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Flash Kinetic Spectroscopy of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$

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Abstract: Laser flash photolysis studies of $Re_2Cl_8^{2-}$ have revealed the presence of a short-lived transient (average $\tau(CH_3CN)$ = 134 nsec, $\tau(CH_2Cl_2)$ = 73 nsec). The same transient is observed upon 337 and 615 nm excitation. The transient exhibits an absorption maximum at 390 nm ($\epsilon \geq 7.5 \times 10^3$). Kinetic data indicate that the transient is an electronic excited state of $Re_2Cl_8^{2-}$, most probably that corresponding to the $\sigma^2\pi^4\delta^1(\delta^*)^1$ configuration. The 390-nm band is assigned to an $e_u(Cl) \rightarrow \delta$ charge-transfer transition. The analogous transient of $Re_2Br_8^{2-}$ (average $\tau(CH_2Cl_2)$ = 51 nsec) exhibits two $e_u(Br) \rightarrow \delta$ charge-transfer bands, at 490 and 555 nm. For $Re_2Cl_8^{2-}$, only 80% of the excitation energy at 337 nm is internally converted to the $\sigma^2\pi^4\delta^1(\delta^*)^1$ state. It is proposed that the remaining 20% of the upper excited states undergoes nonradiative decay to a halide-bridged intermediate, and that this pathway is the source of the photocleavage of Re_2 in acetonitrile.

It has been shown recently that uv irradiation of $[n\text{-}Bu_4N]_2[Re_2Cl_8]$ in acetonitrile solution results in cleavage of the quadruple Re_2 bond and generation of monomeric $[n\text{-}Bu_4N][ReCl_4(CH_3CN)_2]$:[2]

$$[Re_2Cl_8]^{2-} \xrightarrow[CH_3CN]{h\nu} 2[ReCl_4(CH_3CN)_2]^-$$

The photoreaction has a marked wavelength dependence, with increasing quantum yields according to 366 (0.0065) < 313 (0.017) < 254 (0.045) nm.[2,3] Interestingly, irradiation into the least energetic absorption band (680 nm) gives no photoreaction, which establishes that bond cleavage derives from one or more of the higher energy excited states.[2]

The exact mechanism of the photoreaction is not known. It is reasonable to suppose that in the active excited state the dimer dissociates into two $ReCl_4^-$ fragments, which subsequently react with CH_3CN to give the final product. Alternatively, CH_3CN molecules could bind to the excited dimer and assist the fragmentation reaction. It was felt that nanosecond flash photolysis studies of $Re_2Cl_8^{2-}$ in CH_3CN and CH_2Cl_2 (a solvent in which no net reaction occurs) would be useful in resolving this uncertainty, as inferences could then be made about the nature of any observed intermediates.

Experimental Section

The flash photolysis apparatus used either a pulsed nitrogen laser or a dye laser as an excitation source and a xenon flashlamp as a monitoring source. The N_2 laser was a Molectron UV-1000. It produced a pulse of 337-nm light with a duration of 10 nsec. The dye laser (a solution of Rhodamine B in ethanol, pumped by the N_2 laser) produced a pulse of 615-nm light with a 10-nsec duration. The N_2 and dye lasers delivered 1.08×10^{16} and 2.6×10^{15} photons per pulse, respectively, to the samples. The flashlamp produced a 3-μsec pulse of white light for monitoring transient absorptions. Both the laser and the monitoring flashes were focused down to ellipses of area approximately 0.25 cm² on the samples. The detection system consisted of a Bausch and Lomb 0.25-m monochromator and a 1 P28 photomultiplier whose output was measured on a Tektronix 475 oscilloscope (1.4 nsec rise time). Solutions were 10^{-3} to 10^{-2} *M* in the tetrabutylammonium salts of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$, and were either rigorously degassed by three to four freeze-pump-thaw cycles or were saturated with O_2.

Results and Discussion

Flash photolysis of $Re_2Cl_8^{2-}$ in CH_3CN and CH_2Cl_2 solutions produces the transient electronic absorption spectra shown in Figures 1 and 2, respectively. In both solvents the transient shows an absorption maximum at 390 nm. By using the known excitation source intensity and assuming that one photon at 615 nm produces one transient molecule, we calculate $\epsilon_{390} \geq 7.5 \times 10^3$. Lifetime data are given in Table I. First-order kinetic plots are strictly linear at all wavelengths, evidencing a single transient. Further, the similarity of the absorption spectra obtained upon 337 and 615 nm excitation in CH_3CN and CH_2Cl_2 indicates that the same transient is produced in all cases.

The transient observed is in all probability an excited state of $Re_2Cl_8^{2-}$. If it were a dissociated fragment, such as $ReCl_4^-$, it could not decay by first-order kinetics in dichloromethane, where the quantum yield for photoreaction is vanishingly small,[3] nor could it do so in acetonitrile, where we estimate the quantum yield for production of the absorbing transient to be 0.8 for 337-nm excitation (vide infra), as compared with a quantum yield of 0.017 for Re_2 photocleavage.[2] The short transient lifetimes of 73 nsec in CH_2Cl_2 and 134 nsec in CH_3CN are also consistent with this species being an electronic excited state of $Re_2Cl_8^{2-}$. As the least energetic electronic transition (centered at 680 nm in the ground state complex) has been shown[4] to be $\delta \rightarrow \delta^*$, the most reasonable candidate for the transient is an excited state with a $\sigma^2\pi^4\delta^1(\delta^*)^1$ electronic configuration in the Re_2 bond framework. The absence of a large solvent effect on the excited state absorption spectrum conclusively shows that neither CH_3CN nor CH_2Cl_2 coordinates directly to $\sigma^2\pi^4\delta^1(\delta^*)^1$ $Re_2Cl_8^{2-}$.[5]

We observe only marginally significant quenching of the

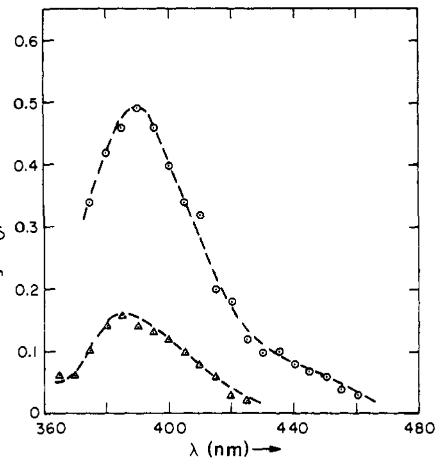

Figure 1. Electronic absorption spectra of the transient observed during flash photolysis of 6.2×10^{-3} *M* $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ acetonitrile solutions: ○, 337 nm excitation; △, 615 nm excitation. Transient absorption was not observed between 500 and 600 nm.

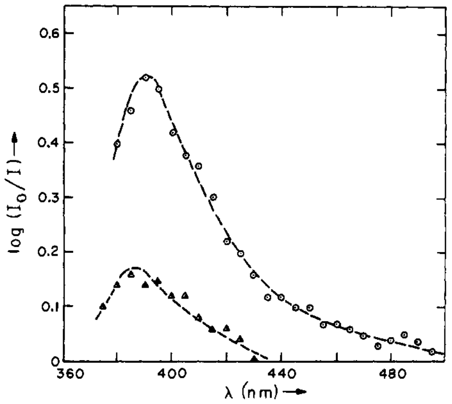

Figure 2. Electronic absorption spectra of the transient observed during flash photolysis of 6.2×10^{-3} *M* $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ dichloromethane solutions: ○, 337 nm excitation; △, 615 nm excitation. Transient absorption was not observed between 500 and 600 nm.

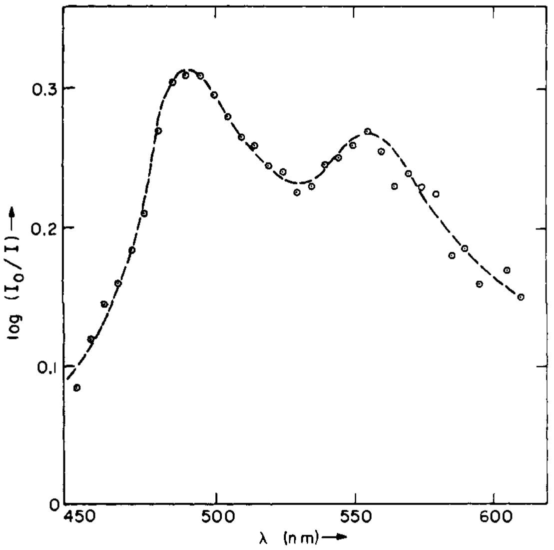

Figure 3. Electronic absorption spectrum of the transient observed during flash photolysis (337 nm excitation) of a 9.4×10^{-4} *M* solution of $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ in dichloromethane.

Table I. Lifetimes of the Transient Absorptions of Flash Photolyzed Solutions of $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ and $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$

Sample	Solvent	λ_{exc}, nm	λ_{obsd}, nm	Lifetime, nsec[a]
$[\text{Re}_2\text{Cl}_8]^{2-}$	CH_2Cl_2 (degassed)	337	400	67 ± 8
	CH_2Cl_2 (O_2 satd)	337	400	73 ± 9
	CH_2Cl_2 (degassed)	615	400	79 ± 14
	CH_3CN (degassed)	337	380	127 ± 9
	CH_3CN (degassed)	337	400	143 ± 12
	CH_3CN (O_2 satd)	337	400	118 ± 9
	CH_3CN (degassed)	615	400	131 ± 16
$[\text{Re}_2\text{Br}_8]^{2-}$	CH_2Cl_2 (degassed)	337	555	50 ± 4
	CH_2Cl_2 (degassed)	337	490	52 ± 4

[a] 95% confidence intervals. Averages of two or three determinations.

$\text{Re}_2\text{Cl}_8{}^{2-}$ transient by O_2. Although the data do not allow an accurate estimation of the O_2 quenching rate, it is clear that it is several orders of magnitude less than diffusion controlled. The low rate is probably due to the metal-metal localized nature of the excitation, in conjunction with the severe steric limitations imposed upon interaction with quenchers by the coordinated chlorides.

Flash photolysis of $\text{Re}_2\text{Br}_8{}^{2-}$ in degassed CH_2Cl_2 at 337 nm produces the transient absorption spectrum shown in Figure 3. Only one transient is observed, with peaks at 490 and 555 nm ($\epsilon_{\max} \geq 5 \times 10^3$) and a lifetime of 51 nsec (Table I). The similarity of the lifetime to that of the $\text{Re}_2\text{Cl}_8{}^{2-}$ transient suggests that once again the excited state is $\sigma^2\pi^4\delta^1(\delta^*)^1$.[6]

The bands in the $\text{Re}_2\text{Br}_8{}^{2-}$ transient are significantly red-shifted (nearly 8000 cm^{-1} in the case of the lower energy maximum) in comparison to the 390-nm peak of $\sigma^2\pi^4\delta^1(\delta^*)^1$ $\text{Re}_2\text{Cl}_8{}^{2-}$, establishing a ligand-to-metal charge transfer (LMCT) assignment. Calculations of the electronic energy levels of $\text{Re}_2\text{Cl}_8{}^{2-}$ predict the lowest allowed LMCT transition in a $\sigma^2\pi^4\delta^1(\delta^*)^1$ state to be $e_u(\text{Cl}) \rightarrow \delta$.[7] An $e_u(\text{Cl}) \rightarrow \delta$ assignment, therefore, is adopted for the 390-nm band in the $\text{Re}_2\text{Cl}_8{}^{2-}$ transient. A similar assignment is reasonable for the 555-nm band in $\sigma^2\pi^4\delta^1(\delta^*)^1$ $\text{Re}_2\text{Br}_8{}^{2-}$. Further, it is likely that the 490-nm absorption represents a second $e_u(\text{Br}) \rightarrow \delta$ transition, as theory shows that there are two rather closely spaced $e_u(\text{X})$ orbitals.[7]

The dominant excited state process in $\text{Re}_2\text{Cl}_8{}^{2-}$ after 337-nm excitation must be internal conversion to the $\sigma^2\pi^4\delta^1(\delta^*)^1$ state. However, measurements of the yields at 337 and 615 nm show that transient production accounts for only 80% of the laser power input at the lower wavelength.[8] Equal energy-loss percentages are observed in CH_3CN and CH_2Cl_2. As we detected no fluorescence or emission of any kind from the solutions upon 337-nm excitation, there must be a nonradiative decay pathway that diverts about 20% of the upper excited states from relaxation to $\sigma^2\pi^4\delta^1(\delta^*)^1$ $\text{Re}_2\text{Cl}_8{}^{2-}$. Our flash photolysis data rule against the production of mononuclear transients, although admittedly we could not have detected any such species with low absorbances between 350 and 600 nm. A likely possibility is that 20% of the upper excited states decays to an intermediate whose geometry is considerably distorted from that of either the ground state or the $\sigma^2\pi^4\delta^1(\delta^*)^1$ state. Whether this new species should, at any point in the decay channel, be regarded as an excited state of $\text{Re}_2\text{Cl}_8{}^{2-}$, or as a high-energy isomer of the ground state, is a semantic question. In any case, an intermediate that would differ structurally from $\sigma^2\pi^4\delta^1(\delta^*)^1$ $\text{Re}_2\text{Cl}_8{}^{2-}$ could be formed by movement of a chloride to a bridged configuration. Such an intermediate would be somewhat analogous to an organic cyclic bromonium ion,[9] and perhaps also to $\text{Re}_2\text{X}_9{}^{-}$ and $\text{Re}_2\text{X}_9{}^{2-}$ species[10] formed by halogen oxidation of $\text{Re}_2\text{X}_8{}^{2-}$. An attractive aspect of this tentative mechanistic

Gray et al. / Flash Kinetic Spectroscopy of $Re_2Cl_8{}^{2-}$ and $Re_2Br_8{}^{2-}$

hypothesis is that one of the rhenium atoms in the intermediate would become quite exposed, making it more susceptible to subsequent attack by nucleophilic solvents. If such a bridged conformer is indeed the source of the photochemical reactivity of $Re_2Cl_8^{2-}$, then the low quantum yield (amounting in CH_3CN to about 10% of the observed energy loss at 337 nm) implies that expulsion of solvent and return to the symmetrical configuration are competitive with Re_2 dissociation.

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The Helium(I) Photoelectron Spectra and Electronic Structure of (η^5-Cyclopentadienyl) d^6 Metal Carbonyls

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Abstract: The He(I) photoelectron spectra of $CpMn(CO)_3$, $CpRe(CO)_3$, and $CpFe(CO)_2X$, where Cp = η^5-C_5H_5 and X = Cl, Br, I, and CH_3, are presented. The low energy ionization bands (binding energies from 7 to 13 eV) are found to be sensitive to metal and ligand substitution. The ionizations which are associated primarily with the cyclopentadienyl ring π e_1'' levels display a characteristic band envelope. Interestingly, the degeneracy of the ionizations associated predominantly with the metal d levels in octahedral $M(CO)_6$ complexes and C_{4v} $Mn(CO)_5X$ complexes is not substantially removed in these lower symmetry $CpM(CO)_3$ and $CpFe(CO)_2X$ analogues. In the case of $CpRe(CO)_3$, a distinct spin–orbit splitting of the predominantly metal ionizations is observed. Comparison of the spectra of the $CpFe(CO)_2X$ complexes with the spectra of the corresponding $Mn(CO)_5X$ complexes provides additional information regarding the assignment of the valence ionization bands of the molecules in both of these series. An ab initio calculation on the cyclopentadienide ion and approximate calculations on the transition metal complexes are used to aid in the interpretation of these ionizations. In addition, the details of a method for interpreting the ionizations of a molecule containing an atom with appreciable spin–orbit interaction are presented, and applied to the spectrum of $CpRe(CO)_3$. The combined knowledge provided by this work and earlier investigations leads to a consistent description of the electronic structure and bonding of d^6 metal η^5-cyclopentadienyl carbonyls and indicates that serious errors may result if ionization potentials are interpreted solely on the basis of Koopmans' theorem. The lowered carbonyl force constants in these π-bonded ring complexes (when compared to the corresponding $M(CO)_6$ and $Mn(CO)_5X$ complexes) are not found to be a result of electron donation from the ring, as previously believed. Instead, the carbonyl ligands and the ring interact with metal orbitals of primarily different symmetry, and the lower carbonyl force constants are a direct result of a decrease in competition for the back-bonding electrons from the metal orbitals of appropriate symmetry.

Major advances, both experimental and theoretical, are being made toward the understanding of the electronic structure and properties of transition metal complexes. Developments in the area of He(I) photoelectron spectroscopy (PES) have had a particularly strong impact on the interpretation of molecular electronic structure. With high-resolution electron energy analyzers, it is now possible to determine the successive ionization potentials for removal of electrons from the valence shells of a gaseous molecule. Initial applications of the technique to transition metal complexes have concerned series of transition metal carbonyls[1-9] and bis(η^5-cyclopentadienyl) metal complexes.[1,10-14] Complementing these developments in photoelectron spectroscopy have been equally important advances in the realm of theoretical quantum mechanics. Quantum mechanical calculations on the ground states of molecules coupled with application of Koopmans' theorem[15] have been valuable for qualitative assignment and interpretation of photoelectron spectra. This is exemplified by the role of approximate and ab initio calculations in the assignment of the $Mn(CO)_5X$ spectra.[16] With the development of increasingly efficient computers, it is becoming possible to perform ab initio LCAO-MO-SCF calculations on many transition metal complexes. Hillier and co-workers[5,13,17-20] have performed ab initio calculations on many of the important transition metal carbonyl complexes, and Veillard and his group[21,22] have investigated certain of the π-bonded organometallics by similar procedures. These calculations have contributed much to an understanding of the ionization process, and in some instances[5,13,22] have seriously challenged the traditional concepts concerning the use of Koopmans' theorem and band intensities for assignment of photoelectron spectra.

The present work represents a combination of experimental and calculational techniques for the purpose of interpreting photoelectron ionizations and the electronic struc-