Articles

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Electron-Transfer Chemistry of Electronically Excited Octachlorodirhenate(III)

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Confacial bioctahedral $Re_2Cl_9^-$ undergoes electrochemically reversible one-electron reduction to $Re_2Cl_9^{2-}$ (0.53 V vs. SCE) in CH_2Cl_2 solution. The mixed-valence complex is reduced further in an irreversible step to quadruply bonded $Re_2Cl_8^{2-}$. Conversely, electrochemical oxidation of $Re_2Cl_8^{2-}$ in CH_2Cl_2 solutions contaminated with Cl^- yields $Re_2Cl_9^{2-}$, and only in highly purified solutions is the heretofore unreported $Re_2Cl_8^{-/2-}$ couple observed (1.25 V vs. SCE). The facile interconversion between confacial bioctahedral and quadruply bonded systems also is demonstrated in a photoreaction in which $Re_2Cl_8^-$, produced by quenching electronically excited $Re_2Cl_8^{2-}$ with chloranil or tetracyanoethylene, combines with Cl^- to give $Re_2Cl_9^{2-}$. When the quencher is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (whose reduction potential is 0.60 V vs. SCE), the photoproduct is $Re_2Cl_9^-$.

Much of our research in recent years has been directed toward understanding oxidation-reduction processes involving electronically excited inorganic species.[1-6] Of special interest in this context is $Re_2Cl_8^{2-}$, whose luminescent excited state ($\delta\delta^*$ singlet, or $^1\delta\delta^*$; 1.75 eV; 140 ns in CH_3CN, 70 ns in CH_2Cl_2)[7] is a strong oxidant and a moderately good reductant.[8]

In previous experiments we have shown that the $\delta\delta^*$ singlet of $Re_2Cl_8^{2-}$ is efficiently quenched by various one-electron acceptors and that the products back-react rapidly to give starting materials.[8] It occurred to us that it might be possible to trap the initial product, $Re_2Cl_8^-$, in the presence of excess Cl^-, thereby giving the confacial bioctahedral $Re_2Cl_9^{2-}$, which could then be oxidized to $Re_2Cl_9^-$. The results of experiments along these lines are reported herein.

Experimental Section

Materials. The tetrabutylammonium salt of $Re_2Cl_8^{2-}$ was prepared by either of two procedures: (i) hypophosphorous acid reduction of $KReO_4$ (Alfa Ventron) or (ii) reductive coupling of NBu_4ReO_4 with benzoyl chloride.[9] Reagent grade solvents and acids were thoroughly deoxygenated prior to use; otherwise, they were used as received. All solvent transfers were carried out under high-purity argon. Tetrabutylammonium perrhenate was prepared by addition of an aqueous solution of NBu_4Br (Eastman) to a hot aqueous solution of $KReO_4$. The white flocculent precipitate was thoroughly washed with diethyl ether and dried under vacuum for 24 h. The crude blue powder of $(NBu_4)_2Re_2Cl_8$, obtained from either of the above synthetic routes, was purified as a microcrystalline solid upon cooling hot acidified methanol solutions that were saturated with the compound.

Confacial bioctahedral $NBu_4Re_2Cl_9$ was prepared from $(NBu_4)_2Re_2Cl_8$ by a standard procedure.[10] Recrystallization of $NBu_4Re_2Cl_9$ from chloroform yielded small, wafer-thin, green platelets. The preparation of $Re_2Cl_9^{2-}$ by the reduction of $Re_2Cl_9^-$ with various metals (Cu, Zn, and Hg)[10] gave violet oils that seldom crystallized. A better synthetic method involved addition of NBu_4Cl (in molar excess to the $Re_2Cl_9^-$ salt) to an acidified CH_2Cl_2/EtOH solution saturated with $NBu_4Re_2Cl_9$. A stream of hydrogen was passed over a platinum gauze that was immersed in solution, causing the green solution to turn violet within minutes. As CH_2Cl_2 evaporated with continued bubbling, purple microcrystalline $(NBu_4)_2Re_2Cl_9$ precipitated from the EtOH-enriched solution. The product was collected, washed with EtOH, and dried.

Tetracyanoethylene (TCNE; Aldrich) was recrystallized from chlorobenzene and vacuum sublimed before use. Chloranil (1,2,5,6-tetrachloro-1,4-benzoquinone; MCB) was recrystallized three times from toluene before use and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; Aldrich) was used without further purification. Tetrabutylammonium perchlorate (TBAP) (NBu_4ClO_4; Southwestern Analytical Chemicals) was dissolved in ethyl acetate, dried over $MgSO_4$, and recrystallized from a pentane/ethyl acetate solution. Tetrabutylammonium chloride (NBu_4Cl; Southwestern Analytical Chemicals) was used without further purification.

Acetonitrile (UV) and dichloromethane were obtained from Burdick and Jackson Laboratories. The acetonitrile was vacuum distilled onto activated grade I alumina (Woelm), allowed to stand for 2 days with mixing, and then vacuum distilled onto 3-Å molecular sieves and stored under vacuum. Dichloromethane was vacuum distilled onto activated 4-Å molecular sieves and stored under vacuum.

Apparatus and Procedures. EPR spectra were recorded on a Varian E-line Century Series X-band spectrometer equipped with an Air Products Heli-Trans low-temperature system. All EPR experiments were performed at 10 K on frozen CH_2Cl_2 solutions that had been subjected to five freeze-pump-thaw cycles.

Cyclic voltammograms were obtained with a Princeton Applied Research (PAR) 173 potentiostat/galvanostat driven by a PAR 175 universal programmer with Pt-button working, Pt-wire auxiliary, and Ag-wire reference electrodes. The auxiliary electrode was concentrically wrapped around the button working electrode in order to provide uniform current densities for scan rates greater than 500 mV s^{-1}. A conventional H-cell design was used for all electrochemical experiments. Electrode potentials were related to the saturated calomel reference by the $Re_2Cl_8^{2-/3-}$ couple,[11] which was present in all cases. Peak separations in the rhenium halide (2 mM solutions with 0.1 M TBAP) cyclic voltammograms were corrected for uncompensated cell resistance by employing ferrocene as an internal standard. Bulk electrolysis experiments were performed with the above electrochemical apparatus in conjunction with a PAR 179 coulometer. A Pt-basket working electrode and a Pt-foil auxiliary electrode were substituted

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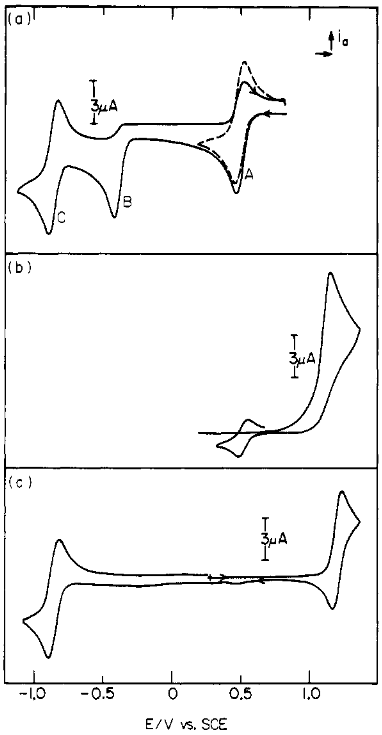

Figure 1. Cyclic voltammograms (CH_2Cl_2, 22 °C; 0.1 M TBAP; scan rate 200 mV s^{-1}): (a) 2 mM $NBu_4Re_2Cl_9$; (b) 2 mM $(NBu_4)_2Re_2Cl_8$/10 mM NBu_4Cl; (c) 2 mM $(NBu_4)_2Re_2Cl_8$.

to facilitate the bulk electrolysis experiment. A Hewlett-Packard Model 8450A spectrometer was used to record optical spectra of electrolysis products.

Photolysis experiments were performed in two-arm evacuable cells equipped with Kontes quick-release Teflon valves. Tetrabutylammonium chloride was placed in one arm of the cell and $(NBu_4)_2Re_2Cl_8$ in the other. Quencher was added to the cell against an argon counterflow after the NBu_4Cl had been dried at 100 °C for 4 h under high vacuum (<1 μm). The cell was reevacuated, and the solvent was transferred by vacuum distillation. All solutions were subjected to five freeze-pump-thaw cycles. Photolyses were performed with a 1000 W high-pressure Hg(Xe) lamp, and high-energy light was eliminated by a series of Corning cutoff filters. In a typical experiment 1 mM $(NBu_4)_2Re_2Cl_8$, 10 mM quencher, and 100 mM NBu_4Cl were irradiated in CH_3CN or CH_2Cl_2 solution at 10 ± 1 °C. Photolysis reactions were monitored by electronic absorption spectroscopy (Cary 17). Photolysis products were isolated by column chromatography.

Results and Discussion

Electrochemistry. Dichloromethane solutions of $NBu_4Re_2Cl_9$ were examined by cyclic voltammetry (Figure 1a). When the potential is cathodically scanned from 0.8 V vs. SCE, three reduction waves are observed, of which two show anodic return waves. The irreversible component (wave B) does not show an anodic return wave for scan rates up to 500 V s^{-1}. The wave illustrated by the dashed line in Figure 1a (wave A) is obtained if the scan is reversed before wave B is reached. A reversible electrode process for wave A is indicated by the linear plots of the anodic and cathodic currents vs. (scan rate)$^{1/2}$ (for scan rates of 20–500 mV s^{-1}), the values of 1.02 ± 0.03 for the ratio of the anodic to cathodic peak currents, and the peak separation of 65 mV.[12] Bulk electrolysis of a green CH_2Cl_2 solution of $Re_2Cl_9^-$ at 0.2 V vs. SCE is complete upon passage of 1.04 equiv of electrons into solution. An optical spectrum of the resulting violet electrolyzed solution is identical with that of $Re_2Cl_9^{2-}$, indicating wave A to be the $Re_2Cl_9^{-/2-}$ couple with a measured half-wave potential of 0.53 V vs. SCE. Bulk electrolysis of the violet $Re_2Cl_9^{2-}$ solution at −0.5 V vs. SCE passes 1.06 equiv of electrons into solution, and an optical spectrum of the blue electrolysis product shows it to be $Re_2Cl_8^{2-}$. These experiments confirm that wave B corresponds to the irreversible one-electron reduction of $Re_2Cl_9^{2-}$ to form $Re_2Cl_8^{2-}$. Wave C of Figure 1a, therefore, corresponds to the reversible $Re_2Cl_8^{2-/3-}$ couple at −0.85 V vs. SCE.[11]

The cyclic voltammogram recorded for $Re_2Cl_8^{2-}$ in CH_2Cl_2 solution (Figure 1c) shows a one-electron-oxidation wave at 1.25 V vs. SCE in addition to the $Re_2Cl_8^{2-/3-}$ couple. The oxidation wave is quasi-reversible for scan rates up to 500 mV s^{-1}. However, at scan rates of 10 V s^{-1}, the ratio of the anodic to cathodic peak current (i_a/i_c) is equal to 1.02 with a peak separation of 70 mV. The ratio remains constant at 1.02 ±0.02 for scan rates from 10 to 100 V s^{-1}. The peak separation increases monotonically with increasing scan rate (130 mV at 100 V s^{-1}), a result of either slow-electron-transfer kinetics at the electrode surface or uncompensated cell resistance. If NBu_4Cl is added to the $Re_2Cl_8^{2-}$ solution, the cyclic voltammogram in Figure 1b is obtained. A large anodic wave with no cathodic component is observed when the potential is anodically scanned from 0.2 V vs. SCE. Presumably, the large anodic wave corresponds to the oxidation of Cl^-, $Re_2Cl_8^{2-}$, and $Re_2Cl_9^{2-}$. Scanning cathodically from the large oxidation wave gives rise to the reversible wave at 0.53 V vs. SCE, indicating the formation of confacial bioctahedral species. The production of $Re_2Cl_9^-$ is observed for scan rates up to 500 V s^{-1}. The cyclic voltammetric results in the presence of anionic donors such as Cl^- explain why the $Re_2Cl_8^{-/2-}$ couple may be observed only for highly purified samples of $Re_2Cl_8^{2-}$.

The reaction of Cl_2 with $Re_2Cl_8^{2-}$ is too slow[13] to account for the observed rate of electrochemical production of $Re_2Cl_9^-$. Thus it is likely that the confacial bioctahedral species is formed by Cl^- addition to the one-electron-oxidized product, $Re_2Cl_8^-$. From cyclic voltammetric measurements a lower limit of 10^3 M^{-1} s^{-1} may be estimated for the rate constant of the reaction of Cl^- with $Re_2Cl_8^-$, indicating that it is an efficient process.

Photochemistry. Dichloromethane and acetonitrile solutions of $Re_2Cl_8^{2-}$, oxidative quencher (TCNE or chloranil, in 10-fold molar excess), and Cl^- (in 100-fold molar excess) were irradiated at >600 nm. Upon irradiation, the absorption band of $Re_2Cl_8^{2-}$ at 685 nm disappeared with concomitant appearance of the 736-nm absorption band of $Re_2Cl_9^{2-}$. Unfortunately, the reaction could not be monitored by optical absorption spectroscopy at higher energy, owing to intense absorption attributable to the red TCNE/Cl^- charge-transfer complex. Spectral data from a typical photolysis experiment are shown in Figure 2. The photolysis reaction is quantitative on the basis of the molar extinction coefficients of the 685-nm absorption band of $Re_2Cl_8^{2-}$ (ϵ_{685} = 2610 M^{-1} cm^{-1}, CH_2Cl_2) and the 736-nm band of $Re_2Cl_9^{2-}$ (ϵ_{736} = 1380 M^{-1} cm^{-1}, CH_2Cl_2). Reaction rates depend on both Cl^- and quencher concentrations. Dichloromethane and acetonitrile solutions identical with those used for photolysis reactions were prepared and stored in the dark at 50 °C. No reaction occurred after 24 h. Photolysis (λ > 660 nm for 3 days) of $Re_2Cl_8^{2-}/Cl^-$ (100-fold molar excess) and $Re_2Cl_8^{2-}$/TCNE (10-fold molar excess in CH_2Cl_2 and CH_3CN) did not lead to the production of $Re_2Cl_9^{2-}$.

In addition to optical absorption spectra, the photolysis reaction mixtures also were characterized by EPR and elec-

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[13] Addition of $Re_2Cl_8^{2-}$ to a deaerated Cl_2-saturated (1.59 M at 20 °C: Vdovichenko, V. T.; Kondratenko, V. I. *Khim. Promst. (Moscow)* **1967**, *43*, 290–291) CH_2Cl_2 solution containing 0.1 M Cl^- produces $Re_2Cl_9^-$. The reaction follows first-order kinetics over 3 half-lives ($k \sim 10^{-3}$ s^{-1}) (Nocera, D. G., unpublished results).

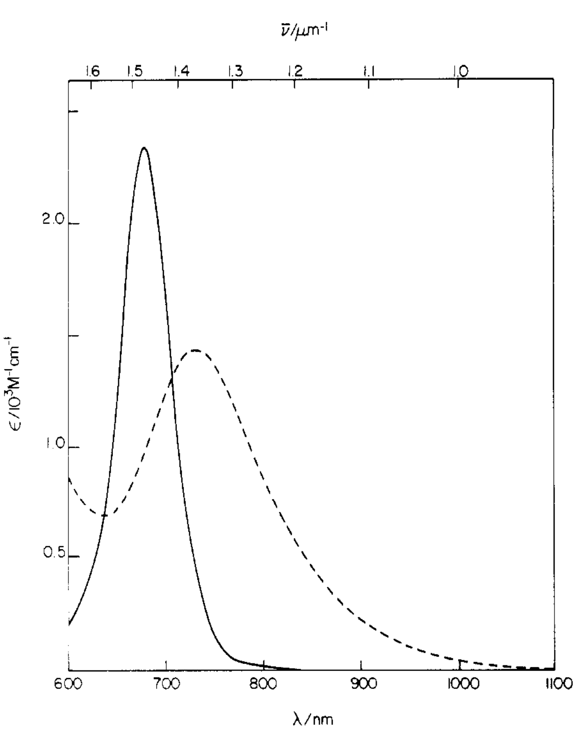

Figure 2. Spectral changes upon irradiation (λ > 660 nm) of a dichloromethane solution of $Re_2Cl_8^{2-}$ (0.6 mM), TCNE (6 mM), and NBu_4Cl (60 mM) at 10 °C: ---, $Re_2Cl_8^{2-}$; —, photolysis product.

trochemical mesurements. EPR spectra of photolysis solutions with TCNE as the oxidative quencher show the characteristic nine-line signal of the radical anion.[14] The EPR spectrum of a frozen CH_2Cl_2 solution displays a weak axial doublet signal with $g_\perp = 2.00$ and $g_\parallel = 1.93$. Unfortunately, these g values are near that of the TCNE radical anion, thereby hindering EPR detection of the $Re_2Cl_9^{2-}$ species in the photolysis reaction mixture. Both the $TCNE^{0/-}$ (0.35 V vs. SCE) and $Re_2Cl_9^{-/2-}$ (0.53 V vs. SCE) couples, however, are observed in the cyclic voltammogram of the photolysis solution.

The photochemical production of $Re_2Cl_9^{2-}$ in the presence of Cl^- and oxidative quencher demonstrates that the Cl^--trapping reaction efficiently competes with the extremely fast thermal back-reaction between $Re_2Cl_8^-$ and $TCNE^-$ ($k = 3.2 \times 10^9$ M^{-1} s^{-1} in CH_2Cl_2) or chloranil(1−) ($k = 1.8 \times 10^9$ M^{-1} s^{-1} in CH_3CN).[8] The rate-determining step for the overall reaction could be either Cl^- trapping of $Re_2Cl_8^-$ or production of $Re_2Cl_8^-$ by excited-state quenching, because both the Cl^- and quencher concentrations markedly affect the photochemical rate of $Re_2Cl_9^{2-}$ production.

In the TCNE and chloranil experiments, the reaction stops at the mixed-valence species, $Re_2Cl_9^{2-}$, because the quenchers cannot oxidize $Re_2Cl_9^{2-}$ to $Re_2Cl_9^-$. However, reactions involving quenchers with reduction potentials greater than 0.53 V vs. SCE, such as DDQ (0.60 V vs. SCE), produce $Re_2Cl_9^-$ at reasonable rates. Irradiation (λ > 660 nm, 10 °C) of a CH_2Cl_2 solution of $(NBu_4)_2Re_2Cl_8$ (1 mM), DDQ (10 mM), and NBu_4Cl (100 mM) led to the disappearance of $Re_2Cl_8^{2-}$ and the production of a species with a weak absorption system that extended to 1000 nm. Discrete features in the optical absorption spectrum of the photolysis mixture could not be distinguished from those of the DDQ/Cl^- charge-transfer complex. Cyclic voltammograms of the photolysis reaction mixture showed only one reversible wave, attributable to the $DDQ^{0/-}$ redox couple. In order to characterize the products, the photolysis solution was chromatographed on Florisil in CH_2Cl_2. A green band immediately separated from a series of yellow and red bands upon introduction of the solution onto the column. Addition of acetonitrile to the CH_2Cl_2 increased the rate of elution of the green band from the column. An optical absorption spectrum of the green product showed it to be $Re_2Cl_9^-$. The remaining yellow and red bands were all DDQ products.[15] Solutions identical with those used for photolysis experiments did not produce $Re_2Cl_9^-$ after 12 h in the dark at 22 °C. The overall photochemical reaction

$$Re_2Cl_8^{2-} + 2DDQ + Cl^- \xrightarrow[CH_2Cl_2]{\lambda > 600\ nm} Re_2Cl_9^- + 2DDQ^-$$

is equivalent to the oxidative addition of a chlorine atom across the metal–metal bond. Thus, a single low-energy photon (λ > 660 nm) facilitates a two-electron oxidation that is (at least) kinetically difficult to bring about.

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Registry No. TCNE, 670-54-2; DDQ, 84-58-2; $NBu_4Re_2Cl_9$, 41772-66-1; $Re_2Cl_9^{2-}$, 48112-92-1; $(NBu_4)_2Re_2Cl_8$, 14023-10-0; Cl^-, 16887-00-6; chloranil, 118-75-2.

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(15) Addition of DDQ/Cl^- solution to Florisil gave rise to five bands that were all identified by optical absorption spectroscopy.