Oxidation by Cobalt(III) Acetate. Part 9.[1] Effect of Substituents on the Oxidative Cleavage of Glycols in Acetic Acid

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The kinetics of oxidative cleavage of glycols by cobalt(III) acetate in acetic acid have been studied. The substrates examined include *cis*- and *trans*-cyclopentane- and cyclohexane-1,2-diols and their mono- and di-methyl derivatives. The rates were first-order in both cobalt(III) acetate and substrate in all cases. In the oxidation of five-membered ring diols, *cis*-diols were generally oxidized faster than the *trans*-isomers. Complex results were obtained in the case of six-membered ring diols. Thermodynamic parameters were calculated for all the substrates. A mechanism involving a bidentate complex of cobalt(III) acetate dimer and the glycol is suggested, except for the case of *trans*-cyclopentane-1,2-diols, for which a monodentate intermediate is proposed.

The oxidative cleavage of 1,2-diols with a variety of oxidants has been thoroughly studied,[2] and the mechanism is conventionally classified into two types. One involves a bidentate complex between the oxidant and the glycol, which breaks down *via* a two-electron process (Scheme 1). The other involves a monodentate complex, which gives an intermediate radical *via* an one-electron process; this is followed by C–C fission and further oxidation (Scheme 2).

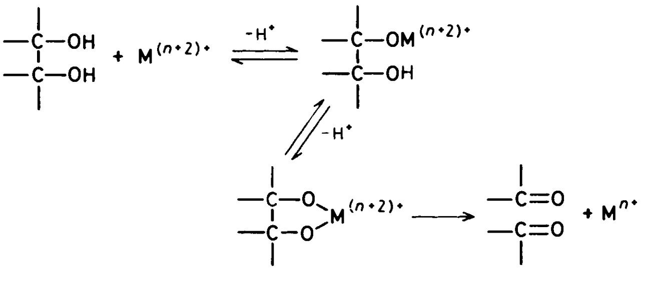
In our previous paper[3] we reported that the oxidative cleavage of 1,2-diols by cobalt(III) acetate was first-order with respect to both oxidant and substrate, and that the oxidation of *trans*-diols was slower than that of the corresponding *cis*-diols, except for the case of cyclohexane-1,2-diols. Cyclohexane-1,2-diol monomethyl ether, however, was oxidized more slowly than the parent diol.

This paper describes a kinetic study of the oxidative cleavage of 1,2-diols by cobalt(III) acetate in acetic acid, and of the effect of methyl substituents on the rates, performed in order to elucidate further the reaction mechanism.

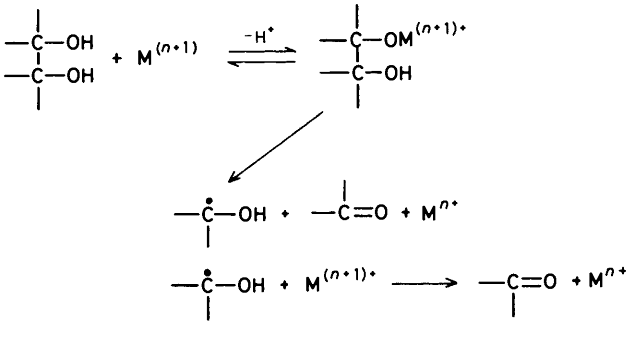
Results

The oxidations of diols by cobalt(III) acetate were carried out in a quartz cell for spectrophotometry; the decrease in absorbance at 610 nm was monitored automatically. In the presence of an excess of *cis*-cyclopentane-1,2-diol, (**1**), first-order plots in cobalt(III) acetate gave a straight line through the origin during the initial stage of the reaction. However, a slight decrease in rate with time was observed. In the reactions of other substrates [cyclic five- and six-membered diols (**2**)—(**12**), propylene glycol (**13**), and pinacol (**14**)], similar results were obtained. The data are shown in Figures 1—3. The deviation from first-order plots was small in the oxidation of the unsubstituted diols [(**1**), (**4**), (**7**), and (**10**)], but it increased with an increase in the number of substituents. The decrease in rate was considered to be due to cobalt(II) acetate formed during the reaction, since the reaction was retarded by addition of anhydrous cobalt(II) acetate to the system (Figure 4). However, attempts to fit the resulting data to any rate law were unsuccessful {*e.g.* reverse first-order in cobalt(II), such as $[\mathrm{Co^{III}}]/[\mathrm{Co^{II}}]$ or $[\mathrm{Co^{III}}]^2/[\mathrm{Co^{II}}]$}. Therefore pseudo-first-order rate constants, obtained from the initial linear plot, were employed for comparisons [equation (1)].

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = k_1[\mathrm{Co^{III}}] \qquad (1)$$



Scheme 1.

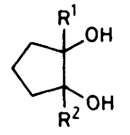


Scheme 2.

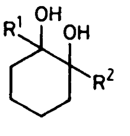
The plots of the first-order rate constants against initial concentration of diol gave straight lines through the origin, showing that the rate was also first-order with respect to the diols. Thus, the rate law may be expressed as in equation (2), at least for the initial stage of the reaction. The kinetic data are summarized in Tables 1, 2, and 3.

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = k_2[\mathrm{Co^{III}}][\text{diol}] \qquad (2)$$

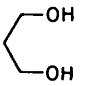
In the oxidation of the cyclopentane-1,2-diols (**1**)—(**6**), the *cis*-diols (**1**)—(**3**) were oxidized more rapidly than the *trans*-isomers (**4**)—(**6**). However, complex results were obtained in the oxidation of the cyclohexane-1,2-diols (**7**)—(**12**). The unsubstituted *cis*-diol (**7**) was oxidized more rapidly than the *trans*-diol (**10**) at 293.15 K, at nearly the same rate at 303.15 K and at 313.15 K, and more slowly at 323.15 K. The monosubstituted *cis*-diol (**8**) was more rapidly oxidized than the *trans*-diol (**11**) over the whole temperature range. In contrast, the disubstituted *cis*-diol (**9**) was oxidized more slowly than the



(1) *cis* $R^1 = R^2 = H$ *trans* **(4)**
(2) *cis* $R^1 = H, R^2 = Me$ *trans* **(5)**
(3) *cis* $R^1 = R^2 = Me$ *trans* **(6)**



(7) *cis* $R^1 = R^2 = H$ *trans* **(10)**
(8) *cis* $R^1 = H, R^2 = Me$ *trans* **(11)**
(9) *cis* $R^1 = R^2 = Me$ *trans* **(12)**



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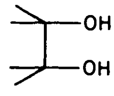

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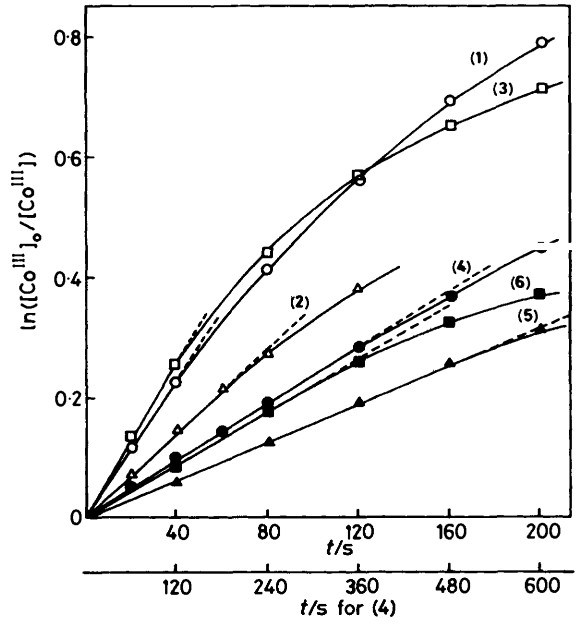


Figure 1. First-order plots for the oxidations of substituted cyclopentane-1,2-diols by Co^{III} in acetic acid at 293.15 K: (**1**), $[\text{diol}]_0 = 4.55 \times 10^{-2}$ mol dm^{-3}; (**2**), $[\text{diol}]_0 = 5.17 \times 10^{-2}$ mol dm^{-3}; (**3**), $[\text{diol}]_0 = 3.76 \times 10^{-2}$ mol dm^{-3}; (**4**), $[\text{diol}]_0 = 6.01 \times 10^{-2}$ mol dm^{-3}; (**5**), $[\text{diol}]_0 = 4.11 \times 10^{-2}$ mol dm^{-3}; (**6**), $[\text{diol}]_0 = 4.16 \times 10^{-2}$ mol dm^{-3}; $[\text{Co}^{III}]_0 = 3.16$—$4.32 \times 10^{-3}$ mol dm^{-3}; $[\text{Co}^{II}]_0/[\text{Co}^{III}]_0 = 0.044$. The lower time scale is used for the oxidation of (**4**) in order to show the deviation from the first-order plot

trans-isomer (**12**). In the case of the open-chain diols, (**13**) was oxidized more slowly than (**14**).

The thermodynamic parameters ($\Delta H^‡$, $\Delta S^‡$, and $\Delta G^‡$) were calculated from the rate constants at the various temperatures (Table 4). In the oxidation of the cyclopentane-1,2-diols (**1**)—(**6**), $\Delta H^‡$ and $\Delta S^‡$ of the *trans*-diols (**4**)—(**6**) were much larger than those of the *cis*-isomers (**1**)—(**3**), and $\Delta G^‡$ for (**4**)—(**6**) was slightly larger than for (**1**)—(**3**). No relationship between methyl substitution and thermodynamic parameters was observed. In the oxidation of the cyclohexane-1,2-diols (**7**)—(**12**), there were only small differences in thermodynamic parameters between *cis*- and *trans*-diols. Values of $\Delta H^‡$ and $\Delta S^‡$ for the *trans*-diols (**10**)—(**12**) decreased slightly with the number of methyl substituents, whereas those for the *cis*-diols (**7**)—(**9**) showed a corresponding increase. Values of $\Delta G^‡$ for (**7**)—(**12**) were approximately constant. In the case of the linear diols (**13**) and (**14**), $\Delta S^‡$ for oxidation of (**13**) was similar to that of (**14**) and $\Delta H^‡$ and $\Delta G^‡$ for (**13**) were slightly larger than those for (**14**).

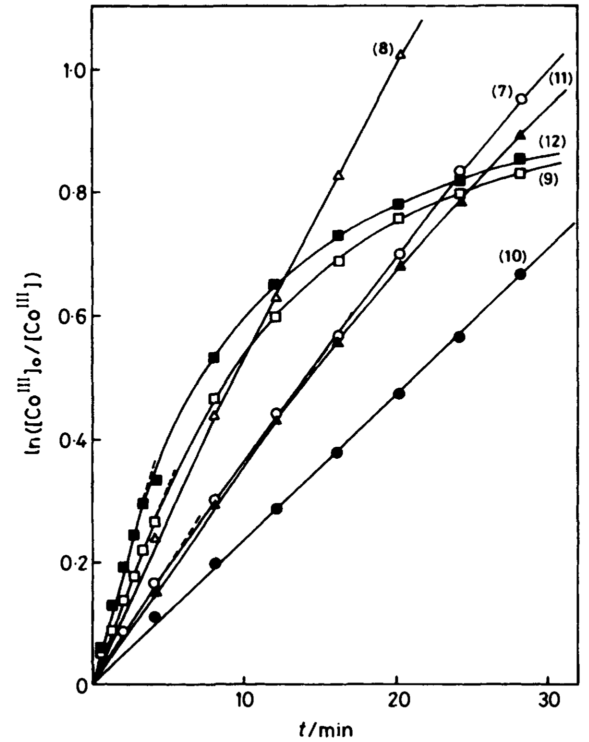


Figure 2. First-order plots for the oxidation of substituted cyclohexane-1,2-diols by Co^{III} in acetic acid at 313.15 K: (**7**), $[\text{diol}]_0 = 4.00 \times 10^{-2}$ mol dm^{-3}; (**8**), $[\text{diol}]_0 = 3.35 \times 10^{-2}$ mol dm^{-3}; (**9**), $[\text{diol}]_0 = 3.22 \times 10^{-2}$ mol dm^{-3}; (**10**), $[\text{diol}]_0 = 3.26 \times 10^{-2}$ mol dm^{-3}; (**11**), $[\text{diol}]_0 = 3.39 \times 10^{-2}$ mol dm^{-3}; (**12**), $[\text{diol}]_0 = 3.32 \times 10^{-2}$ mol dm^{-3}; $[\text{Co}^{III}]_0 = 3.03$—$3.54 \times 10^{-3}$ mol dm^{-3}; $[\text{Co}^{II}]_0/[\text{Co}^{III}]_0 = 0.044$

Discussion

We propose the mechanism illustrated in Scheme 3 for the oxidative cleavage of glycols by cobalt(III) acetate in acetic acid.

The *cis*-diols (**1**)—(**3**) were more rapidly oxidized than the *trans*-isomers (**4**)—(**6**) in the cyclopentane series. It is well known that the five-membered ring is of considerable rigidity, and that substituents bear a fixed relationship to each other. In the five-membered diols, the two hydroxy groups of the *cis*-diols lie on the same side of the ring, and in the *trans*-isomers one they are on opposite sides. Thus the *cis*-diols may form a stable bidentate complex with cobalt(III) acetate dimer, but the *trans*-isomer cannot. Oxidative fission of a glycol is considered to be faster when a bidentate complex can be formed between substrate and oxidant, as in oxidations by periodate[4] and lead(IV).[5] *cis*-Isomers, therefore, should be oxidized faster, as observed.

The thermodynamic parameters ($\Delta H^‡$, $\Delta S^‡$, and $\Delta G^‡$), especially $\Delta S^‡$, are considered to support the mechanism described in Scheme 3. The values of $\Delta S^‡$ for the *cis*-isomers (**1**)—(**3**) are considerably smaller than those of the *trans*-isomers (**4**)—

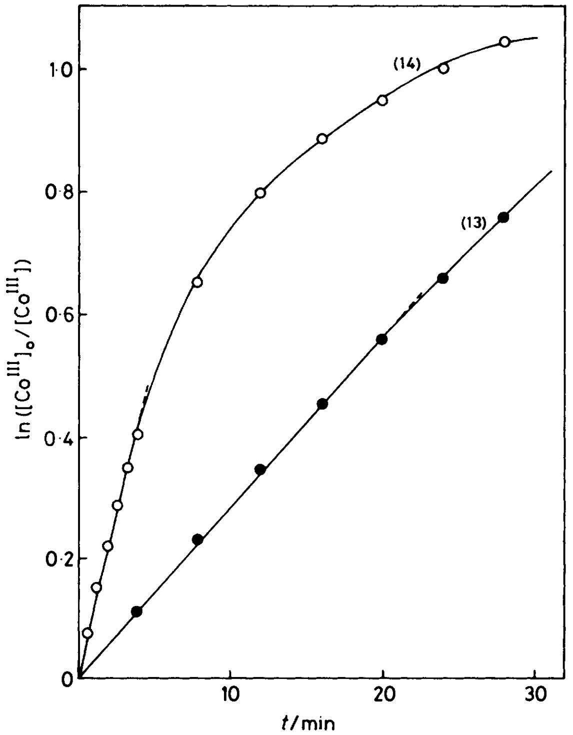


Figure 3. First-order plots for the oxidation of open-chain diols by Co^{III} in acetic acid at 313.15 K: (**13**), $[diol]_0 = 6.40 \times 10^{-2}$ mol dm^{-3}, $[Co^{III}]_0 = 3.26 \times 10^{-3}$ mol dm^{-3}; (**14**), $[diol]_0 = 6.07 \times 10^{-2}$ mol dm^{-3}, $[Co^{III}]_0 = 3.30 \times 10^{-3}$ mol dm^{-3}; $[Co^{II}]_0/[Co^{III}]_0 = 0.044$

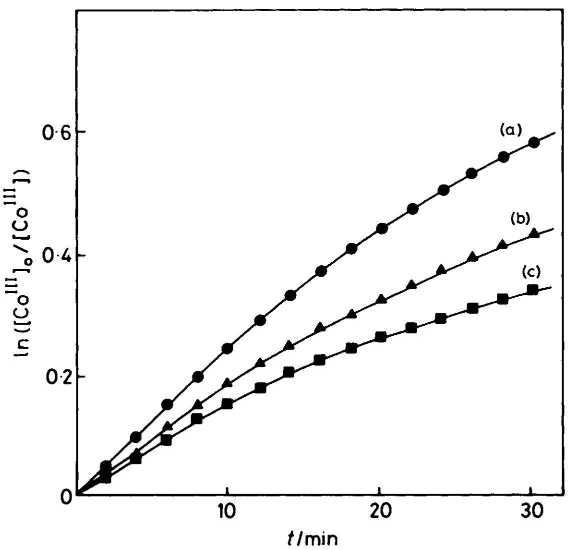


Figure 4. The effect of Co^{II} in the oxidation of *trans*-1-methylcyclohexane-1,2-diol (**11**) by Co^{III} in acetic acid at 313.15 K: (a) $[Co^{II}]_0/[Co^{III}]_0 = 0.337$; (b) $[Co^{II}]_0/[Co^{III}]_0 = 0.692$; (c) $[Co^{II}]_0/[Co^{III}]_0 = 0.869$; $[diol]_0 = 5.31 \times 10^{-2}$ mol dm^{-3}

Table 1. Rate constants for the oxidation of cyclopentanediols by cobalt(III) acetate in acetic acid

10^2[diol] / mol dm^{-3}	$10^3[Co^{III}]$ / mol dm^{-3}	Temp. (K)	k_1/s^{-1}	k_2 / dm^3 mol^{-1} s^{-1}
cis-Cyclopentane-1,2-diol (**1**)				
4.55	5.41	283.15	2.50×10^{-3}	5.50×10^{-2}
4.55	4.09	293.15	5.96×10^{-3}	1.31×10^{-1}
4.55	5.29	303.15	1.12×10^{-2}	2.47×10^{-1}
cis-1-Methylcyclopentane-1,2-diol (**2**)				
5.17	3.40	293.15	3.68×10^{-3}	7.13×10^{-2}
4.13	3.47	293.15	3.40×10^{-3}	8.22×10^{-2}
3.10	3.57	293.15	2.77×10^{-3}	8.95×10^{-2}
5.17	3.03	298.15	5.30×10^{-3}	1.03×10^{-1}
5.17	3.68	303.15	8.14×10^{-3}	1.58×10^{-1}
cis-1,2-Dimethylcyclopentane-1,2-diol (**3**)				
3.76	4.32	293.15	6.69×10^{-3}	1.71×10^{-1}
3.76	6.76	303.15	1.36×10^{-2}	3.49×10^{-1}
trans-Cyclopentane-1,2-diol (**4**)				
6.01	3.16	293.15	8.07×10^{-4}	1.34×10^{-2}
6.01	3.07	298.15	1.63×10^{-3}	2.72×10^{-2}
6.01	3.80	303.15	3.42×10^{-3}	5.70×10^{-2}
4.81	3.32	303.15	2.55×10^{-3}	5.31×10^{-2}
3.61	3.56	303.15	2.06×10^{-3}	5.71×10^{-2}
trans-1-Methylcyclopentane-1,2-diol (**5**)				
4.11	2.82	283.15	3.05×10^{-4}	7.12×10^{-3}
4.11	3.42	293.15	1.57×10^{-3}	3.82×10^{-2}
4.11	3.96	303.15	5.61×10^{-3}	1.37×10^{-1}
5.14	3.78	303.15	6.53×10^{-3}	1.27×10^{-1}
3.29	3.76	303.15	4.33×10^{-3}	1.32×10^{-1}
2.47	3.95	303.15	3.65×10^{-3}	1.48×10^{-1}
trans-1,2-Dimethylcyclopentane-1,2-diol (**6**)				
4.16	3.73	293.15	2.27×10^{-3}	5.46×10^{-2}
4.16	3.92	303.15	7.18×10^{-3}	1.73×10^{-1}

(**6**) in the cyclopentane series. These values of $\Delta S^{\ddagger}$ may be compared with those for oxidation by cerium(IV), although the reaction conditions differ.[6] The value of $\Delta S^{\ddagger}$ for *trans*-cyclopentane-1,2-diol (**4**) (70.3 J mol^{-1} K^{-1}) in the present reaction is close to that reported for cerium(IV) oxidation (64.4 J mol^{-1} K^{-1}), whereas values for the *cis*-isomer (**1**) differ considerably from each other [-87.9 J mol^{-1} K^{-1} for cobalt(III) acetate oxidation and 61.5 J mol^{-1} K^{-1} for cerium(IV) oxidation]. Furthermore, in the oxidation of cyclopentane-1,2-diols (**1**) and (**4**) by cerium(IV), $\Delta S^{\ddagger}$ for the *cis*-diol (**1**) is nearly equal to that of the *trans*-isomer (**4**), suggesting formation of an acyclic intermediate. On the basis of these comparisons, it can be concluded that the oxidation of *trans*-cyclopentane-1,2-diols (**4**)—(**6**) by cobalt(III) acetate proceeds *via* an acyclic mechanism, that is, a monodentate mechanism, whereas that of the *cis*-isomer (**1**)—(**3**) proceeds *via* a cyclic intermediate (probably six-membered), formed from the diol and cobalt(III) acetate dimer.

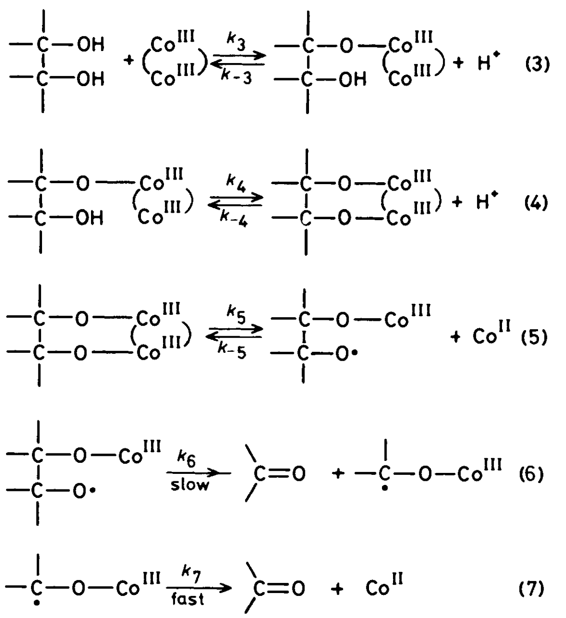
In the cyclohexane series, thermodynamic parameters for the *cis*-diols (**7**)—(**9**) are nearly equal to those of the *trans*-isomer (**10**)—(**12**). These results may indicate that both *cis*- and *trans*-diols react *via* the same mechanism, probably involving a bidentate complex as for the *cis*-cyclopentane-1,2-diols (**1**)—(**3**). If this mechanism applies, the *cis*- and *trans*-cyclohexane-1,2-diols (**7**)—(**12**) may form the complexes (**15a**) and (**15b**), respectively. In (**15a**) there is no steric hindrance between R^1 and R^2, since they are far from each other. Thus the methyl group functions only as an electron donor and can stabilize the cyclic intermediate (**15a**). Hence when R^1 and R^2 are methyl groups, the bulk of the intermediate is relatively small. This situation is compatible with the observation that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ become smaller with an increasing number of methyl sub-

Table 2. Rate constants for the oxidation of cyclohexanediols by cobalt(III) acetate

10^2[diol] / mol dm^{-3}	10^3[Co^{III}] / mol dm^{-3}	Temp. (K)	k_1/s^{-1}	k_2 / dm^3 mol^{-1} s^{-1}
cis-Cyclohexane-1,2-diol (**7**)				
4.00	3.17	293.15	6.00×10^{-5}	1.50×10^{-3}
4.00	3.17	303.15	1.66×10^{-4}	4.14×10^{-3}
5.00	3.19	313.15	6.29×10^{-4}	1.26×10^{-2}
3.20	3.13	313.15	4.60×10^{-4}	1.44×10^{-2}
2.40	2.95	313.15	3.06×10^{-4}	1.28×10^{-2}
4.00	3.28	323.15	1.24×10^{-3}	3.11×10^{-2}
cis-1-Methylcyclohexane-1,2-diol (**8**)				
4.18	3.34	293.15	9.03×10^{-5}	2.16×10^{-3}
4.18	2.09	303.15	4.07×10^{-4}	9.73×10^{-3}
3.35	3.11	313.15	9.30×10^{-4}	2.78×10^{-2}
2.51	3.19	313.15	6.08×10^{-4}	2.42×10^{-2}
4.18	2.85	323.15	3.15×10^{-3}	7.53×10^{-2}
cis-1,2-Dimethylcyclohexane-1,2-diol (**9**)				
4.02	3.08	293.15	1.00×10^{-4}	2.49×10^{-3}
4.02	2.93	303.15	4.47×10^{-4}	1.11×10^{-2}
4.02	3.19	313.15	1.36×10^{-3}	3.38×10^{-2}
5.02	3.40	313.15	1.71×10^{-3}	3.40×10^{-2}
3.22	3.13	313.15	1.11×10^{-3}	3.45×10^{-2}
2.41	2.92	313.15	8.89×10^{-4}	3.69×10^{-2}
trans-Cyclohexane-1,2-diol (**10**)				
4.07	3.21	293.15	4.78×10^{-5}	1.17×10^{-3}
4.07	3.27	303.15	2.06×10^{-4}	5.05×10^{-3}
3.26	3.04	313.15	4.15×10^{-4}	1.27×10^{-2}
5.09	3.14	313.15	6.77×10^{-4}	1.33×10^{-2}
5.03	3.39	313.15	6.18×10^{-4}	1.23×10^{-2}
4.02	3.13	313.15	4.53×10^{-4}	1.13×10^{-2}
3.02	3.36	313.15	3.73×10^{-4}	1.24×10^{-2}
4.07	2.03	323.15	2.13×10^{-3}	5.23×10^{-2}
trans-1-Methylcyclohexane-1,2-diol (**11**)				
4.24	3.22	293.15	5.70×10^{-5}	1.35×10^{-3}
4.24	3.17	303.15	2.17×10^{-4}	5.12×10^{-3}
4.24	1.51	313.15	7.05×10^{-4}	1.66×10^{-2}
5.30	3.04	313.15	9.65×10^{-4}	1.82×10^{-2}
3.39	3.54	313.15	6.22×10^{-4}	1.83×10^{-2}
2.54	3.28	313.15	4.80×10^{-4}	1.89×10^{-2}
trans-1,2-Dimethylcyclohexane-1,2-diol (**12**)				
4.02	3.17	293.15	1.78×10^{-4}	4.43×10^{-3}
4.02	3.21	303.15	7.16×10^{-4}	1.78×10^{-2}
5.18	3.55	313.15	2.19×10^{-3}	4.22×10^{-2}
3.32	3.03	313.15	1.60×10^{-3}	4.82×10^{-2}
2.49	3.22	313.15	1.27×10^{-3}	5.10×10^{-2}

Table 3. Rate constants for the oxidation of open-chain diols by cobalt(III) acetate

10^2[diol] / mol dm^{-3}	10^3[Co^{III}] / mol dm^{-3}	Temp. (K)	k_1/s^{-1}	k_2 / dm^3 mol^{-1} s^{-1}
Propylene glycol (**13**)				
6.40	3.38	293.15	5.98×10^{-5}	9.35×10^{-4}
6.40	3.37	303.15	1.68×10^{-4}	2.63×10^{-3}
6.40	3.26	313.15	4.75×10^{-4}	7.42×10^{-3}
7.60	3.23	323.15	1.66×10^{-3}	2.18×10^{-2}
5.43	3.28	323.15	1.22×10^{-3}	2.25×10^{-2}
3.26	3.31	323.15	7.13×10^{-4}	2.19×10^{-2}
Pinacol (**14**)				
6.07	3.54	293.15	2.32×10^{-4}	3.82×10^{-3}
6.07	3.38	303.15	6.38×10^{-4}	1.05×10^{-2}
4.85	3.33	303.15	5.02×10^{-4}	1.03×10^{-2}
4.25	2.81	303.15	4.60×10^{-4}	1.08×10^{-2}
3.64	3.38	303.15	3.85×10^{-4}	1.06×10^{-2}
2.43	3.40	303.15	2.48×10^{-4}	1.02×10^{-2}
6.07	3.30	313.15	1.86×10^{-3}	3.07×10^{-2}



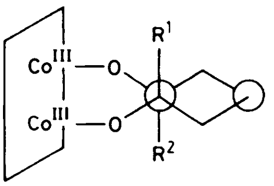
Scheme 3.

stituents. On the other hand, there is some crowding between R^1 and R^2 in (**15b**), since these groups are on the same side of the plane defined by the diol and cobalt(III) acetate. Thus the methyl group not only functions as an electron donor but also causes steric repulsion, which makes (**15b**) unstable and bulky. This agrees with the facts that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the *cis*-diols (**7**)—(**9**) increase with an increasing number of methyl groups. In the oxidation of (**7**)—(**9**), retardation due to the repulsion between the two methyl groups surpasses the acceleration due to their electron-donating ability. The effect of the methyl group as an electron donor was also observed in the oxidation of the linear diols (**13**) and (**14**).

The reaction rate deviated below the first-order plot at extended reaction times, and the deviation became larger with an increasing number of methyl groups in both systems. There is no doubt that this behaviour is attributable to cobalt(II) ion formed by reduction of cobalt(III) acetate. This was confirmed by the addition of cobalt(II) acetate to the reaction mixture (Figure 4). Similar retardation has been often observed in the oxidation of organic compounds by cobalt(III) acetate and it is reported that such reactions obey rate laws such as $[\mathrm{Co^{III}}]/[\mathrm{Co^{II}}]$[7] or $[\mathrm{Co^{III}}]^2/[\mathrm{Co^{II}}]$.[8] However, our attempts to fit the present data to these rate laws were unsuccessful.

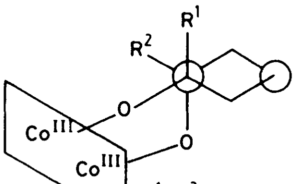
In Scheme 3 the steady state assumption gives the rate law[7] (8).

The lack of a fit with any simple rate law may show that the rate of forward reaction in equation (5) is similar to that of the reverse reaction, equation (4), *i.e.* the assumption $k_{-3}k_{-4}k_{-5}[\mathrm{Co^{II}}] \gg k_{-3}k_{-4}k_6 + k_{-3}k_5k_6 + k_4k_5k_6$ or its reverse is unjustified. Hence the complex curves obtained for these oxid-



(R^1,R^2 = H or Me)

(15 a)



(R^1,R^2 =H or Me)

(15 b)

Table 4. Thermodynamic parameters for the oxidation of glycols by cobalt(III) acetate at 298.15 K

Diol	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ kJ mol^{-1}
(**1**)	51.0	−87.9	77.4
(**2**)	46.9	−106	78.2
(**3**)	50.2	−87.9	76.6
(**4**)	110	70.3	82.0
(**5**)	110	78.7	79.5
(**6**)	87.9	13.3	91.6
(**7**)	78.2	−31.8	91.6
(**8**)	89.1	10.3	85.8
(**9**)	98.3	41.1	85.8
(**10**)	94.1	21.2	87.9
(**11**)	92.5	15.3	87.9
(**12**)	88.3	10.3	84.9
(**13**)	80.3	−28.7	88.7
(**14**)	77.0	−28.7	85.8

$$-\frac{d[\mathrm{Co^{III}}]}{dt} = \frac{k_3k_4k_5k_6[\mathrm{diol}][\mathrm{Co^{III}\ dimer}]}{k_{-3}k_{-4}k_{-5}[\mathrm{Co^{II}}] + k_{-3}k_{-4}k_6 + k_{-3}k_5k_6 + k_4k_5k_6} \tag{8}$$

ations. Since the deviation is larger in the oxidation of the more branched diols, steric or inductive effects of the methyl groups must be responsible. Unfortunately, we cannot determine which is the more important, because of limited data.

The large deviations in the oxidations of (**9**) and (**12**) cannot be explained in terms of retardation by the formation of cobalt(II) ion, because the plot for the rate law [diol][Co$^{\mathrm{III}}$]/[Co$^{\mathrm{II}}$][7] also deviates below the straight line. The same downward deviation was observed from the plot for the rate law [diol][Co$^{\mathrm{III}}$]^2/[Co$^{\mathrm{II}}$],[8] which is reported for oxidations of alkyl aromatic compounds and others. These results lead us to predict the deactivation of cobalt(III) acetate by some substance formed during the reaction. Indeed, if it is assumed that four molecules of cobalt(III) acetate are consumed for every molecule of diol, the first-order plot gives a fairly good straight line through the origin.

In order to investigate the deactivation further, the product from (**9**) and (**12**), octane-2,7-dione, was added to the reaction mixture of cobalt(III) acetate and the unsubstituted diol [(**7**) or (**10**)] for which the deviations were small, and the rates were measured. However, nearly the same reaction curves were obtained in the presence and in the absence of the dione, showing that retardation by the product can be excluded. The same results were obtained in the oxidations of (**9**) and (**12**).

Hanotier and his co-worker[8c] suggested the deactivation of cobalt(III) acetate by 1 : 1 complex formation with cobalt(II) ion in the oxidation of ethylbenzene. This agrees well with our results for the oxidation of (**9**) and (**12**) by cobalt(III) acetate. However, it is well established that two moles of cobalt(III) acetate react with every one mole of organic substrate in the oxidation of various compounds.[2–4] Furthermore, if the retardation is attributable to the deactivation of cobalt(III) acetate by cobalt(II) ion, all the reactions should be retarded.

Thus it is not clear why only the oxidations of (**9**) and (**12**) deviate severely from the first-order plot [equation (1)]. Further study is necessary.

Conclusions

In the oxidation of glycols by cobalt(III) acetate in acetic acid the reactions of *trans*-cyclopentane-1,2-diols (**4**)—(**6**) proceed *via* acyclic intermediates like those for cerium(IV) oxidation, and those of the other diols (**1**)—(**3**) and (**7**)—(**12**) proceed *via* cyclic intermediates. When there is no steric hindrance between the substituents, as in (**10**)—(**12**), methyl groups function only as electron donors and can stabilize the intermediate, but when there is crowding, as in (**7**)—(**9**), they not only function as electron donors but also cause steric repulsion.

Experimental

M.p.s were measured with a Yamato capillary apparatus. Visible spectra were recorded with a Hitachi UV-124 spectrophotometer; the cell chamber was maintained at a constant temperature by circulating water. Preparative g.l.c. was carried out with a Shimadzu GC-4A instrument attached to a Shimadzu APP-5 fraction collector through a heated glass joint.

Materials.—Cobalt(III) acetate was prepared by the method described in the literature.[9]

Propylene glycol, pinacol, cyclohexanone, cyclopentanone, 1-methylcyclohexanone, and diethyl adipate were commercially available. *cis*- and *trans*-cyclopentane-1,2-diol (**1**) and (**4**), and *cis*- and *trans*-cyclohexane-1,2-diol (**7**) and (**10**) were prepared as described in a previous paper.[3]

1-Methylcyclopentene, b.p. 347.15 K, and 1-methylcyclohexene, b.p. 383.15 K, were prepared by dehydration of 1-methylcyclopentanol and 1-methylcyclohexanol, obtained in turn by reactions of methylmagnesium iodide with cyclopentanone and cyclohexanone, respectively.

2-Methylcyclopentanone was prepared from diethyl adipate with sodium metal in anhydrous toluene by a method similar to that reported.[10]

1,2-Dimethylcyclopentene and 1,2-dimethylcyclohexene were prepared by dehydration of 1,2-dimethylcyclopentanol and 1,2-dimethylcyclohexanol, obtained in turn by the reactions of methylmagnesium iodide with 2-methylcyclopentanone and 2-methylcyclohexanone, respectively. They were purified by fractional g.l.c. (Silicone SE-30 on Celite 545, 2 m, 333.15 K and 343.15 K respectively, N_2 carrier gas, 30 ml min^{-1}).

The *trans*-forms of 1-methyl- [m.p. 334 K (lit.,[11] 346 K)] and 1,2-dimethyl- [m.p. 378 K (lit.,[12] 378—380 K)] cyclopentane-1,2-diol (**5**) and (**6**) were made from the corresponding cyclopentenes by the method for (**4**) as described in a previous paper.[3]

The *trans*-forms of 1-methyl- [m.p. 356 K (lit.,[13] 357 K)] and 1,2-dimethyl- [m.p. 365 K (lit.,[14] 365—366 K)] cyclohexane-1,2-diol (**11**) and (**12**) were made from the corresponding cyclohexenes by the method above.

The *cis*-forms of 1-methylcyclopentane-1,2-diol (**2**) and 1-methylcyclohexane-1,2-diol (**8**) [m.p. 339 K (lit.,[15] 341 K)] were prepared by oxidation of the corresponding cyclopentene and cyclohexene with osmium tetraoxide and t-butyl hydroperoxide in t-butyl alcohol containing aqueous 10% tetraethylammonium hydroxide.[16] The former diol (**2**) was purified by t.l.c. (Wakogel B-5F; ether).

The *cis*-forms of 1,2-dimethylcyclopentane-1,2-diol (**3**) and 1,2-dimethylcyclohexane-1,2-diol (**9**) [m.p. 321 K (lit.,[17a] 323; lit.,[17b] 321 K)] were obtained by treating the corresponding cycloalkenes with osmium tetraoxide in ether. The diol (**3**) was purified by t.l.c. as above.

Kinetic Measurements.—A solution of the glycol in acetic acid (4.0 cm^3) was placed in a quartz cell with a glass joint stopper (the cell was then almost full). The cell was flushed with nitrogen, then kept in the cell chamber until the temperature of the solution was constant. Cobalt(III) acetate solution in acetic acid (0.05—0.1 cm^3), previously kept at the same temperature, was then added through a syringe. The reaction was monitored by following the decrease in absorption of cobalt(III) acetate at 610 nm. The molar absorption of cobalt(III) acetate in acetic acid at this wavelength is 213 $dm^3\ mol^{-1}\ cm^{-1}$; that of cobalt(II) acetate is 4.0 $dm^3\ mol^{-1}\ cm^{-1}$.

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