produced *cis*-2-methylthiocyclopentanol (9.8 g, 74%), bp 52–54° (0.3 mm); nmr δ 4.05 (m, 1 C*H*OH), 3.03 (d, 1, J = 2.5 Hz, OH), 2.95 (m, 1, C*H*SCH$_3$), 2.08 (s, 3, SCH$_3$), and 1.74 (m, 6, (CH$_2$)$_3$).

2-Methoxy-1-propanol and 1-methoxy-2-propanol were prepared by the acid-catalyzed ring opening of propylene oxide in methanol according to a known procedure,[26] and the isomers were separated by preparative glpc.

1-Methylthio-2-propanol was prepared by the procedure of Bordwell and Andersen:[27] bp 67–69° (20 mm) [lit.[27] bp 55–58° (10 mm)].

2-Methylthio-1-propanol was prepared as follows: a mixture of 1-propenyl acetate (10 g, 0.1 mol), methanethiol (60 g), and benzoyl peroxide (0.5 g) was illuminated with a uv lamp as described earlier for *cis*-2-methylthiocyclopentanol. The 2-methylthiopropyl acetate obtained (4.8 g, 34%, bp 128°) was hydrolyzed with 10% KOH solution (60 ml) at room temperature. The mixture was extracted with ether several times, and the combined extracts were washed with water saturated with sodium chloride, dried (MgSO$_4$), and concentrated. The product was separated and purified by preparative glpc; overall yield 18%; bp 65–71° (12 mm); nmr (CDCl$_3$) δ 3.55 (d, 2, J = 6.0 Hz, C*H*$_2$OH), 2.85 (s, 1, OH), 2.79 (m, 1, C*H*SCH$_3$), 2.05 (s, 3, SCH$_3$), and 1.27 (d, 3, J = 6.0 Hz, CHC*H*$_3$).

Acknowledgment. We are indebted to Dr. Wesley Huntress of the Jet Propulsion Laboratories, Pasadena, for his help with regard to both the instrumental and conceptual aspects of this work.

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Anodic Oxidations. IX. Anodic Oxidation of 2-Methoxyethanol

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Abstract: The anodic oxidation of 2-methoxyethanol in the presence of tetraethylammonium fluoroborate as supporting electrolyte results in the formation of formaldehyde, bis(2-methoxyethyl)formal (I), 2-hydroxyethyl-2′-methoxyethylformal (II), and 2,4,6,9-tetraoxadecane (III), with the major oxidation products resulting from attack on the ether rather than the alcohol function of 2-methoxyethanol. With tetraethylammonium nitrate as supporting electrolyte, an additional product, 3-hydroxymethyl-2,4,7-trioxaoctane (IV), is obtained. The mechanisms of these oxidations have been discussed.

The saturated aliphatic alcohols and ethers have ionization potentials exceeding 9 eV.[1,2] Since there is a parallelism between anodic oxidation potentials and gas-phase ionization potentials,[3] it is not surprising that the anodic oxidation of aliphatic alcohols and ethers requires extreme positive potentials.[4] By using fluoroborates as the supporting electrolyte, it is possible to extend the potential range to beyond 3.0 V *vs.* Ag|Ag$^+$ (10^{-2} M),[5] and to determine the half-wave potentials for oxidation of aliphatic alcohols by cyclic voltammetry.[6]

Sundholm[7] has shown that methanol and ethanol can be electrooxidized to give, in good yield, aldehydes with sodium alkoxides as the supporting electrolytes and acetals with perchlorates or fluoroborates as the supporting electrolytes. The proposed mechanism involves reaction I as the primary process, with subsequent chemical steps leading to products. Shono and Matsumura[8] have anodically methoxylated saturated ethers in methanol containing a methoxide, a nitrate, or a p-toluenesulfonate as the supporting electrolyte. This reaction introduces methoxy groups in the α position of the ether and fails when no α hydrogens are available. The authors, therefore, favored a mechanism in which an anodically generated radical abstracts hydrogen from the α position of the ether.

$$\mathrm{RCH_2OH \longrightarrow R\overset{+}{C}HOH + 2e + H^+} \qquad \text{(I)}$$

A mechanism involving direct electron transfer from an ether to form a cationic species should be possible, since such a mechanism has been observed for the alcohols.[6,7] To explore this possibility, the anodic oxidation of 2-methoxyethanol, which contains both the alcohol and the ether function, has been investigated. The products formed indicate the locus of attack, and the extent of attack at the two available sites affords some indication of the relative ease of anodic oxidation of the two functions.

Results

Cyclic voltammograms of a solution of 0.1 M tetraethylammonium fluoroborate in acetonitrile over the potential range −1.20 to +2.1 V *vs.* E (Ag|Ag$^+$ (0.1 N)) at scan rates of 100 and 200 mV sec^{-1} are comparable to those previously reported[9] for a more concentrated solution of this salt and show an increase in current at E > 1.8 V. The addition of 0.47 M 2-methoxy-

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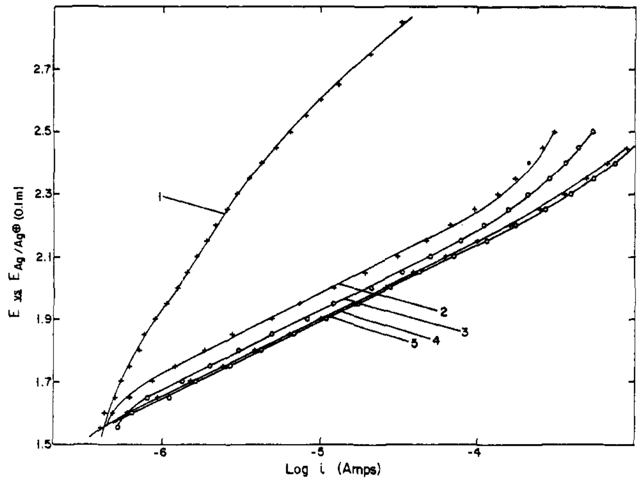


Figure 1. Plots of log *i vs.* E for the anodic oxidation of 2-methoxyethanol in acetonitrile containing 0.1 M tetraethylammonium fluoroborate. Curve 1 is without 2-methoxyethanol added. Curves 2-5 are for solutions containing 10^{-1}, 2×10^{-1}, 8×10^{-1}, and 1 M 2-methoxyethanol, respectively.

ethanol does not result in a new peak potential, but there is a marked increase in current when the potential is more anodic than 1.60 V.

These results were amplified with the steady-state, potentiostatic measurements shown in Figure 1. The upper curve is for 0.1 M tetraethylammonium fluoroborate in acetonitrile, and the remaining curves, going from top to bottom, are with 0.1, 0.2, 0.8, and 1.0 M 2-methoxyethanol added. A comparison of the background current (the upper curve in Figure 1) and the current observed in the presence of 0.1 M 2-methoxyethanol suggests that at 1.9 V as much as 80% of the observed current is attributable to 2-methoxyethanol oxidation. At higher potentials and with greater concentrations of 2-methoxyethanol, the current is virtually all due to oxidation of 2-methoxyethanol.

The four log *i vs.* E curves for 2-methoxyethanol oxidation (Figure 1) are linear over at least 2 decades of current and give Tafel slopes of 245–250 mV/decade of current. Plots of log *i vs.* log of the 2-methoxyethanol concentration, determined at four voltages from 1.8 to 2.3 V, were also linear. The slopes of these lines represent the reaction order in 2-methoxyethanol and were found to vary between 0.4 and 0.5. Both the Tafel slopes and the observed reaction orders indicate that the rate-determining step is complex and not a simple one-electron transfer.

Cyclic voltammetry of a 0.05 M solution of tetraethylammonium fluoroborate in 2-methoxyethanol affords evidence for the occurrence of an electrode reaction at potentials as low as 1.0 V *vs.* Ag|Ag$^+$ (0.1 N). This reaction is self-inhibiting, with the currents at the potentials of interest decreasing with decreasing scan speed as shown in Figure 2. This oxidation is comparable to the self-inhibiting oxidation of methanol observed in the methanol–fluoroborate system[9] and probably involves attack on the hydroxyl function of 2-methoxyethanol.

Despite the electrochemical complexity of the reaction, 2-methoxyethanol can be oxidized anodically at constant current at both carbon and platinum anodes to give isolable and identifiable products in good yield. If a 0.16 M solution of tetraethylammonium fluoroborate in 2-methoxyethanol is electrolyzed until 0.2 F of charge has been passed, it can be demonstrated by two procedures that a quantitative oxidation of 2-methoxyethanol has occurred. Treatment of the electrolysis mixture with 2,4-dinitrophenylhydrazine permits the isolation of a quantitative yield, based on the assumption of a two-electron change/mole of oxidation product formed, of the 2,4-dinitrophenylhydrazone of formaldehyde. When, in a separate experiment, the electrolysis solution was refluxed, under a Dean–Stark trap, with benzene containing a catalytic quantity of sulfuric acid, a quantitative yield of the formal, I, was formed.

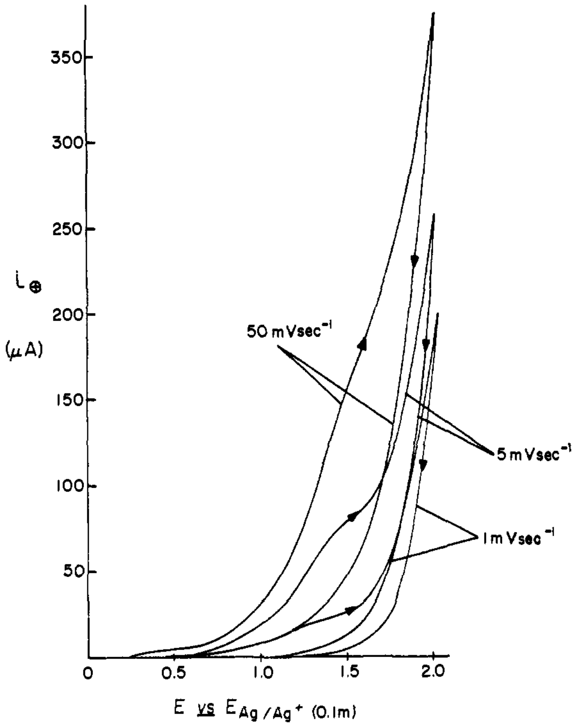
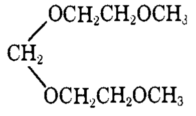
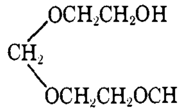


Figure 2. Cyclic voltammograms for a 0.05 M solution of tetraethylammonium fluoroborate in 2-methoxyethanol at three different sweep rates.

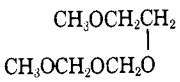


I

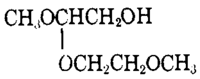
Although both the formal, I, and formaldehyde are present in all the electrolyzed solutions, it is highly probable that neither is a primary product of the electrochemical reaction. When tetraethylammonium fluoroborate is the supporting electrolyte, II and III are also formed, and with tetraethylammonium nitrate as the supporting electrolyte, IV is obtained in addition to the foregoing products. The structural proofs for these compounds will be given in the Discussion, and in what immediately follows the focus will be on the reaction



II



III



IV

parameters which determine the relative amounts of these compounds.

The studies involved experiments with two anode materials, platinum and carbon, and with two supporting electrolytes, tetraethylammonium fluoroborate and tetraethylammonium nitrate. In early experiments, the predominant product obtained was generally the symmetrical formal, I, but it quickly became apparent that some acidity was being generated during the electrolyses and that acid-catalyzed interconversion of the products was taking place during the electrolyses and particularly during the work-up. In fact, if a small amount of sulfuric acid is added prior to initiation of the electrolysis, coulombic yields of I varying from 61 to 77% are obtained, and lesser amounts of the unsymmetrical formal, II, are found. The interconversion during work-up was obviated by making the solution basic with sodium carbonate immediately after electrolysis, and studies with pyridine added to the electrolysis solutions were carried out to determine to what extent this would alter the product composition.

Table I compiles some representative values for the amounts of the products obtained in the anodic oxidation of 2-methoxyethanol. These determinations were made using analytical vpc but did not include a determination of formaldehyde. As already noted, if all of the products obtained using the fluoroborate salt were converted to either I or the 2,4-dinitrophenylhydrazone of formaldehyde, the coulombic yield would be essentially 100%. It, therefore, follows that formaldehyde must be present in these electrolysis solutions and that the difference between 100% and the sum of the percentages shown in Table I is a measure of the amount of formaldehyde present.

Table I. Coulombic Yields of Products in the Anodic Oxidation of 2-Methoxyethanol

Anode	Supporting electrolyte	Coulombic yield, % I	II	III	IV
Pt	$Et_4N^+ BF_4^-$	3.9	37.1	5.5	
Pt[a]	$Et_4N^+ BF_4^-$	61.1	15.3	0.85	
C	$Et_4N^+ BF_4^-$	19.3	30.4	8.1	
C[a]	$Et_4N^+ BF_4^-$	77.5	17.8	2.1	
Pt	$Et_4N^+ NO_3^-$	Trace	11.4	2.1	20.6
C	$Et_4N^+ NO_3^-$	Trace	29.6	2.1	14.4

[a] With 1.2% (by volume) concentrated sulfuric acid added initially.

For reasons to be discussed later, the reactions with the nitrate salt are probably not 100% efficient. Nevertheless, it can be shown that formaldehyde is present in these product solutions as well. Treatment of the solutions with 2,4-dinitrophenylhydrazine results in an intractable mixture of the dinitrophenylhydrazone of formaldehyde and the osazone of glycolaldehyde. Acid-catalyzed reaction using benzene and the Dean–Stark procedure converts free formaldehyde to I, II to I, each mole of III to 2 mol of I, and IV to the di-2-methoxyethyl acetal of glycolaldehyde. The use of this procedure gave 32.6% I for the experiment at platinum and 60.6% I for the experiment at carbon, indicating the presence of at least 17% formaldehyde in the former case and 26.8% formaldehyde in the latter case.

Table II records the results of some experiments to determine the effect of initially added pyridine on the product composition. The observed coulombic yields of both I and II are lowered, probably because pyridine is electroactive at the anodic potentials attained. The significant point to note is that the ratios of II:I are significantly increased with pyridine added. Since II is probably a primary product and I is an interconversion product, the addition of pyridine suppresses but does not completely eliminate equilibration during the electrolysis.

Table II. Effect of Initially Added Pyridine on the Product Composition in the Anodic Oxidation of 2-Methoxyethanol with Tetraethylammonium Fluoroborate as the Supporting Electrolyte

Anode	% pyridine	Coulombic yield, % I	II	III
C	6.3	7.0	28.2	8.6
C	12.5	3.7	24.2	8.6
Pt	6.3	1.0	19.3	2.6

All of the foregoing experiments were carried out in a cell that was not fully protected from the atmosphere. The 2-methoxyethanol used was distilled at atmospheric pressure, and the water content, determined by Karl Fisher titration, varied from 0.02 to 0.11% depending on the time elapsed between distillation and use.

A solution of tetraethylammonium fluoroborate (0.5 g) in freshly distilled 2-methoxyethanol (15 ml) contained 0.02% water initially and 0.70% water after the solution had been standing unprotected for 19 hr. An actual electrolysis solution contained 0.30% water after oxidation at 2.0 A for 163 min, this being our typical electrolysis time and condition. This percentage of water is, of course, in addition to any amounts that were consumed by hydrolytic reactions during the course of the anodic oxidation.

This absorbed water and the hydrolytic reactions that it makes possible account for the significant amounts of formaldehyde observed in our anodic oxidations. This hypothesis was given credence by carrying out the anodic oxidations with water initially added and in a cell protected from the atmosphere. The results are shown in Table III.

Table III. Effect of Added Water on the Product Composition in the Anodic Oxidation of 2-Methoxyethanol at a Carbon Anode in the Presence of Tetraethylammonium Fluoroborate

% water added initially	Coulombic yield, % I	II	III
0	30.9	32.8	7.8
0	19.3	30.4	8.1
3.1	10.2	26.0	9.9
6.3	5.0	21.2	9.6

The first entry in Table III is for an experiment conducted in an all glass cell, protected from the atmosphere with a drying tube, with the electrodes sealed into the cell. The remaining three experiments were carried out in the usual water-jacketed beaker. For all four experiments, an aliquot of the reaction mixture treated with 2,4-dinitrophenylhydrazine gave an essentially quantitative yield of the 2,4-dinitrophenylhydrazone of formaldehyde. The addition of water results in increased yields of formaldehyde and decreased yields of I and II, with the increase in formaldehyde being more at the expense of I than of II.

Experimental Section

Materials. Fisher certified 2-methoxyethanol was distilled at atmospheric pressure, bp 123–124°. The preparations of tetraethylammonium nitrate[10] and tetraethylammonium fluoroborate[11] have been described.

Electrochemical Measurements. The two-compartment cell, electronic equipment, and techniques used for making the electrochemical measurements have all been described previously.[9]

Constant Current Electrolyses. The electrolysis cell and electrode assemblies are those previously described for use in constant-current procedures.[12] A solution of 0.025 mol of supporting electrolyte in 2-methoxyethanol (160 ml) was electrolyzed at a current of 2.0 A until the desired amount of charge (usually 0.2–0.3 F) was passed. A 25-ml aliquot was removed and treated with a solution prepared from 2,4-dinitrophenylhydrazine (5 g), concentrated sulfuric acid (25 ml), water (35 ml), and ethanol (50 ml). The precipitate was filtered and crystallized from ethanol, mp 163–165°, undepressed on mixture melting point with authentic formaldehyde 2,4-dinitrophenylhydrazone.

Another 25-ml aliquot was dissolved in benzene (150 ml). Concentrated sulfuric acid (1 ml) was added, and the solution was refluxed under a Dean-Stark trap until the separation of water was complete. Sodium carbonate (5 g) was added, and the mixture was stirred magnetically. The mixture was washed twice with water, the sodium carbonate being carried along, and the benzene solution was dried over anhydrous magnesium sulfate. The benzene and 2-methoxyethanol were distilled from a warm water bath at the water pump, and the residue was made up to 10 ml with acetone for vpc analysis.

The remainder of the electrolysis solution was stirred for 0.5 hr with sodium carbonate. After filtration on a sintered-glass funnel, the solution was distilled at the water pump from a warm water bath to remove the unreacted 2-methoxyethanol. The distillation residue was stirred magnetically with ether, and the quaternary ammonium salt which solidified was separated by filtration. The ether solution was concentrated to a small volume by distillation and made up to 50 ml with acetone for vpc analysis.

With tetraethylammonium fluoroborate as the supporting electrolyte, the development of acidity during electrolysis could be demonstrated with pH paper, while with tetraethylammonium nitrate as the supporting electrolyte, no acidity developed.

Isolation of Products. All of the oxidation products, I, II, III, and IV, were isolated from the anodic oxidations. I and II were synthesized independently by procedures to be described, and the structures of III and IV were determined by chemical and physical methods. The pure isolated or synthesized compounds were then used as standards for the analytical determination of the product compositions by vpc.

Isolation of Bis(2-methoxyethyl)formal (I). Following the normal work-up procedure of an electrolysis mixture from 2-methoxyethanol and tetraethylammonium fluoroborate at a carbon anode, the final liquid residue was fractionally distilled at the water pump. A main cut, having bp 90–105° (20 mm) and $n^{24}\text{D}$ 1.4150, was retained and redistilled through a Vigreux column, yielding the pure formal, bp 101° (20 mm), $n^{19}\text{D}$ 1.4147. This product was shown to be a single compound by vpc, and its infrared spectrum was identical with that of an authentic sample of I.

Anal. Calcd for $C_7H_{16}O_4$: C, 51.20; H, 9.82. Found: C, 51.06; H, 9.69.

Isolation of 2-Hydroxyethyl-2′-methoxyethylformal (II). The analytical solution from a typical electrolysis was fractionally distilled and four fractions were taken. Examination of the fractions by analytical vpc showed that the fourth fraction was enriched in II. Pure II, $n^{23}\text{D}$ 1.4280, was isolated from this fraction by preparative vpc on an Aerograph Autoprep, Model A-700, using a 10 ft × $^3/_8$ in. column packed with 10% UCON on Teflon 6 and maintained at 200°. The isolated formal was shown to be identical with an authentic sample through the identity of its infrared spectrum and vpc retention time.

Isolation of 2,4,6,9-Tetraoxadecane (III). The analytical solution from a typical electrolysis was fractionated at the pressure of the water pump, and the earlier fractions were found by analytical vpc to be enriched in III. Further separation was achieved with the Autoprep using the column described above at 175°. The sample finally isolated had $n^{23}\text{D}$ 1.4049 and was 96% pure by vpc.

Anal. Calcd for $C_6H_{14}O_4$: C, 47.98; H, 9.40. Found: C, 47.49; H, 9.34.

A sample of III (0.0887 g, 0.000591 mol) was treated with a solution of 2,4-dinitrophenylhydrazine (0.496 g) in concentrated sulfuric acid (2.5 ml), water (4 ml), and ethanol (8 ml), yielding 0.253 g (0.00123 mol) of the crude formaldehyde 2,4-dinitrophenylhydrazone. The yield of crude product was 104% based on the expected formation of 2 mol of hydrazine/mol of III. After crystallization from ethanol, the hydrazone melted at 163–165° and showed no depression on mixture melting point with an authentic sample of formaldehyde 2,4-dinitrophenylhydrazone.

A solution of III (0.368 g) in methanol (10 ml), water (0.5 ml), and concentrated sulfuric acid (2 drops) was refluxed 3 hr. Solvent (8 ml) was removed by distillation, and the residue was stirred with sodium bicarbonate. After filtration, the solution was taken up in ether and dried over anhydrous magnesium sulfate. The dried ether solution was concentrated to a volume of 5 ml for vpc analysis, which showed the presence of 0.076 g (41%) of 2-methoxyethanol.

The nmr spectrum of III, described and discussed in the Discussion, was fully consistent with the chemical evidence and structure proposed for III.

Isolation of 3-Hydroxymethyl-2,4,7-trioxaoctane (IV). The analytical solution from an electrolysis using tetraethylammonium nitrate as the supporting electrolyte was first distilled to obtain a fraction enriched in IV, and the final separation was made with the Autoprep using the column described above at 175°. The finally isolated product has $n^{24}\text{D}$ 1.4271.

Anal. Calcd for $C_6H_{14}O$: C, 47.98; H, 9.40. Found: C, 47.96, 47.77; H, 9.32, 9.17.

A solution of IV (0.319 g, 0.00213 mol) in ethanol (10 ml) was added to a solution of 2,4-dinitrophenylhydrazine (1.5 g) in concentrated sulfuric acid (7.5 ml), water (10 ml), and ethanol (15 ml). The mixture was left standing 1 hr, after which time the precipitate was filtered and crystallized from nitrobenzene-ethanol to yield 0.453 (50.9%) of the bis-2,4-dinitrophenylhydrazone of glyoxal, mp 316–317° dec.

Treatment of either glyoxal or glycolaldehyde with 2,4-dinitrophenylhydrazine gave the same derivative, all three products having identical infrared spectra and the same melting point.

Conversion of IV to the *p*-nitrobenzoate gave an oil, which was purified by distillation in a short-path still.

Anal. Calcd for $C_{13}H_{17}NO_7$: N, 4.68. Found: N, 4.13.

Vpc Analyses. Solutions were analyzed by vpc using a F & M Model 720 gas chromatograph and a 6-ft, 0.25-in. i.d. column packed with 5% Carbowax 20M on Haloport F. The unknown solutions were compared with standards prepared from the identified components.

Bis(2-methoxyethyl)formal (I). A mixture of paraformaldehyde (30 g, 1 mol), 2-methoxyethanol (193.2 g, 2.54 mol), *p*-toluenesulfonic acid (1 g), and toluene (500 ml) was refluxed under a Dean-Stark trap until water no longer separated. The reaction mixture was stirred with sodium carbonate (5 g), extracted two times with 75-ml portions of water, and dried over anhydrous magnesium sulfate. Distillation at 24 mm yielded 111.5 g (67.9%) of the formal; bp 100–101°, $n^{21}\text{D}$ 1.4139. A sample redistilled for analysis had bp 98° (22 mm), $n^{22}\text{D}$ 1.4134.

Anal. Calcd for $C_7H_{16}O_4$: C, 51.20; H, 9.82. Found: C, 50.98; H, 9.73.

2-Hydroxyethyl-2′-methoxyethylformal, (II). Concentrated sulfuric acid (1 ml) was added to a solution of I (50 ml) in ethylene glycol (20 ml), and the mixture was left standing overnight at room temperature. It was stirred with sodium carbonate (5 g) and again left standing overnight. The sodium carbonate was removed by filtration, 1 g of fresh sodium carbonate was added, and the mixture was distilled to yield 8.8 g of II, bp 66–77° (0.43 mm), $n^{23}\text{D}$ 1.4294. A sample redistilled for analysis had bp 68° at 0.43 mm and $n^{22}\text{D}$ 1.4290.

Anal. Calcd for $C_6H_{14}O_4$: C, 47.99; H, 9.40. Found: C, 48.03; H, 9.42.

Conversion of II to I. A solution of II (0.527 g, 0.00351 mol) and concentrated sulfuric acid (12 drops) in 2-methoxyethanol (50 ml) was left standing at room temperature for 24 hr. The solution was taken up in ether and stirred magnetically with a saturated solution of sodium carbonate and some solid sodium bicarbonate. The

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ether solution was separated and dried over sodium carbonate. After filtration, the solution was distilled at the water pump to remove the ether and 2-methoxyethanol, and the residue was made up to 10 ml with acetone. Analysis by vpc indicated the presence of 0.478 g (83.2%) of I.

1,6-Dichloro-2,5-dioxahexane. The procedure of Lichtenberger and Martin,[13] in which dry hydrogen chloride was passed into a mixture of paraformaldehyde and ethylene glycol, was used. The yield of product was 66%, bp 90–94° (14 mm), $n^{23}\text{D}$ 1.4630.

2,4,7,9-Tetraoxadecane. 1,6-Dichloro-2,5-dioxahexane (31.8 g, 0.2 mol) was added, dropwise with stirring, to a solution of sodium methoxide, prepared by allowing sodium (9.29 g, 0.4 g-atom) to react with methanol (300 ml). Stirring was continued for 1 hr after the addition. The sodium chloride was removed by filtration, and the methanol was removed at the water pump. The residue was taken up in methylene chloride, filtered to remove the last traces of sodium chloride, and distilled at 10 mm. The yield was 21 g (70%), $n^{24}\text{D}$ 1.4028, bp 58°.

2,4,7,9-Tetraoxadecane (0.171 g, 0.000114 mol) was treated with a solution of 2,4-dinitrophenylhydrazine (1.02 g) in concentrated sulfuric acid (5 ml), water (8 ml), and ethanol (10 ml), yielding 0.452 g (94.6%) of crude formaldehyde 2,4-dinitrophenylhydrazone. Crystallization from ethanol gave 0.354 g of the hydrazone, mp 165–167°.

A solution of 2,4,7,9-tetraoxadecane (0.202 g) and concentrated sulfuric acid (2 drops) in methanol (10 ml) and water (0.5 ml) was refluxed 3 hr. Solvent (5 ml) was removed by distillation, and the residue was stirred with sodium bicarbonate. Methanol was added. The solution was filtered and concentrated to a volume of 2 ml for vpc analysis, which showed the presence of 0.031 g (36%) of ethylene glycol.

The following compounds, which were considered to be possible oxidation products, were prepared but not found in the electrochemical reaction mixtures.

(1) **Tris(2-methoxyethyl) orthoformate** was prepared using the procedure of Sah and Ma,[14] yield 23%, bp 112–114° (1 mm), $n^{28}\text{D}$ 1.4268.

Anal. Calcd for $C_{10}H_{22}O_6$: C, 50.41; H, 9.31. Found: C, 50.29; H, 9.29.

(2) **Bis(2-hydroxyethyl)formal** was prepared from paraformaldehyde and ethylene glycol *via* the Dean-Stark procedure, yield 15.3%, bp 109° (0.15 mm), $n^{21}\text{D}$ 1.4478.

Anal. Calcd for $C_5H_{12}O_4$: C, 43.85; H, 9.42. Found: C, 44.27; H, 8.88.

(3) **Tetrakis(2-methoxyethyl)glyoxal diacetal** was prepared from 40% aqueous glyoxal and 2-methoxyethanol using the Dean-Stark procedure, yield 54.6%, bp 144–146° (0.8 mm), $n^{27}\text{D}$ 1.4350.

Anal. Calcd for $C_{14}H_{30}O_8$: C, 51.52; H, 9.26. Found: C, 51.53; H, 9.37.

Discussion

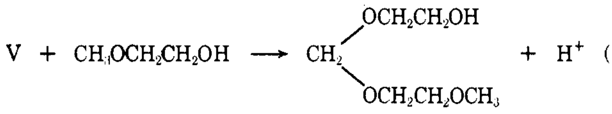
Both cyclic voltammetry and steady-state, potentiostatic measurements on solutions of 2-methoxyethanol in acetonitrile containing tetraethylammonium fluoroborate as the supporting electrolyte point to electron transfer from the ether function of 2-methoxyethanol as the initiation process for the major products of oxidation. The specifics of this electron transfer cannot be detailed, but the products obtained make it clear that the overall process, probably occurring in a series of steps, is one in which a cationic species, V, is formed, as shown in eq 1.

$$CH_3OCH_2CH_2OH \longrightarrow 2e + H^+ + \underset{+}{C}H_2OCH_2CH_2OH \qquad (1)$$

V

There is no cleavage of V to give either formaldehyde and ethylene oxide or formaldehyde and a new cation, $HOCH_2CH_2^+$, which could then react with 2-methoxyethanol to give the methyl ether of diethylene glycol. Neither of these possible cleavage products was found in our reaction mixtures.

Reaction of V with 2-methoxyethanol results in the unsymmetrical formal, II, which is probably a primary



$$V + CH_3OCH_2CH_2OH \longrightarrow CH_2\begin{cases}OCH_2CH_2OH\\OCH_2CH_2OCH_3\end{cases} + H^+ \qquad (2)$$

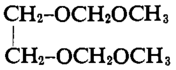
II

product in this oxidation. Since some acid is generated in the reactions forming V,[15] II can react further with 2-methoxyethanol to give the symmetrical formal, I, and I, II, or V reacting with water can result ultimately in formaldehyde.

The structures of both I and II were confirmed by synthesis. I was prepared by a standard procedure, and II was prepared by equilibrating I with a limited amount of glycol in the presence of acid and was isolated by distillation after the mixture was made basic. Pure II was also reconverted to I using the Dean-Stark procedure and an acid catalyst.

Although III was obtained in only limited amount, it is a product of unusual structure and considerable interest. It can be isolated from the oxidation reactions by preparative vpc, but it was not possible to devise a nonelectrochemical method for its synthesis, since, to our best knowledge, there is no suitable method for introducing the grouping, $-OCH_2-OCH_2-O$, in an organic compound. Its nmr spectrum shows two separate singlets at τ 5.19 and 5.27, each corresponding to two hydrogens and indicating two different $-OCH_2-O-$ groupings. In addition, it gives an A_2B_2 pattern centered at τ 6.34 from the $-CH_2-CH_2-$ group and a singlet at τ 6.59, corresponding to six hydrogens and the two methyl groups. On hydrolysis it yields 2 mol of formaldehyde, isolated as the 2,4-dinitrophenylhydrazone, and 1 mol of 2-methoxyethanol.

For comparison purposes, the symmetrical compound, VII, was prepared by chloromethylation of



$$\begin{array}{l}CH_2-OCH_2OCH_3\\ |\\ CH_2-OCH_2OCH_3\end{array}$$

VII

glycol, followed by reaction with sodium methoxide in methanol. Its nmr spectrum shows three singlets, one at τ 5.94 corresponding to the two identical $-OCH_2O-$ groups, one at τ 6.33 for the $-CH_2CH_2-$ group, and one at τ 6.65 for the two methyl groups. On hydrolysis it yields 2 mol of formaldehyde and 1 mol of ethylene glycol.

The origin of III cannot be indicated with certainty. Cyclic voltammetry of a solution of the fluoroborate salt in 2-methoxyethanol indicates that there is some self-inhibiting oxidation of the alcohol function. This could lead to an electron-deficient oxygen species, VIII, as shown in (3). If VIII rearranged, with carbon migrating, a new cation, IX, would form, and reaction of IX with 2-methoxyethanol would give rise to III.

$$CH_3OCH_2CH_2OH \longrightarrow 2e + H^+ + \underset{\text{VIII}}{CH_3OCH_2CH_2O^+} \qquad (3)$$

$$\underset{\text{VIII}}{CH_3OCH_2CH_2O^+} \longrightarrow \underset{\text{IX}}{CH_3OCH_2OCH_2^+} \qquad (4)$$

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(13) J. Lichtenberger and L. Martin, *Bull. Soc. Chim. Fr.*, **12**, 114 (1945).

(14) P. P. T. Sah and T. S. Ma, *J. Amer. Chem. Soc.*, **54**, 2964 (1932).

(15) At sufficiently high anodic potentials, discharge of fluoroborate anion and hydrogen atom abstraction by the resulting radical are another possible source of acid.

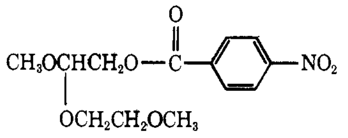
The foregoing results indicate that the major focus of anodic attack on 2-methoxyethanol is on the ether function rather than the hydroxyl group, and this observation accords with a prior expectation, since ethers have lower ionization potentials than alcohols.[1,2] It should also be noted that in the reactions with the fluoroborate supporting electrolyte, the proton transfer occurs solely from the methyl group, and there is no formation of acetals of glycolaldehyde, which would result, ultimately, if the proton were transferred from the methylene group.

In these reactions the initiating electrode mechanism is some form of direct electron transfer from 2-methoxyethanol. With an anion oxidizable at a potential lower than that required for the oxidation of 2-methoxyethanol, an alternative mechanism becomes possible. Nitrate ion is just such an anion[9] and makes possible a reaction sequence in which the initiating step is electron transfer from nitrate ion to give a nitrate radical, as shown in (5). The final products in this mechanism will

$$NO_3^- \longrightarrow e + NO_3\cdot \qquad (5)$$

depend not on a proton transfer, but on the position or positions from which a hydrogen atom is abstracted by the nitrate radical. Abstraction from the methylene group will result in acetals of glycolaldehyde, and abstraction from the methyl group will give rise to formals. Also reactions with nitrate ion might be somewhat less efficient than reactions with fluoroborate supporting electrolyte, since there is some disproportionation of the nitrate radical to give oxygen and oxides of nitrogen.

These hoped for differences between oxidations in the presence of nitrate ion and oxidations in the presence of fluoroborate ion did materialize. The reactions with nitrate ion were, in fact, less efficient, and an additional product, IV, was obtained. The nmr spectrum of IV gave chemical shifts too closely spaced to permit analysis. The infrared spectrum of IV showed a strong hydroxyl band, and it was, therefore, converted to the *p*-nitrobenzoate, X. The nmr spectrum of X proved tractable and showed a singlet at τ 1.78 for the aromatic hydrogens, an AB_2 pattern ranging from τ 5.07 to 5.67 for the $-CH-CH_2$ grouping and a somewhat merged but distinguishable conglomerate consisting of an A_2B_2 pattern centered at τ 6.36 for the $-CH_2-CH_2-$ moiety, and singlets at τ 6.57 and 6.68 for the two methyl groups. Hydrolysis of IV gave glycolaldehyde, isolated as the 2,4-dinitrophenylosazone.



X

The formation of IV in these reactions is strong evidence to support the availability of two mechanisms for the oxidation of 2-methoxyethanol. IV results only from the hydrogen abstraction mechanism, but I and II could arise either from this mechanism or the mechanism observed with the fluoroborate supporting electrolyte. Since III is also obtained in the nitrate reactions, albeit in lower coulombic yield, it is probable that anode potentials high enough to effect direct electron transfer from 2-methoxyethanol are attained in the nitrate reactions, and I and II could be products of either or both mechanisms.

Electrochemical Reduction Studies of Several Bicyclo[6.1.0]nona-2,4,6-trienes and of *cis*-Bicyclo[6.2.0]deca-2,4,6-triene. Search for a Polarographic Criterion of Homoaromaticity

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Abstract: The reduction of *cis*- (**6**) and *trans*-bicyclo[6.1.0]nona-2,4,6-trienes (**9**), the 2,3-benzo derivative of **6** (**11**), and *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**12**) has been studied by the techniques of polarography and cyclic voltammetry in tetrahydrofuran and acetonitrile solutions. In all cases, the first electron transfer occurs with considerably greater difficulty than cyclooctatetraene and is observed in the region characteristic of medium-ring trienes. Also, **9**, **11**, and **12** exhibit only one-electron reductions. The probable causative factors underlying these differences are elaborated.

The observation of effective electronic delocalization in a number of charged two- and six-electron systems in which conjugation is interrupted by one or more methylene groups (*e.g.*, **1–3**) has stimulated considerable interest in homoaromatic phenomena.[2-4] Other investigations have shown that related nonclassical structures can also arise in nine-[5] and ten-electron sys-

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(1) Holder of a NATO postdoctoral fellowship (1970–1972), administered by the Science Research Council.

(2) For an extensive review of homoaromaticity, see S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 1 (1967).

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