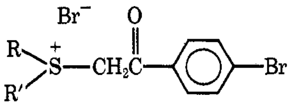
TABLE V[a]



R	R′	Registry no.	Mp, °C	p*K*	Calcd, % C	Calcd, % H	Calcd, % Br	Calcd, % S	Found, % C	Found, % H	Found, % Br	Found, % S
C_2H_5	C_2H_5	6320-83-8	122–123	6.46	39.15	4.38	43.41	8.71	39.22	4.33	43.46	8.76
$-CH_2(CH_2)_2CH_2-$		19158-69-1	123–125	7.54	39.37	3.85	43.65	8.76	40.18	3.93		
$-CH_2(CH_2)_3CH_2-$		33046-62-7	141–142	7.00	41.07	4.24	42.04	8.43	40.47	4.07	42.43	8.56
$-CH_2(CH_2)_4CH_2-$		33046-63-8	149–150		42.66	4.60	40.55	8.13	42.66	4.96	40.17	7.99

[a] R = R′ = CH_3, reference 4; R, R′ = $-CH_2CH_2SCH_2CH_2-$ and $-(CH_2)_3S(CH_2)_3-$ supplied by Professor N. J. Leonard.

borates.—The procedure used is illustrated by methylphenyl-4′-chlorophenacylsulfonium tetrafluoroborate. Phenyl-4-chlorophenacyl sulfide (26.2 g, 0.1 mol) was added to trimethyloxonium tetrafluoroborate (14.8 g, 0.1 mol) in 200 ml of methylene chloride at room temperature. The mixture, after standing for 10 days, was diluted with ether and filtered. The methylphenyl-4-chlorophenacylsulfonium tetrafluoroborate was obtained as a white solid which after washing with ether and drying gave 34.2 g (94%), mp 155–157°. The salts prepared are listed in Table II.

Preparation of Dialkyl-4′-bromophenacylsulfonium Bromides.—The procedure used is illustrated with 4′-bromophenacyltetramethylenesulfonium bromide. Tetrahydrothiophene (17.6 g, 0.2 mol) and 2,4′-dibromoacetophenone (55.6 g, 0.2 mol) were mixed in 200 ml of benzene and heated to effect solution. After allowing the mixture to stand for 5 days the solid was removed by filtration. It was washed with benzene and dried in air to give 54.5 g (75%) of product, mp 123–125°. The sulfonium bromides prepared are listed in Table V.

Silver(I)-Catalyzed Oxidative Cleavage Reactions of Cyclic 1,2-Diols by Peroxydisulfate[1]

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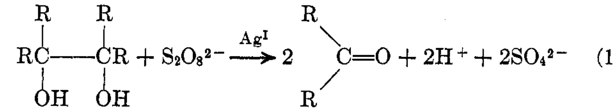
Received June 11, 1971

The oxidative cleavage rates of *cis*- and *trans*-1,2-cycloalkanediols by peroxydisulfate ($S_2O_8^{2-}$) in Ag^I-catalyzed reactions have been measured. The mechanistic implications of the observed reaction rates are discussed in terms of two mechanistic paths for the oxidative cleavage reactions. Path I proceeds by interaction of Ag^{III} with the diol. The kinetic data suggest the possible formation of a dsp^2 square planar complex as a reaction intermediate in oxidative cleavage by path I. The more rapid oxidative cleavage by path II is a free-radical chain reaction involving attack of the diol by Ag^{II} and apparently does not require formation of a cyclic complex between Ag^{II} and the diol.

The oxidative cleavage reactions of glycols by peroxydisulfate in silver(I)-catalyzed reactions reported by Greenspan and Woodburn[2] have been the object of several mechanistic investigations.[3-8] Recently we



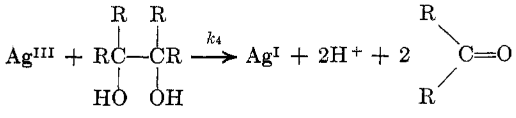
$$R\underset{OH}{\overset{R}{C}}-\underset{OH}{\overset{R}{C}}R + S_2O_8^{2-} \xrightarrow{Ag^I} 2\,R_2C{=}O + 2H^+ + 2SO_4^{2-} \qquad (1)$$

reported, on the basis of the kinetics of the reactions, that these oxidative cleavages were accomplished by two paths.[9] One route (path I) involves Ag^{III}, formed by oxidation of an $Ag^I(S_2O_8^{2-})_x$ complex, as the cleaving agent. The other route (path II) is a chain sequence of free-radical reactions involving Ag^{II} as the oxidative cleaving agent. Initiation of the chain sequence 6–8 is accomplished by reaction of Ag^{III} with Ag^I (reaction 5) yielding the chain-carrying Ag^{II} radical. Formation of Ag^{III} is the rate-determining factor for reaction by path I, whereas the rate of oxidative cleavage by path II, which is generally more rapid than reaction by path I, may depend on a variety of factors. Most significant of these is the partitioning of the Ag^{III} formed in reaction 3 between the substrate, resulting in cleavage by path I, and Ag^I which initiates the more rapid oxidation *via* the chain sequence. The relative amounts of cleavage by paths I and II depend on both the concentration of the substrate and its ability to interact with Ag^{III}. Thus, at lower substrate concentrations the overall rates of oxidative cleavage are faster, since more of the reaction is occurring by the more rapid free-radical chain sequence. On the other hand, if the substrate is capable of reacting readily with Ag^{III}, cleavage by the slower path I will be more prevalent than with substrates that react less readily with Ag^{III}. The latter situation allows for more extensive reaction of Ag^{III} with Ag^I, thereby initiating the faster oxidative cleavage by the free-radical chain reaction.

Path I

$$Ag^I + xS_2O_8^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ag^I(S_2O_8^{2-})_x \qquad (2)$$

$$Ag^I(S_2O_8^{2-})_x \xrightarrow{k_3} Ag^{III} + 2SO_4^{2-} + (x-1)S_2O_8^{2-} \qquad (3)$$



$$Ag^{III} + R\underset{HO}{\overset{R}{C}}-\underset{OH}{\overset{R}{C}}R \xrightarrow{k_4} Ag^I + 2H^+ + 2\,R_2C{=}O \qquad (4)$$

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[1] This work was supported by a grant (AM-08517) from the U. S. Public Health Service.

[2] P. Greenspan and M. Woodburn, *J. Amer. Chem. Soc.*, **76**, 6345 (1954).

[3] D. D. Mishra and S. Ghosh, *J. Indian Chem. Soc.*, **41**, 397 (1964).

[4] M. M. Mhala and R. V. Iyer, *Indian J. Chem.*, **3**, 568 (1965).

[5] N. Venkatasubramanian and A. Sabesan, *Curr. Sci.*, 632 (1967).

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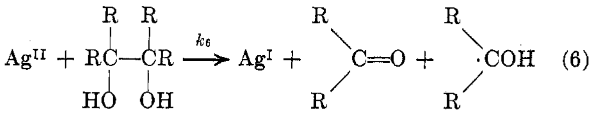
[7] G. V. Bakore and S. N. Joshi, *Z. Phys. Chem. (Leipzig)*, 250 (1965).

[8] G. D. Manghani and G. V. Bakore, *Bull. Chem. Soc. Jap.*, **41**, 2574 (1967).

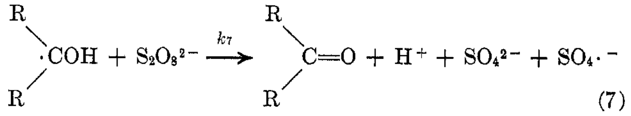
[9] E. S. Huyser and L. G. Rose, *J. Org. Chem.*, **37**, 649 (1972).

Path II

$$Ag^{III} + Ag^{I} \xrightarrow{k_5} 2Ag^{II} \quad (5)$$



$$Ag^{II} + R_2C(OH)\text{—}C(OH)R_2 \xrightarrow{k_6} Ag^{I} + R_2C{=}O + R_2\dot{C}OH \quad (6)$$

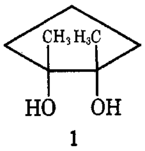


$$R_2\dot{C}OH + S_2O_8^{2-} \xrightarrow{k_7} R_2C{=}O + H^+ + SO_4^{2-} + SO_4\cdot^- \quad (7)$$

$$SO_4\cdot^- + Ag^{I} \xrightarrow{k_8} SO_4^{2-} + Ag^{II} \quad (8)$$

$$R_2\dot{C}OH + SO_4\cdot^- \xrightarrow{k_9} SO_4^{2-} + H^+ + R_2C{=}O \text{ (termination reaction)} \quad (9)$$

Both Ag^{II} and Ag^{III} form dsp^2 square planar complexes with bifunctional species such as glycols.[10] If the Ag^I-catalyzed peroxydisulfate oxidative cleavages of diols proceed *via* such intermediates, the reactions would be expected to have stereochemical requirements of the hydroxy groups similar to those encountered in periodic acid[11] and lead tetraacetate[12] cleavage reactions which proceed by decomposition of cyclic intermediates formed from the diol and the oxidative cleavage agent. Cyclic intermediates capable of decomposition in this manner are formed more readily from cis 1,2-diols than from the corresponding trans isomers, as evidenced by the more rapid rates of cleavage of cis diols.[13]



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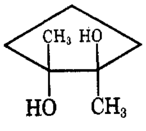

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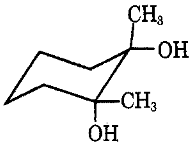

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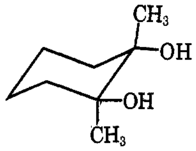


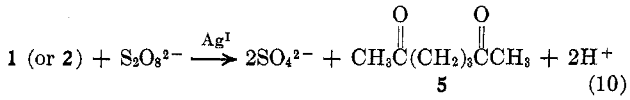
4

TABLE I

INITIAL OXIDATIVE CLEAVAGE RATES[a] OF CYCLIC 1,2-DIOLS BY PEROXYDISULFATE AT 30° [c]

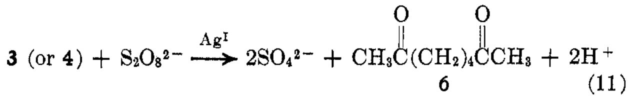
Diol	$[Ag^I] \times 10^3$	[Diol] 0.0375	[Diol] 0.00938
1	5.12	0.565	
1	2.56	0.296 (0.040)[b]	0.355
2	5.12	0.879	
2	2.56	0.457 (0.079)[b]	0.516
3	5.12	0.299	
3	2.56	0.160 (0.113)[b]	0.225
4	5.12	0.916	
4	2.56	0.488 (0.120)[b]	0.597

[a] Rate expressed in mol l.$^{-1}$ min^{-1} × 10^4 and measured over the first 10% of the reaction. [b] Rate of oxidative cleavage in presence of 0.1 *M* allyl acetate. [c] pH = 1.7, $[S_2O_8^{2-}]$ = 0.01 *M*.



$$\mathbf{1} \text{ (or } \mathbf{2}) + S_2O_8^{2-} \xrightarrow{Ag^I} 2SO_4^{2-} + CH_3C(=O)(CH_2)_3C(=O)CH_3 + 2H^+ \quad (10)$$

5



$$\mathbf{3} \text{ (or } \mathbf{4}) + S_2O_8^{2-} \xrightarrow{Ag^I} 2SO_4^{2-} + CH_3C(=O)(CH_2)_4C(=O)CH_3 + 2H^+ \quad (11)$$

6

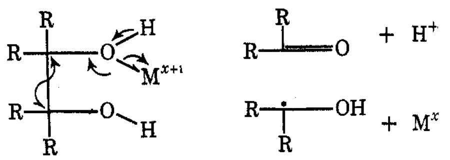
To determine if the dsp^2 square planar cyclic complexes are intermediates in the Ag^I-catalyzed peroxydisulfate reactions, we have examined oxidative cleavages of *cis*- and *trans*-1,2-dimethylcyclopentane-1,2-diols (**1** and **2**, respectively) and *cis*- and *trans*-1,2-dimethylcyclohexane-1,2-diols (**3** and **4**, respectively) with these reagents. The cleavage products from **1** and **2** and from **3** and **4** are the expected diketones 2,6-heptadione (**5**) and 2,7-octadione (**6**), respectively. Table I lists the initial rates of oxidative cleavage of these diols by peroxydisulfate in silver(I)-catalyzed reactions. The reaction rates follow the rate law

$$\text{rate} = \frac{k_2k_3\,[Ag^I][S_2O_8^{2-}]^{x+1}}{k_3\,[S_2O_8^{2-}] + k_{-2}} + \left(\frac{k_2k_3k_7k_8}{k_9(k_3[S_2O_8^{2-}] + k_{-2})}\right)[Ag^I][S_2O_8^{2-}]^{(x+1)^{1/2}+1} \quad (12)$$

where the first term is the rate of cleavage by path I and the second term that for path II provided chain termination occurs only by reaction 9, the most likely termination route under these conditions.[9]

The reactions are very nearly first order in $[Ag^I]$. However, changes in the diol concentration have an inverse effect on the oxidative rate, which is indicative of more reaction of Ag^{III} with Ag^I at the lower diol concentration, thereby initiating the more rapid cleavage by the free-radical chain mechanism (path II). That some cleavage occurs by path II in each case is also evidenced by the effect of allyl acetate, a free-radical chain inhibitor, on decreasing the overall reaction rate.

Assuming that the observed oxidative cleavage rates at the lower diol concentrations reflect mainly reaction by path II, then the similarities of the rates of oxidative cleavage of the trans diols relative to the corresponding cis diols obviate the necessity of formation of a cyclic intermediate of the diol with Ag^{II} for cleavage *via* the free radical chain mechanism. The necessity of cyclic complexes as reaction intermediates has been disposed of in oxidative cleavage reactions effected by Ce^{IV} and V^V.[14] These species also effect one-electron oxidations generating a free radical from the glycol in a manner



$(M^{x+1} = Ag^{II}, Ce^{IV}, V^V)$

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[10] J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962).

[11] C. C. Price and H. Kroll, *J. Amer. Chem. Soc.*, **60**, 2726 (1938); C. C. Price and M. Knell, *ibid.*, **64**, 552 (1942); G. J. Buist and C. A. Burton, *J. Chem. Soc.*, 1406 (1954).

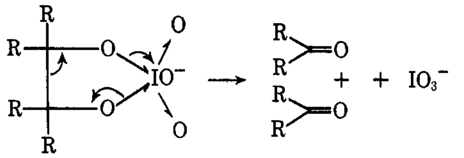
[12] R. Criegee, L. Kraft, and R. Bank, *Justus Liebigs Ann. Chem.*, **507**, 159 (1933); R. Criegee, E. Buchner, and W. Walther, *Ber.*, **73**, 571 (1940); R. Criegee, E. Hager, G. Huber, P. Kruck, R. Marktscheffel, and H. Schellenberger, *Justus Liebigs Ann. Chem.*, **599**, 81 (1956).

[13] Evidence is available, however, that indicates that *trans*-1,2-diols not capable of forming cyclic intermediates can be cleavaged by lead tetraacetate but at slower rates than encountered for those diols that are able to form cyclic intermediates. See C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960).

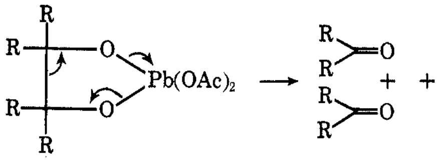
[14] J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 2767 (1960); H. L. Hintz and D. C. Johnson, *J. Org. Chem.*, **32**, 556 (1967).

similar to the reactions of Ag^{II}. Involvement of both oxygens of the diol is not required in these processes.

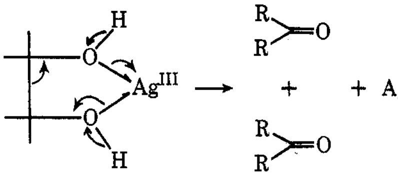
Cyclic intermediates have been suggested to be necessary only in oxidative cleavage reactions that involve two-electron oxidants [*e.g.*, IO_4^-, $Pb(OAc)_4$]. In such oxidations, the electron movement involves all of the atoms of the rings and apparently is more facile if the participating atoms are coplanar (or very nearly so). Oxidative cleavage by path I involving Ag^{III}, a two-electron oxidant, may require the formation of a cyclic intermediate. By analogy with the periodic acid and lead tetraacetate reactions, cyclic complexes that decompose yielding the oxidative cleavage products should be formed more readily between Ag^{III} and the cis diols than with the trans isomers.[15] Although there is no direct evidence for a cyclic intermediate in the oxidative cleavages by path I, the formation and participation of such a species can be inferred from the kinetic data in Table I. Since the cis diols would be expected to undergo cleavage by path I more readily than the trans isomers, less Ag^{III} would react with Ag^I to initiate oxidative cleavage by the more rapid free-radical chain sequence of path II. Initiation of the chain reaction could be expected to occur more readily in the reactions of the trans isomers because the Ag^{III} is not so efficiently consumed by the trans diols as it is by the corresponding cis diols, which can form the cyclic intermediates that decompose by path I. The somewhat faster rates of cleavage of the trans isomers with respect to the corresponding cis isomers may reflect, therefore, a greater amount of cleavage by the more rapid path II.



(13)



(14)



(15)

In the case of *cis*-1,2-dimethylcyclohexane-1,2-diol (**3**), not only is the oxidative cleavage rate decidedly slower than that of the trans isomer under similar conditions, but allyl acetate is considerably less effective in inhibiting the reaction rate of the cis isomer. Both factors suggest that a significant amount of the oxidative cleavage of **3** occurs by path I because Ag^{III} complexes readily with this diol. The more effective retardation of the overall cleavage rate of **1**, **2**, and **4** reflects a larger proportion of the available Ag^{III} being partitioned in the reaction with Ag^I to initiate cleavage by path II.

Experimental Section

Materials.—1,2-Dimethylcyclohexene, bp 129–135°, n^{20}D 1.4601, was prepared by dehydration of 1,2-dimethylcyclohexan-1-ol, which in turn was obtained by reaction of methylmagnesium iodide with 2-methylcyclohexanone (Aldrich Chemical Co.). ***trans*-1,2-Dimethylcyclohexane-1,2-diol**, mp 92–93° (lit.[16] 93°), was obtained in 22% yield from the performic acid hydroxylation[17] of 1,2-dimethylcyclohexene. ***cis*-1,2-Dimethylcyclohexane-1,2-diol**, mp 51° (lit.[18] 50°), was obtained in about 2% conversion from the reaction of 1,2-dimethylcyclohexene with osmium tetroxide and hydrogen peroxide.[19] ***trans*-1,2-Dimethylcyclopentane-1,2-diol**, mp 104–105° (lit.[20] 105–107°), was prepared in 16% conversion by performic acid hydroxylation[17] of 1,2-dimethylcyclopentane (K and K Laboratories, Inc.). ***cis*-1,2-Dimethylcyclopentane-1,2-diol**, mp 23° (lit.[21] 24°), was obtained in about 7% conversion from the osmium tetroxide catalyzed hydroxylation of 1,2-dimethylcyclopentene with hydrogen peroxide.[18]

Oxidative Cleavage of *cis*- and *trans*-1,2-Dimethylcyclopentane-1,2-diol.—A reaction mixture consisting of *cis*-1,2-dimethylcyclopentane-1,2-diol (0.130 g, 1 mmol), potassium peroxydisulfate (0.270 g, 1 mmol), and silver nitrate (0.0136 g, 0.08 mmol) in 20 ml of water was allowed to stand at room temperature under a nitrogen atmosphere for 2 days. A saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl (120 ml) was added to the reaction mixture. 2,6-Heptadione bis-2,4-dinitrophenylhydrazone, mp 184–185° (lit.[21] 183–185°), was isolated in 79% yield (0.387 g). In a similar experiment the 2,6-heptadione bis-2,4-dinitrophenylhydrazone, mp 184°, was obtained from *trans*-1,2-dimethylcyclopentane-1,2-diol (0.466 g, 95% of theory).

Oxidative Cleavage of *cis*- and *trans*-1,2-Dimethylcyclohexane-1,2-diols.—A solution of *cis*-1,2-dimethylcyclohexane-1,2-diol (0.144 g, 1 mmol), potassium peroxydisulfate (0.270 g, 1 mmol), and silver nitrate (0.135 g, 0.08 mmol) was allowed to react under a nitrogen atmosphere for 2 days. Addition of 120 ml of a 2 *N* HCl solution saturated with 2,4-dinitrophenylhydrazine resulted in formation of 0.242 g (48% of theory) of 2,7-octanedione bis-2,4-dinitrophenylhydrazone, mp 218–219° (lit.[22] 219°). In a similar experiment employing 1.5 mmol of potassium peroxydisulfate, the 2,7-octanedione bis-2,4-dinitrophenylhydrazone was obtained in 71% yield. Oxidative cleavage of 0.144 g (1 mmol) of *trans*-1,2-dimethylcyclohexane-1,2-diol with 0.27 g (1 mmol) of potassium peroxydisulfate and 0.0136 g (0.08 mmol) of silver nitrate yielded 0.492 g (96% of theory) of 2,7-octanedione bis-2,4-dinitrophenylhydrazone which melted at 218–218.5°.

Kinetic Measurements.—The reactions were performed in distilled water buffered to a pH of 1.7 by 0.25 *M* sodium sulfate and 0.25 *M* sodium bisulfate. The organic substrate and potassium peroxydisulfate were dissolved in the buffered solution and placed in a painted three-neck 500-ml flask. The flask was placed in a water bath maintained at 30 ± 0.1° and nitrogen was bubbled through the solution for 1 hr to remove any dissolved oxygen. An appropriate amount of 0.4 *M* silver nitrate was added and immediate reaction ensured. Aliquots of the reaction mixture were removed at appropriate time intervals and the unreacted peroxydisulfate was determined by the iodometric method described by Bartlett and Cotman.[23]

Registry No.—**1**, 33046-19-4; **2**, 33046-20-7; **3**, 33046-21-8; **4**, 33046-22-9; silver(I) ion, 14701-21-4; peroxydisulfate, 15092-81-6; 2,7-octanedione bis-2,4-DNP, 33046-95-6.

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[15] A cyclic complex having essentially the same strain as that obtained from the *cis*-cyclohexane-1,2-diol (**3**) should be formed from the *trans*-diequatorial cyclohexane-1,2-diol (**4**). However, a low-energy transition state for the decomposition of the trans isomers complex cannot be attained owing to the conformational aspects of the cyclohexane ring that prevent 1,2-diequatorial substituents from becoming coplanar.

[16] C. A. Bunton and M. D. Carr, *J. Chem. Soc.*, 5854 (1963).

[17] A. Roebuck and H. Adkins, *Org. Syn.*, **28**, 35 (1948).

[18] S. Namerthin and N. Delekarsky, *Ber.*, **57**, 583 (1924).

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[22] S. Shimizu and S. Tate, *J. Agr. Chem. Soc. Jap.*, **23**, 286 (1950).

[23] P. D. Bartlett and J. D. Cotman, *J. Amer. Chem. Soc.*, **71**, 1419 (1949).