Oxidation by Cobalt(III) Acetate. Part 4.[1] Kinetics and Mechanism of the Oxidation of Glycols in Acetic Acid

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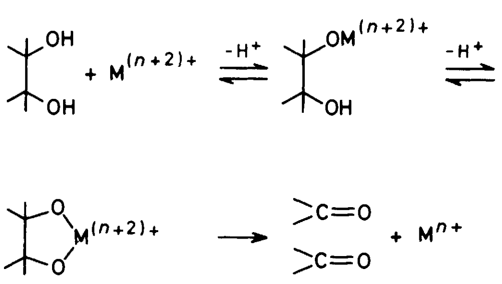
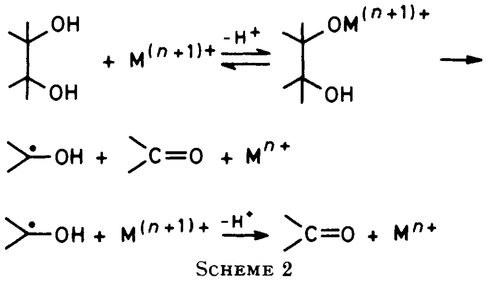
The oxidative cleavage of 1,2-glycols by cobalt(III) acetate in acetic acid was studied kinetically in order to clarify the reaction mechanism. The rates were first-order in both cobalt(III) acetate and substrate for the oxidation of all the diols used. *cis*-Cyclopentane-1,2-diol and decalin-9,10-diol were more rapidly oxidized than the corresponding *trans*-isomers, respectively, whereas *cis*-cyclohexane-1,2-diol was more slowly oxidized than the *trans*-isomer. The oxidation of *trans*-2-methoxycyclohexanol was much slower than that of the corresponding diol. The mechanism involving the formation of a bidentate complex between cobalt(III) acetate dimer and glycol is discussed.

THE oxidative cleavage of 1,2-glycols has been studied for a variety of oxidants.[2] There are two types of mechanism of the reaction. One involves the formation of a bidentate complex which then breaks down to products *via* a two-electron process (Scheme 1). Support for this mechanism comes from the facts that *cis*-glycols are more rapidly oxidized than the corresponding *trans*-isomers and *threo*-diols are more rapidly oxidized than the corresponding *erythro*-isomers.[3] These are well established for lead(IV) acetate and periodate oxidations.[2a]


SCHEME 1

The other mechanism involves a monodentate complex which then gives an intermediate radical *via* a one-electron oxidation, followed by C–C fission and further oxidation (Scheme 2). Support for this mechanism lies in the similar rates of the oxidation of 1,2-glycols and their monomethyl ethers [4] and of *threo*- and *erythro*-isomers,[5] and in the successful trapping of a radical intermediate.[6] This mechanism is proposed for the cerium(IV) ion oxidation of 1,2-glycols.[5]

We found previously that oxidation of styrene by cobalt(III) acetate in acetic acid gave the corresponding glycol monoacetate and further oxidation products, but not the glycol.[7] When styrene glycol was treated with cobalt(III) acetate in order to examine the intermediacy of the glycol in the formation of further oxidation products, we observed that it was oxidized very quickly. The difference in reactivities between glycol and its monoacetate towards cobalt(III) acetate led us to expect that the reaction of the glycol with cobalt(III) acetate proceeded through a bidentate-complex mechanism. Cobalt(III) acetate is considered, however, to be a one-electron rather than a two-electron oxidant. Indeed, several aromatic compounds react with the reagent in the presence of strong acid to generate radical cations, which are derived from a one-electron abstraction from the benzene ring.[8] This inconsistency stimulated us to investigate the mechanism of the oxidative cleavage of 1,2-glycols by cobalt(III) acetate in acetic acid.


SCHEME 2

This paper deals with a kinetic study of the oxidative cleavage of cyclic glycols, the hydroxy-groups of which are fixed relative to each other, by cobalt(III) acetate in acetic acid.

RESULTS

Reactions were carried out in a quartz cell maintained at constant temperature by circulating water kept at a constant temperature to a cell chamber. The reaction rates were measured by following the decrease of the absorbance of cobalt(III) acetate at 610 nm in acetic acid and recorded automatically. With an excess of substrate, the rate of the oxidation of *trans*-cyclohexane-1,2-diol was first-order in cobalt(III) acetate (Figure). Pseudo-first-order rate constants were maintained constant by changing the initial concentration of cobalt(III) acetate and also by adding anhydrous cobalt(II) acetate which is known to retard the oxidation of hydrocarbons by the oxidant in acetic acid.[9]

Plots of the pseudo-first-order rate constants against the initial concentrations of *trans*-cyclohexane-1,2-diol gave a straight line through the origin, showing that the rate is also first-order in substrate [equation (1)]. The kinetic data are summarized in Table 1.

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Co^{III}}][\mathrm{Diol}] \qquad (1)$$

The same kinetic laws were obtained for the oxidation of *trans*-cyclopentane-1,2-diol and *trans*-decalin-9,10-diol by cobalt(III) acetate. All the oxidations of the corresponding

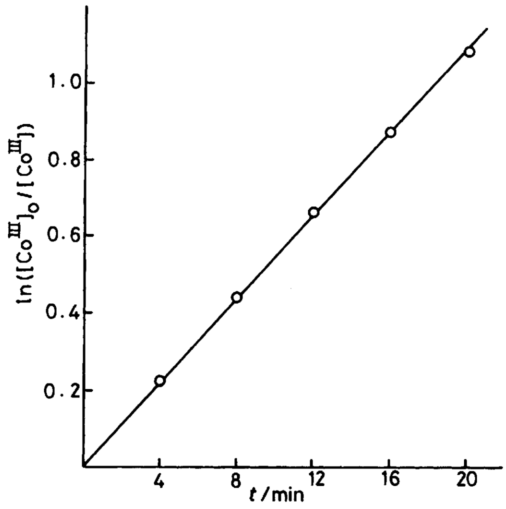


FIGURE First-order plot of the oxidation of *trans*-cyclohexane-1,2-diol by cobalt(III) acetate in acetic acid at 50 °C. $[Co^{III}]_0$ 2.20×10^{-3}M; $[Diol]_0$ 4.67×10^{-2}M.

cis-diols were also found to obey the same kinetic laws, although the effects of cobalt(II) acetate on the rates were not examined. The data are listed in Table 2.

The oxidations of *cis*- and *trans*-cyclohexane-1,2-diols with the oxidant were conducted in n-butyric and pivalic acids in order to examine ligand effects. The rates are shown in Table 3.

TABLE 1

The oxidation of *trans*-cyclohexane-1,2-diol in acetic acid at 50 °C

10^2 $[Diol]_0$/ M	10^3 $[Co^{III}]_0$/ M	10^3 $[Co^{II}]_0$/ M	10^2 k'/min^{-1}	k_{obs}/l mol^{-1} min^{-1}
4.64	2.20	0	5.07	1.09
4.67	3.24	0	5.36	1.15
4.59	3.75	0	5.16	1.12
4.61	4.25	0	4.77	1.04
4.05	3.24	1.61	4.88	1.20
4.08	3.24	3.21	4.56	1.12
2.63	3.24	0	3.12	1.19
4.21	3.24	0	4.97	1.18
5.45	3.24	0	6.33	1.16
6.73	3.24	0	7.92	1.18

$k' = k_{obs} [Diol]_0$.

The oxidation of *trans*-2-methoxycyclohexanol with cobalt(III) acetate was much slower than that of the corresponding diol in acetic acid under similar conditions (Table 2). Cyclohexanol was oxidized more slowly than the diols in acetic acid, although the rate did not obey a first-order rate law.

TABLE 2

The rate constants of the oxidation of cycloalkanediols and 2-methoxycyclohexanol with cobalt(III) acetate in acetic acid at 50 °C

10^2 $[Diol]_0$/ M	10^3 $[Co^{III}]_0$/ M	10^3 $[Co^{II}]_0$/ M	10^2 k'/min^{-1}	k_{obs}/l mol^{-1} min^{-1}
cis-Cyclohexane-1,2-diol				
2.60	3.24	0	2.45	0.940
4.57	3.24	0	3.80	0.832
5.50	3.24	0	4.65	0.845
5.83	3.24	0	5.12	0.878
trans-Cyclopentane-1,2-diol				
5.49	4.40	0	3.56	0.649
8.94	4.40	0	5.75	0.643
4.16	2.10	0	2.81	0.676
4.16	4.71	0	2.84	0.683
4.16	3.95	4.20	2.63	0.632
cis-Cyclopentane-1,2-diol				
1.89	4.40	0	6.61	3.49
3.36	4.40	0	11.8	3.51
4.30	4.40	0	13.3	3.09
5.91	4.40	0	20.7	3.50
trans-Decalin-9,10-diol				
2.84	3.37	0	0.351	0.124
6.14	3.37	0	0.749	0.122
10.38	3.37	0	1.22	0.117
4.06	3.24	2.39	0.511	0.126
4.12	3.24	8.04	0.517	0.125
cis-Decalin-9,10-diol				
2.90	3.37	0	7.41	2.55
3.99	3.37	0	10.0	2.51
4.84	3.37	0	14.2	2.93
6.65	3.37	0	15.9	2.39
trans-2-Methoxycyclohexanol				
5.55	3.45	0	0.308	0.0556

TABLE 3

The rate constants of the oxidation of *cis*- and *trans*-cyclohexane-1,2-diol with cobalt(III) acetate in n-butyric and pivalic acids at 50 °C

	10^2 $[Diol]_0$/ M	10^3 $[Co^{III}]_0$/ M	10^2 k'/ min^{-1}	k_{obs}/l mol^{-1} min^{-1}
In n-butyric acid				
trans	3.56	3.33	2.34	0.657
	5.62	3.33	3.68	0.655
cis	4.87	3.33	2.18	0.448
	5.53	3.33	2.37	0.429
In pivalic acid				
trans	3.81	2.85	0.730	0.192
	5.39	2.85	1.13	0.209
cis	3.34	2.85	0.416	0.125
	5.34	2.85	0.616	0.115

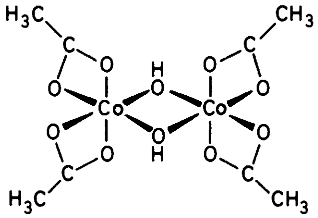
DISCUSSION

The results, except for the fact that *trans*-cyclohexane-1,2-diol is more rapidly oxidized than the *cis*-isomer, indicate that a bidentate complex intervenes as an intermediate in the oxidation of diols by cobalt(III) acetate in acetic acid.

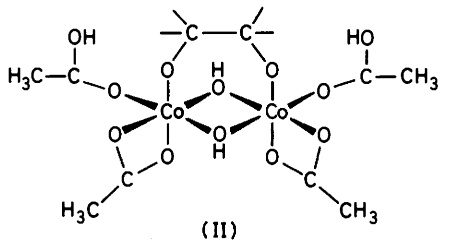
The oxidation of *trans*-2-methoxycyclohexanol was much slower than that of the parent diol. The relative rate of oxidative cleavage of the diol to its monomethyl ether (*ca.* 21) is similar to that of hydrobenzoin to its monomethyl ether with lead(IV) acetate, the glycol fission by which is believed to proceed through a bidente complex mechanism, as opposed to the situation with cerium(IV) ion.[4,5] Additional support for the intermediacy of this bidentate complex comes from the observation that *cis*-cyclopentane-1,2-diol and *cis*-decalin-9,10-diol were more rapidly oxidized than the corresponding *trans*-isomers. The relative rates (5.4 for cyclopentane-1,2-diol and 21.7 for decalin-9,10-diol) are much smaller than the values observed for their oxidation by lead(IV) acetate (*ca.* 3 000 and *ca.* 100,[10] respectively) and by periodate.[11] But the value for cyclopentane-1,2-diol in the present reaction is larger than that for the reaction with cerium(IV) ion.[12] Unfortunately, the relative rate for decalin-9,10-diol could not be compared with that with cerium(IV) ion since no datum was available. It is difficult to explain the relative rate by the difference of electronic effects of the stability of the *cis*- and *trans*- isomers, because these compounds differ only in the direction of the two hydroxy-groups and in the arrangement of the two rings. The relative rate is attributable to the difference in the structure of the transition state or intermediate; that is, the *cis*-isomer can form a stable bidentate complex but the *trans*-isomer cannot.

trans-Cyclohexane-1,2-diol was more rapidly oxidized by cobalt(III) acetate in acetic acid than the *cis*-isomer. The same results were obtained for their oxidation in n-butyric and pivalic acids. These results are contrary to the occurrence of a bidentate complex mechanism since the *cis*-isomer can form such a complex more easily than the *trans*-isomer and, indeed, in oxidation by lead(IV) acetate and periodate the *cis*-isomer is more rapidly oxidized than the *trans*-isomer.[3,13] These results may show that glycol cleavage by cobalt(III) acetate proceeds *via* a bidentate complex mechanism and the structure of the intermediate is different from that suggested for the lead(IV) acetate and periodate oxidations.

Cobalt(III) acetate is dimeric in the solid state and also in organic solvents [14] and there are some reports suggesting that dimeric cobalt(III) acetate, rather than the monomer, is the reactive species for the oxidation of hydrocarbons in acetic acid.[9] The same dimeric species may attack diols in the present reaction.

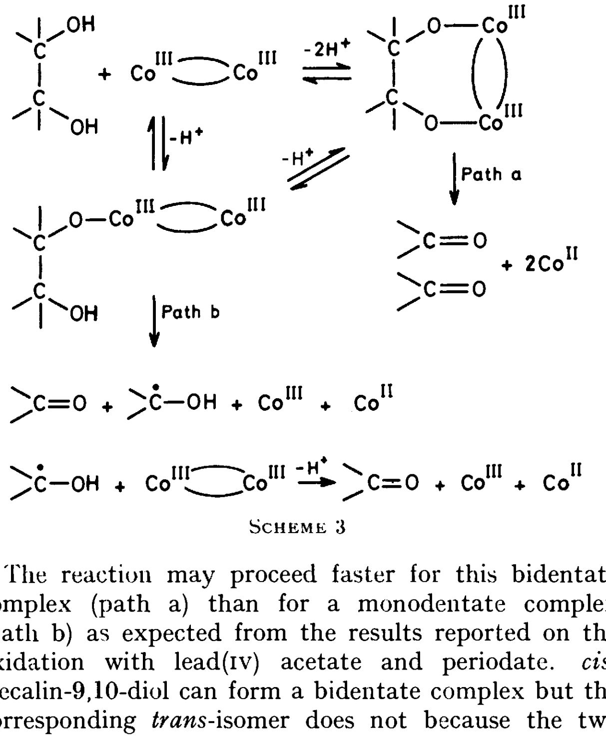


(I)



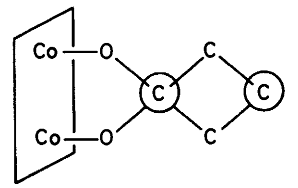
(II)

The structure of the dimer is reported as (I).[14a,b] If the hydroxy-groups in the glycol occupied positions on the same side of the two cobalt(III) ions displacing the oxygen atoms of the acetoxy-groups at the same time or by a stepwise process, then the bidentate complex (II) can be formed and the mechanism in Scheme 3 can be written.

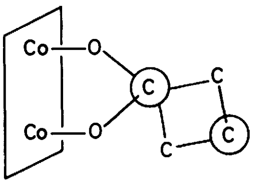


SCHEME 3

The reaction may proceed faster for this bidentate complex (path a) than for a monodentate complex (path b) as expected from the results reported on the oxidation with lead(IV) acetate and periodate. *cis*-Decalin-9,10-diol can form a bidentate complex but the corresponding *trans*-isomer does not because the two hydroxy-groups lie in opposite directions and are thus far from each other for the purpose of forming such a bidentate complex. The *trans*-isomers, therefore, are oxidized through a monodentate complex. Indeed, its oxidation rate is close to that of *trans*-2-methoxycyclohexanol which cannot form a bidentate complex. The distance between the two hydroxy-groups of *trans*-cyclopentane-1,2-diol is shorter than that of *trans*-decalin-9,10-diol but still it is not short enough to form a bidentate complex. Thus, path b is favoured for *trans*-cyclopentane-1,2-diol. In contrast, the *cis*-isomer does not resist forming a stable bidentate complex.



(III)



(IV)

The distance between the two cobalt(III) ions in (I) is relatively long and the intermediate (II) has a flexible structure compared with the five-membered ring of the intermediate in the lead(IV) acetate and periodate oxidations of diols. Since the distance between the two hydroxy-groups of *trans*-cyclohexane-1,2-diol is similar to that of the *cis*-isomer, both compounds may form stable bidentate complex (III) and (IV).

Hence, both *cis*- and *trans*-cyclohexane-1,2-diol react smoothly with cobalt(III) acetate and at a comparable rate. Species (III) formed from *trans*-cyclohexane-

1,2-diol and cobalt(III) acetate has a structure in which the cyclohexane ring is perpendicular to the plane constructed by cobalt(III) ions and the ligands. In (IV) which is derived from the *cis*-isomer, the cyclohexane ring inclines toward the plane. The shorter distance between the ring and the plane decreases the stability of (IV) because of repulsion. This agrees with the observation that *trans*-cyclohexane-1,2-diol is more rapidly oxidized than the *cis*-isomer. This is supported by the fact that k_{cis}/k_{trans} becomes smaller with increasing bulk of the solvent. It has been reported that cobalt(III) acetate is converted into the corresponding carboxylate in carboxylic acid.[15] Thus, cobalt(III) acetate is converted into cobalt(III) n-butyrate and pivalate in n-butyric and pivalic acids, respectively [reaction (2)].

$$\mathrm{Co^{III}(OAc)_3 + 3RCOOH \longrightarrow Co^{III}(OCOR)_3 + 3AcOH} \quad (2)$$

The increasing size of ligands decreased the stability of the intermediate in both cases. The decrease in stabilization is smaller with (III) than with (IV), because the distance between the cyclohexane ring and the ligands of cobalt(III) acetate dimer is smaller in (IV) than in (III). Thus, the decrease in rate is larger in the oxidation of the *cis*-isomer than in the *trans*.

EXPERIMENTAL

M.p.s were measured on a Yamato capillary apparatus and were uncorrected. Visible spectra were recorded with a Hitachi UV-124 spectrophotometer and the cell chamber was maintained at a constant temperature by circulating water.

Starting Materials.—*cis*-Cyclohexane-, m.p. 93—95 °C, and *cis*-cyclopentane-1,2-diol, m.p. 28—29 °C, were prepared by the oxidation of cyclohexene and cyclopentene by potassium permanganate.[16] *trans*-Cyclohexane-, m.p. 101.5—103 °C, and *trans*-cyclopentane-1,2-diol, b.p. 97—98 °C at 5 mmHg) were prepared from the olefins by treatment with formic acid and hydrogen peroxide.[17] *cis*-Decalin-9,10-diol, m.p. 88—89 °C, was prepared from 1,2,3,4,5,6,7,8-tetrahydronaphthalene with osmium tetraoxide,[18] and the *trans*-isomer was prepared from the olefin with *m*-chloroperbenzoic acid.[19] Cobalt(III) acetate was prepared by the oxidation of cobalt(II) acetate tetrahydrate with ozone in acetic acid in the presence of acetic anhydride.[1]

Kinetic Measurements.—A solution of diol in acetic acid (3.5 ml) was placed in a quartz cell with a glass joint stopper and flushed with nitrogen. The cell was kept in the cell chamber till the temperature of the solution became constant. Cobalt(III) acetate solution in acetic acid (0.1—0.5 ml) was then added by means of a hypodermic syringe under a gentle flow of nitrogen, and the reaction was started. The reaction was monitored by following the decrease of the absorption of cobalt(III) acetate at 610 nm. The molar absorption of cobalt(III) acetate in acetic acid at this wavelength was 213 l mol^{-1} cm^{-1} and that of cobalt(II) acetate was 4.0 l mol^{-1} cm^{-1}.

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