

a double doping of DNA by  $ET^+$  and  $MV^{2+}$  (Figure 1).

**Electron Transfer.** The interaction of  $ET^+$  and  $MV^{2+}$  in water is indicated by the quenching of fluorescence of  $ET^+$  by an increasing concentration  $c_{MV^w}$  (Figure 2). After correcting the data for ion-ion interaction (Debye-Hückel), we obtain for the relative intensity  $I/I_0$  a Stern-Volmer relation  $I_0/I - 1 = K_Q^w c_{MV^w}$  with  $K_Q^w = 1.5 M^{-1}$  (Figure 2). Quenching is enhanced by NaCl (Figure 2). For infinite concentration of salt we extrapolate  $K_Q^s = 27.5 M^{-1}$ . We assign the quenching to electron transfer considering the redox potentials<sup>15</sup>  $E'_0(ET^{+*}/ET^{2+}) = -0.52 V_{NHE}$  (from  $E'_0(ET^+/ET^{2+}) = 1.68 V_{NHE}$ ) and  $E'_0(MV^+/MV^{2+}) = -0.44 V_{NHE}$ . In fact, after flash excitation of  $ET^+$  we observe reduced  $MV^+$ . The maximal rate constant with salt is  $k_{el}^s = 1.6 \times 10^{10} M^{-1} s^{-1}$ , considering  $K_Q^s = k_{el}^s \tau_{ET}^s$  with a lifetime  $\tau_{ET}^s = 1.7 ns$ .

With  $ET^+$  bound to DNA ( $\nu_{ET} = 0.02/bp$ ), its fluorescence is quenched by  $MV^{2+}$  most efficiently (Figure 2). At low concentration we obtain a Stern-Volmer relation with  $K_Q^{DNA} = 7.6 \times 10^5 M^{-1}$ . The DNA matrix enhances the yield of electron transfer by a factor  $K_Q^{DNA}/K_Q^w = 507000$ . Saturation is observed around  $I_0/I = 10$  above  $c_{MV^w} = 10^{-5} M$ .

Five contributions may be responsible for the dramatic effect: (i) enhanced lifetime of  $ET^{+*}$ , (ii) reduced repulsion of approaching reactands, (iii) enhanced interfacial concentration  $c_{MV^i}$ , (iv) restriction of diffusion, and (v) modulation of electron transfer. With  $\tau_{ET}^{DNA} = 20 ns$  the first effect contributes a factor of  $\tau_{ET}^{DNA}/\tau_{ET}^s = 12$ . The factor of vanishing repulsion is indicated by the salt effect  $K_Q^s/K_Q^w = 18$ . Accumulation is estimated as  $c_{MV^i}/c_{MV^w} = 2.2 \times 10^3$ . (From  $c_{MV^i} = \nu_{MV}/V_i$  with an interfacial volume  $V_i = \pi(2r_H w_i + w_i^2) h_{bp} = 1.34 nm^3/bp$ , with helix radius  $r_H = 1 nm$ , width of interfacial shell  $w_i = 0.5 nm$ , and height of base pair  $h_{bp} = 0.34 nm/bp$ , considering  $\nu_{MV} = \bar{\nu}_{MV} K_{MV} c_{MV^w}$  at low concentration). Thus the cumulative effect of the contributions i-iii could be 100 times larger than the enhancement actually observed. The discrepancy may indicate a slowing down of electron transfer itself (diffusion or reaction).

We restrict a mechanistic interpretation to a sketch of two limiting aspects, diffusion control at low occupation and reaction control near saturation. **Diffusion control:** In the limit of low occupation we describe fluorescence quenching by diffusion control in 1D as  $I_0/I - 1 = 1.8(4D_{MV} \tau_{ET}^{DNA} / \pi h_{bp}^2)^{1/2} \nu_{MV}$ . (The non-stationary term of diffusion<sup>16</sup> dominates in 1D.) Comparison with the data by using  $\nu_{MV} = \bar{\nu}_{MV} K_{MV} c_{MV^w}$  yields a diffusion coefficient  $D_{MV} = 2.5 \times 10^{-7} cm^2/s$ . The mobility of  $MV^{2+}$  along the double helix appears to be restricted. **Reaction control:** In the limit of saturation we consider electron transfer between localized reactands in the nonadiabatic limit with  $k_{el} = k_{el}^0 \exp(-E^*/kT)$  with  $k_{el}^0 = V_{el}^2 (h^2 \lambda kT / 4\pi^3)^{-1/2}$  and  $E^* = (1 + \Delta/\lambda)^2 (\lambda/4)$  (interaction energy  $V_{el}$ , Planck's constant  $h$ , drop of redox potential  $\Delta$ , reorganization energy  $\lambda$ ).<sup>17</sup> The rate constant is obtained from  $I_0/I - 1 = k_{el} \tau_{ET}^{DNA}$ . From an Arrhenius plot between 5 and 40 °C we determine  $k_{el}^0 = 1.1 \times 10^{12} s^{-1}$  with  $E^* = 0.180 eV$ . With  $\Delta = 0.1 eV$ , the reorganization energy is  $\lambda = 0.95 eV$  and the interaction energy  $V_{el} = 8 meV$ . This large value indicates an intimate contact of donor and acceptor. Without further knowledge of the precise location of  $MV^{2+}$  and of the redox potentials in DNA, we avoid a more detailed analysis.<sup>18</sup>

**Summary.** We use the double helix as a medium for an organized reaction. The well-defined matrix allows a detailed evaluation of photoinduced electron transfer between intercalated ethidium and condensed methylviologen. In preliminary time-resolved studies we have observed that the nonexponential decay of  $ET^{+*}$  occurs within 1 ns on one hand and that the lifetime of

hole and electron as  $ET^{2+}$  and  $MV^+$  is beyond 1 ms on the other hand. We proceed in the assembly of a photosynthetic reaction chain in defined sequences of DNA.

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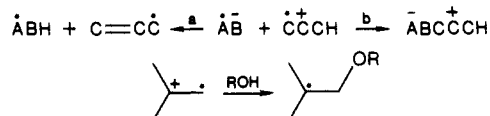
## Photolysis of *N*-(2-Methyl-2-propenyl)phthalimide in Methanol. Evidence Supporting Radical-Radical Coupling of a Photochemically Generated Radical Ion Pair

Paul H. Mazzocchi\* and Gregory Fritz

Department of Chemistry and Biochemistry  
University of Maryland, College Park, Maryland 20742

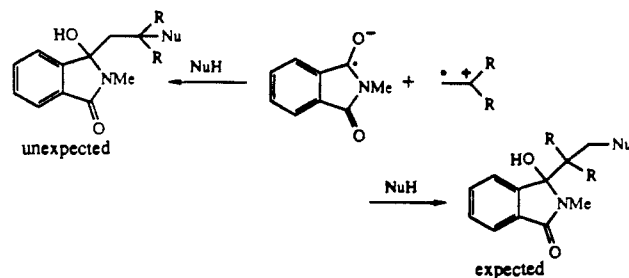
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The nature of radical cation-radical anion interactions is a topic of current interest. For photochemically generated radical ion pairs in the absence of nucleophiles the major process is usually back electron transfer or proton transfer to give a radical pair<sup>1</sup> (path a) although radical-radical coupling of the radical ion pair



(path b) to a zwitterion has been suggested in several cases.<sup>2</sup> In nucleophilic solvents, such as alcohols, it is well established that the alcohol adds to the radical cation in an anti-Markovnikov manner<sup>3</sup> to give the most stable radical which can then undergo subsequent reactions. To date there is no convincing data available to support radical-radical coupling of the radical ion pair (path b) and the conclusive demonstration that this process occurs would establish a new reaction of photochemically generated radical ion pairs.

It appeared to us that the most convincing evidence for radical-radical coupling of a photochemically generated radical ion pair would be to trap the resultant zwitterionic intermediate, most conveniently by addition to a nucleophile. To accomplish this, conditions would have to be set up to favor radical coupling over nucleophilic addition to the radical cation and an unexpected product, that which would have been formed from "Markovnikov" addition of the nucleophile to the radical cation, would have to result.



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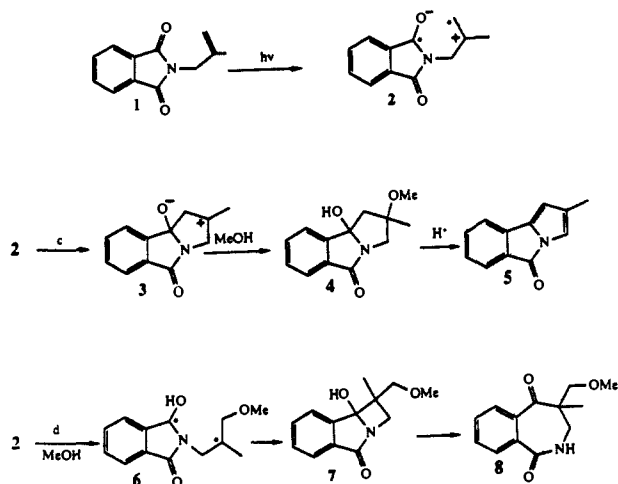
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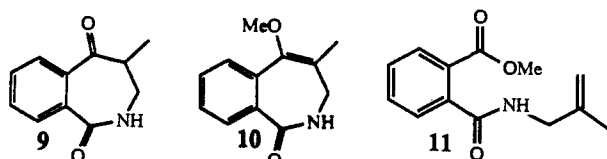
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We chose *N*-(2-methyl-2-propenyl)phthalimide (**1**) as our substrate. Intramolecular electron transfer in this system should be reasonably efficient<sup>4</sup> on the basis of the fact that it is known to occur in the analogous intermolecular system and the expectation that the proximity of the two radical ions should favor the desired radical coupling process through a five-membered transition state. The resultant stable tertiary cation **3** could be trapped by methanol to yield **4** which could undergo acid-catalyzed loss of water and methanol to **5**.



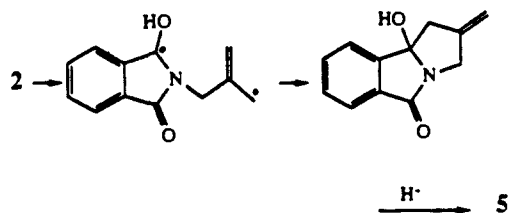
The typical reaction of the radical cation with methanol would afford biradical **6** which would close to **7** and subsequently reopen to **8**, a process which has numerous precedents.<sup>5</sup>

We were quite gratified when, on irradiation of **1** in methanol, we obtained **4**, **5**, and **8** since the formation of these products appeared to support paths c and d. We were perplexed, however, when we observed that compounds **9** and **10** were also formed along with **11**.<sup>6</sup> Although **11** arises from simple methanolysis of **1**, compounds **9** and **10** correspond to the excision of a  $\text{CH}_2$  unit from **1** and might represent a further and unwanted complication in its photochemistry.

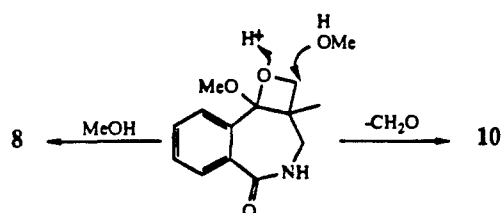


Careful examination of the photolysis reaction by HPLC showed that **4** and **8** were the only primary photoproducts, ap-

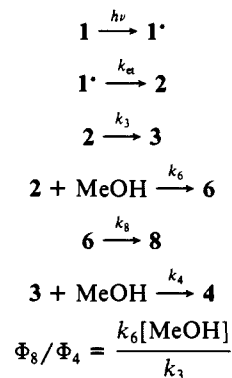
pearing in the early stages of the reaction along with **11** which was subsequently shown to be a thermal product in equilibrium with **1** under the reaction conditions. Compound **5** was shown to arise from **4** presumably via acid-catalyzed dehydration and demethanolysis, thus ruling out the sequence outlined below.



Since **9** and **10** are not photoproducts of **1** they must be photoproducts of **11**. We suggest that the first step in this reaction is a [2 + 2] intramolecular photoaddition of the alkene to the ester carbonyl<sup>9</sup> to give the unobserved oxetane **12** which can then lose formaldehyde to give the enol ether **10**. Subsequent hydrolysis of **10** during the isolation process would give the ketone **9**. It is quite possible that **8** also arises via acid-assisted methanolysis of the oxetane<sup>10</sup> in addition to formation via path d, and we are presently conducting experiments to decide this question.



Scheme I



Our conclusion is that **4** and **8** are the only primary photoproducts of the reaction and are generated via the mechanism outlined in Scheme I. Consistent with expectations for Scheme I a linear relationship between the  $\Phi_8/\Phi_4$  ratio and methanol concentration<sup>11</sup> was observed, and the slope of the line indicates that the rate of radical-radical coupling ( $k_3$ ) is an order of magnitude greater than the rate of methanol addition to the radical cation ( $k_6$ ). Strong supporting evidence for the intermediacy of **2** was provided by a solvent effect study. If the polar intramolecular radical anion-radical cation is a true intermediate, the formation of **4** and **8** should be favored in polar solvents. In fact, when **1** was irradiated in 4 M solutions of methanol in methylene chloride, methyl acetate, and acetonitrile the relative quantum yield for the formation of **4** (and **8**) increased from 1 to 1.29 to 2.18. These data, along with the formation of **8**, support our

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(11) Irradiations of **1** were conducted in parallel in pure methanol (24.7 M) and 18.5, 12.3, and 6.2 M methanol in acetonitrile.

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(6) (a) Products were isolated by column chromatography (silica gel, ethyl acetate-hexane) followed by preparative TLC. Isolated products: **4** (5%); **8** (11%); **11** (3%); **9** (3%); **10** (2%). (b) Selected physical data. **4**: IR ( $\text{CHCl}_3$ ) 3460 (br), 1700  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3/\text{Me}_2\text{Si}$ )  $\delta$  7.75 (1 H, m), 7.58 (2 H, m), 7.49 (1 H, m), 4.95 (1 H, brs), 3.82 (1 H, dd,  $J = 0.6, 12.6$  Hz), 3.52 (1 H, d,  $J = 12.6$  Hz), 3.42 (3 H, s), 2.57 (1 H, d,  $J = 13.4$  Hz), 1.65 (1 H, dd,  $J = 0.6, 13.4$ ), 1.43 (3 H, s). **5**: mp 79–81 °C; mass spectrum  $\text{C}_{12}\text{H}_{15}\text{NO}$ ,  $m/z$  found  $M^+$  183; IR ( $\text{CHCl}_3$ ) 3020, 1740  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3/\text{Me}_2\text{Si}$ )  $\delta$  7.60 (1 H, m), 7.40 (1 H, m), 7.11–7.26 (2 H, m), 6.75 (1 H, brs), 6.05 (1 H, s), 2.03 (3 H, brs). **10**: IR ( $\text{CHCl}_3$ ) 3440, 1750, 1665  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3/\text{Me}_2\text{Si}$ )  $\delta$  7.92 (1 H, m), 7.60–7.73 (3 H, m), 7.13 (1 H, brt,  $J = 6.5$  Hz), 3.85 (1 H, dd,  $J = 6.5, 16.9$  Hz), 3.74 (3 H, s), 3.48 (1 H, dd,  $J = 6.5, 16.9$  Hz), 1.57 (3 H, s). **11**:  $^1\text{H NMR}$  ( $\text{CDCl}_3/\text{Me}_2\text{Si}$ )  $\delta$  7.40–7.93 (5 H, m), 4.95 (2 H, m), 4.03 (2 H, m), 3.90 (3 H, s), 1.85 (3 H, brs). (c) Compound **4** was unstable and readily converted to **5**. (d) Compound **8** was characterized by alkylation (NaH, MeI, DMF) and comparison of its *N*-methyl derivative with an authentic sample prepared by photochemical addition of 2-(methoxymethyl)propene to *N*-methylphthalimide.<sup>7</sup> (e) Compound **9** was compared to an authentic sample.<sup>8</sup> (f) Compound **11** was unstable, readily closing to **1**.

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contention that the excited state of **1** undergoes intramolecular electron transfer and conclusively demonstrates that the intramolecular radical ion pair must be a key intermediate to **4** and **8**. These results show that radical-radical coupling of the radical ion pair (path b) occurs, establishes that this process can occur in competition with back electron transfer and proton transfer, and requires that it be considered as a possible route in other systems. We are presently searching for other examples of this process.

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### One- and Two-Electron Photooxidation of a Molybdenum(III) Thiocyanate Complex

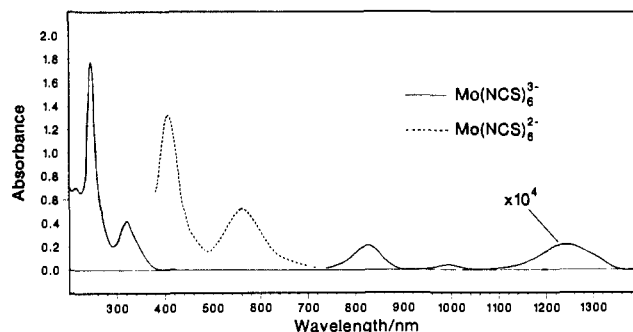
Qin Yao and Andrew W. Maverick\*

Department of Chemistry, Washington University  
St. Louis, Missouri 63130

Received April 1, 1986

There has been continuing interest in the properties of excited states of transition-metal complexes and in their use as catalysts for redox reactions. However, photoredox processes have generally been confined to one-electron transfers, while many desirable redox reactions require the transfer of two or more electrons in a single substrate molecule. One-electron photoredox reactions, such as those of polypyridine complexes of chromium(III)<sup>1</sup> and ruthenium(II),<sup>2</sup> and multielectron redox activity in ruthenium- and osmium-based systems,<sup>3</sup> have been investigated separately. Our goal has been to generate multielectron oxidants photochemically by beginning with d<sup>3</sup> complexes of the early transition metals: initial excited-state electron transfer is to be followed by a second thermal electron transfer, thus producing a net two-electron transformation. In addition to our recent work with vanadium(II),<sup>4</sup> we have been interested in the heavier d<sup>3</sup> ions, whose photoredox properties have not been studied before. We now report facile ground- and excited-state oxidation of the hexakis(thiocyanato-N)molybdate(3-) ion, Mo(NCS)<sub>6</sub><sup>3-</sup>, and the disproportionation of the initial electron-transfer product Mo(NCS)<sub>6</sub><sup>2-</sup> to generate the molybdenum(V) dimer (SCN)<sub>3</sub>MoO(μ-O)<sub>2</sub>MoO(NCS)<sub>3</sub><sup>4-</sup>. These observations constitute the first photoredox reactions ever recorded in a molybdenum(III) complex. They indicate not only that a broad new class of transition-metal complexes can be used as redox sensitizers but that many such systems are likely to be useful in photoinitiated net two-electron-transfer processes.

Octahedral d<sup>3</sup> complexes have the <sup>4</sup>A<sub>2g</sub> ground state and the low-lying d-d excited states <sup>4</sup>T<sub>2g</sub>, <sup>2</sup>E<sub>g</sub>, <sup>2</sup>T<sub>1g</sub>, and <sup>2</sup>T<sub>2g</sub>.<sup>1</sup> The phosphorescent <sup>2</sup>E<sub>g</sub> excited state is long-lived if it is lower in energy than <sup>4</sup>T<sub>2g</sub>; for chromium(III) this occurs only with strong-field ligands such as CN<sup>-</sup> and 1,10-phenanthroline. In second- and third-row metal complexes, on the other hand, all three doublets lie below <sup>4</sup>T<sub>2g</sub>; this has been shown recently for MoCl<sub>6</sub><sup>3-</sup> in the elegant absorption and emission spectroscopic study of Flint and Paulusz.<sup>5</sup> A variety of molybdenum(III) complexes, then, should have excited states sufficiently long lived for photoredox reactions. We chose Mo(NCS)<sub>6</sub><sup>3-</sup> for our initial experiments because its



**Figure 1.** Room-temperature electronic absorption spectra: (—) K<sub>3</sub>Mo(NCS)<sub>6</sub> in water (2 × 10<sup>-5</sup> M, 200–420 nm; 0.2 M, 740–1400 nm); (---) Mo(NCS)<sub>6</sub><sup>2-</sup> in CH<sub>3</sub>CN (2 × 10<sup>-5</sup> M).

**Table I.** Half-Wave Potentials from Cyclic Voltammetry

couple	E <sub>1/2</sub> /V <sup>a</sup>
Mo(NCS) <sub>6</sub> <sup>2-/3-</sup>	0.05
TCNE <sup>0/-b</sup>	-0.16
1,4-C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>0/-</sup>	-1.08
1,3-C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>0/-</sup>	-1.27

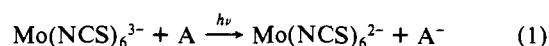
<sup>a</sup> Reversible one-electron couples in CH<sub>3</sub>CN (0.1 M (C<sub>4</sub>H<sub>9</sub>)(O<sub>3</sub>SCF<sub>3</sub>)), vs. Fc/Fc<sup>+</sup> (Fc = ferrocene). <sup>b</sup> TCNE = ethene-tetracarboxitrile.

spectral and redox properties had been studied before.

The weak absorption bands between 740 and 1400 nm in Mo(NCS)<sub>6</sub><sup>3-</sup> (Figure 1) have been assigned to the three quartet → doublet transitions,<sup>6</sup> with <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> probably obscured by the intense ligand-to-metal charge-transfer absorption that begins near 400 nm.<sup>7</sup> The ion has not been reported to luminesce.

Sykes and co-workers showed that IrCl<sub>6</sub><sup>2-</sup> oxidizes Mo(NCS)<sub>6</sub><sup>3-</sup> to the deep red-brown molybdenum(IV) complex Mo(NCS)<sub>6</sub><sup>2-</sup>, which is stable in nonaqueous solvents but disproportionates in water to give Mo(NCS)<sub>6</sub><sup>3-</sup> and a molybdenum(V) species.<sup>8</sup> Thus, Mo(NCS)<sub>6</sub><sup>3-</sup> is subject to one-electron oxidation, and the initial molybdenum(IV) product can readily undergo a second electron transfer. We have now accomplished these one- and two-electron oxidations of Mo(NCS)<sub>6</sub><sup>3-</sup> photochemically.

Conventional flash irradiation (350–450 nm) of solutions of K<sub>3</sub>Mo(NCS)<sub>6</sub>·4H<sub>2</sub>O<sup>8</sup> and 1,4-dinitrobenzene in CH<sub>3</sub>CN<sup>9</sup> leads to transient absorption signals characteristic of Mo(NCS)<sub>6</sub><sup>2-</sup> (410 and 560 nm; see Figure 1).<sup>10</sup> These absorptions decay with second-order kinetics, as expected for reaction 2 (A = 1,4-di-



nitrobenzene). Based on kinetic data, and on absorption spectral data for Mo(NCS)<sub>6</sub><sup>2-</sup> (ε<sub>560</sub> = 2.6 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup><sup>10</sup>), k<sub>b</sub> is approximately 8 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>, a reasonable value for a diffusion-controlled reaction between two anions. Comparable experiments in acetone solution give transient-absorption signals attributable to A<sup>-</sup> (λ > 750 nm<sup>11</sup>) as well as those expected for Mo(NCS)<sub>6</sub><sup>2-</sup>.

Electrochemical data for Mo(NCS)<sub>6</sub><sup>3-</sup> and several electron acceptors are shown in Table I. Mixtures of Mo(NCS)<sub>6</sub><sup>3-</sup> and TCNE undergo slight spontaneous electron transfer; absorption spectra of the mixtures yield an equilibrium constant for the reaction Mo(NCS)<sub>6</sub><sup>3-</sup> + TCNE ⇌ Mo(NCS)<sub>6</sub><sup>2-</sup> + TCNE<sup>-</sup> of 0.0004 in CH<sub>3</sub>CN at room temperature. This is in agreement with the half-wave potentials for the two redox couples. With

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