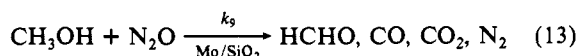
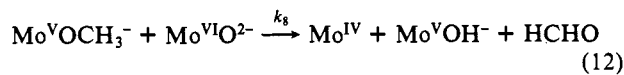


Even in this case the methoxide ion is considered to be an important intermediate. These and subsequent oxidation reactions may be described by the equations



Methyl formate, a known byproduct in the partial oxidation of methanol to formaldehyde, was also detected in this study.

On the basis of this mechanism the overall rate equation for the conversion of methane may be derived. Making the usual steady-state approximation for $d[\text{Mo}^{\text{V}}]/dt$, $d[\text{O}^-]/dt$, and $d[\text{CH}_3^-]/dt$, and recognizing that $[\text{Mo}^{\text{V}}] \ll [\text{Mo}]_{\text{total}}$ enables one to obtain the rate equation for the disappearance of methane

$$-\frac{d[\text{CH}_4]}{dt} = \left(1 + \frac{k_3}{k_2} [\text{N}_2\text{O}]\right) k_1 [\text{Mo}]_{\text{total}} \quad (14)$$

Since reaction 7 occurs at 25 °C and reaction 5 at much higher temperatures⁵

$$\frac{k_3}{k_2} [\text{N}_2\text{O}] \gg 1 \quad (15)$$

eq 14 becomes

$$\frac{d[\text{CH}_4]}{dt} = -\frac{k_1 k_3}{k_2} [\text{N}_2\text{O}] [\text{Mo}]_{\text{total}} \quad (16)$$

which is in agreement with the experimental rate equation with respect to the gas-phase reactants. The order of the reaction with respect to $[\text{Mo}]_{\text{total}}$ has not been tested; however, a simple first-order relationship is unlikely because of the various phases of Mo which might exist on the surface; i.e., the form of Mo which appears in eq 16 is probably a subset of the actual total amount of Mo.

Conclusions

The selective oxidation of methane to methanol and formaldehyde occurs over a supported molybdenum via a catalytic cycle in which O^- is the reactive form of oxygen. This ion initiates a reaction sequence in which methyl radicals and then methoxide ions are formed. The methoxide ions may decompose directly to formaldehyde or they may react with water to form methanol. The reaction of N_2O to O^{2-} rather than O^- results in the nonselective oxidation.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-8112893.

Registry No. Mo, 7439-98-7; N_2O , 10024-97-2; methane, 74-82-8.

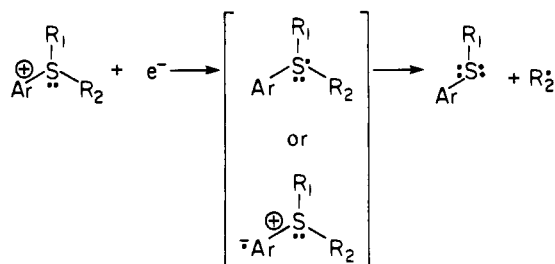
Mechanism of One-Electron Electrochemical Reductive Cleavage Reactions of Sulfonium Salts

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Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. Received October 11, 1983

Abstract: Irreversible one-electron reduction potentials (E_p) were measured for 12 arylmethyl(substituted-alkyl)sulfonium salts (aryl = phenyl and 1-naphthyl). One-electron reduction produced homolytic sulfur-carbon σ -bond cleavage in each of the sulfonium salts studied, providing the observed irreversible electrochemical behavior. The E_p values were extremely sensitive to the electronegativity of the fragmenting radical, suggesting that the electrochemical one-electron reductive cleavage reaction of sulfonium salts occurs by a concerted or nearly concerted mechanism in which bond breaking is concomitant with electron acceptance.

One-electron electrochemical or chemical reduction of sulfonium salts is generally irreversible, as a consequence of carbon-sulfur σ -bond cleavage, providing a sulfide and a carbon radical.¹⁻³ The rate-determining step for fragmentation has been attributed to the formation of an intermediate sulfuranyl radical¹ via direct addition of an electron to sulfur or an intermediate π -ligand radical-anion sulfonium cation³ preceding homolytic cleavage of a σ carbon-sulfur bond.



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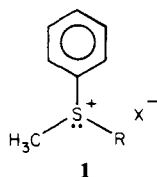
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The proposed two-step mechanism for reductive cleavage of sulfonium salts can be compared to the one-electron reduction of aryl halides with an electron-withdrawing substituent such as nitro or cyano.⁴ These systems produce dehalogenation, i.e., heterolytic σ -bond cleavage, after initial formation of an anion radical. The dehalogenation has been viewed as an intramolecular electron-transfer reaction whereby the electron initially added to the π system of the aryl ring is transferred in a second step to the C-X σ bond to form X^- and a carbon-centered radical.⁴ The delay in the electron transfer has been attributed to the lack of overlap between the π system and the σ bond.

In contrast to the two-step fragmentation via an intermediate ion radical, there are several systems, e.g., reduction of alkyl halides, oxidation of carboxylates, and reduction of diaryl peroxides, that are thought to occur by a synchronous electron-transfer/bond-cleavage reaction.⁵ The sulfuranyl radical postulated to be the intermediate in the reductive cleavage process contains the 9-S-3 system, by the classification scheme proposed by Perkins et al.,⁶ where nine valence-shell electrons are associated

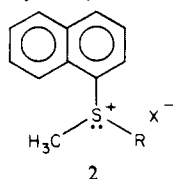
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Table I. Electrochemical Peak (E_p) Potentials for the Reduction of Substituted Phenylmethylsulfonium Salts

compd	R	X	E_p^a	
			Pt	GC
1a	CH ₃	CF ₃ SO ₃	-1.64	-1.73
1b	CH(CH ₃) ₂	BF ₄	-1.61	-1.63
1c	H ₂ CC ₆ H ₅	BF ₄	-1.20	-1.31
1d	H ₂ CC ₆ H ₄ - <i>p</i> -CN	BF ₄	-0.95	-0.99
1e	H ₂ CCOC ₆ H ₅	OTf	-0.73	-0.93
1f	H ₂ CC(C ₆ H ₅)=C(CN) ₂	BF ₄	-0.23	-0.26

^aVolts vs. SCE in CH₃CN (50 mV/s scan rate) with 0.1 N tetrabutylammonium fluoroborate (TBAF) as electrolyte. Sulfonium salt concentration was 1.0×10^{-4} M. A platinum button (Pt) and a glassy-carbon (GC) electrode were used as the working electrode.

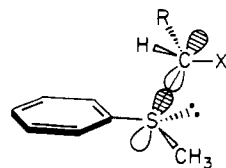
Table II. Electrochemical Peak (E_p) Potentials for the Reduction of Some Substituted 1-Naphthylmethylsulfonium Salts

compd	R	X	E_p^a	
			Pt	GC
2a	CH ₃	CF ₃ SO ₃	-1.51	-1.46
2b	CH(CH ₃) ₂	BF ₄	-1.49	-1.40
2c	H ₂ CC ₆ H ₅	BF ₄	-1.23	-1.06
2d	H ₂ CC ₆ H ₄ - <i>p</i> -CN	BF ₄	-0.92	-0.82
2e	H ₂ CCOC ₆ H ₅	CF ₃ SO ₃	-0.74	-0.80
2f	H ₂ CC(C ₆ H ₅)=C(CN) ₂	CF ₃ SO ₃	-0.17	-0.15

^aVolts vs. SCE in CH₃CN (50 mV/s scan rate) with 0.1 N tetrabutylammonium fluoroborate (TBAF) as electrolyte. Sulfonium salt concentration was 1.0×10^{-4} M. A platinum button (Pt) and a glassy-carbon (GC) electrode were used as the working electrode.

sulfur-carbon antibonding orbital is accessible for a concerted electron-transfer/cleavage mechanism, as shown below. Approach from either the carbon or the sulfur side of the σ^* orbital should be equally effective at bringing about reduction. The electrochemical observations, however, are not controlled by surface effects, as indicated by the experimental results obtained with platinum and glassy-carbon working electrodes (see Tables I and II).

An alternative mechanism for consideration is reduction of the R group prior to fragmentation. This mechanism is not consistent with the extremely large cathodic potentials for the reduction of R alone or R substituted with a good leaving group. For example, toluene and *p*-tolunitrile, which are models for benzyl and *p*-cyanobenzyl R groups, would be expected to reduce at potentials more cathodic than benzonitrile, which is reduced at -2.6 V (vs. SCE in dimethylformamide).¹⁰ The reduction potential of acetophenone is also quite cathodic, i.e., -1.99 V, under the same conditions as the benzonitrile reduction.¹¹ With **1f** or **2f**, the hydrocarbon analogue of the R group, i.e., phenyldicyanopropene, reduces at -1.32 V (E_p vs. SCE at 50 mV/s scan rate in CH₃CN). The incorporation of an electron-withdrawing group on R such as 1-thionaphthalene in a position to be a sulfonium salt model tends to produce a minor shift (e.g., <300 mV) of the reduction



electrode surface	
X	R
H	H
CH ₃	CH ₃
	H
	H
	H
	H

potential to less cathodic values. In this propene derivative, reduction clearly involves the olefinic moiety, as indicated by the observation of electrodimers.¹² Also, one would not expect to shift the reduction potential of an R group whose lowest unoccupied molecular orbital (LUMO) level is of π character by greater than 1 V in a two-step mechanism by simply attaching an electron-withdrawing group through a σ bond.

Summary

The mechanism of reduction of phenyl- and naphthylalkylsulfonium salts is consistent with a concerted σ sulfur-carbon bond breaking concomitant with electron acceptance. This conclusion is supported by the sensitivity of E_p to the electron-withdrawing behavior of the leaving group, which determines the relative energy of the σ^* molecular orbital of the bond being broken in the reduction.

Experimental Section

Equipment. A Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer were used in the standard three-electrode configuration to obtain reduction potentials by cyclic voltammetry. Platinum-inlay and glassy-carbon electrodes were used as the working electrode along with a platinum auxiliary electrode and a standard calomel electrode. The electrolyte was 0.1 M tetrabutylammonium fluoroborate (TBAF) recrystallized from ethyl acetate/pentane in dry acetonitrile (propionitrile) (distilled from CaH₂ under argon). Coulometry was performed on a Princeton Applied Research Model 179 digital coulometer. ¹H NMR spectra were determined on a Varian EM-390 (90 MHz) NMR spectrometer. Combustion analyses were performed by the Analytical Sciences Division of the Kodak Research Laboratories.

Phenyldimethylsulfonium Trifluorosulfonate (1a). Phenyl methyl sulfide (0.05 mol, 6.21 g, Aldrich) was dissolved in methylene chloride (40 mL) and cooled in an ice bath before dropwise addition of methyl trifluoromethanesulfonate (0.05 mol, 5.50 mL, Fluka). The mixture was refluxed for 15 h, cooled, and poured into 150 mL of diethyl ether. The product crystallized and was collected by suction filtration and air-dried. Recrystallization from isopropyl alcohol gave 2.60 g (97% yield) of purified product: mp 103–105 °C; ¹H NMR (acetone-*d*₆) δ 3.46 (s, 6 H). Anal. Calcd for C₉H₁₁S₂F₃O₃: C, 37.7; H, 3.8; S, 21.9. Found: C, 37.5; H, 3.8; S, 22.2.

Phenylmethylisopropylsulfonium Tetrafluoroborate (1b). Thioanisole (8.05 mmol, 1.0 g, Aldrich), isopropyl bromide (8.05 mmol, 0.99 g, Kodak Laboratory Chemicals), and silver tetrafluoroborate (8.05 mmol, 1.57 g, Aldrich) were added to a 50-mL flask along with 25 mL of dry

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methylene chloride, and the mixture was stirred for 27 h at room temperature. The reaction mixture was filtered into 100 mL of diethyl ether, and the product oiled out of solution. The product was converted to the PF₆⁻ salt as described³ and recrystallized from diethyl ether/acetonitrile at ~8 °C, giving 1.5 g (60% yield) of the purified product: mp 85–86 °C; ¹H NMR (CD₃CN) δ 3.15 (s, 3 H), 3.89 (7 lines, 1 H, *J* = 6.0 Hz).

Phenylmethylbenzylsulfonium Tetrafluoroborate (1c). Thioanisole (1.0 mmol, 1.24 g, Aldrich), benzyl bromide (1.0 mmol, 1.71 g, Aldrich), and silver tetrafluoroborate (1.0 mmol, 1.94 g, Aldrich) were added to a 100-mL round-bottom flask along with 30 mL of dry methylene chloride, and the mixture was stirred at room temperature for 2 days. The reaction mixture was filtered into 100 mL of diethyl ether. The product crystallized and was collected by suction filtration. Recrystallization from acetonitrile/diethyl ether gave 2.5 g (83% yield) of purified product: mp 123–124 °C; ¹H NMR (CD₃CN) δ 3.18 (s, 3 H), 4.80 (q, 2 H, Δ*ν*_{AB} = 21.0 Hz). Anal. Calcd for C₁₄H₁₅BF₄S: C, 55.7; H, 5.0. Found: C, 55.7; H, 5.1.

Phenylmethyl(*p*-cyanobenzyl)sulfonium Tetrafluoroborate (1d). Thioanisole (10 mmol, 1.24 g, Aldrich), α-bromo-*p*-tolunitrile (1 mmol, 1.96 g, Aldrich), and silver tetrafluoroborate (1 mmol, 1.94 g, Aldrich) were added to 30 mL of dry methylene chloride, and the mixture was stirred at room temperature for 3 days. The reaction mixture was filtered and flash evaporated to dryness; the product crystallized after diethyl ether was added to the colorless oil. The white crystalline product was recrystallized from acetonitrile/diethyl ether, giving 3.2 g (85% yield) of purified product: mp 129–131 °C; ¹H NMR (CD₃CN) δ 3.20 (s, 3 H), 4.84 (q, 2 H, Δ*ν*_{AB} = 21.0 Hz). Anal. Calcd for C₁₅H₁₄BF₄NS: C, 60.7; H, 4.3; N, 3.7. Found: C, 60.9; H, 4.3; N, 4.2.

Phenylmethylphenacylsulfonium *p*-Toluenesulfonate (1e). Thioanisole (5 mmol, 0.62 g, Aldrich) and phenacyl *p*-toluenesulfonate (5 mmol, 1.45 g) was dissolved in 25 mL of acetonitrile; the solution was refluxed for 15 h and cooled in ice. The product crystallized from the reaction mixture and was filtered, dried, and recrystallized from isopropyl alcohol, giving 190 mg (92% yield) of purified product: mp 187–188 °C; ¹H NMR (Me₂SO-*d*₆) δ 2.28 (s, 3 H), 3.37 (s, 3 H), 5.90 (s, 2 H). Anal. Calcd for C₂₂H₂₂S₂O₄: C, 63.7; H, 5.3. Found: C, 63.7; H, 5.4.

α-(Bromoethyl)-β,β-dicyanostyrene. (1-Phenylethylidene)malononitrile (0.1 mol, 16.82 g) synthesized by the method of Mowry¹³ was dissolved in carbon tetrachloride (200 mL) along with *N*-bromosuccinimide (0.1 mol, 17.79 g, Aldrich). A catalytic quantity of benzoyl peroxide (Aldrich) was added, and the mixture was heated to reflux for 7 days. The mixture was cooled to room temperature, the succinimide was filtered off, and the solvent was flash evaporated. The resulting solid was recrystallized from absolute ethanol, giving 21.0 g (85% yield) of purified product: mp 116–117 °C; ¹H NMR (CDCl₃) δ 4.52 (s, 2 H). Anal. Calcd for C₁₁H₇BrN₂: C, 53.5; H, 2.9; N, 11.3. Found: C, 53.4; H, 2.9; N, 11.3.

Phenylmethyl(2-phenyl-3,3-dicyanoprop-2-enyl)sulfonium Tetrafluoroborate (1f). Thioanisole (1.0 mmol, 1.24 g, Aldrich), α-(bromoethyl)-β,β-dicyanostyrene (1.0 mmol, 2.47 g), and silver tetrafluoroborate (1.0 mmol, 1.94 g, Aldrich) were added to a 100-mL single-neck round-bottom flask along with 30 mL of dry methylene chloride, and the mixture was stirred at room temperature for 2 days. The reaction mixture was filtered into 100 mL of diethyl ether. The product crystallized and was collected by suction filtration. Recrystallization from acetonitrile/diethyl ether at ~8 °C gave 3.0 g (80% yield) of purified product: mp 160–163 °C; ¹H NMR (CD₃CN) δ 3.33 (s, 3 H), 5.11 (q, 2 H, Δ*ν*_{AB} = 17.0 Hz). Anal. Calcd for C₁₈H₁₅BF₄N₂S: C, 57.2; H, 4.0; N, 7.4. Found: C, 57.3; H, 4.1; N, 7.6.

1-Naphthyl Methyl Sulfide. Methyl iodide (30 mmol) in 30 mL of anhydrous tetrahydrofuran (THF) was added to a solution of 30 mmol of sodium 1-naphthalenethiolate in 50 mL of THF at room temperature. The thiolate had been made from 1-naphthalenethiol (Kodak Laboratory Chemicals) and sodium hydride in argon-purged THF. The mixture was stirred for 30 min and poured into 200 mL of water. The aqueous solution was extracted with ether (3 × 100 mL). The combined extracts were washed with 5% aqueous sodium carbonate, dried over MgSO₄, filtered, and flash evaporated. The colorless oil was distilled under reduced pressure (100 °C/0.4 mmHg), and the desired product (3.60 g, 67% yield) was collected: ¹H NMR (CDCl₃) δ 2.5 (s, 3 H). Anal. Calcd for C₁₁H₁₀S: C, 75.8; H, 5.8; S, 18.4. Found: C, 76.0; H, 6.0; S, 18.6.

1-Naphthyl dimethylsulfonium Trifluoromethanesulfonate (2a). 1-Naphthyl methyl sulfide (10 mmol) was dissolved in 25 mL of dry methylene chloride. To this solution was added via syringe 10 mmol of methyl trifluoromethanesulfonate at room temperature. After 15 h the solvent was flash evaporated, diethyl ether was added, and the product (1.60 g, 47% yield) crystallized. Recrystallization from isopropyl alcohol gave 0.97 g of the desired product: mp 90–92 °C; ¹H NMR (acetone-*d*₆)

δ 3.6 (s, 6 H). Anal. Calcd for C₁₃H₁₃F₃O₃S₂: C, 46.1; H, 3.9; S, 19.0. Found: C, 46.1; H, 4.1; S, 18.7.

1-Naphthylmethylisopropylsulfonium Tetrafluoroborate (2b). 1-Naphthyl methyl sulfide (5.7 mmol, 1.0 g), isopropyl bromide (5.7 mmol, 1.0 g), and silver tetrafluoroborate (5.7 mmol, 1.12 g, Aldrich) were added to a 50-mL single-neck flask along with 25 mL of dry methylene chloride, and the mixture was stirred for 15 h at room temperature. The reaction mixture was filtered into 100 mL of diethyl ether. The product oiled out of solution and was crystallized from diethyl ether/acetonitrile at ~8 °C, giving 0.30 g (17% yield) of purified product: mp 111–112 °C; ¹H NMR (CD₃CN) δ 3.26 (s, 3 H), 4.1 (hep, 1 H, Δ*ν*_{AB} = 6.0 Hz). Anal. Calcd for C₁₄H₁₇BF₄S: C, 55.3; H, 5.6. Found: C, 55.4; H, 5.6.

1-Naphthylbenzylmethylsulfonium Tetrafluoroborate (2c). 1-Naphthyl methyl sulfide (1.0 mmol, 1.21 g), benzyl bromide (1.0 mmol, 1.71 g, Aldrich), and silver tetrafluoroborate (1.0 mmol, 1.94 g, Aldrich) were added to a 100-mL single-neck flask along with 30 mL of dry methylene chloride, and the mixture was stirred at room temperature for 2 days. The reaction mixture was filtered into 100 mL of diethyl ether. The product crystallized and was collected by suction filtration. Recrystallization from acetonitrile/diethyl ether at ~8 °C gave 2.90 g (82% yield) of purified product: mp 146–147 °C; ¹H NMR (CD₃CN) δ 3.28 (s, 3 H), 4.88 (q, 2 H, Δ*ν*_{AB} = 25.5 Hz). Anal. Calcd for C₁₈H₁₇BF₄S: C, 61.4; H, 4.9. Found: C, 61.5; H, 5.0.

1-Naphthyl(4-cyanobenzyl)methylsulfonium Tetrafluoroborate (2d). 1-Naphthyl methyl sulfide (1.0 mmol, 1.21 g), α-bromo-*p*-tolunitrile (1.0 mmol, 1.96 g, Aldrich), and silver tetrafluoroborate (1.0 mmol, 1.94 g, Aldrich) were added to 30 mL of dry methylene chloride, and the mixture was stirred at room temperature for 2 days. The reaction mixture was filtered into 100 mL of diethyl ether, and the product crystallized. The crude product was recrystallized from acetonitrile/diethyl ether at ~8 °C, giving 3.2 g (85% yield) of purified product: mp 121–122 °C; ¹H NMR (CD₃CN) δ 3.32 (s, 3 H), 4.90 (q, 2 H, Δ*ν*_{AB} = 27.0 Hz). Anal. Calcd for C₁₉H₁₆BF₄NS: C, 60.7; H, 4.3; N, 3.7. Found: C, 61.0; H, 4.3; N, 3.8.

1-Naphthyl Phenacyl Sulfide. 1-Naphthalenethiol (1.0 mmol, 1.60 g, Kodak Laboratory Chemicals) was dissolved in 30 mL of dry tetrahydrofuran, and the solution was purged with argon. After 10 min sodium hydride (1.0 mmol, 0.24 g, J. T. Baker) was added, producing the thiolate anion. Phenacyl bromide (1.0 mmol, 1.87 g, Aldrich) was dissolved in 25 mL of dry tetrahydrofuran and added dropwise to the reaction mixture at room temperature. After 2 h the mixture was poured into 200 mL of water, which was then extracted with diethyl ether (3 × 50 mL). The combined ether extracts were washed with 5% aqueous sodium carbonate, dried over MgSO₄, filtered, and condensed. The crude product was recrystallized from heptane, giving 1.98 g (71% yield) of purified product: mp 80–82 °C; ¹H NMR (CDCl₃) δ 4.27 (s, 3 H). Anal. Calcd for C₁₈H₁₄SO: C, 77.7; H, 5.1; S, 11.5. Found: C, 77.8; H, 5.1; S, 11.6.

1-Naphthylphenacylmethylsulfonium Trifluoromethanesulfonate (2e). Methyl trifluoromethanesulfonate (1.0 mmol, 1.64 g, Fluka) was added to 1-naphthyl phenacyl sulfide (1.0 mmol, 2.78 g) in 30 mL of dry methylene chloride. The reaction mixture was stirred at room temperature for 3 days, and 100 mL of diethyl ether was added. The solution was placed in a refrigerator at ~6 °C, and after several hours the product crystallized. Recrystallization from isopropyl alcohol gave 3.98 g (90% yield): mp 156–158 °C; ¹H NMR (acetone-*d*₆) δ 3.74 (s, 3 H), 6.23 (s, 2 H). Anal. Calcd for C₂₀H₁₇F₃O₄S₂: C, 54.3; H, 3.9; S, 14.5. Found: C, 54.3; H, 3.9; S, 14.3.

1-Naphthyl 2-phenyl-3,3-dicyanoprop-2-enyl Sulfide. 1-Naphthalenethiol (1.0 mmol, 1.60 g, Kodak Laboratory Chemicals) was dissolved in 30 mL of dry tetrahydrofuran, the solution was purged with argon, and sodium hydride (1.0 mmol, 0.24 g, J. T. Baker) was added. α-(Bromoethyl)-β,β-dicyanostyrene (1.0 mmol, 1.14 g) was dissolved in 20 mL of tetrahydrofuran and added dropwise to the reaction mixture at room temperature. After 2 h the reaction mixture was poured into 200 mL of water, which was then extracted with diethyl ether (3 × 50 mL). The combined ether extracts were washed with 5% aqueous sodium carbonate, dried over MgSO₄, filtered, and condensed. The crude product was recrystallized from isopropyl alcohol, giving 1.10 g (34% yield) of purified product: mp 120–120.5 °C; ¹H NMR (CDCl₃) δ 4.20 (s, 2 H). Anal. Calcd for C₂₁H₁₄N₂S: C, 77.3; H, 4.3; N, 8.6; S, 9.8. Found: C, 77.0; H, 4.4; N, 8.6; S, 10.0.

1-Naphthylmethyl(2-phenyl-3,3-dicyanoprop-2-enyl)sulfonium Trifluoromethanesulfonate (2f). 1-Naphthyl 2-phenyl-3,3-dicyanoprop-2-enyl sulfide (1.0 mmol, 3.26 g) was dissolved in 30 mL of dry methylene chloride along with methyl trifluoromethanesulfonate (1.0 mmol, 1.64 g, Fluka), and the mixture was refluxed for 5 days. The reaction mixture was poured into 150 mL of diethyl ether and placed in a refrigerator at ~8 °C. The product crystallized and was recrystallized from acetonitrile/diethyl ether at ~6 °C, giving 2.75 g (56% yield): mp 149–150.5

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$^{\circ}\text{C}$; ^1H NMR (CD_3CN) δ 3.50 (s, 3 H), 5.30 (q, 2 H, $\Delta\nu_{\text{AB}} = 21.0$ Hz). Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_3\text{S}_2$: C, 56.3; H, 3.5; N, 5.7. Found: C, 56.9; H, 3.6; N, 5.9.

Phenylmethyl(*m*-cyanobenzyl)sulfonium Tetrafluoroborate. Thioanisole (8.05 mmol, 1.00 g, Aldrich), α -bromo-*m*-tolunitrile (8.05 mmol, 1.57 g, Aldrich), and silver tetrafluoroborate (8.05 mmol, 1.57 g, Aldrich)

were added to 30 mL of dry methylene chloride, and the mixture was stirred at room temperature for 20 h. The reaction mixture was filtered and flash evaporated to dryness, and attempted crystallization from acetonitrile/diethyl ether gave the product as a colorless oil [2.5 g (95% yield)]: ^1H NMR (CH_3CN) δ 3.22 (s, 3 H), 4.70 (q, 2 H, $\Delta\nu_{\text{AB}} = 15.6$ Hz); mass spectrum (FDMS), m/e 240 (M^+).

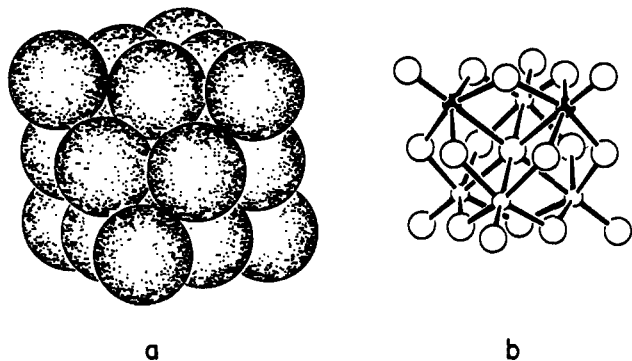
The $\{[(\text{CH}_3)_5\text{C}_5]\text{Rh}(\text{cis-Nb}_2\text{W}_4\text{O}_{19})\}^{2-}$ Isomers: Synthesis, Structure, and Dynamics

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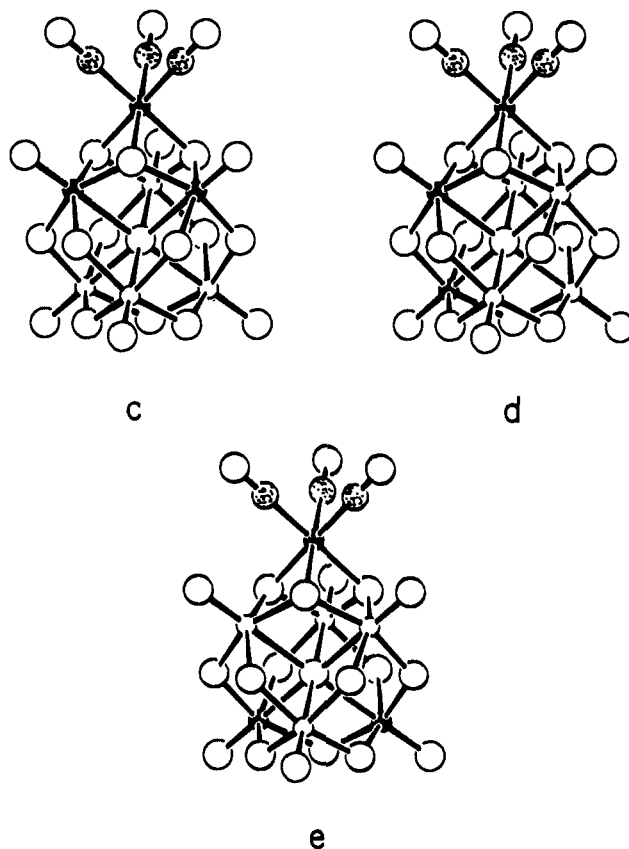
Abstract: The $\text{cis-Nb}_2\text{W}_4\text{O}_{19}^{4-}$ anion reacts with $\{[(\text{CH}_3)_5\text{C}_5]\text{RhCl}_2\}_2$ in CH_2Cl_2 to form the title complex. According to a single-crystal X-ray diffraction study, the $\text{cis-Nb}_2\text{W}_4\text{O}_{19}^{4-}$ ion behaves as a tridentate ligand in this complex, utilizing three contiguous bridging oxygen atoms for the rhodium binding site. Of the three diastereomers possible for this adduct, only two are formed under the reaction conditions. The third diastereomer is formed from a mixture of these two in CH_3NO_2 at room temperature in the presence of a catalyst, solvated $\{[(\text{CH}_3)_5\text{C}_5]\text{Rh}^{2+}$. Employing the results of ^1H and ^{17}O NMR spectroscopic studies, mechanisms are proposed for the formation and isomerization of $\{[(\text{CH}_3)_5\text{C}_5]\text{Rh}(\text{Nb}_2\text{W}_4\text{O}_{19})\}^{2-}$. The former involves the intermediate $\{[(\text{CH}_3)_5\text{C}_5]\text{RhCl}_2(\text{Nb}_2\text{W}_4\text{O}_{19})\}^{4-}$; the latter involves the $\{[(\text{CH}_3)_5\text{C}_5]\text{Rh}_2(\text{Nb}_2\text{W}_4\text{O}_{19})\}$ molecule as an intermediate.

The $\text{cis-Nb}_2\text{W}_4\text{O}_{19}^{4-}$ anion²⁻⁵ has a structure tailor-made for systematically examining the reaction chemistry of small, closed-packed oxygen surfaces. Its 19 oxygen atoms form the octahedral, cubic close-packed array shown in the space-filling representation a.⁶ The six d^0 Nb^{V} and W^{VI} centers occupy octahedral interstices within this array, and they are themselves arranged in the cis-octahedral fashion illustrated in b.



The $\text{Nb}_2\text{W}_4\text{O}_{19}^{4-}$ anion is sufficiently basic to form air-stable metal tricarbonyl adducts $[(\text{OC})_3\text{M}(\text{cis-Nb}_2\text{W}_4\text{O}_{19})]^{3-}$, $\text{M} = \text{Mn}^{\text{I}}$ and Re^{I} .⁵ In these complexes, the polyoxoanion behaves as a tridentate ligand, utilizing a triangle of bridging oxygen atoms

as the metal tricarbonyl binding site. Three diastereomers c-e are possible for this structure, and low-resolution 13.5-MHz ^{17}O NMR spectroscopy has shown that isomer d predominates for the $\text{M} = \text{Re}$ complex.⁵



Simple electrostatic considerations would dictate that $\text{M}(\text{CO})_3^+$ cations prefer $\text{Nb}_2\text{W}_4\text{O}_{19}^{4-}$ binding sites adjacent to pentavalent

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(6) M_6O_{19} units were drawn using O_h -idealized $\text{W}_6\text{O}_{19}^{2-}$ coordinates;⁷ $\{[(\text{CH}_3)_5\text{C}_5]\}$ units were drawn using D_{5h} -idealized coordinates with 1.43 Å ring carbon-ring carbon distances and 1.51-Å methyl carbon-ring carbon distances.⁸ Rhodium-oxygen and rhodium-carbon bond lengths were fixed at 2.20 and 2.16 Å, respectively. Van der Waals radii⁹ for oxygen (1.4 Å), carbon (1.7 Å), chlorine (1.8 Å), and methyl groups (2.0 Å) were used for space-filling drawings.