catalyst for the carbonylation of organic sulfur compounds.

Experimental Section

General Remarks. Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer. Varian EM360A and XL300 instruments were used for NMR spectral determinations, and a VG5050 micromass spectrometer was used for recording mass spectra. Reactant halides, cobalt carbonyl, and phase-transfer agents were purchased from commercial sources. Thiiranes were prepared by literature methods,[18,19] Bis(triphenylphosphine)-nitrogen(1+) tetracarbonylcobaltate was synthesized according to the procedure of Gladysz and co-workers.[20] Solvents were dried and distilled by standard techniques.

General Procedure for the Carbonylation of Thiiranes. Carbon monoxide was bubbled through a 3 N KOH (15 mL) solution containing 0.3 mmol of PEG-400. After 15 min, a degassed solution of $Co_2(CO)_8$ (0.3 mmol) in benzene (20 mL) was added followed 1 h later by the halide (2 mL) and 30 min later by the thiirane (2.0 mmol) in benzene (5 mL). The reaction mixture was stirred under carbon monoxide at room temperature and one atmosphere (see Table I for reaction times). Standard workup [separation of the phases, acidification of the aqueous phase (1 M HCl), ether extraction (4 × 25 mL), and flash chromatography of the concentrated ether extract (Al_2O_3; C_6H_{14}/$CH_3COOC_2H_5$ as eluant)] gave pure β-mercapto acid.

Reaction of 2-Phenylthiirane with Bis(triphenylphosphine)nitrogen(1+) Tetracarbonylcobaltate. Carbon monoxide was bubbled, for 15 min, through an aqueous solution (15 mL) of cetyltrimethylammonium bromide (0.364 g, 1.0 mmol). Bis(triphenylphosphine)nitrogen(1+) tetracarbonylcobaltate (0.709 g, 1.0 mmol), in degassed methylene chloride (20 mL), was added, and the solution was stirred under carbon monoxide for 1 h.

Methyl iodide (2 mL) was added, followed 30 min later by a methylene chloride (5 mL) solution of 2-phenylthiirane (0.136 g, 1.0 mmol). The reaction mixture was stirred under carbon monoxide for 18 h at room temperature and one atmosphere. The phases were separated, the aqueous phase was extracted with ether, the combined organic phase was concentrated, and flash chromatography of the crude product on alumina using hexane/ethyl acetate as the eluant afforded the pure β-mercapto acid in 41% yield.

Phase-Transfer-Catalyzed Cleavage of Thietan-2-one. Carbon monoxide was bubbled through a solution of potassium hydroxide (15 mL, either 0.1 or 3.0 M) and PEG-400 (0.12 g, 0.30 mmol). After 15 min, a degassed solution of benzene (20 mL) was added, followed by thietan-2-one (0.176 g, 2.0 mmol) in benzene (5 mL). The reaction mixture was stirred overnight at room temperature (1 atm). The phases were separated, and the aqueous phase was acidified with 1 M HCl and then extracted with ether (4 × 25 mL). The ether extract was dried ($MgSO_4$) and concentrated, and flash chromatography on alumina with hexane/ethyl acetate gave 3-mercaptopropionic acid in 94–100% yield (two runs).

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Electrochemical Oxidation of Rhenium Alkyl Complexes of the Formula (η⁵-C₅H₅)Re(NO)(PPh₃)(R): Evidence for One-Electron Charge Transfer

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The redox properties of rhenium alkyl complexes R–(Re) ((Re) = (η⁵-C₅H₅)Re(NO)(PPh₃)) with R = PhCH₂ (**1**), (CH₃)₂CHCH₂ (**2**), and Ph(CH₃)CH (**3**) are studied electrochemically. Cyclic voltammetric, peak current, heterogeneous charge transfer, and chronoamperometric studies in a variety of solvents indicate that **1–3** undergo initial one-electron oxidation to cation radicals R–(Re)•⁺. These decompose by an EC mechanism at rates that correlate with solvent donor ability. Intermediates, possibly R–(Re/solvent)•⁺, are detected by cyclic voltammetry. Coulometric experiments further suggest that R–(Re)•⁺ can catalytically oxidize solvent via R–(Re/solvent)•⁺. These data contrast with an earlier report describing evidence for a two-electron oxidation of **3**.

Introduction

An earlier investigation of the electrochemical oxidation of rhenium alkyl complexes (η⁵-C₅H₅)Re(NO)(PPh₃)(R), abbreviated here as R–(Re), suggested that two types of processes take place.[2] Type I complexes (R = CH₃, CH₂CH₃, CH₂CH₂CH₃, CH₂CH₂Ph, CH₂CH(CH₃)₂, CH₂-C(CH₃)₃, CH(CH₃)CH₂Ph, CH₂Ph) were thought to undergo one-electron charge transfer to give R$_I$–(Re)•⁺ (**I**),

(1) (a) University of Utah. (b) University of Trondheim.

(2) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, S. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020.

Table I. Cyclic Voltammetry Data for the Oxidation of Alkyl Complexes R–(Re) in CH₃CN[a]

| compd	R	ΔE^p/mV[b]
1	PhCH₂	82 ± 3
2	(CH₃)₂CHCH₂	60 ± 2
3	Ph(CH₃)CH	69 ± 1

[a] Containing $Bu_4N^+BF_4^-$ (0.1 M); substrate concentration 0.5 mM. [b] Peak potential separations measured by derivative cyclic voltammetry at 100 V/s using a Pt electrode (0.8 mm) at 290 K.

while type II complexes (R = CH(CH₃)Ph, CH(CH₂Ph)Ph, CH(CH₂CH₃)Ph) were thought to undergo two-electron charge transfer to give R_{II}–$(Re)^{2+}$ (II). Since the alkyl ligands in neither type are expected to support a charge, this implies that depending on rather subtle changes in R, either a cation radical I or a dication II is the thermodynamically favored product of charge transfer of R–(Re). This represents a unique situation that has not yet been demonstrated in any related systems. We have recently reported compelling evidence that hydride abstraction from both type I and type II alkyl complexes R–(Re) by Ph_3C^+ occurs by initial one-electron transfer to give R–(Re)·⁺ and Ph_3C·.[3] Hence, we set out to further characterize the redox properties of these complexes and independently evaluate the previous conclusions.

$$R_I\text{–}(Re)^{\cdot+} \qquad R_{II}\text{–}(Re)^{2+}$$
$$\text{I} \qquad\qquad\qquad \text{II}$$

Results

1. Cyclic Voltammetry of R–(Re) Complex Oxidation. Three complexes, representative of both type I and type II, were chosen for study: PhCH₂–(Re) (1, type I),[4] (CH₃)₂CHCH₂–(Re) (2, type I),[5] and (SR,RS)-Ph(CH₃)-CH–(Re) (3, type II).[5] The peak potential separations during cyclic voltammetry were determined by derivative techniques in both CH₃CN (Table I) and CH₂Cl₂ (Table II) by using procedures outlined in earlier publications.[6]
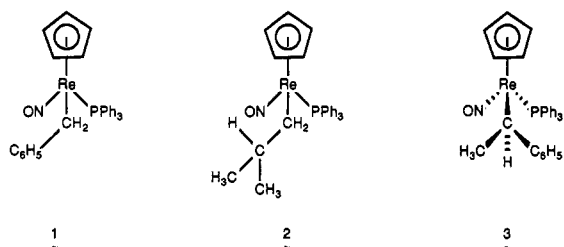
The results obtained in CH₃CN (Table I) at a voltage sweep rate (ν) of 100 V/s and with substrate concentrations of 0.5 mM indicate quasi-reversible oxidation for all three complexes, with some differences in heterogeneous charge-transfer rate constants. Under these conditions, the peak currents for 2 (type I) and 3 (type II) were very similar. This suggests that both complexes undergo one-electron charge transfer. Since the peak currents are similar for the different substrates, any possible error due to uncompensated resistance cancels for the purpose of comparison. Heterogeneous charge-transfer rate constants could be calculated from the data, but since the responses

Table II. Comparison of Heterogeneous Kinetic Parameters for the Oxidation of Alkyl Complexes R–(Re) in CH₂Cl₂[a]

	2		3	
ν/V s⁻¹	$\Delta\Delta E^p$/mV[b]	$k_s/D^{1/2}$[c]	$\Delta\Delta E^p$/mV[d]	$k_s/D^{1/2}$[c]
0.100	3.7	22.5	4.0	20.8
0.150	5.7	17.9	4.8	21.2
0.200	6.4	18.4	5.5	21.4
0.300	6.3	22.9	6.8	21.2
0.400	7.3	22.8	7.7	21.6
0.600	9.4	21.7	9.1	22.4
0.800	9.2	25.6	11.2	21.0
1.00	11.7	22.5	11.7	22.5
		21.8 ± 2.5		21.5 ± 0.6

[a] Containing $Bu_4N^+BF_4^-$ (0.1 M) at 292 K; substrate concentration 0.5 mM. [b] $\Delta\Delta E^p = \Delta E^p - 61$ mV as explained in the text. [c] The heterogeneous rate constant divided by the square root of the substrate diffusion coefficient. Units of k_s and D are cm/s and cm²/s, respectively. [d] $\Delta\Delta E^p = \Delta E^p - 59$ mV as explained in the text.
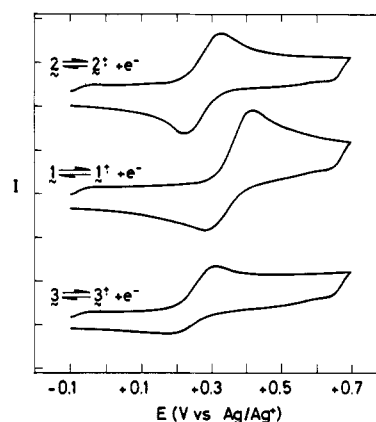

Figure 1. Cyclic voltammograms of complexes 1–3 in Me₂SO/$Bu_4N^+BF_4^-$ (0.1 M) at 10 V/s and 293 K.

are affected by some adsorption problems, this was not pursued further.

A more quantitative study was carried out at lower sweep rates for the oxidation of 2 (type I) and 3 (type II) in CH₂Cl₂ (Table II). In this solvent, all of the cation radicals were long-lived and the CV data were free of complications due to follow-up reactions. In these cases, the data are suitable for heterogeneous charge-transfer studies. The quantity determined was $\Delta\Delta E^p$, defined as the observed peak potential separation minus that for a diffusion-controlled process (Nernstian) under the same conditions.[7] Since the response was not ideal for either substrate, the quantity subtracted from ΔE^p was adjusted to give the smallest deviations in $k_s/D^{1/2}$ (k_s is the heterogeneous rate constant and D is the diffusion coefficient of the substrate). The values of $k_s/D^{1/2}$ were calculated from eq 1, which was presented earlier[9] from an analysis

$$\Delta\Delta E^p = 2.303RT/F(2^{-1} - 2^{-3} + 2^{-5})\psi^{-1}$$

$$\psi = k_s/(\pi DF\nu/RT)^{1/2} \qquad (1)$$

of theoretical electrode potential data. The results indicate that $k_s/D^{1/2}$ is identical, within experimental error, for the two substrates. Diffusion coefficients for 2 and 3 are not known, but k_s can be estimated as about 0.07 cm/s by

(3) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757.

(4) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

(5) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4972.

(6) (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem.* **1981**, *121*, 57. (b) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

(7) The peak separation for a Nernstian process is independent of sweep rate but depends somewhat upon the temperature and the difference in switching and reversible potentials.[8]

(8) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980.

(9) Ahlberg, E.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 71.
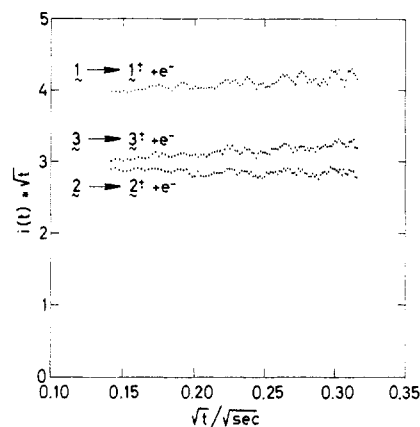
Figure 2. Chronoamperometry data for the oxidation of complexes 1–3 in $Me_2SO/Bu_4N^+BF_4^-$ (0.1 M).

Table III. Summary of Peak Current and Chronoamperometric Data for the Oxidation of Alkyl Complexes R–(Re)

complex/solv	$(i^p)_{rel}$[a]	$(it^{1/2})_{rel}$[b]
1/Me₂SO	1.6	1.4
2/Me₂SO	1.0	1.0
3/Me₂SO	1.2	1.1
1/CH₂Cl₂	1.7	1.9
2/CH₂Cl₂	1.0	1.0
3/CH₂Cl₂	0.8	1.4

[a] Measurements at 0.100 V/s. [b] Average value between 10 and 100 ms as shown in Figure 2.

employing the common assumption that D are equal to 10^{-5} cm^2/s.

Cyclic voltammograms for the oxidation of **1**, **2**, and **3** (all 1.0 mM) in $Me_2SO/Bu_4N^+BF_4^-$ (0.1 M) at 10 V s⁻¹ are illustrated in Figure 1.

2. Comparison of Peak Current and Chronoamperometry Data for R–(Re) Complex Oxidation. Since the data in Tables I and II do not confirm the existence of type II oxidation processes for **3**, further tests were made. Chronoamperometry, which measures the transient current after a potential step into the region where the charge transfer is diffusion-controlled,[8] was used as a diagnostic tool for the oxidation of all three substrates in both Me₂SO and CH₂Cl₂. The results of chronoamperometry in Me₂SO are demonstrated by the plots of $it^{1/2}$ vs. $t^{1/2}$ shown in Figure 2. If the diffusion coefficients for the three substrates were identical and there were no complications such as adsorptions or interfering chemical follow-up reactions, $it^{1/2}$ would be constant and equal for each. This is seen to be very nearly the case for substrates **2** (type I) and **3** (type II), but the quantity is somewhat greater for **1** (type I). The fact that $it^{1/2}$ is constant for all three processes suggests that the apparent number of electrons transferred is time independent and the follow-up reactions that take place are of the eC type (charge transfer followed by a first-order or pseudo-first-order irreversible chemical reaction).

The relative CV peak heights in both Me₂SO and CH₂Cl₂ show similar trends as the chronoamperometric $it^{1/2}$ values (Table III). In all cases, the results for **2** (type I) and **3** (type II) are similar, while both $(i^p)_{rel}$ and $(it^{1/2})_{rel}$ for **1** (type I) are considerably greater than for the other two substrates. From these results, together with those in Tables I and II, we conclude that all three substrates undergo quasi-reversible one-electron oxidation under all conditions studied. The larger currents during cyclic voltammetry and chronoamperometry during the oxidation of **1** could be explained in part by a larger diffusion

Table IV. Dependence of Chronoamperometry Data for the Oxidation of Alkyl Complexes R–(Re) on Solvent Composition

CH_2Cl_2/CH_3CN[a]	ferrocene	$(it^{1/2})_{rel}$		
		1	2	3
5/0	1.00	1.37	0.76	0.95
5/1	1.00	1.26	0.80	0.93
5/2	1.00	1.22	0.84	0.95
5/3	1.00	1.22	0.88	0.94
5/5	1.00	1.21	0.91	0.93
5/5[b]	1.00	1.22	0.93	0.94

[a] v/v, Bu_4N^+ PF_6^- (0.1 M). [b] This experiment utilized a substrate solution initially comprised of equal volumes of both solvents. Data in the preceding entries were obtained by the successive addition of CH_3CN to CH_2Cl_2 solutions of substrates.

coefficient, but it is likely that other complicating factors such as adsorption play a role. In any event, **3**, which was proposed to be a type II substrate, gives current intermediate between those observed for the type I substrates **1** and **2**.

In cases where diffusion coefficients are not known, the number of electrons transferred during voltammetric measurements is often determined by comparison with a well-defined electrode process. Chronoamperometry experiments were carried out for the oxidation of ferrocene and alkyl complexes R–(Re) in CH₂Cl₂ and mixtures of CH₂Cl₂ and CH₃CN. The data are summarized in Table IV. Under all conditions, $it^{1/2}$ during the oxidation of **3** was about 94% of that during the oxidation of ferrocene. Interestingly, as the solvent mixture becomes richer in CH₃CN, $it^{1/2}$ for **1** decreases to approach that for ferrocene while $it^{1/2}$ for **2** increases toward that for ferrocene. In 50:50 (v/v) CH_2Cl_2/CH_3CN, $it^{1/2}$ is 1.3 times greater for **1** than **2**. By taking ferrocene as a standard for one-electron transfer, it is clear that the oxidations of **2** and **3** involve the transfer of one electron. The larger than expected $it^{1/2}$ for **1** cannot be explained by a two-electron process. We conclude that all three alkyl complexes R–(Re) undergo quasi-reversible one-electron oxidation in aprotic solvents. None of the processes behave ideally, and this could give rise to the trends in the relative $it^{1/2}$ values.

3. Kinetic and Activation Parameters for the Reactions of R–(Re)·⁺ Complexes. The voltammetric data discussed in the previous sections show that the initial steps in the oxidations are, for all substrates, quasi-reversible one-electron oxidations to give cation radicals. The chronoamperometry results ($it^{1/2}$ = constant) as well as the CV current function data ($i^p/v^{1/2}$ = constant)[10] reported earlier show that only one electron is transferred even under conditions where there is considerable decomposition of the cation radical. These results are then consistent with either an eC (rate-determining first-order reaction following charge transfer) or an eC(dim) (rate-determining dimerization following charge transfer) mechanism. The second-order reaction was ruled out by showing that the apparent decomposition rates are independent of the substrate concentration. Thus, the chemical follow-up reactions of the rhenium alkyl cation radicals are of the eC type.

Rate constants obtained by DCV measurements assuming an eC mechanism at 20 °C in a number of aprotic solvents are summarized in Table V. The magnitudes of the rate constants depended upon both the solvent and the R group. When possible, rate constants were determined over a range of temperature (from −30 to +50 °C depending upon the particular reaction). The Arrhenius activation energies E_a derived from plots of the data varied from 7.5 to 16.5 kcal/mol, but no clear relationships be-

**Table V. Rate Constants for the Decomposition of R–(Re)·⁺ Complexes in Aprotic Solvents at 293 K[a]**

sol	k_1/s^{-1}	k_2/s^{-1}	k_3/s^{-1}	DN[b]
CH_2Cl_2	2		0.086^c	0
CH_3CN	0.65	0.009^c	0.72	14.1
PC^d		0.07^c		15.1
DMF	10.1	0.33	23.3	26.6
Me_2SO	17.4	0.43	25.2	29.8
HMPA		197		47.2

[a] Containing $Bu_4N^+BF_4^-$ (0.1 M); measured by derivative cyclic voltammetry (DCV). [b] Solvent donor number from ref 20. [c] Rate constants lower than about 0.1 s^{-1} are highly uncertain. [d] Propylene carbonate.

Table VI. Arrhenius Activation Energies for the Decomposition of R–(Re)·⁺ Complexes in Aprotic Solvents[a]

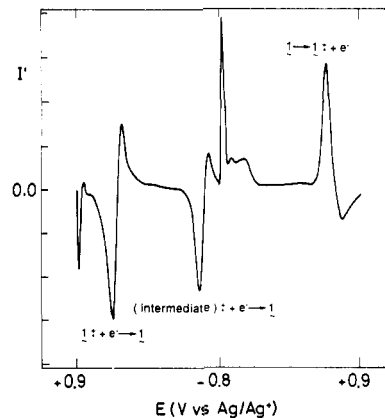| sol	$(E_a)_1/$ kcal mol^{-1}	$(E_a)_2/$ kcal mol^{-1}	$(E_a)_3/$ kcal mol^{-1}
CH_2Cl_2	too slow	too slow	too slow
CH_3CN	16.5	too slow	15.0
PC^b			14
DMF	9.4	8.2	9.9
Me_2SO	7.5	12.2	11
HMPA/CH_2Cl_2 (4/1)^c	too fast	10.8	too fast

[a] Measurements of rate constants at temperatures ranging from 243 to 323 K depending upon the particular reaction. [b] Propylene carbonate. [c] Cosolvent CH_2Cl_2 was necessary to keep HMPA solutions fluid at low temperatures.
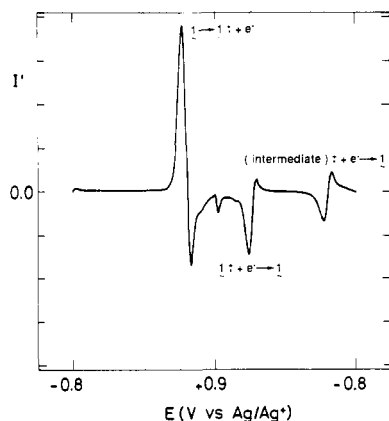
Figure 3. Derivative cyclic voltammogram (DCV) for the oxidation of $PhCH_2$–(Re) (1, 1 mM) in CH_2Cl_2/$Bu_4N^+BF_4^-$ (0.1 M) at 100 mV/s and 293 K.

Figure 4. Derivative cyclic voltammogram (DCV) showing the reduction of $PhCH_2$–(Re)·⁺ (1·⁺) and $PhCH_2$–(Re/solvent)·⁺ at 50 V/s in CH_2Cl_2/$Bu_4N^+BF_4^-$ (0.1 M).
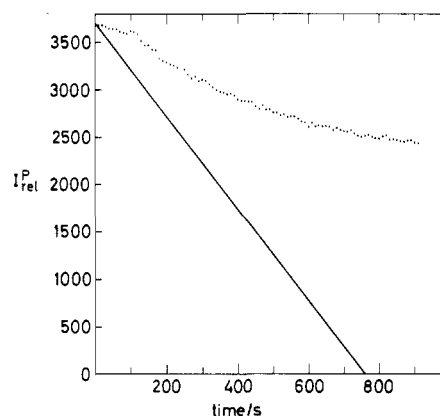
Figure 5. Constant current coulometry of $PhCH_2$–(Re) (1) in Me_2SO/$Bu_4N^+BF_4^-$ (0.1 M). The solid line defines that expected for the consumption of 4.0 faradays/mol.

Table VII. Coulometric n Values Obtained during Constant Current Coulometry Experiments on R–(Re) Complex Oxidations

substrate	solv	% conversn	n_{app}
1	CH_2Cl_2	90	4.5
2	CH_2Cl_2	56	7
1	Me_2SO	20	10
1	Me_2SO	32	6
2	Me_2SO	20	10
3	Me_2SO	33	6
3	Me_2SO	44	9

tween E_a and rate constants are apparent (Table VI).

4. Observation of a Reaction Intermediate. DCV scans over a wide potential range (–0.8 to +0.9 V vs. Ag⁺/Ag) showed a reduction process ($E_p \simeq -0.7$ V) in addition to that of the primary quasi-reversible redox couple involving the substrate/cation radical. This process was only observed under conditions where R_I' (the derivative peak ratio) was considerably less than unity, indicating significant reaction of the cation radical. This behavior is illustrated by the DCV in Figure 3 for the oxidation of 1 in CH_2Cl_2/$Bu_4N^+BF_4^-$ at 100 mV/s. The presence of the intermediate is further demonstrated by the DCV shown in Figure 4. In this case, the rest potential of the electrode (+0.9 V) was positive of the oxidation potential of 1 so that R–(Re) in the diffusion layer was converted to R–(Re)·⁺ and further reaction products. In this case, the derivative peak for the reduction of the intermediate was nearly as great as that for reduction of R–(Re)·⁺.

5. Coulometric Analysis of R–(Re) Complexes. Constant current (8–12 mA) electrolyses at a large plati-

num mesh electrode ($\simeq 25$ cm^2) were carried out in a divided cell. The cell was equipped with the same electrodes used for the DCV studies so that the disappearance of substrate could be monitored by recording DCV scans at regular intervals (10 or 20 s) during the oxidations. The data, $(I')^P_{rel}$ (the derivative peak height expressed in arbitrary units), were plotted as a function of electrolysis time. A typical plot is shown in Figure 5. The solid line is the theoretical plot for a process involving the consumption of 4 faradays/mol. In this case, the substrate was $PhCH_2$–(Re) (1) and the oxidation was carried out in Me_2SO/$Bu_4N^+BF_4^-$ (0.1 M). It is obvious from the figure that the oxidation is a nonstoichiometric process involving a large number of electrons per molecule of substrate consumed. Thus, a meaningful coulometric n value for this process, or the others studied, cannot be assigned. In order to provide an indication of the efficiency of consumption of the R–(Re) complexes during constant current oxidation, n values were calculated at particular degrees of conversions for several different oxidations. These are summa-

rized in Table VII for reactions carried out in CH_2Cl_2 and Me_2SO. The values observed varied from 4.5 to 10 electrons/molecule consumed.

Discussion

1. Consecutive Charge Transfer in Solution. For two consecutive one-electron oxidations (or reductions) of a species A in solution, forming first the cation (or anion) and then the dication (or dianion), the difference in electrode potentials for the two processes reflects the ionization potential (or electron affinity) difference of A and $A^{\bullet+}$ (or $A^{\bullet-}$) as well as the relative solvation energies of the singly and doubly charged ions. Due to charge repulsion, the gas-phase ionization potential difference corresponding to equation 2 is generally fairly large. In

$$A - e^- \underset{}{\overset{-E_1^\circ}{\rightleftharpoons}} A^{\bullet+} - e^- \underset{}{\overset{-E_2^\circ}{\rightleftharpoons}} A^{2+} \qquad (2)$$
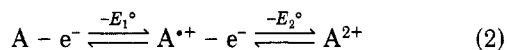
solution, the electrode potential difference ΔE° can be considerably smaller due to the larger solvation energy of the doubly charged ion. However, apparent two-electron charge transfers resulting when the second step is more favorable than the first are relatively rare and have only been observed when special structural features are present in A. For example, apparent two-electron oxidation of tetraarylethylenes (4) where $X = Me_2N$ or MeO has been observed.[11-13] The structural feature that contributes to the unusual stability of 4^{2+} is the twisted conformation about the central bond, which allows the positive charges to be essentially out of conjugation and relatively far removed from each other. An illustrative example is provided by the series of dimethoxyarenes 5 and 6. In
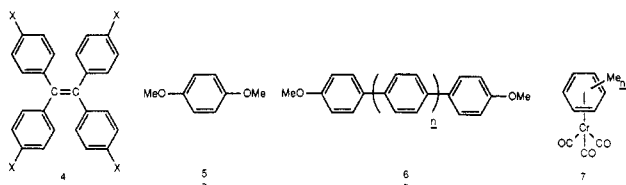

$CH_2Cl_2/TFAn/TFA$ (45:5:1; TFA = CF_3COOH and TFAn = $(CF_3CO)_2O$), ΔE° was 710 mV for the consecutive oxidations of 5 and declined progressively to 220 mV as *n* in structure 6 was varied from 0 to 2.[14] The variations in ΔE° can be attributed to twisting about the biphenyl linkages as well as increased charge separation as the methoxy groups, which bear considerable charge in the dications, become more distant.

In general, the HOMOs of organo-transition-metal compounds are largely metal-centered and have appreciable d character.[15] This gives rise to relatively small ligand-substituent effects upon oxidation potentials. For example, the oxidation potentials of (methylbenzene)tricarbonylchromium complexes $(C_6H_{6-n}Me_n)Cr(CO)_3$ (7) vary by only 212 mV as *n* ranges from 0 to 6.[16] There is little separation of charge in the dications of mononuclear

organo-transition-metal compounds, and thus a fairly large separation between the first and second oxidation potentials is expected in most cases.

Apparent reversible two-electron redox processes have been observed for some mononuclear organo-transition-metal complexes. Reduction of certain (arene)chromium tricarbonyl complexes, $ArCr(CO)_3$, is accompanied by cyclic voltammetric peak separations of about 30 mV.[17] These reactions are believed to involve fast reversible isomerizations as shown for $8^{\bullet-}$ to $9^{\bullet-}$. The η^4-anion radical $9^{\bullet-}$
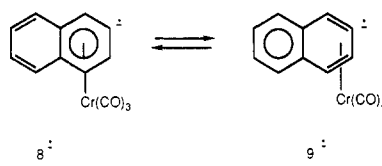

is more easily reduced than starting neutral η^6-complex 8, which gives rise to the apparent two-electron process. Similarly, isomerization occurs during reduction of $(\eta^6-C_6Me_6)_2Ru^{2+}$, which results in a single two-electron process in CH_3CN and two closely spaced one-electron reductions in CH_2Cl_2.[18] An analogous two-electron reduction accompanied by a change in hapticity has been observed for the mixed-sandwich complex $(\eta^5-C_5Me_5)(\eta^6-C_6Me_6)Ir^{2+}$.[19] In all of these cases, a substantial structural change takes place after the initial one-electron transfer to produce a species that is more readily reduced than the substrate.

In view of the above, the existence of reversible one- and two-electron processes for rhenium alkyl complexes R–(Re), depending upon small structural changes in the alkyl groups, is not expected. The data presented in this paper clearly indicate that all of the complexes studied undergo quasi-reversible one-electron oxidation to give cation radicals that can be observed by cyclic voltammetry.

2. The Behavior of R–(Re)$^{\bullet+}$ Complexes in Solution. The cation radicals of all three complexes, R–(Re)$^{\bullet+}$, are found to be relatively stable in CH_2Cl_2 at 293 K (Table V). The first-order rate constants for the reactions of the cation radicals correlate reasonably well with solvent donor numbers,[20] implying that the solvents are intimately involved in the reactions. These results suggest an analogy to related work with iron phenanthroline complexes in aprotic solvents.[21] Kinetic studies were carried out and the results interpreted in terms of reactions 3 and 4. In

$$Fe^{III} + solv \rightleftharpoons Fe^{III}(solv) \qquad (3)$$

$$Fe^{III}(solv) \rightarrow Fe^{II} + (solv)^{\bullet+} \qquad (4)$$
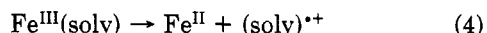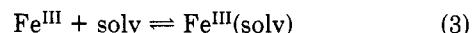
fact, our coulometry data (Table VII) indicate that the decomposition reactions of cation radicals R–(Re)$^{\bullet+}$ are nonstoichiometric and involve the transfer of several electrons, the number of which depends upon the solvent, the conditions, and the degree of conversion. This implies a catalytic oxidation of solvent—i.e., reaction 5, which is

$$R–(Re/solv)^{\bullet+} \rightarrow R–(Re) + (solv)^{\bullet+} \qquad (5)$$
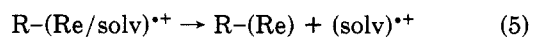
accompanied by the regeneration of substrate R–(Re). It

(10) The $i^p/\nu^{1/2}$ values reported in ref 2 for type II complexes are apparently in error by a factor of 2.

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is tempting to assign the reduction peaks observed at negative potentials to the reduction of the solvates (eq 7) formed in reaction 6. However, to be consistent with this

$$R-(Re)^{•+} + solv \rightleftharpoons R-(Re/solv)^{•+} \qquad (6)$$

$$R-(Re/solv)^{•+} + e^- \rightarrow R-(Re) + solv \qquad (7)$$
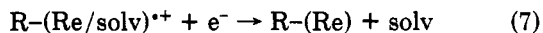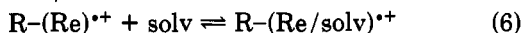
interpretation K_6, the equilibrium constants for the formation of the solvates, would have to be of the order of 10^{15} M^{-1} s^{-1} (K_6 are readily estimated from the potential differences for the reduction of the cation radicals and of the reduction peaks observed for the intermediates). We regard this to be unlikely in view of the fact that the intermediates are formed in relatively slow reactions.

The question may arise concerning the observation of clean first-order kinetics during DCV analysis while the coulometry experiments clearly suggest a catalytic decomposition of solvent. We do not view this as an inconsistency but rather a reflection of the difference in time scale of the two types of experiments. Our result indicate that the rate-determining step in the diffusion layer is first order in cation radicals $R-(Re)^{•+}$. The catalytic reaction takes place at a lower rate in the bulk solution.

The identity of the intermediates giving rise to the reduction processes at negative potentials as well as the products and mechanisms of the decomposition reactions are being investigated. These results will be described in a future publication.

Conclusions

The rhenium alkyl complexes R-(Re) undergo quasi-reversible one-electron oxidation to cation radicals R-(Re)$^{•+}$ in a number of aprotic solvents. The cation radicals are relatively stable in solvents that do not coordinate with cations—i.e., those with low donor numbers. Heterogeneous charge-transfer rate constants in CH_2Cl_2 are observed to be of the order of 0.07 cm/s. The reactions that do take place in CH_2Cl_2 could involve impurities, such as water, that can coordinate with the cation radicals. The predominant decomposition pathway of the cation radicals appears to be a catalytic oxidation of solvent regenerating R-(Re).

Experimental Section

Chemicals. Complexes 1–3 were prepared as described previously.[4,5] The supporting electrolyte Bu$_4$N$^+$BF$_4^-$ was prepared from Bu$_4$N$^+$HSO$_4^-$ and aqueous HBF$_4$. Reagent grade solvents containing supporting electrolyte (0.1 M) were passed through a column of active neutral alumina (ICN, W200 neutral, super grade 1) before use.

Electrodes and Cells. The working electrode for DCV studies was a 0.6-mm platinum wire sealed in glass and polished to a planar surface. Reference electrodes were Ag/AgNO$_3$ (0.01 M in CH$_3$CN/Bu$_4$N$^+$BF$_4^-$ (0.1 M)) constructed in the manner described by Moe.[22] Leakage from the reference electrode was negligible as was the current consumed by the small electrodes for short times, which enabled use of a single compartment cell consisting of a cylindrical (25-mL volume) tube fitted with a joint to accommodate a Teflon electrode holder equipped with an inlet tube for purified nitrogen. The working electrode for constant current coulometry (carried out in the manner described earlier)[23] was a platinum gauze (25 cm^2) place in the anode chamber of a two-compartment cell separated from the cathode chamber by a glass frit. The DCV analysis during constant current coulometry was carried out with the electrodes described above.

Instrumentation. The potentiostat was a PAR Model 173D driven by a Hewlett-Packard HP 3314A function generator interfaced to a Hewlett-Packard 9825 desk computer. The data were digitized by a Nicolet 2090 digital oscilloscope and processed with the desk computer. The oscilloscope had a time resolution of 0.5 μs/point with 12-bit precision.

Data Collection. Data initially stored in the oscilloscope memory, 0.2 mV/data point, were transferred to computer memory. The computer was programmed to find the peak heights and the potentials where the derivative of the current–voltage curve passed through the zero line. Compensation of iR drop in solution was accomplished by positive feedback. The feedback necessary was determined as described earlier.[6]

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