electron reduction of radical VI followed by protonation of the resulting carbanion (Scheme II) would account for the high level of C-9 deuteration of product III for reaction in acetonitrile–D_2O as well as the absence of aminoalkyl radical–VI combination product. The formation of aminoalkyl radical combination products in some amine photooxidation reactions (e.g., with stilbene[2,12] or pyridine[8]) but only redox products in others (e.g., with I or benzophenone[9]) may be determined by the electron affinity of the other member of the radical pair.[20]

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Electron-Transfer Chemistry of the Luminescent Excited State of Octachlorodirhenate(III)†

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Previous studies in our laboratory have established that the luminescent excited state[1] of $Re_2Cl_8^{2-}$ ($Re_2Cl_8^{2-*}$; 1.75 eV, 0.14 μs, CH_3CN soln; 25 °C)[2] is a $\delta\delta^*$ singlet.[3] Owing to our interest in photoredox processes involving polynuclear inorganic complexes,[4] we decided to explore the chemistry of $Re_2Cl_8^{2-*}$ with potential donor and acceptor molecules. These experiments have revealed that $Re_2Cl_8^{2-*}$ functions as a strong oxidant as well as a moderately good reductant in nonaqueous solutions.

Various electron acceptors (e.g., TCNE, chloranil, $PW_{12}O_{40}^{3-}$) quench the $Re_2Cl_8^{2-*}$ luminescence in nonaqueous solutions (25 °C), thereby producing $Re_2Cl_8^-$ and the reduced acceptor. A transient signal attributable to $TCNE^-$ was observed in flash kinetic spectroscopic studies[5] of dichloromethane solutions containing TCNE (10^{-3} M) and $(Bu_4N)_2Re_2Cl_8$ (10^{-4} M) (25 °C); the decay of the transient was found to follow second-order kinetics ($k = 3.2\ (7) \times 10^9\ M^{-1}\ s^{-1}$).[6] Similar flash spectroscopic experiments on the $Re_2Cl_8^{2-}$/chloranil system revealed second-order kinetic behavior for the disappearance of the photogenerated chloranil anion ($k = 1.8\ (7) \times 10^9\ M^{-1}\ s^{-1}$ in CH_3CN solution; $k = 1.5\ (2) \times 10^9\ M^{-1}\ s^{-1}$ in acetone solution).[6] Our observation that the rates of the back-reactions are near the diffusion limit suggests that very little internuclear reorganization is associated with electron transfer to the δ orbital of $Re_2Cl_8^-$.

The luminescence of $Re_2Cl_8^{2-*}$ also is quenched by secondary and tertiary aromatic amines[7] in acetonitrile solution. Neither the electronic absorption nor the emission spectrum of $Re_2Cl_8^{2-}$ changes in the presence of the quenchers, and no evidence for the formation of new chemical species was observed in flash spectroscopic or steady-state emission experiments. The measured rate constants for the steady-state quenching of the $Re_2Cl_8^{2-*}$ luminescence are given in Table I. In accord with expectation for electron-transfer quenching,[8,9] a plot of log k_q vs. $E_{1/2}(D^+/D)$ is linear for large $E_{1/2}(D^+/D)$ values (slope = 12.7 (3) V^{-1}; quenchers 3–9) and approaches a limiting value when $E_{1/2}(D^+/D)$ is small (quenchers 1 and 2) (Figure 1). We propose that the products of the quenching reaction form a strongly associated ion pair,[10] $Re_2Cl_8^{3-}\cdot D^+$; that separated $Re_2Cl_8^{3-}$ and D^+ species were not observed in flash spectroscopic experiments indicates unusually efficient back-electron-transfer.

Table I. Rate Constants for Quenching of $Re_2Cl_8^{2-*}$ by Aromatic Amines in Acetonitrile Solution at 25 °C

quencher (D)	$E_{1/2}$[a]	k_q(obsd)[b]	k_q(corr)[c]
(1) *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine	0.10	5.4×10^9	7.6×10^9
(2) *N*,*N*,*N*′,*N*′-tetramethylbenzidine	0.36	2.2×10^9	2.5×10^9
(3) dimethoxydiphenylamine	0.58	1.1×10^9	1.2×10^9
(4) phenothiazine	0.59	8.4×10^8	8.8×10^8
(5) *N*,*N*-dimethyl-*p*-toluidine	0.70	1.3×10^7	1.3×10^7
(6) 10-methylphenothiazine	0.73	9.5×10^6	9.5×10^6
(7) diphenylamine	0.79	6.1×10^6	6.1×10^6
(8) *N*,*N*-diethylaniline	0.76	2.2×10^6	2.2×10^6
(9) *N*,*N*-dimethylaniline	0.81	1.5×10^6	1.5×10^6

[a] Reduction potentials (D^+/D, V vs. SCE) from cyclic voltammetric measurements in CH_3CN solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP). [b] Second-order rate constants ($M^{-1}\ s^{-1}$); $[(Bu_4N)_2Re_2Cl_8] = 5 \times 10^{-4}$ M; $\mu = 0.1$ M (TBAP). [c] Rate constants ($M^{-1}\ s^{-1}$) corrected for diffusion effects.

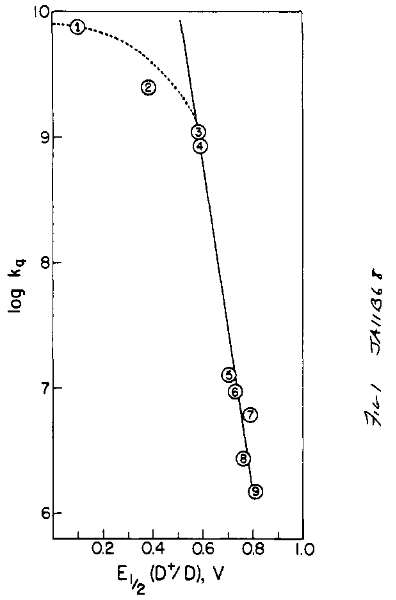

Figure 1. Plot of log k_q vs. $E_{1/2}(D^+/D)$; conditions and quencher numbering as in Table I.

The two reduction potentials involving $Re_2Cl_8^{2-*}$ (−/2−*; 2−*/3−) may be estimated from the results of spectroscopic and electrochemical[11] experiments, as displayed below in the form of

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† Happy 60th birthday to George Sims Hammond, who first encouraged one of us (H.B.G.) to do research in inorganic and organometallic photochemistry.

(1) Trogler, W. C.; Solomon, E. I.; Gray, H. B. *Inorg. Chem.* **1977**, *16*, 3031–3033.

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(3) Miskowski, V. M.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 86–89.

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(5) Experiments were performed with a flash spectroscopic instrument described previously (Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 6761–6764).

(6) Rate constants were calculated by using the following ε values ($M^{-1}\ cm^{-1}$): $TCNE^-$, ε (438 nm) 7.43×10^3 (CH_2Cl_2 solution); chloranil anion, ε (460 nm) 4.98×10^3 (CH_3CN solution); ε (466 nm) 4.92×10^3 (acetone solution).

(7) Primary amines react thermally with $Re_2Cl_8^{2-}$.

(8) (a) Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519–2523 and references therein. (b) Bock, C. R.; Connor, J. A.; Buitterez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815–4824.

(9) The triplet energies of the quenchers are substantially greater than the $\delta\delta^*$ energy (1.75 eV) of $Re_2Cl_8^{2-}$, thereby ruling out an energy-transfer quenching mechanism. For example, the triplet energy of quencher 4 is 2.62 eV (Alkaitis, S. A.; Grätzel, M.; Henglein, A. *Berg. Bunsenges. Phys. Chem.* **1975**, *79*, 541–546). Selected others are as follows: quenchers 7, 3.12 eV (Terenin, A.; Ermolaev, V. *Trans. Faraday Soc.* **1956**, *52*, 1042–1052); 8, 2.95 eV (Dubroca, C.; Loazno, P. *Chem. Phys. Lett.* **1974**, *24*, 49–54); 9, 2.99 eV (Lim, E. C.; Chakrabarti, S. K. *Chem. Phys. Lett.* **1967**, *1*, 28–31).

(10) Ion-pair intermediates have been proposed to explain the lack of transient formation in the oxidative quenching of $Ru(bpy)_3^{2+*}$ by nitroaromatics (Bock, C. R.; Whitten, D. G.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 2909–2911). In our case the lifetime of such an intermediate ($Re_2Cl_8^{3-}\cdot D^+$) would be expected to be much too short (<1 μs) to be detectable with the instrumentation employed.[5]

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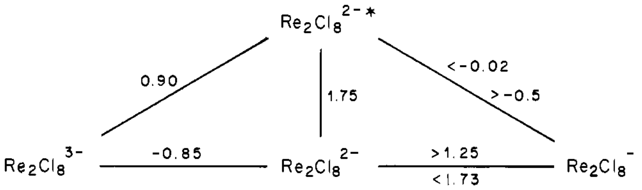
a modified Latimer diagram (excited-state energy in eV; electrode potentials vs. SCE in CH_3CN solution):



The $Re_2Cl_8^{2-*/3-}$ reduction potential of 0.90 V vs. SCE is consistent with the relatively low k_q values measured for quenchers 5–9 (Table I). The corresponding value for $Re_2Cl_8^{-/2-*}$ is not well determined, because the electrochemical oxidation of $Re_2Cl_8^{2-}$ to $Re_2Cl_8^{-}$ is not reversible. The estimated upper limit [$E°(Re_2Cl_8^{-/2-*} < -0.02$ V vs. SCE) is based on our finding that chloranil is an efficient quencher.[12] This in turn places an upper limit of 1.73 V vs. SCE on the $Re_2Cl_8^{-/2-}$ reduction potential in acetonitrile solution.

The rich redox chemistry of $Re_2Cl_8^{2-*}$ is potentially exploitable for photochemical energy storage applications. In this connection we emphasize that the $\delta\delta^*$ singlet provides a facile route to an extremely powerful inorganic oxidant, $Re_2Cl_8^{-}$, a species that has not been generated cleanly by other means. The goal of experiments now in progress in our laboratory is to elucidate the chemistry of various photogenerated octachlorodirhenates (2–*, –, 3–) in aqueous solution.

Acknowledgment. We thank Dan Buttry for assistance with the electrochemical experiments and R. A. Marcus and A. W. Maverick for several helpful discussions. This research was supported by National Science Foundation Grant CHE78-10530.

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(11) Cyclic voltammetric measurements; our value of –0.85 V vs. SCE for $E_{1/2}(Re_2Cl_8^{2-/3-})$ in acetonitrile solution ($[(Bu_4N)_2Re_2Cl_8] = 1 \times 10^{-3}$ M, [TBAP] = 0.1 M, 25 °C) accords closely with the results of earlier electrochemical experiments (Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 383–387).

(12) For chloranil/chloranil⁻ in acetonitrile solution (25 °C), $E_{1/2} = -0.02$ V vs. SCE (Peover, M. E. *Nature (London)* **1961**, *191*, 702–703).

Stable Simple Enols. 2.[1] Correlated Rotation in Two β,β-Dimesityl-α-arylethenols. A Probable Example of a Three-Ring Flip

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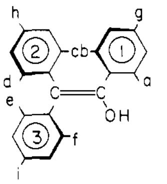
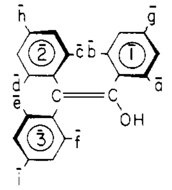
Molecular propellers of the form Ar_3X and Ar_3XY (X = C, B, N) show correlated rotation.[2b,c] Four different rotational modes[2] which lead to helicity reversal involve zero-, one-, two-, and three-ring flips. In the zero- and three-ring flips all three rings rotate in the same direction; in the one- and two-ring flips, two rings rotate in one direction and the third rotates in the opposite direction.[3] It has been established that the rotational mode of lowest activation energy is the two-ring flip.[4]

The triarylvinyl system $Ar^3Ar^2C{=}C(Y)Ar^1$ is the vinyl "propeller" analogue of $Ar^1Ar^2Ar^3CY$. Because of the presence of the double bond there are additional potential routes and less degeneracy of the flipping routes, leading to enantiomerization and a larger maximum number of stereoisomers. To our knowledge, these routes have not been studied or analyzed previously.

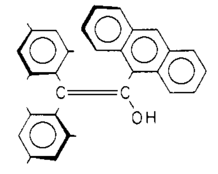
Several triarylethenols are stable in the enol form.[5] In a continuation of our studies of their properties,[1,6] the ^{1}H NMR spectra and internal rotation of several enols were studied. Most investigated was trimesitylethenol (**1**)[5c] which by X-ray diffraction is a distorted molecular propeller[7] capable of existing as enantiomeric right- or left-handed forms **1a** and **1b** (letters with an overbar indicate enantiomeric sites). All the six *o*-methyl groups,



1a



1b



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the three *p*-methyl groups, and the six aromatic protons of each enantiomer are diastereotopic. The 300-MHz ^{1}H NMR spectrum ($C_6D_5NO_2$, 298 K) shows 16 separate singlets, 9 methyl groups (δ 1.84–2.68), 1 OH group (δ 5.46), and 6 aromatic protons (δ 6.39–6.98).

NMR signals were assigned by isotopic labeling of the methyl groups of the β rings and by synthesis of β-*p*-*tert*-butyl- and α-2,6-dimethylphenyl analogues.[8] The saturation transfer technique[9] was valuable for identifying unequivocally the coalescing protons on each ring. Irradiation of one *o*-Me (or Ar–H) signal to saturation caused an intensity diminution of another *o*-Me (or Ar–H) peak and vice versa, indicating pairs of protons which are involved in a dynamic exchange process.[9]

Upon raising the temperature the three pairs of *o*-methyl groups and the three pairs of aromatic protons coalesce. We measured four coalescence temperatures (T_c) with practically identical $\Delta G_c^‡$ values: 18.1 (Ar–H in a β ring; $\Delta\nu = 16$ Hz) and 18.4 (c → d or e → f; $\Delta\nu = 10$ Hz) kcal mol^{-1} at 352 K and 18.2 (c → d or e → f; $\Delta\nu = 84$ Hz), and 18.4 (a → b; $\Delta\nu = 61$ Hz) kcal mol^{-1} at 376 K.[10]

Four different dynamic processes may account for the coalescence. (a) Rotation around the double bond—this has precedents[11] but is excluded since the *p*-methyls (h, i) of the β rings do not coalesce. (b) Reversible S_N1 ionization of the OH group to form a vinyl cation—this is unlikely due to the low nucleofugality of the OH group and the slowness of vinylic solvolysis.[12,13] (c) Ketonization followed by enolization—this is excluded since trimesitylethanone cannot be prepared,[5c] the CF_3COOH-catalyzed

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(3) A "flip" is a passage through a plane perpendicular to the reference plane with no edge interchange. The nonflipping rings pass through the reference plane with edge interchange.

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(13) With good nucleofuges, this route should be considered together with possible degenerate rearrangements across the double bond of the intermediate ion.[12]

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