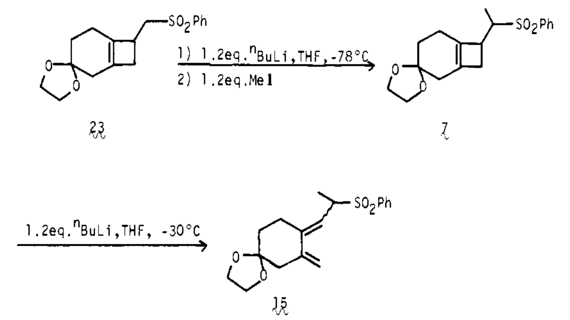
Scheme III



compound **10**[7] was obtained by a similar treatment of **5**.

In case of sulfoxy compounds **6** and **8**, the compounds which resulted from subjecting them to the same reaction conditions as **4** were **13**, **14**, and **16**,[8] respectively. The formation of **13** and **16** could be explained by the intervention of double [2.3] sigmatropic rearrangement of the initial products **17** and **18** via **19** and **20**. Actually compound **14**, which resulted from nucleophilic substitution of the phenyl group of compound **6** by *n*-butyl on treatment with *n*-butyllithium followed by ring opening, was transformed quantitatively into compound **22**[9] on standing at room temperature via **21** (Scheme II). In the case of compound **6** lithium diisopropylamide was also used as a base in place of *n*-butyllithium under the same conditions to give compound **13** (74.3%) as the sole product.[10]

A very attractive feature of this method of diene generation is that alkylation of **23** and **6**, involving essentially the same conditions as above, *n*-BuLi/THF, can be carried out at -78 °C, at which temperature the butene ring remains intact. Thus, compounds **7** and **8** were obtained in almost quantitative yields by using 1.2 equiv of *n*-butyllithium and 1.2 equiv of methyl iodide, 2.2 equiv of base and electrophile was used for **9** and **10**. Monomethylated compounds **7** and **8** were then subjected to a ring-opening reaction to give dienes **15** and **16**, respectively. Thus it can be seen that alkylation and/or ring-opening reactions of such butenes are readily brought about by control of the reaction temperature (Scheme III).

It is clear that the presence of an active proton next to the arylsulfoxy or -sulfonyl group is critical for this new ring-opening reaction of butenes, since compounds **9** and **10**, which have no active protons, were recovered unchanged when subjected to the above treatment. We plan to report further studies on this reaction and its application to the synthesis of natural products in the near future.

Acknowledgment. We thank staff of the Central Analytical Laboratory of Tohoku University, Sendai, Japan, for assistance.

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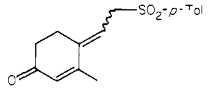
[7] **11**: UV (EtOH) (log ϵ) 238 nm (3.94); NMR (CCl_4) δ 2.45 (s, 3 H), 3.71 (d, *J* = 8 Hz, 2 H), 3.83 (s, 4 H), 4.6 (br s, 1 H), 4.86 (br s, 1 H), 5.4 (distorted t, *J* = 8 Hz, 1 H), 7.25 (d, *J* = 8 Hz, 2 H), 7.66 (d, *J* = 8 Hz, 2 H); *m/e* 334 (M^+). To confirm its structure, **11** was treated with 10% hydrochloric acid in methanol to give **24**: IR ($CHCl_3$) 1665 cm^{-1}; NMR



(CCl_4) δ 2.03 (s, 3 H), 2.43 (s, 3 H), 3.88 (d, *J* = 8 Hz, 2 H), 5.73 (s, 1 H), 5.85 (distorted t, *J* = 8 Hz, 1 H), 7.26 (d, *J* = 8 Hz, 2 H), 7.7 (d, *J* = 8 Hz, 2 H); *m/e* 290 (M^+). **10**: oil; UV (EtOH) (log. ϵ) 237 nm (3.93); NMR (CCl_4) δ 3.76 (d, *J* = 8 Hz, 2 H), 3.84 (s, 4 H), 4.66 (br s, 1 H), 4.90 (br s, 1 H), 5.10 (distorted t, *J* = 8 Hz, 1 H), 7.40–8.0 (m, 5 H); *m/e* 320 (M^+).

[8] **13**: oil; UV (EtOH) (ϵ) 243 nm (4.20); NMR (CCl_4) δ 3.4 (d, *J* = 12 Hz, 1 H), 3.7 (d, *J* = 12 Hz, 1 H), 3.85 (s, 4 H), 4.8 (d, *J* = 10 Hz, 1 H), 5.03 (d, *J* = 16 Hz, 1 H), 6.27 (dd, *J* = 10 and 16 Hz, 1 H), 7.43 (br s, 5 H); *m/e* 304 (M^+). **14**: oil; UV (EtOH) (log ϵ) 235 nm (4.06); NMR (CCl_4) δ 3.38 (d, *J* = 9 Hz, 2 H), 3.9 (s, 4 H), 4.63 (br s, 1 H), 4.93 (br s, 1 H), 5.52 (t, *J* = 9 Hz, 1 H); *m/e* 284 (M^+). **16**: oil; UV (EtOH) (log ϵ) 253 nm (4.09); NMR (CCl_4) δ 1.64 (d, *J* = 5 Hz, 3 H), 3.4 (d, *J* = 12 Hz, 1 H), 3.67 (d, *J* = 12 Hz, 1 H), 3.86 (s, 4 H), 5.56 (m, 1 H), 5.92 (d, *J* = 14 Hz, 1 H), 7.3–7.6 (m, 5 H); *m/e* 318 (M^+).

[9] **22**: UV (EtOH) (log ϵ) 246 nm (4.17); NMR (CCl_4) δ 3.5 (br s, 1 H), 3.9 (s, 4 H), 5.05 (d, *J* = 11 Hz, 1 H), 5.2 (d, *J* = 16 Hz, 1 H), 6.68 (d, d, *J* = 11 and 16 Hz, 1 H); *m/e* 284 (M^+).

[10] The formation of the initial product **17** was recognized in the NMR spectrum of the crude product from this experiment showing the typical olefinic signals, although this was very labile and spontaneously isomerized to give **13** on purification. **17**: oil; NMR ($CDCl_3$) δ 3.65 (d, *J* = 8 Hz, 2 H), 3.93 (s, 4 H), 4.66 (br s, 1 H), 4.90 (br s, 1 H), 5.39 (distorted t, *J* = 8 Hz, 1 H), 7.50 (br s, 5 H).

[11] **15**: oil; UV (EtOH) (log ϵ) 240 nm (3.97); NMR (CCl_4) δ 1.46 (d, *J* = 7 Hz, 3 H), 3.0–3.4 (m, 1 H), 3.87 (s, 4 H), 4.67 (br s, 1 H), 4.94 (br s, 1 H), 5.25 (d, *J* = 10 Hz, 1 H), 7.5–8.0 (m, 5 H); *m/e* 334 (M^+).

Photochemistry of Metal–Metal Bonded Complexes: One-Electron Oxidation of Photogenerated Seventeen-Valence-Electron Radicals

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Though M–M bond homolysis according to eq 1 is generally

$$>M-M< \xrightarrow{h\nu} 2\cdot M< \tag{1}$$

the main result of photoexcitation[1] of metal–metal bonded complexes such as $M_2(CO)_{10}$ (M = Mn, Re)[2] and $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$,[3] efficient formation of metal carbonyl cations and anions has been observed upon irradiation of metal–metal bonded complexes in polar media.[4] We wish to report results that show that clean, 1-electron oxidation of photogenerated 17-valence-electron radicals can be an important thermal reaction pathway. Oxidation is thus added to halogen abstraction,[1-3,5] radical coupling,[1-3,6,7] radical trapping,[8] and ligand substitution[9,10] as reaction paths for the primary photoproducts from dinuclear metal–metal bonded

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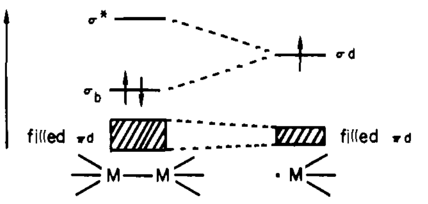
Scheme I. Qualitative Orbital Diagrams for M-Centered Radical and Its $>M-M<$ Parent



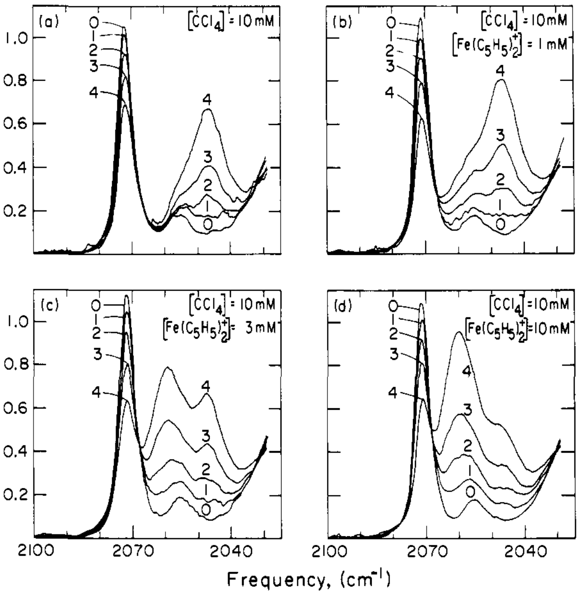


Figure 1. Infrared spectral changes accompanying the irradiation (355 ± 15 nm) of $Re_2(CO)_{10}$ in deoxygenated CH_2Cl_2/0.1 M n-Bu_4NClO_4 solutions containing 10 mM CCl_4 and variable amounts of ferricenium at 25 °C. Curve 0 is the zero-time spectrum and 1, 2, 3, and 4 are after different irradiation periods. The 2073-cm^{-1} band is due to $Re_2(CO)_{10}$; the 2048-cm^{-1} band is due to $Re(CO)_5Cl$; and the 2060-cm^{-1} band is due to $Re(CO)_5ClO_4$.

complexes. Loss of CO from $M_2(CO)_{10}$ or $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ is at best a small fraction of the primary photoreactions and is not believed to be very important in the photochemistry.[1-3,6,11]

Radicals from homolysis of $M_2(CO)_{10}$ or $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ and related species should be more easily oxidized and reduced than their metal-metal bonded precursors. This point can be concluded from the simple orbital diagrams in Scheme I for the M-M species and the M-centered radical;[1] the σ_b level is more stable and the σ^* level less stable than the σd orbital for the radical. Thus, it is easier to add an electron to, or remove an electron from, the radical. Rates and mechanisms of redox reactions may be very different for the radical and its precursor, and this may cloud the energetic differences between them.

We have studied the irradiation of three radical precursors, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, or $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$, in the presence of variable amounts of CCl_4, a known halogen atom donor,[1-3] and one of several one-electron oxidants, A^+ (A^+ = ferricenium, 1,1′-dimethylferricenium, decamethylferricenium, tropylium, or *N*,*N*′-dimethyl-4,4′-bipyridinium). The solvent/electrolyte system was either CH_2Cl_2/0.1 M n-Bu_4NClO_4 or CH_3CN/0.1 M n-Bu_4NClO_4. We find that the products and their ratio accord well with the mechanistic scheme represented by eq 1-3. Since processes 2 and 3 are first order in radical concentration, the ratio

$$>M\cdot + CCl_4 \xrightarrow{k_x} >M-Cl \tag{2}$$

$$>M\cdot + A^+ \xrightarrow[L]{k_{ox}} >M^+-L + A \tag{3}$$

Table I. Oxidation of Photogenerated Radicals Relative to Chlorine Atom Abstraction from CCl_4

radical precursor[a]	oxidant, A^+	$E°(A^+/A)$ vs. SCE, V	k_{ox}/k_x[b]	
			CH_2Cl_2	CH_3CN
$(\eta^5\text{-}C_5H_5)_2W_2\text{-}(CO)_6$	$[Fe(\eta^5\text{-}C_5H_5)_2]^+$	+0.45	13[c]	143
	$[Fe(\eta^5\text{-}C_5H_4Me)_2]^+$	+0.36	7[c]	139
	$[Fe(\eta^5\text{-}C_5Me_5)_2]^+$	−0.11	1[c]	17
	$[C_7H_7]^+$ (−0.18)[d]			110
	$[MV^{2+}]$[e] (−0.45)			12
$Mn_2(CO)_{10}$	$[Fe(\eta^5\text{-}C_5H_5)_2]^+$	+0.45	135	380
	$[Fe(\eta^5\text{-}C_5H_4Me)_2]^+$	+0.36	8.5	54
	$[Fe(\eta^5\text{-}C_5Me_5)_2]^+$	−0.11	<0.01[f]	1
	$[C_7H_7]^+$ (−0.18)[d]			0.25
$Re_2(CO)_{10}$	$[Fe(\eta^5\text{-}C_5H_5)_2]^+$	+0.45	4.2	
	$[Fe(\eta^5\text{-}C_5H_4Me)_2]^+$	+0.36	2.3	
	$[Fe(\eta^5\text{-}C_5H_5)_2]^+$	−0.11	0.01[g]	

[a] The M–M precursors (~5 mM) were irradiated in CH_3CN/0.1 M n-Bu_4NClO_4 or CH_2Cl_2/0.1 M n-Bu_4NClO_4 solution at 25 °C. Samples were deoxygenated and the solutions containing CCl_4 and/or $A^+BF_4^-$ were illuminated at 355 ± 15 nm (2×10^{-6} einstein/min) in matched NaCl infrared cells. IR analyses in the infrared region 2200–1800 cm^{-1} were made after various irradiation times. Products $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, $Mn(CO)_3Cl$, $Re(CO)_5Cl$, $Mn(CO)_5ClO_4$, $Re(CO)_5ClO_4$, $Mn(CO)_5NCCH_3^+$, and $(\eta^5\text{-}C_5H_5)W(CO)_3NCCH_3^+$ were quantitated by comparison to authentic samples. The metal carbonyl chloride products have been characterized previously (ref 2a, 3, 12, and 13). The oxidation products, or derivatives, are also known substances: Trogler, W. C. *J. Am. Chem. Soc.* 1979, *101*, 6459. Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* 1975, *14*, 1579. Wimmer, F. L.; Snow, M. R. *Aust. J. Chem.* 1978, *31*, 267. Uson, R.; Riera, V.; Gimeno, J.; Laguna, M.; Gamasa, M. P. *J. Chem. Soc., Dalton Trans.* 1979, 996. Burckett-St. Laurent, J. C. T.; Field, J. S.; Haines, R. J.; McMahon, M. *J. Organomet. Chem.* 1979, *181*, 117. [b] k_{ox}/k_x values are from linear plots like those in Figure 2; see text, eq 4. Values given are average from slopes of plots where $[A^+]$ is fixed and $[CCl_4]$ is varied and vice versa. Ratio is ±10% except where noted otherwise. $E°(A^+/A)$ was determined by cyclic voltammetry. [c] These values of k_{ox}/k_x are determined from plots of $(1 - [(\eta^5\text{-}C_5H_5)W(CO)_3Cl])/[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ vs. $[A^+]$ and $[CCl_4]^{-1}$, since no stable oxidation product was observed. There is a slow thermal reaction of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ with ferricenium at 25 °C; no other combination shows thermal reaction on a timescale similar to that for the photoreaction. [d] This redox couple is not reversible; −0.18 is the $E_{1/2}$ value from: Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* 1976, *98*, 4222. [e] $MV^{2+} \equiv$ *N*,*N*′-dimethyl-4,4′-bipyridinium as the triflate salt. [f] No detectable reaction corresponding to oxidation. [g] Error is larger than ±10% owing to low rate of oxidation. We estimate ~±25% error.

of the metal carbonyl products, $>M^+-L$ to $>M-Cl$, at a given irradiation time t_i is related to k_x and k_{ox} by eq 4. Thus, slopes

$$\left(\frac{[>M^+-L]}{[>M-Cl]}\right)_{t=t_i} = \frac{k_{ox}[A^+]}{k_x[CCl_4]} \tag{4}$$

of the linear plots of product ratio against $[A^+]$ at fixed $[CCl_4]$ or against $[CCl_4]^{-1}$ at fixed $[A^+]$ give the ratio k_{ox}/k_x.

Irradiation of $M_2(CO)_{10}$ in CH_2Cl_2/0.1 M n-Bu_4NClO_4 containing variable amounts of CCl_4 and A^+ give $M(CO)_5Cl$ from chlorine atom abstraction and $M(CO)_5ClO_4$ from oxidation by A^+; ClO_4^- scavenges the 16-valence-electron $M(CO)_5^+$. Infrared spectral changes in a restricted region of the spectrum for the $Re_2(CO)_{10}$ system as a function of ferricenium concentration are given in Figure 1 and qualitatively show the expected variation in $Re(CO)_5ClO_4/Re(CO)_5Cl$ ratio. Figure 2 shows plots confirming the mechanistic scheme represented by eq 1-3. Similar data were obtained for $Mn_2(CO)_{10}$ in CH_2Cl/0.1 M n-Bu_4NClO_4 and in CH_3CN/0.1 M n-Bu_4NClO_4 ($Mn(CO)_5NCCH_3^+$ is the oxidation product from $Mn_2(CO)_{10}$ in CH_3CN solvent). Data for $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ were also obtained in the two solvent systems, but in CH_2Cl_2 no oxidation product was observed. The addition of A^+ suppressed the yield of $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, but $(\eta^5\text{-}C_5H_5)W(CO)_3ClO_4$ was not observed. Plots of (1 − [(η^5-

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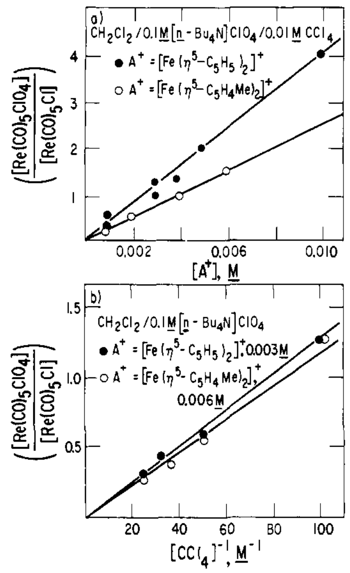

Figure 2. Plots of product ratios against $[A^+]$ and $[CCl_4]^{-1}$ for the $Re_2(CO)_{10}$ system. Data are from experiments like those represented by Figure 1. See eq 1–4 in text.

$C_5H_5)W(CO)_3Cl])/[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ vs. $[A]^+$ or $[CCl_4]^{-1}$ are linear and allow us to extract k_{ox}/k_x from the slope. In CH_3CN, irradiation of the $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ gives $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$ and $(\eta^5\text{-}C_5H_5)W(CO)_3NCCH_3^+$. Table I gives values of k_{ox}/k_x for the various systems.

The infrared analyses are rather complicated, but the linear plots as in Figure 2 and the zero intercepts substantiate the mechanistic scheme represented by eq 1–3. That only two products are formed in the presence of A^+ and CCl_4 is confirmed by the fact that the mass balance is initially 100% with an estimated error of ±10%. Straightforward experiments where the starting dinuclear complex was irradiated only in the presence of A^+ were carried out, and the quantum yield for the reaction was found to be the same, within experimental error, for reaction in the presence of CCl_4.[1a,2a,3]

Four main conclusions can be drawn from the data. First, oxidation of the radicals generated by cleavage of M–M bonds is a viable reaction pathway, even competing against a good halogen donor such as CCl_4. Second, the oxidation rate constant, k_{ox}, depends on A^+ and seems to correlate with the formal potential of the A^+/A redox couple. The lack of a strong difference between $C_7H_7^+$, decamethylferricenium, and ferricenium for the $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ case rules out steric effects as the major contribution to rate variation. Third, k_{ox}/k_x is sensitive to the solvent used; oxidation is relatively more important in CH_3CN than in CH_2Cl_2. Fourth, the value of k_{ox}/k_x for a given A^+ depends on the radical. It is known that the value of k_x for the three radicals is ordered: $(\eta^5\text{-}C_5H_5)W(CO)_3\cdot$ relative $k_x = 1.0$, $Mn(CO)_5\cdot$ relative $k_x = 1.85$, and $Re(CO)_5\cdot$ relative $k_x \geq 15$ in hydrocarbon solutions of CCl_4.[12] Earlier work has led to a value of $k_x = 1.0 \times 10^4\ M^{-1}\ s^{-1}$ for $(\eta^5\text{-}C_5H_5)W(CO)_3\cdot$ in tetrahydrofuran solutions of CCl_4.[13] Thus, the values of k_{ox} for the various A^+ oxidants can be calculated,[12,13] assuming no solvent effect on the reaction with CCl_4. The calculation of k_{ox} is straightforward from the ratios in Table I and the data above. For example, k_{ox} for oxidation of $(\eta^5\text{-}C_5H_5)W(CO)_3\cdot$ by ferricenium in CH_3CN solution is 143 times $1.0 \times 10^4\ M^{-1}\ s^{-1}$, or $k_{ox} = 1.43 \times 10^6\ M^{-1}\ s^{-1}$. The value of k_{ox} for $Mn(CO)_5\cdot$ is $7.03 \times 10^6\ M^{-1}\ s^{-1}$ under the same conditions. The value for $Re(CO)_5\cdot$, even within the framework of our assumptions, can only be limited on the low side due to the fact that the value of k_x, relative to that for the W-centered radical, is not known. Thus with ferricenium, the fastest oxidant, we find k_{ox} to be below the diffusion-controlled limit in every case, with the possible exception of reactions of $Re(CO)_5$. The A^+ reagents used are generally fast, outer sphere, one-electron oxidants, but the radicals likely have significant geometry changes upon oxidation, accounting for the relatively slow rates of oxidation[14] assuming that the energetics are sufficiently favorable. We attribute variation in k_{ox} to be due mainly to energetic factors, since the structural requirements would appear to be rather similar for the series of A^+ based on ferrocene. For a given radical then we would attribute the dimunition in k_{ox} for the more alkylated ferricenium with the reduced driving force for reaction. By comparison to either the Mn- or Re-centered radical, the W-centered radical shows modest variation in k_{ox} for the series of A^+ used, and we conclude that even the weakest oxidant is capable of oxidizing the W-centered radical at a rate as fast as the most powerful oxidant used. For the Mn- or Re-centered radical the value of k_{ox} is much lower for the peralkylated ferricenium, and we conclude that these radicals are weaker reductants than the W-centered radical on these grounds. The dinuclear W species is the most easily oxidized of the three dinuclear complexes studied, but the reactivity of the W-centered radical toward CCl_4 is the least of the three radicals studied.[12]

Our work has several other important implications. First, the slow rate of decamethylferricenium reduction by the $M(CO)_5$ radicals suggests that the reaction of $M(CO)_5$ does not proceed by prior reduction of the CCl_4 to $CCl_4^-\cdot$, since the $E_{1/2}$ for CCl_4 reduction is about ~−0.8 V vs. SCE[15] compared to −0.11 V vs. SCE for the decamethylferricenium. The reaction of $M(CO)_5$ with CCl_4 would therefore best be thought of as an abstraction or in one sense an inner sphere redox process.[16] Second, the increased tendency for redox processes in CH_3CN accords well with the general findings that the photoinduced formation of metal carbonyl anions occurs most efficiently[4] in polar, donor solvents, e.g., pyridine, THF, and CH_3CN. Thus, we regard homolytic scission as the major primary photoreaction of the dinuclear complexes; products that would appear to arise from heterolytic cleavage can be accounted for by disproportionation of 17-valence-electron radicals.[17] The key here is that the M–M bond homolysis is the *primary* chemical event following excitation. The resulting fragments may well lose CO or pick up other ligands, but for the conditions used in our experiments, it would appear that either A^+ or CCl_4 reacts with the radicals prior to degradation of the coordination sphere. For example, we do not see $ClMn(CO)_4(CH_3CN)$ as a primary product that could arise from abstraction of Cl by $Mn(CO)_4$ followed by reaction with CH_3CN. Finally, a prior electron transfer from photogenerated radicals should be considered in the halogen "abstraction" reactions from thermodynamically reducible species such as HgX_2 and CuX_2.[5] Redox reactions of organometallics are well documented[18,19] for other types of radicals and should be of importance for the 17-valence-electron radicals that can be produced by the photochemical cleavage of M–M bonds. Studies of redox mechanism and reactivity of other photogenerated, 17-valence-electron radicals are in progress.

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[16] Radical traps[8] can be regarded as inner sphere oxidants; preliminary results for interception of $Mn(CO)_5\cdot$ by tetracyanoethylene (see ref 8e), $E° = +0.24$ V vs. SCE,[15] competing against CCl_4 show that the k_{ox}/k_x is greater than for 1,1′-dimethylferricenium, $E° = +0.36$ V vs. SCE, but most of the reaction is inner sphere to form the $Mn(CO)_5TCNE$ radical.

[17] Disproportionation-like reactions could occur by first substitution of a CO by solvent[9,10] at the radical stage to provide a driving force for electron transfer, e.g.

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5 \xrightarrow{S} Mn(CO)_5 + Mn(CO)_4S + CO \rightarrow Mn(CO)_5^- + Mn(CO)_4S^+$$

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Fermi Level Pinning of p-Type Semiconducting Indium Phosphide Contacting Liquid Electrolyte Solutions: Rationale for Efficient Photoelectrochemical Energy Conversion

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A recent report[1] concerning p-type InP-based photoelectrochemical cells prompts us to give this preliminary account of our work on p-type InP/liquid interfaces. We report data that show that p-type InP gives a photovoltage E_V, of $\sim$0.8 V with respect to solution redox couples where the formal potential of the redox couple, E°, can vary over a potential range that significantly exceeds the magnitude of the band gap, E_g, of InP. Indeed, for E°'s more negative than $\sim$-0.40 V vs. SCE in CH_3CN/0.1 M n-Bu$_4$NClO$_4$, we find essentially a constant value for E_V. When E_V is independent of E° for a semiconductor/liquid interface the semiconductor is said to be "Fermi level pinned".[2-7] One intriguing finding is that the ratio E_V/E_g for p-type InP is the highest reported thus far for a semiconductor/liquid interface.

Single-crystal p-type InP, fabricated into photocathodes,[8] has been studied in CH_3CN/0.1 M n-Bu$_4$NClO$_4$ or aqueous electrolyte solutions containing fast, outer sphere, reversible, one-electron transfer reagents whose E°'s span a wide potential range. The strategy in using such redox reagents is to explore interface energetics without the complication of poor electrode kinetics.[2-7,9] The use of CH_3CN as a solvent is necessary owing to the fact that H_2O has a rather restricted negative potential window because H_2O can be (photo)reduced at (photo)cathodes. We have performed cyclic voltammetry studies and steady-state current-potential experiments with illuminated ($\geq E_g$ light) p-type InP contacting various solvent/electrolyte/redox couple combinations.

Figure 1 illustrates typical cyclic voltammetry behavior, and Table I summarizes some of the quantitative data that we have collected. Consider first the cyclic voltammetry in Figure 1. The CH_3CN/0.1 M n-Bu$_4$NClO$_4$ electrolyte solution contains a number of one-electron reducible materials at $\sim$1 mM concentration where the associated E°'s span a wide range of potential. Compared to the cyclic voltammetric peaks at Pt (a reversible electrode), the cathodic peak associated with reduction of the various oxidized species at illuminated p-type InP is shifted to a more positive value (Table I). Three facts are crucial: (1) all of the oxidized species are photoreducible at illuminated p-type InP at an electrode potential more positive than at Pt; (2) the extent to which the photocathodic current peak is more positive is nearly the same for the couples whose E° is more negative than -0.4 V vs. SCE; (3) the potential range of E°'s spanned significantly exceeds the magnitude of E_g = 1.35 eV for InP.[1] Taking the difference in position of the cathodic current peak at Pt and at illuminated p-type InP to be a reasonable relative measure of E_V,[4-6] we see that for many E°'s the E_V is very large, $\sim$0.8 V.[10]

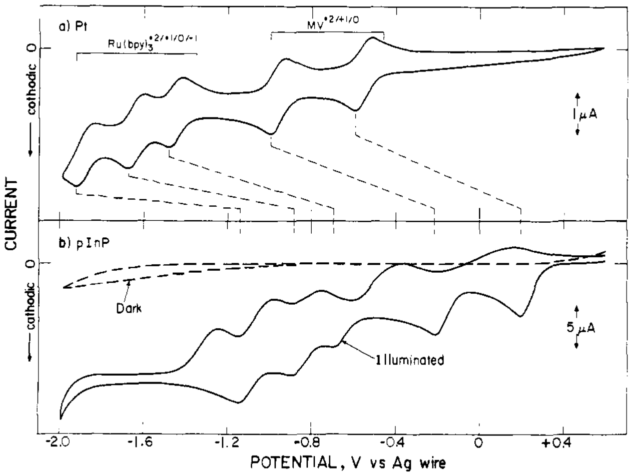

Figure 1. Cyclic voltammetry of a CH_3CN solution containing 0.1 M TBAP, $\sim$1 mM MV^{2+} and $\sim$1 mM Ru(bpy)$_3^{2+}$ at (a) Pt and (b) p-InP in the dark and under irradiation with 632.8-nm light. Scan rate employed is 100 mV/s. Light intensity was $\sim$50 mW/cm^2.

Table I gives the values of E_V for p-type InP contacting various redox couples. In addition to the data from CH_3CN solvent, we include data for CH_3CN containing CH_3COOH and for H_2O at different pH's. For the MV^{2+}/MV$^{+\cdot}$ system we make special note of the fact that the value of E_V is essentially independent of the medium.

From steady-state current-voltage scans for illuminated p-type InP in the presence of various redox couples, we have found high efficiency for the conversion of light to electricity, as was previously reported for the p-InP/VCl_3-VCl_2-HCl/C cell.[1] Short-circuit photocurrents, open-circuit photovoltage, and fill factors are high, and we concur with the conclusion of other workers[1] that the efficiency of p-type InP-based photoelectrochemical energy conversion devices can be quite high. But on the basis of the data presented in Table I, we conclude, in contrast to earlier workers,[1] that p-type InP is indeed "Fermi level pinned". This is most certainly the case in CH_3CN where various redox couples having a very wide range of E°'s give essentially the same value of E_V. The similar E_V for the MV$^{2+/+\cdot}$ system in H_2O and CH_3CN and the pH independence of E_V provide support for the contention that p-type InP departs from ideal semiconductor/liquid interface behavior.[2,11]

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(8) Electrodes were constructed by using a Zn-doped p-type InP, $\langle 111\rangle$ or $\langle\bar{1}\bar{1}\bar{1}\rangle$ face exposed, with a carrier concentration $\sim 1 \times 10^{18}$ cm^{-3}. Ohmic contacts were made by ultrasonic soldering of a copper wire to the crystal back with In/Zn (saturated with Zn) solder. The InP surface was etched in 5% Br_2/MeOH for 60 s at 25 °C followed by rinsing with MeOH. The electrochemical equipment has been described previously;[4] solutions were degassed and typically contained 1 mM of electroactive material.

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(10) The value of E_V increases only modestly from the $\sim$0.8 V upon increasing light intensity beyond the $\sim$50 mW/cm^2 used. The highest E_V observed has been 0.86 V at $\sim$10 W/cm^2. The $\sim$50 mW/cm^2 approximates the visible intensity from the AM1 solar spectrum. Other workers have investigated p-InP in nonaqueous media[9d] and found a smaller E_V. This may be due to lower quality InP samples or to a poor ohmic contact. However, even the earlier work[9d] revealed a photovoltage for a range of E°'s exceeding E_g of InP.

(11) An earlier study [Van Wezemael, A.-M.; Laflrere, W. H.; Cardon, F.; Gomes, W. P. *J. Electroanal. Chem.* **1978**, *87*, 105] of the p-InP/H_2O interface as a function of pH suggested that the value of E_V would be fixed relative to the H^+/H_2 because the so-called flat-band potential was found to shift 59 mV/pH unit in the same direction as $E^\circ(H_2O/H_2)$. Since the E_V relative to MV^{2+}/M$^{+\cdot}$ is independent of pH, we conclude that the potential determining species in such a case is MV^{2+}/M$^{+\cdot}$. A shift in the flat-band potential with pH is apparently ruled out when the MV^{2+}/M$^{+\cdot}$ system is present. For interpretation of the constant E_V relative to H_2O/H_2 in the absence of deliberately added redox couples, we offer the suggestion that the p-InP is Fermi level pinned by a mechanism not involving acid-base equilibrium of surface functionality.

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