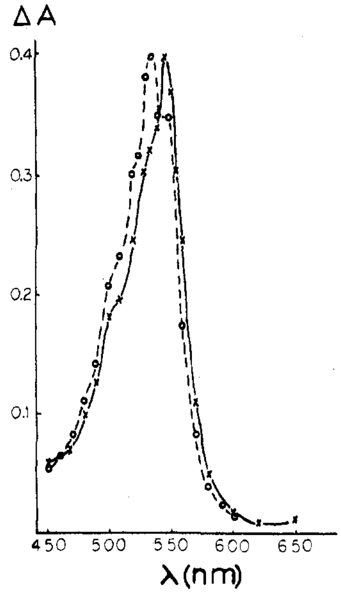

Figure 5. Absorption at different wavelengths after the flash (1 ms) of a solution of $Ru(bpy)_3^{2+}$ (1×10^{-5} M), dtc^- (10^{-3} M), and anthraquinone (5×10^{-4} M): (×) 0.1 M CH_3CN–Et_4NClO_4; (o) CH_3CN without electrolyte.

Our attempt to build up the radical anion of the anthraquinone, $A^{-}\cdot$, by a continuous irradiation in acetonitrile was unsuccessful. Moreover, a series of successive flashes showed that the concentration of $A^{-}\cdot$ reaches a maximum and then decreases. The reason why it is impossible to build up $A^{-}\cdot$ in solution is probably ascribable to photochemistry of the radical anion induced by visible light which has been demonstrated in water.[27] The excited state, $A^{-}\cdot{}^*$, can give the dianion A^{2-} by photoreduction ($E_{1/2} = -1.45$ V)[22] and A^{2-} is, no doubt, able to reduce the disulfide, $(dtc)_2$, very rapidly. The very slow disappearance of $A^{-}\cdot$ after the flash is probably due to the slow oxidation of $A^{-}\cdot$ by the disulfide (eq 10). A decay similar

$$A^{-}\cdot + {}^1/_2(dtc)_2 \rightarrow A + dtc^- \qquad (10)$$

to that observed for $Ru(bpy)_3^+$ as a function of the concentration of disulfide was obtained, giving $k_2 = (2.4 \pm 0.5) \times 10^3$ M^{-1} s^{-1} for the reaction between the anthraquinone radical anion and the disulfide. The disproportionation of $A^{-}\cdot$ into A and AH_2 by the residual water in acetonitrile, which has been observed for some quinones[28] (eq 11, 12, 13), did not seem

$$A^{-}\cdot + H_2O \rightarrow AH\cdot + OH^- \qquad (11)$$

$$A^{-}\cdot + AH\cdot \rightleftarrows A + AH^- \qquad (12)$$

$$AH^- + H_2O \rightarrow AH_2 + OH^- \qquad (13)$$

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[23] Maki, A. H.; Geske, D. H. *J. Chem. Phys.* **1960**, *33*, 825.

[24] It is impossible to use paraquat as acceptor ($E_{1/2} = -0.44$ V) because there is formation of a strong charge-transfer complex with dtc^- ($\lambda_{max} = 571$ nm).

[25] We have checked that $A^{-}\cdot$ is not produced by a flash of a solution where A and dtc^- only were present.

[26] Osa, T.; Kuwana, T. *J. Electroanal. Chem.* **1969**, *22*, 389. Cruver, G. A.; Kuwana, T. **1972**, *36*, 85.

[27] Inoue, H.; Hida, M. *Chem. Lett.* **1979**, 107.

[28] Cauquis, G.; Marbach, G. *Bull. Soc. Chim. Fr.* **1971**, 1908.

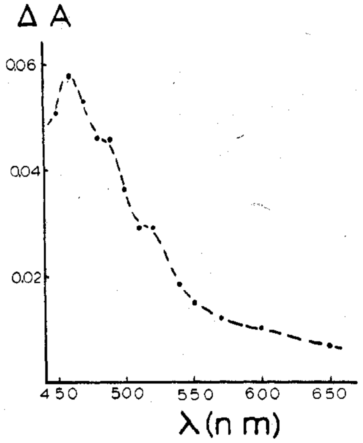
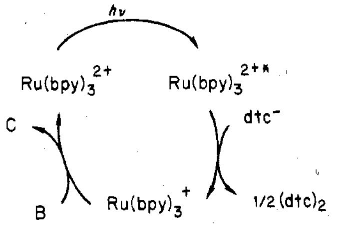


Figure 6. Absorption at different wavelengths after the flash (1 ms) of a solution of $Ru(bpy)_3^{2+}$ (1×10^{-5} M), dtc^- (10^{-3} M), and *o*-dinitrobenzene (5×10^{-4} M) in 0.1 M $CH_3CN-Et_4NClO_4$.

Scheme I



to be of significant importance in our work. This is indicated by the fact that the quantity of $A^{-}\cdot$ produced after the flash is identical with the quantity of $Ru(bpy)_3^+$ obtained under the same conditions without added A, at least within experimental error.

A good agreement is also found for the spectrum of the radical anion of *o*-dinitrobenzene (see the spectrum in Figure 6) obtained after the flash and that published in the literature for the similar compounds nitrobenzene and *p*-nitrotoluene[29] in solution and also with the spectrum of *o*-dinitrobenzene radical anion obtained in a glassy frozen solution.

The experiments described above show that dithio anions like dtc^- can quench $Ru(bpy)_3^{2+*}$ to give $Ru(bpy)_3^+$ and that such systems have potential in photochemical applications for catalysis on the basis of Scheme I. In Scheme I, a compound B is converted into C by an irreversible process which is sufficiently rapid to prevent the oxidation of $Ru(bpy)_3^+$ by the disulfide. In this case (with anthraquinone) the overall scheme is only transient, but in principle it illustrates the ability of such excited-state systems to drive reactions in photochemical or photoelectrochemical applications and to create and observe transients which would otherwise be difficult to observe.

Conclusions

The results of our studies on the system $Ru(bpy)_3^{2+}-dtc^-$ are worth noting in a catalytic sense because we have shown that it is possible in acetonitrile to build up, if transiently, the powerful reductant $Ru(bpy)_3^+$. Unfortunately, the system is limited in any useful sense by the rapidity of the reduction of the disulfide $(dtc)_2$ which was a surprise to us. However, our experiments do demonstrate the potential value of such systems photocatalytically and for the generation of usually unobservable transients. In the future it may be possible to exploit a more appropriate dithio anion or other reductive quencher which will allow the buildup of significant concentrations of Ru^I.

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Registry No. I, 392-74-5; II, 28563-38-4; III, 71141-39-4; IV, 40898-92-8; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_3^+$, 56977-24-3; $Ru(bpy)_2(CN)_2^-$, 73746-84-6; $Ru(4,4'-[(CH_3)_2CHOOC]_2bpy)_3^+$, 73746-85-7; $Ru(bpy)_2(4,4'\text{-bpyMe})_2^{3+}$, 73746-86-8; $(dtc)_2$, 97-77-8.

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Stereochemistry and Quantum Yields for the Ligand Field Photolysis of Rhodium(III) Complexes. 3.[1,2] *cis*- and *trans*-$Rh(en)_2XI^{n+}$

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Ligand field excitations of *cis*- and *trans*-$Rh(en)_2XI^{n+}$ complexes (X = I, NH_3, H_2O), in all cases but one, lead exclusively to the formation of *trans*-$Rh(en)_2(H_2O)I^{2+}$ as the photoproduct. The exception is the *cis*-$Rh(en)_2(NH_3)I^{2+}$ complex, where irradiation leads to the formation of both *trans*-$Rh(en)_2(H_2O)I^{2+}$ and *cis*-$Rh(en)_2(NH_3)(H_2O)^{3+}$. The stereochemistry of all of the photochemical products is consistent with ligand labilization from the lowest electronic excited state and rearrangement of the triplet, five-coordinate, square-pyramidal fragments as originally proposed by Vanquickenborne and Ceulemans. The three separate reaction channels observed for the photolysis of the spectroscopically similar *trans*- and *cis*-$Rh(en)_2(NH_3)I^{2+}$ complex ions have been interpreted as a strong preference for the Rh(III) metal center not to break a Rh(III)–en bond in a ligand field excited state. For the series of *cis*- and *trans*-$Rh(en)_2XY^{n+}$ (X = Cl, Br, I; Y = X, NH_3), qualitative series for ease of halogen labilization (Cl > Br > I) and trans-labilizing ability (I ≫ Br > Cl) have been proposed.

Introduction

The ligand field photolysis of rhodium(III) amine complexes has been extensively studied over the past 8 years.[1-11] This activity is due, in part, to the substitutional inertness and stereoretention of the thermal substitution reactions[12] and the

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