reaction. We have now established that the addition of CF_3SO_3Cl to the cis and trans isomers of CFH=CFH is stereospecific and that the displacement of Cl from a single stereoisomer of $CF_3CO_2CFH\text{-}CFHCl$ proceeds with retention of configuration. These results suggest that CF_3SO_3Cl and its bromine analogue[5] could be very useful reagents in organic chemistry, the main drawback to the latter being the control of the reactions in certain cases (*Caution! explosions can result from contact of CF_3SO_3Cl with readily oxidizable materials*).

The addition of CF_3SO_3Cl to *cis*-CFH=CFH proceeds readily in the absence of solvent at −111 to −40 °C to give an 88% (GLC) yield of $CF_3SO_3CFH\text{-}CFHCl$. Reaction of CF_3SO_3Cl with a 3:2 mixture of cis-trans CFH=CFH proceeds under the same conditions to give a 90% (GLC) yield of $CF_3SO_3CFH\text{-}CFHCl$. By ^{19}F NMR it was readily apparent that two stereoisomers are present in the latter reaction in the ratio of ~3:2 and that the more abundant isomer is the same as that formed using the pure cis olefin. Similar conclusions are arrived at by examination of the ^1H NMR spectra, but these spectra are rather extreme examples of complicated second-order spectra.[6]

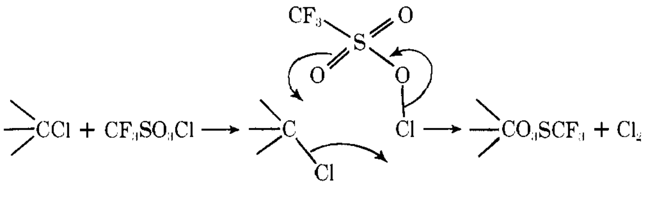
The distinction as to which stereoisomer is erythro and which is threo cannot be made with great certainty. In these compounds, one has vicinal $^3J_{HF}$, $^3J_{FF}$, and $^3J_{HH}$ couplings available as structural probes, but only the $^3J_{HH}$ coupling is completely reliable. Unfortunately, the latter is the most difficult to extricate from the observed ^1H or ^{19}F spectra. $^3J_{FF}$ is the easiest value to ascertain, but it is the least reliable. These uncertainties not withstanding, we tentatively assign the stereoisomers in the following way.

In the additions of CF_3SO_3Cl, CF_3SO_3Br[5], CF_3OCl[7], and CF_3CO_2Cl[8] to cis and trans CFH-CFH, a single stereoisomer is obtained with each geometrical isomer in every case. $^3J_{FF}$ values for these cis and trans adducts are, respectively, as follows: CF_3SO_3Cl (15.8, 20.5), CF_3SO_3Br (19.5, 25.5), CF_3OCl (14.5, 20.0), and CF_3CO_2Cl (15.4, 20.4 Hz). These values indicate an inverse dependence of $^3J_{FF}$ on the electronegativity of the substituents and a clear dependence on the dihedral angle assuming the same average rotomer populations. If one assumes that the most abundant rotomer in both erythro and threo has the R_fO group trans to Cl or Br, then the vicinal fluorines are trans for erythro and gauche for threo. For this related series of compounds only, it may then be a reasonable conclusion that the larger $^3J_{FF}$ belongs to the threo isomer and the smaller $^3J_{FF}$ to the erythro isomer, making the addition cis.[9-12]

Reaction of CF_3SO_3Cl with the stereoisomer formed by addition of CF_3CO_2Cl to cis CFH=CFH yields a single stereoisomer as indicated by ^{19}F NMR:

$$CF_3CO_2CFH\text{-}CFHCl + CF_3SO_3Cl \xrightarrow{-111\text{ to }22\ ^\circ C} CF_3CO_2CFH\text{-}CFHO_3SCF_3 + Cl_2$$

Because CF_3SO_3 is more electronegative than Cl, one expects $^3J_{FF}$ to be 10–15 Hz if the substitution proceeds with retention of configuration and 15–20 Hz if inversion occurs. The observed $^3J_{FF}$ value is 10.8 Hz, suggesting that the reaction proceeds with retention of configuration. We propose that the substitution proceeds by an S_Ei-type mechanism[13] like the following:



Precedent for reactions of this type are limited and we hope to provide other examples via additional reactions of CF_3SO_3Cl and reactions of CF_3SO_3Br and $BrOSO_2F$. The latter compound has previously been shown to undergo this type of reaction, but no systems were investigated that allowed any mechanistic conclusions to be made.[14]

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(12) Additional support for this conclusion can be obtained from the ^{19}F chemical shift of the CHF groups. In a series of 2-fluoro-3-halobutanes and related compounds, the ^{19}F signal for the CHF group is at higher field for the threo isomers: G. A. Olah, M. Bollinger, and J. Brinch, *J. Am. Chem. Soc.*, **90**, 2587 (1968); R. Fields, *Annu. Rep. NMR Spectrosc.*, **5A**, 99 (1972), pp. 101, 102. For the series of compounds for which $^3J_{FF}$ values are given here, the addition product to the trans isomer has the two ^{19}F signals for the CHF groups at higher field in every case than the product with the cis isomer.
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Yutaka Katsuhara, Darryl D. DesMarteau*[15]
Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

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Electrochemical Oxidation of Some Mesocyclic Dithioethers and Related Compounds

Sir:

Evidence supporting the hypothesis that suitable neighboring groups can facilitate oxidation at sulfur of substituted dialkyl sulfides has been previously presented.[1] Since all of these oxidations are irreversible, thermodynamic parameters cannot be directly secured from the data. Recently, the existence of unusually stable aliphatic cation radicals derived from certain mesocyclic dithioethers was reported.[2] Further one-electron oxidation affords the corresponding dications which have been obtained as solid salts.[3] The unusual stability of these compounds compared with ordinary alkyl sulfide cation radicals and dications has been attributed to intramolecular transannular interaction between the sulfur atoms in which an S–S bond is formed. These results suggested that reversible electrochemical oxidation might be observed with these compounds from which thermodynamic parameters could readily be obtained and that transannular participation by one sulfur atom might facilitate oxidation of the other.

This paper reports the electrochemical oxidation of some mesocyclic dithioethers and a series of other mono- and dithioethers. The most remarkable findings are that a number of the mesocyclic dithioethers studied undergo reversible oxidation with unusual ease. Further, the formal potential, $E_2°'$, for the second one-electron oxidation is equal to or less than that of the first.[4] These properties are, as far as we are aware, unprecedented in saturated aliphatic sulfide electrochemistry.

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Table I. Anodic Oxidation of Mono- and Dithioethers

compd	E_p[a]	$nD^{2/3} \times 10^4$ [b]
1,3-dithietane	1.13	10.8
1,4-dithiacyclohexane	1.25	5.4
1,5-dithiacyclooctane (1,5-DTCO)[c]	0.343[d]	13.6
1,5-dithiacyclononane (1,5-DTCN)[c]	0.424[d]	12.7
1,6-dithiacyclodecane (1,6-DTCD)[c]	0.424[d]	11.2
1,3-dithiacyclohexane	1.14	12.3
1,4-dithiacycloheptane (1,4-DTCH)[c]	0.75	11.9
1,4-dithiacyclooctane (1,4-DTCO)[c]	0.81	11.8
7,8-benzo-1,5-dithiacyclononane	0.48	11.2
3,4,8,9-dibenzo-1,6-dithiacyclodecane	0.62	9.8
2,5-dithiahexane	0.97	10.0
2,6-dithiaheptane	0.66	12.3
2,7-dithiaoctane	0.67	
thiolane (tetramethylene sulfide)	1.13	11.1
thiane (pentamethylene sulfide)	1.32	
4-oxathiane	1.31	15.5
1-thiacyclooctan-5-ol	0.72	12.4

[a] Peak potentials of first oxidation peaks determined at a Pt electrode (1 cm^2), 0.1-V/s scan rate, and measured in acetonitrile, 0.1 M $NaClO_4$ vs. Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode. [b] Estimated from platinum rotating disc electrode measurements. These values reflect overall 2e$^-$ oxidations, except for 1,4-dithiacyclohexane, in which an irreversible one-electron oxidation to form a dimer is suggested. [c] Structures given in ref 3. [d] Concentration 0.2 mM.

The electrochemical studies were carried out by computer-controlled cyclic voltammetry at a platinum electrode in acetonitrile. Electrochemical parameters related to the first oxidation peak are shown in Table I. All of the oxidations were irreversible as evidenced by the absence of corresponding cathodic peaks even at scan rates up to 50 V/s, except for the mesocyclic dithioethers 1,5-dithiacyclooctane (1,5-DTCO), 7,8-benzo-1,5-dithiacyclononane, 1,5-dithiacyclononane (1,5-DTCN), and 1,6-dithiacyclodecane (1,6-DTCD). The peak potentials for a number of the dithioethers are significantly more cathodic than observed for typical dialkyl sulfides.[5]

The most easily oxidized dithioether (1,5-DCTO) was studied in greater detail. At slow scan rates (0.01 V/s), a quasi-reversible ($k_s \geq 5 \times 10^{-2}$ cm s^{-1}) cyclic voltammogram is obtained for 2 mM 1,5-DTCO (Figure 1). The anodic peak current and peak shape suggest a one-electron oxidation. As the scan rate is increased, the only initial oxidation peak (O_1) is broadened while R_1 shifts to more negative potentials and decreases rapidly at the expense of R_2 and O_2. Such behavior is characteristic of a reversible EC mechanism (dimerization) illustrated previously by the oxidation of 2,6-di-*tert*-butyl-4-ethylphenoxide.[6] At high (>0.5 mM), increasing concentrations, the anodic peak potential shifts to more negative values consistent with expected behavior. Visible spectra taken during the course of a controlled potential electrolysis reveal a band at 410 nm (yellow) identified previously as due to the cation radical[3] which increases to a maximum value in the half-electrolyzed solution and then decreases to yield again a colorless solution. This latter solution is produced by passage of 1.94 electrons/mol of 1,5-DTCO and will regenerate the yellow color upon addition of the parent compound.

Because the peak-current functions are dependent upon electrode kinetics, the semi-integral method[7] was used to distinguish kinetic and diffusion control. The semi-integral computed directly from the voltammogram is shown in Figure 1 to reach a maximum limiting value at ~0.5 V which is independent of scan rate and again characteristic of a one-electron process. When the potential is returned to more negative values, the semi-integral eventually approaches zero, giving a better than 90% recovery of starting material. The sloping nature of the curve in the −0.1-V region is indicative of a process controlled by a chemical reaction rather than diffusion or slow heterogeneous electron transfer.

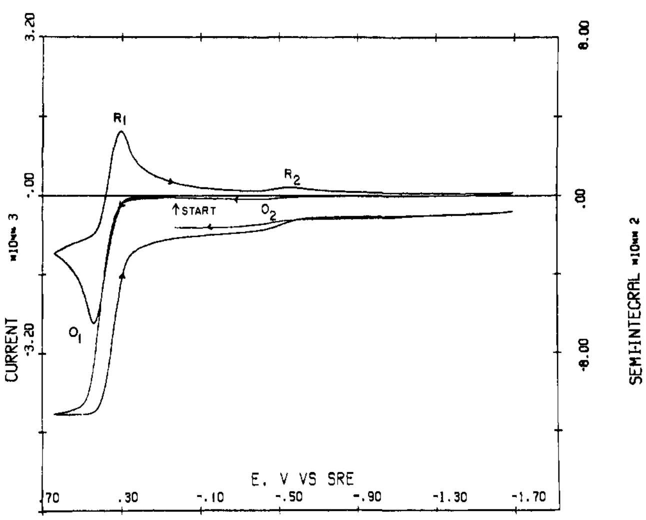

Figure 1. Cyclic voltammogram of 2 mM DTCO in MeCN, 0.1 M $NaClO_4$: potentials vs. Ag/0.1 M $AgNO_3$ reference (SRE); scan rate, 0.1 V/s.

At high concentrations, it seems likely that 1,5-DTCO is oxidized by one electron to form a cation-radical dimer. This route is suggested by the overall stoichiometry, the lack of a reversible cathodic peak, and independent chemical evidence.[3] The dimer is not electroactive in the 0.5-V region but can be reduced directly at −0.6 V. If the scan rate is not too rapid, the dimer can be completely reduced indirectly by slow dissociation into the cation radical. As the concentration of 1,5-DTCO is lowered to 0.05 mM, the anodic peak-current and scan rate independent semi-integral gradually increase to yield a limiting overall 2e$^-$ process and production of the dication. Even at high concentrations, controlled potential electrolysis yields an overall 2e$^-$ oxidation because conditions are favorable for dimer dissociation. The most reasonable structure for this dimer is $R_2S^+{-}{}^+SR_2$. Such dimerization of 1,5-DTCO cation radical in the solid state has been suggested previously.[3] This dimerization is distinct from the well-known reaction of aliphatic sulfur cation radicals with their corresponding sulfides to form $R_2S^{\cdot+}SR_2$.[8]

Transannular interaction in the electrochemical oxidation products of 1,5-DTCO, 1,5-DTCN, 1,6-DTCD, and 7,8-benzo-1,5-dithiacyclononane are suggested to account for their facile, reversible oxidation. The structural features necessary for electrochemically reversible oxidation are the formation of two five-, two six-, or a five- and a six-membered fused ring. Formation of a five- or six-membered ring alone or fused to a three- or four-membered ring is insufficient. Although formation of two six-membered fused rings is a necessary condition for electrochemically reversible oxidation, it is not a sufficient condition because oxidation of 3,4,8,9-dibenzo-1,6-dithiacyclodecane is irreversible. Thus it appears that electrochemical reversibility requires formation of five- or six-membered rings *and* geometric constraint.

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George S. Wilson,* Dale D. Swanson
Jacob T. Klug, Richard S. Glass*
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Michael D. Ryan
Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233

W. Kenneth Musker
Department of Chemistry, University of California
Davis, California 95616

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Electrochemical Generation of $[Rh(diphos)_2]^0$ and Its Role in an Electrocatalytic Reduction of Cyclohexyl Halides

Sir:

The role of odd-electron complexes in the chemistry of oxidative addition reactions, radical-chain processes, and the activation of C–H bonds is a subject of current interest.[1] An important factor in this last category is the selectivity of the activation process, which is related to the "energy content" of the M· species. Electrochemical methods for generating odd-electron complexes are appealing because no additional reagents are needed, the reduction potential provides a measure of M· reactivity, and the subsequent chemical reactions of M· generation can be monitored by both chemical and electrochemical techniques. In this report we describe the electrochemical formation of the d^9 Rh(0) species $[Rh(diphos)_2]^0$ (diphos = 1,2-bis(diphenylphosphino)ethane) and some of its chemical reactions.

Our results contrast with the previous report[2] of Pilloni, Vecchi, and Martelli on the electrochemistry of $[Rh(diphos)_2]Cl$ and its Ir analogue. These authors reported that the electrochemical reduction of these d^8 complexes proceeded by an EC mechanism involving a single $2e^-$ reduction to give an anionic intermediate which was quenched by proton abstraction from solvent to give the metal hydrides,

$$M^+ + 2e^- \rightarrow M^- \qquad (1)$$

$$M^- + S\text{-}H \rightarrow M\text{-}H + S^- \qquad (2)$$

Ginsberg et al.[3] reexamined the electrochemistry of $[Ir(diphos)_2]^+$ and established by cyclic voltammetry and constant potential coulometry experiments that the hydride forms via an ECE mechanism

$$M^+ + e^- \rightarrow M\cdot \qquad (3)$$

$$M\cdot + S\text{-}H \rightarrow M\text{-}H + S\cdot \qquad (4)$$

$$S\cdot + e^- \rightarrow S^- \qquad (5)$$

in which $1e^-$ transfer occurs to generate an Ir(0) species, followed by H-*atom* abstraction and reduction of the solvent radical. The rhodium complex, $[Rh(diphos)_2]Cl$, reduces at approximately the same potential as its iridium analogue, yet shows reversible cyclic voltammetric behavior under similar conditions. It was thus of interest to determine whether electrochemically generated $[Rh(diphos)_2]^0$ could be both a reactive and also selective reagent.

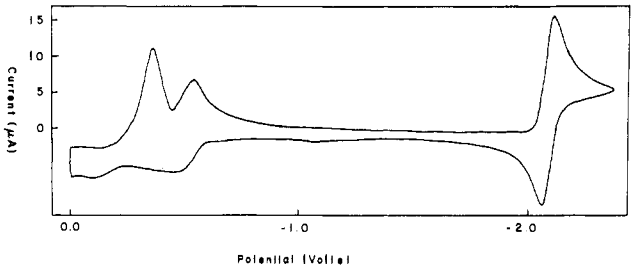

Figure 1. Cyclic voltammogram of 1×10^{-3} M $[Rh(diphos)_2]Cl$ in 0.1 M $(n\text{-}Bu_4N)ClO_4$ in CH_3CN at a scan rate of 100 mV/s on HMDE vs. a 0.1 M $Ag/AgNO_3$ reference.

Table I. Cyclic Voltammetry Data for the Reduction of $[Rh(diphos)_2]Cl$

scan rate, mV s^{-1}	$E_p^{red,a}$ V	ΔE_p, mV	$\Delta E_p^{cor,b}$ mV	i_p^{red}/i_p^{ox}
200	−2.16	72.5	65.3	1.00
150	−2.16	68.9	65.7	1.00
100	−2.16	66.0	66.0	1.05
90	−2.16	65.3	65.3	1.09
80	−2.16	63.8	63.8	1.10
70	−2.16	61.7	61.7	1.12
60	−2.15	58.1	58.1	1.09
50	−2.15	55.8	55.8	1.17
40	−2.15	54.4	54.4	1.18
30	−2.15	50.8	50.8	1.21
20	−2.14	47.2	47.2	1.22
10	−2.14	43.5	43.5	1.27

[a] Scans were made on a HMDE in CH_3CN containing 0.1 M $(n\text{-}Bu_4N)ClO_4$. Voltage are vs. a 0.1 M $Ag/AgNO_3$ reference at 23 °C. [b] $\Delta E_p^{corr} = (\Delta E_p^{Rh}/\Delta E_p^{Fe}) \times 65.3$.

Cyclic voltammetry of $[Rh(diphos)_2]Cl$ on a hanging mercury drop electrode (HMDE) in acetonitrile exhibits a reversible redox couple centered about −2.12 V at a scan rate of 100 mV s^{-1}, corresponding to the reduction of the complex, Figure 1.[4,5] The redox couple centered about −2.12 V displays a variance in peak potential separation, ΔE_p, with scan rate, Table I. In order to compensate for the ohmic contribution to ΔE_p in acetonitrile and to demonstrate the behavior of a purely reversible one-electron system under identical conditions, the Fe(II)/Fe(I) redox couple of $[Fe(bpy)_3]^{2+/1+}$ (bpy = 2,2′-bipyridine) was used.[6] At scan rates of 100 mV s^{-1}, or slower, the reversible one-electron couple for $[Fe(bpy)_3]^{2+/1+}$ exhibits a peak separation of 65.3 mV. At fast scan rates, from 200 mV s^{-1} to ~90 mV s^{-1}, $[Rh(diphos)_2]Cl$ mimics the behavior of $[Fe(bpy)_3]^{2+}$. At slower scan rates, the behavior of the Rh system begins to depart from the one-electron transfer model, $\Delta E_p = 65.3$ mV, and shows increasingly smaller values of ΔE_p. This decrease in ΔE_p is the expected behavior for an ECE reduction such as eq 3–5 when the chemical reaction (eq 4) becomes kinetically significant and the second one-electron transfer is anodic to the first.[7] Concomitant with the decrease in ΔE_p below 65.3 mV is an increase in the ratio of the reduction peak current to the oxidation peak current, i_p^{red}/i_p^{ox}. The system also agrees with the Nicholson and Shain diagnostic criterion[7] for an ECE reduction such as eq 3–5. That is, an increase in $i_p^{red}/v^{1/2}$, where v is the scan rate, is observed as the scan rate decreases. Similar cyclic voltammetric results were obtained for the reduction of $[Rh(diphos)_2]Cl$ in dimethyl sulfoxide, dimethylacetamide, and benzonitrile. These cyclic voltammetric results suggest that eq 3–5 are also valid for the mechanism of the reduction of $[Rh(diphos)_2]Cl$.

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