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# Electrochemical Reduction of Cyclic and Acyclic Sulfates

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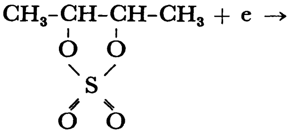
It was confirmed that cyclic and acyclic sulfates of diols and monoalcohols could be reduced at cathodes in nonaqueous solvents. The reduction products were greatly affected by the molecular structures of the sulfates. The reduction of the cyclic sulfates of 1,2-diols yielded the corresponding alkenes and disulfate dianions of the parent diols in high yields and current efficiencies were based on one-electron reduction. On the other hand, the cyclic sulfates of 1,3- and 1,4-diols were also reduced by one-electron transfer under similar conditions, but the cycloalkanes expected were not formed and the products were cyclic ethers along with acyclic alkane or unsaturated alcohol. The reduction of the cyclic sulfate of hydrated formaldehyde, which is regarded as a 1,1-diol, did not give any identified products except for a small amount of methane. Finally, acyclic dialkyl sulfates were reduced by one-electron transfer to give complicated mixtures consisting of monomeric alkanes and alkenes, dimeric alkanes, ethers, and/or alkyl metals. Based on the results obtained, the mechanism of reduction of sulfates (mainly cyclic sulfates of 1,2-diols) is discussed.

It is known that 1,2-diols themselves are electrochemically reduced only with great difficulty. However when the hydroxyl groups are derivatized to a good "leaving group" -OR, reduction leads to alkenes or alkanes. The diacetate of hydrobenzoin is reduced to bibenzyl in the presence of proton donors,[1] while the dioxalate also is reduced at a relatively low potential to give stilbene.[2] Highly aryl-substituted epoxides are reduced but selectivities for the corresponding alkenes are low.[3]

The above examples show that derivatives of only 1,2-diols involving di- or higher aryl-substituents can be reduced. This may suggest considerable difficulty in the reduction of derivatives of 1,2-diols which are not aryl-substituted. In fact, only one successful result had been reported prior to our previous report. Dey and Sullivan[4] found that propylene carbonate was reduced not directly but indirectly with electrogenerated lithium metal.

In previous works,[5,6] we showed the first example of the direct reduction of derivatives of 1,2-diols which are not aryl-substituted,[7] and the following points were established: (a) The sulfate was coulometrically reduced by one-electron transfer and (b) the yield of 2-butene formed did not exceed 50% based on the starting sulfate. Equation 1 was tentatively given as a stoichiometry for this reduction, postulating the elimination of radical anion $SO_4^{\cdot-}$ and its dimerization. This is distinguished by the one-electron transfer reduction, as contrasted to the four-[1] and two-electron[2–4] transfer reductions of other 1,2-diol derivatives.



$$\text{CH}_3\text{-CH=CH-CH}_3 + \frac{1}{2}\text{S}_2\text{O}_8{}^{2-} \qquad (1)$$

More detailed examination of the reduction of sulfate of 2,3-butanediol and extension of the reduction to sulfates of other 1,1-, 1,2-, 1,3-, and 1,4-diols and of monoalcohols are reported here.

## Results an Discussion

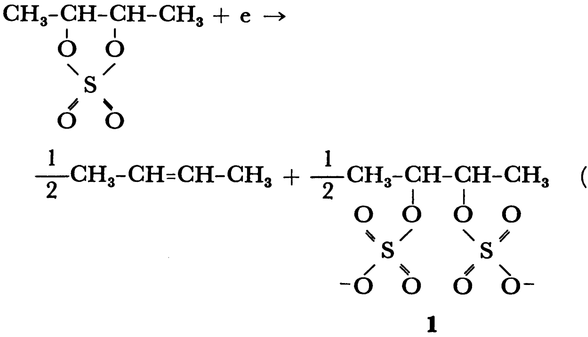
*Reduction of the Cyclic Sulfate of 2,3-Butanediol. Stoichiometry*: In order to establish the stoichiometry, the separation of products containing sulfur was attempted.

When the sulfate was reduced at a mercury cathode in $Et_4NClO_4$/DMF, very small amounts of precipitates, which decomposed in acid solutions, were formed. They were presumed to be a mercury salt of an oxyacid containing sulfur, *e.g.* Caro's acid,[9] from their properties.

If peroxodisulfate ions were formed according to Eq. 1, they would be present as the tetraethylammonium salt (soluble in DMF) and should be easily reduced to sulfate ions.[10] In fact, it was confirmed that ammonium peroxodisulfate was reduced consuming 2F (1F=96480C)/mole of charge at a less negative potential than the cyclic sulfate of 2,3-butanediol.

Peroxodisulfate ion can be regarded as equivalent to sulfate anion radical ($SO_4^{\cdot-}$) in some cases. Therefore, it was attempted to trap the anion radical in electrolyses in the presence of aniline[11] and styrene,[12] but the yield of 2-butene was not affected in both cases and also in the latter case neither styrene oxide nor polystyrene could not be detected.

A further investigation was made of products which are soluble in the catholyte and not volatile. After a complicated work-up procedure of the catholyte, the bis(tetrabutylammonium) salt of the acyclic disulfate dianion (**1**) of 2,3-butanediol was separated and derivatized to the dipotassium salt. The molecular structure of the dipotassium salt was confirmed by spectral and analytical data, and by the recovery of 2,3-butanediol and sulfuric acid after its hydrolysis. These results indicate Eq. 2 to be the most likely stoichiometry for the main reaction. The yield of **1** separated as the dipotassium salt was 42% according to Eq. 2; such a value lower than 100% seemed to be due to mainly to material loss in the complicated multi-step procedure for the separation. On the other hand, yields of 2-butene, which were tentatively reported to be lower (39—49%) than 50% according to Eq. 1 in the previous work,[5] can be re-evaluated as 78—99% according to Eq. 2.



$$\mathrm{CH_3\text{-}CH(O)\text{-}CH(O)\text{-}CH_3 \cdot SO_2} + e \rightarrow \frac{1}{2}\mathrm{CH_3\text{-}CH{=}CH\text{-}CH_3} + \frac{1}{2}\mathrm{CH_3\text{-}CH(OSO_3^-)\text{-}CH(OSO_3^-)\text{-}CH_3} \quad (2)$$

1

*Reaction Mechanism*: The initial steps of the reduction were investigated by voltammetric methods. As shown in Fig. 1, cyclic voltammetry indicated a totally irreversible process, since a more negative shift of reduction peak potentials at higher sweep rates and no oxidation peak were observed. The cyclic sulfate also gave a single polarographic wave ($E_{1/2}$ −1.86 V *vs.* $Ag^+/Ag$), the wave height of which was proportional to concentration and had a linear relationship to the square root of the mercury column height. The wave analysis of the polarograms gave a slope of *ca.* 160 mV. Since it has been confirmed that the cyclic sulfate undergoes one-electron reduction, the slope larger than 59 mV should indicate that the electron transfer step is also irreversible. Combining this result with that of cyclic voltammetry, a possible reaction route from the cyclic sulfate to a ring-opened anion radical (**3**) *via* another one (**2**) is shown in Scheme 1. This manner of ring-opening should be more favorable than others, in view of the higher electron negativity of oxygen than carbon and the strong electron-withdrawing power of the $-SO_2-$ part of **3**.

As the simplest route from **3** to the final products (2-butene and **1**), disproportionation (route A in Scheme 1) of **3** is conceptually proposed without either highly negative or positive experimental evidence. Since it is known that a radical with a leaving group at its $\beta$-position looses the latter as a radical and yields an olefin,[13] **3** may loose $SO_4^{\dot{-}}$ to give 2-butene (route **B**). Although it has been confirmed by the electrolysis in the presence of $SO_4^{\dot{-}}$ trapping reagents that the reaction does not involve any free $SO_4^{\dot{-}}$ in the bulk of the catholyte, the formation of **1** by addition reaction of $SO_4^{\dot{-}}$ to **3** or 2-butene in cathode interface can not be excluded in a case where the trapping reagents can

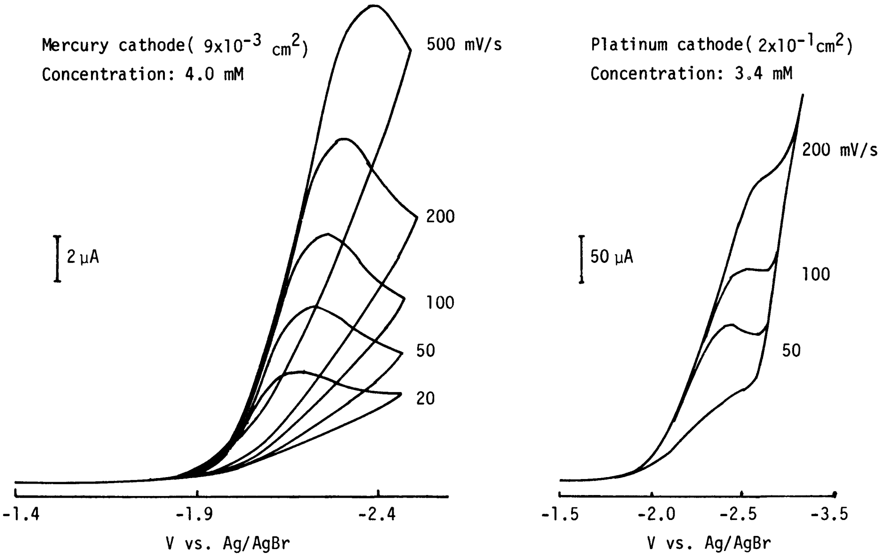
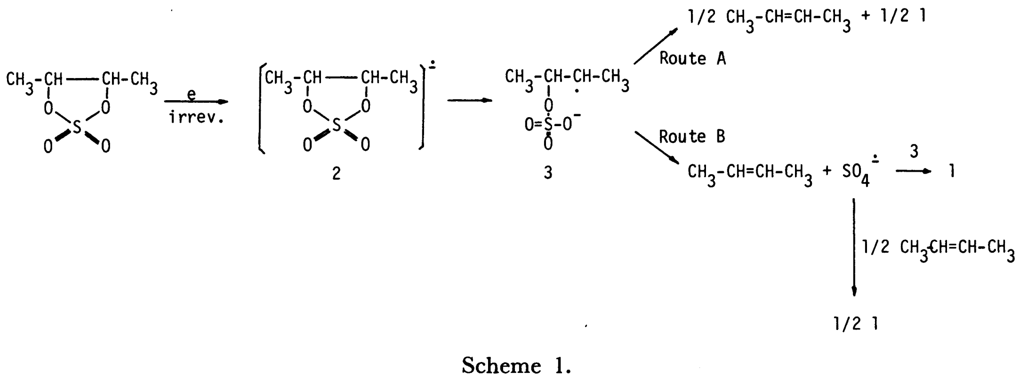


Fig. 1. Cyclic voltammograms of cyclic sulfate of 2,3-butanediol at various potential sweep rates in 0.2 M tetrabutylammonium perchlorate/DMF.



Scheme 1.

not enter the interface. However, it may be difficult to explain why $SO_4^{\cdot -}$, a strong oxidizing reagent, could not be reduced if it had been formed; a rationalization is possible if the rate of the addition reaction is very much higher than that of the reduction. In such a case, there should be no apparent difference between routes A and B, and at least they can not be distinguished by ordinary means. The reaction of $SO_4^{\cdot -}$ with mercury, if it occurred, should be considered separately from the main pathways.

*Reduction of Cyclic Sulfates of 1,2-Diols Other Than 2,3-Butanediol.* *i-E* Curves of the cyclic sulfate of four kinds of 1,2-diols including 2,3-butanediol were measured by a stationary method. As shown in Fig. 2, the reduction potential of the sulfates was apparently affected by steric hindrance of the diol molecules.

Table 1 shows results of controlled potential electrolyses of the sulfates at a mercury cathode in $Et_4NClO_4$/DMF. Yields and current efficiencies of the corresponding alkenes formed were estimated according to the stoichiometry of Eq. 2.

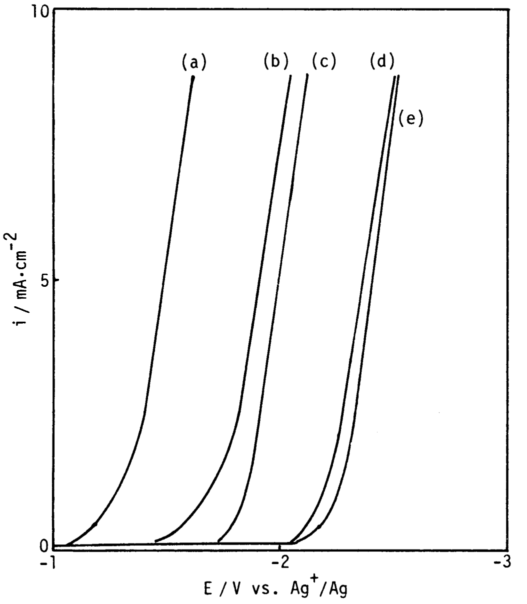


Fig. 2. *i-E* Curves of cyclic sulfates of 1,2-diols (0.04 M) at a mercury cathode.
Cyclic sulfates of 1,2-diols: (a) 1,2-ethanediol, (b) 2,3-butanediol, (c) 2,3-dimethyl-2,3-butanediol, (d) *trans*-1,2-cyclohexanediol, (e) background (0.4 M tetraethylammonium perchlorate/DMF).

The cyclic sulfate of 1,2-ethanediol showed a unique phenomenon in the current-time relation during electrolysis. As shown in Fig. 3, the current decreased rapidly to the background level when the electrolysis was carried out at −1.3 V *vs.* Ag$^+$/Ag and only 0.6 F/mole of charge was passed. The current efficiency for ethene in this period was 22%. When the applied potential was reset now at −1.6 V, the current increased. Additional 0.3 F/mole of charge could be passed at this potential, till the current decreased again. The current efficiency in this period was 42%. The current could be increased again by resetting the potential at −1.8 V and 0.2 F/mole of charge was passed. The current efficiency was 44%. No more significant increase of the current was observed, when the potential was changed more cathodically after diminution of the current at −1.8 V. The overall current efficiency and total yield were 30 and 34%, respectively. No original sulfate remained unreacted. The above phenomenon is very intriguing but it seems difficult to explain; an attempted explanation is that electrogenerated species might initiate polymerization of the cyclic sulfate to form linear poly(1,2-ethanediol sulfate)s whose reduction

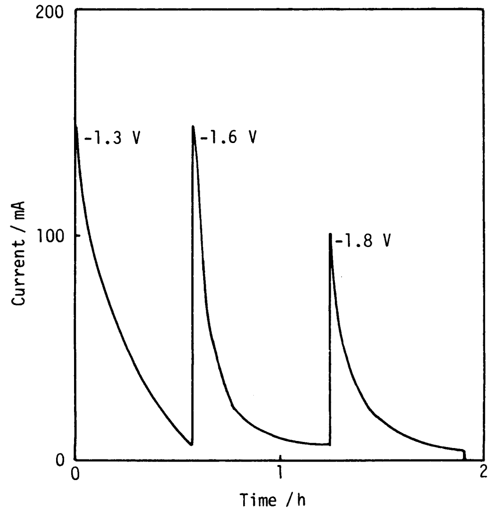


Fig. 3. Current-time relation in the electroreduction of the cyclic sulfate of 1,2-ethanediol at potentials changed stepwise.

Table 1. Results of electrolytic reduction of cyclic sulfates of 1,2-diols at a mercury cathode in tetraethylammonium perchlorate/DMF

| Diol | Cathodic potential/ V *vs.* Ag$^+$/Ag | Charge passed[a] /F·mol | Alkene | |
|---|---|---|---|---|
| | | | Yield[b] /% | Current efficiency /% |
| 1,2-Ethanediol | −1.3, −1.6, −1.8[c] | 1.1 | 34 | 30 |
| 2,3-Butanediol | −1.7 | 1.0 | 78 | 78 |
| 2,3-Butanediol | −2.0 | 1.0 | 99 | 99 |
| 2,3-Dimethyl-2,3-butanediol | −1.9 | 1.1 | 66 | 60 |
| trans-1,2-Cyclohexanediol | −2.4 | 2.3[d] | 100 | 46 |

a) Corresponding to coulometric *n*-value. b) Estimated according to the stoichiometry of Eq. 2 in the text. c) Changed stepwise during the electrolysis (See Fig. 3.) d) Not coulometric.

potentials are more negative than that of the cyclic sulfate, depending on the degree of polymerization.

Beside the results given above, here, some informations about the reduction of the cyclic sulfate of 2,3-butanediol are supplemented. As shown in Table 1, a lower current efficiency and yield of 2-butene was obtained at a less negative potential at a mecury cathode; such a dependence of the efficiency and yield on the potential was not observed at a platinum cathode. This fact may suggest the occurrence of side reaction of **3** with a less negatively polarized mercury cathode. A gas chromatogram of the catholyte just after the electrolysis showed only a very small peak for 2-butanone(in addition to 2-butene), while the catholyte treated with aqueous sulfuric acid at 70 °C gave several small peaks which could not be identified. This result also suggests occurrence of side reactions.

The cyclic sulfate of 2,3-dimethyl-2,3-butanediol could be coulometrically reduced by one-electron transfer to give 2,3-dimethyl-2-butene in current efficiency and yield lower than those in the reduction of the sulfate of 2,3-butanediol. The tetrabutylammonium salt of the disulfate dianion of 2,3-dimethyl-2,3-butanediol could be separated pure from a catholyte consisting of $Bu_4NClO_4$ and acetonitrile.

The cyclic sulfate of *trans*-1,2-cyclohexanediol was reduced at such a negative potential(−2.4 V *vs.* $Ag^+/Ag$) that supporting electrolyte cation ($Et_4N^+$) was discharged; amalgam formation was observed indicating that indirect reduction with electrogenerated amalgam occurred simultaneously. The yield of cyclohexene was 100% when 2.3 F/mole of charge were passed.

*Reduction of Cyclic Sulfates of Diols Other Than 1,2-Diols.* The cyclic sulfate of hydrated formaldehyde, so-called methylene sulfate, can be regarded as the cyclic sulfate of a 1,1-diol and presents as an equilibrium mixture with the cyclic dimer.[14] As the sulfate decomposed exothermically in DMF, acetonitrile was used as a solvent for the electrolysis. The *i-E* curve of the sulfate is shown in Fig. 4, together with that of sulfates of other diols. As shown in Figs. 2 and 4, it is plain that the sulfate of 1,1-diol can be reduced at a considerably less negative potential than that required for any other diols, though different cathodes and/or solvents were used. The two-step reduction wave of the sulfate of the 1,1-diol may be due to the monomer/dimer equilibrium described above. The sulfate was reduced consuming coulometrically 1.0 F/mole of charge at −1.0 V *vs.* $Ag^+/Ag$ corresponding to the first reduction wave at a mercury cathode in acetonitrile, but no product could be detected by gas-chromatographic analysis. When 0.9 F/mole of charge was coulometrically passed at a more negative potential (−1.8 V) corresponding to the second wave, small amounts (2% yield) of methane were formed. Using a platinum cathode, similar results were given. Because no ethene could be detected in any case, the generation of a carbene as an intermediate was not be verified.

The cyclic sulfate of 1,3-propanediol was reduced consuming 1 F/mole of charge at −1.9 V *vs.* $Ag^+/Ag$ at mercury and platinum cathodes in DMF. The former cathode gave no gas-chromatographically detectable product, while the latter gave allyl alcohol in 10% yield and one more product which had the same molecular weight as allyl alcohol but was not either propylene oxide or oxetane.

The reduction of the cyclic sulfate of 1,4-butanediol at a mercury cathode gave a result similar to that of 1,3-propanediol under the same conditions. Reduction at a platinum cathode resulted in the formation of

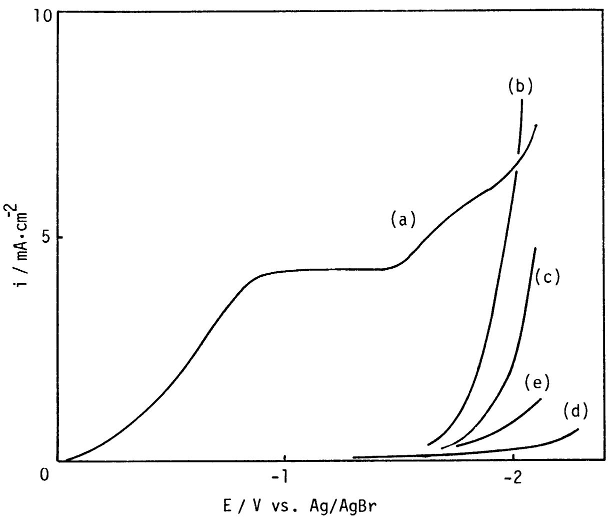


Fig. 4. *i-E* Curves of cyclic sulfates of 1,1-, 1,3-, and 1,4-diols.
(a) 0.1 M Cyclic sulfate of hydrated formaldehyde at a mercury cathode in 0.5 M tetrabutylammonium perchlorate/acetonitrile, (b) 0.1 M cyclic sulfate of 1,3-propanediol at a platinum cathode in 0.5 M tetrabutylammonium perchlorate/DMF, (c) 0.1 M cyclic sulfate of 1,4-butanediol at the same cathode in the same solution, (d) background for (a), (e) background for (b) and (c).

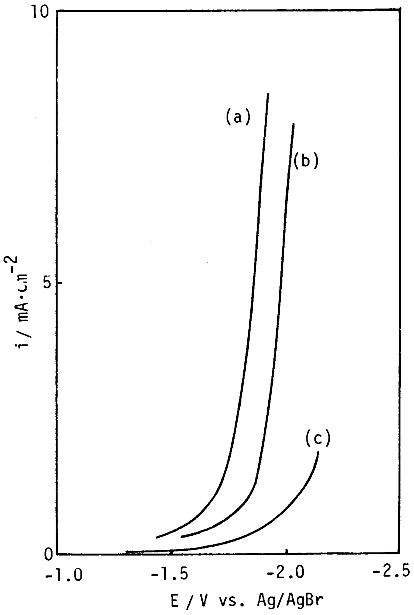
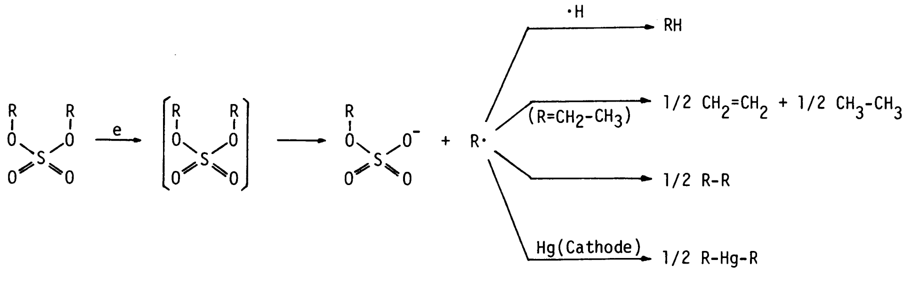


Fig. 5. *i-E* Curves of dialkyl sulfates (0.2 M) at a platinum cathode.
(a) Dimethyl sulfate, (b) diethyl sulfate, (c) background, 0.5 M tetrabutylammonium perchlorate/DMF.



Scheme 2.

butane(16% yield) and THF(11%).

Although there have been some ambiguous points in the reduction of the cyclic sulfates of diols other than 1,2-diols, it is interesting to note that the manner of the reduction was quite different from that of 1,2-diols.

*Reduction of Acyclic Sulfates of Monoalcohols.* *i-E* curves of dialkyl sulfates are shown in Fig. 5. Dimethyl sulfate was reduced at a less negative potential than diethyl sulfate.

Dimethyl sulfate was completely reduced by about 1 F/mole at −1.9 V *vs.* $Ag^+/Ag$ at a mercury cathode in DMF. The products detected were dimethyl ether and dimethylmercury. At a platinum cathode, methane(6% yield) was formed in addition to dimethyl ether(13%). Diethyl sulfate also was reduced by 1 F/mole at a mercury cathode to give diethyl ether in 38% yield, but the presence of diethylmercury was not checked. The reduction at a platinum cathode resulted in the formation of a variety of products: Diethyl ether (17% yield), ethanol(12%), ethane(37%), ethene(16%), and butane(trace). The formation of hydrocarbons and dialkylmercury in the reduction of dialkyl sulfates suggests the generation of alkyl radicals as intermediates, shown in Scheme 2. On the other hand, it seems difficult, just as in the reductions of the cyclic sulfates of diols other than 1,2-diols, to propose specific routes for the products containing oxygen from dialkyl sulfates; they may involve alkoxyl radicals, alkoxide anions and/or alkyl radicals.

## Conclusions

This comparative study of the electrochemical reduction of a variety of types of organic sulfates leads to the following principal conclusions:

(a) All the sulfates used were reduced by one-electron transfer.

(b) The reduction products were greatly affected by the type of sulfates; cyclic/acyclic, diol/monoalcohol, and 1,1-/1,2-/1,3-/1,4-diols.

(c) Among the cyclic sulfates of diols, those of 1,2-diols were reduced in a unique manner to give the corresponding alkenes and 1,2-disulfate dianions.

## Experimental

*Voltammetry.* Cyclic voltammograms were recorded at room temperature in 0.1—0.2 M[†] $Bu_4NClO_4$/DMF by using a potentiostat (Nikko Keisoku Co. Model MPGS-301), a function generator (Nikko Keisoku Co. Model NPS-2) and an X-Y recorder (Rikendenshi Co. Model F-3DH). Polarograms were measured using Yanaco Model P-1100. Working electrodes for the voltammetries were a platinum wire (diameter, 0.04 cm; length, 1.5 cm; area, $2\times10^{-1}$ cm$^2$), a hanging mercury electrode (drop weight, 1.1 mg; area, $9\times10^{-3}$ cm$^2$) and a dropping mercury electrode (drop weight at −2.10 V *vs.* $Ag^+/Ag$ and 43.5 cm mercury column height, 1.3 mg; area, $1\times10^{-2}$ cm$^2$). Cathodic potentials were referred to a silver bromide electrode in 0.1 M $Bu_4NClO_4$/DMF. Three-electrode systems with large platinum counter electrodes were employed for all measurements.

Steady state *i-E* curves were measured by using the equipment and solutions similar to those used in the preparative electrolyses described below.

*Preparative Electrolyses.* An H-type divided cell, a potentiostat (Wenking Model ST-72 or Hokutodenko Model HA-105) and a coulometer (Hokutodenko Model HF-201) were used for electrolyses which were carried out at constant potentials at a mercury pool cathode (diameter, 4 cm; area, 12.5 cm$^2$ or diameter, 3 cm; area, 7.1 cm$^2$) and a platinum plate cathode (3×4 cm; area, 12 cm$^2$) at 20 °C. Catholytes were 50 cm$^3$ of DMF or acetonitrile containing 0.4 M $Et_4NClO_4$ or 0.5 M $Bu_4NClO_4$ and 0.04—0.10 M starting sulfates.

*Product Analyses.* Gaseous products were introduced into a gas burette with a nitrogen stream and analyzed by gas chromatography (Porapak Q, 2 m, 40—100 °C). Products in the catholytes also were analyzed by gas chromatography (Porapak Q, 2 m, 100—200 °C for dimethyl ether, diethyl ether, THF, oxetane, propylene oxide, styrene oxide, ethanol and 2,3-butanediol; PEG 20M, 0.5 and 2 m, 30—150 °C for butane, 2-butene, 2-butanone, cyclohexene, 2,3-dimethyl-2-butene and allyl alcohol). Mass spectra were measured by a spectrometer (Jeol Model D-100) connected with gas chromatograph (Joel Model GJC-20K) or none.

The separation of salts of the acyclic disulfate dianion (**1**) of 2,3-butanediol from the catholytes and their identification were carried out by the following procedures: After the electrolysis of the cyclic sulfate of 2,3-butanediol, DMF was evaporated at 50 °C under reduced pressure from the catholyte containing tetrabutylammonium perchlorate; water was added to the residue. The perchlorate was removed from the resulting mixture by extraction with dichloromethane. The aqueous layer was evaporated to dryness under reduced pressure. The residual white solid, which was contaminated with water and DMF, seemed to consist mainly of the bis(tetrabutylammonium) salt of **1** (IR spectrum), but it could not be purified enough to confirm the molecular structure. Next, the separation from a catholyte containing acetonitrile instead of DMF was attempted in a different procedure. Acetonitrile was evaporated at room temperature under reduced pressure and then 30 cm$^3$ of water and 9 cm$^3$ of 0.5 M perchloric acid were added to the residue. The resulting mixture was extracted with two potions of 20 cm$^3$ of dichlo-

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[†] 1 M=1 mol dm$^{-3}$.

romethane to remove the tetrabutylammonium perchlorate. The aqueous layer was neutralized (pH 7.0) with potassium hydroxide solution and concentrated at room temperature under reduced pressure. The precipitated potassium perchlorate was removed from the solution by filtration. To the filtrate was added ethanol, and the precipitated potassium salt of **1** as white crystals was collected on a filter paper and washed repeatedly with ethanol. Yield, 42%; mp, 249.0—252.5 °C (dec); IR (KBr), 3010 ($\nu_{C-H}$) and 1220—1290 cm$^{-1}$ ($\nu_{S=O}$) MS (70 eV), *m/z* 88 (corresponding to the molecular weight of 3,4-dimethyldioxetane) and 72 (2,3-epoxybutane); $^1$H-NMR (in $D_2O$), $\delta$=1.37 (m, 6H) and 4.55 (m, 2H) (multiplet signals may be due to stereoisomers, *dl/meso*, of **1**); flame test, violet (potassium). Found: C, 14.82; H, 2.66; S, 18.80%. Calcd for $C_4H_8S_2O_8K_2$: C, 14.72; H, 2.47; S, 19.64%. Further confirmation of the structure was obtained by hydrolysis. 0.192 g (0.59 mole) of the potassium salt of **1** was heated for 6 h at 95 °C in 2 cm$^3$ of water containing three drops of 2 M hydrochloric acid. 2,3-Butanediol (45% yield) in the reaction mixture was detected by gas chromatography and barium sulfate (52% yield) was precipitated by addition of barium chloride solution.

A small amount of the bis(tetrabutylammonium) salt of the acyclic disulfate dianion of 2,3-dimethyl-2,3-butanediol also could be separated fairly pure from the corresponding catholyte of DMF. Mp, 94.5—95.0 °C; IR(KBr), 1110—1240 cm$^{-1}$ ($\nu_{S=O}$). Found: C, 59.57; H, 11.24; N, 4.36; S, 9.02%. Calcd for $C_{38}H_{84}N_2S_2O_8$: C, 59.96; H, 11.12; N, 3.68; S, 8.42%.

Partial confirmation of the composition of the suspended pale gray particles formed in the electrolysis of the cyclic sulfate of 2,3-butanediol in DMF was made as follows: The particles were collected on a filter paper and washed with DMF and water. The fine powder thus obtained dissolved in dilute nitric acid generating gas. From the resulting nitric acid solution, black and yellow powders precipitated by adding to it aqueous solutions of sodium sulfide and potassium iodide, respectively. The former and the latter seemed to be probably HgS and $\beta$-$HgI_2$ which latter was slightly soluble in ether. The original powder also seemed to decompose in dilute sulfuric and hydrochloric acids and be transposed to finer white powders. The resulting acid solution did not oxidize iodide ions. The original powder was not organic as judged by the IR spectrum. The properties of the powder indicated that it was an inorganic mercury salt. Identification as $HgSO_4$ and $Hg(ClO_4)_2$ was excluded by comparison with authentic samples. From these results, the powder was presumed to be a mercury salt of an oxyacid containing sulfur, *e.g.* Caro's acid. No further structure determination of this powder was made, since, because of the very small quantity involved it should not be important in determining the main reaction paths.

Dimethylmercury was analyzed by mass spectroscopy combined with gas chromatography: MS (20 eV), *m/z* 234 ($M^+$), 232 ($M^+$), 231 ($M^+$), 230 ($M^+$), 229 ($M^+$), 219 ($M^+-CH_3$), 217 ($M^+-CH_3$), 216 ($M^+-CH_3$), 215 ($M^+-CH_3$), 214 ($M^+-CH_3$) and 213 ($M^+-CH_3$).

*Materials.* Chemicals, except for the cyclic sulfates, were commercially supplied from Tokyo Kasei Kogyo Co., Ltd., Aldrich Chemical Co. and Pfaltz & Bauer, Inc. The cyclic sulfates mentioned below, unless stated otherwise, were prepared by literature methods: The cyclic sulfates of 1,2-ethanediol,[15] 2,3-butanediol,[16] 2,3-dimethyl-2,3-butanediol,[17] *trans*-1,2-cyclohexanediol,[18] and hydrated formaldehyde.[19]

*Cyclic Sulfate of 1,3-Propanediol*: To a suspension of 42.6 g (0.56 mole) of 1,3-propanediol in 200 cm$^3$ of dichloromethane was dropwise added 72.6 g (0.62 mole) of thionyl chloride; the reaction mixture was reluxed for 1 h. The mixture was poured into 100 cm$^3$ of ice water and the organic layer was washed with 100 cm$^3$ of water and aqueous sodium hydrogencarbonate, and again with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure. By fractional distillation of the residual oil the cyclic sulfite of 1,3-propanediol was obtained. Yield, 71%; bp, 52—54 °C/ 8 Torr (1 Torr= 101×325/760 Pa); IR (liquid film), 1180 cm$^{-1}$ ($\nu_{S=O}$). To a solution of 20.0 g (0.16 mole) of the cyclic sulfite in 150 cm$^3$ of acetic acid was added dropwise below 14 °C a solution of 20.0 g (0.13 mole) of potassium permanganate in 200 cm$^3$ of water. After the reaction mixture was stirred for 1 h at room temperature, 100 cm$^3$ of water was added and then a solution of sodium sulfite until the precipitating manganese dioxide disappeared. When the mixture was neutralized with sodium carbonate, considerable amounts of the cyclic sulfate of 1,3-propanediol precipitated as white solid. The mixture was thoroughly extracted with ether and the resulting ethereal solution after being washed with water was dried over anhydrous magnesium sulfate. The solution was evaporated and the recrystallization of the residual white solid from a mixture of ether and hexane afforded the pure sulfate of 1,3-propanediol as white needles. Yield, 20%; mp, 60.5—62.0 °C (lit,[20], 63 °C); IR(KBr), 1380 and 1190 cm$^{-1}$ ($\nu_{S=O}$). Found: C, 26.11; H, 4.54; S, 23.25%. Calcd for $C_3H_6SO_4$: C, 26.01; H, 4.38; S, 23.21%.

*Cyclic Sulfate of 1,4-Butanediol*: Prepared by a procedure similar to that for the cyclic sulfate of 1,3-propanediol. The cyclic sulfite of 1,4-butanediol: Yield, 67%; bp, 71.0—72.0 °C/ 6 Torr (lit,[18], 90.5—91.0 °C/13 Torr); IR (liquid film), 1200 cm$^{-1}$ ($\nu_{S=O}$). The cyclic sulfate of 1,4-butanediol (recrystallized from a mixture of benzene and hexane): Yield, 50% (based on the sulfite); mp, 41.5—43.0 °C (lit,[18] 44—45 °C); IR(KBr), 1360—1395 and 1195 cm$^{-1}$ ($\nu_{S=O}$). Found: C, 31.41; H, 5.41; S, 20.81%. Calcd for $C_4H_8SO_4$: C, 31.57; H, 5.50; S, 21.07%.

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