J. CHEM. SOC. PERKIN TRANS. II 1983

Oxidation by Cobalt(III) Acetate. Part 5.[1] Kinetics and Mechanism of the Oxidative Cleavage of Hydrobenzoins

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The mechanism of the oxidative cleavage of hydrobenzoin by cobalt(III) acetate in acetic acid has been studied by following the kinetics of the reaction. The rate is first order in cobalt(III) acetate, inverse first order in cobalt(II) ion, and first order in substrate. DL-Hydrobenzoin is oxidized 4.5 times faster than the *meso*-isomer. A mechanism involving a bidentate complex formed from the reaction of cobalt(III) acetate dimer with glycol is discussed.

Oxidative fissions of a number of glycols have been well studied for several oxidants.[2] There are two types of mechanism: (a) a bidentate complex mechanism and (b) a monodentate complex mechanism.

In Part 4,[1] we found that *cis*-cyclopentane-1,2-diol and *cis*-decalin-9,10-diol were more rapidly oxidized than the corresponding *trans*-isomers, while *cis*-cyclohexane-1,2-diol is oxidized more slowly. To explain the contrasting results, we suggested a mechanism in which a bidentate complex resulting from the reaction of cobalt(III) acetate dimer [3] and diols intervened as an intermediate.

In this paper, we report the reaction of hydrobenzoins with cobalt(III) acetate in acetic acid in order to clarify the mechanism.

Results and Discussion

The oxidation of hydrobenzoin with cobalt(III) acetate in acetic acid gave benzaldehyde in high yield and the reaction proceeded through the stoicheiometry (1). This stoicheiometry was also observed in the oxidation of benzpinacol and 1,2-dimethylhydrobenzoin.

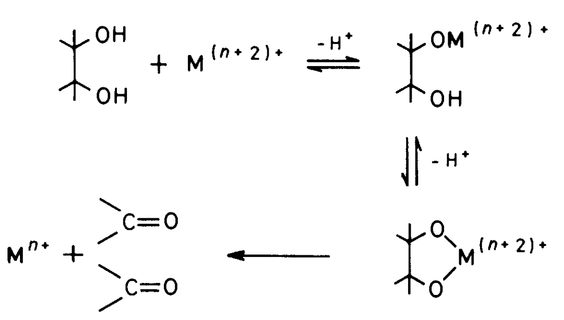
The rates of the oxidation of hydrobenzoins by cobalt(III) acetate in acetic acid were determined by following the decrease of the absorption peak of cobalt(III) acetate at 610 nm and the reaction was carried out in the quartz cell kept at a constant temperature.

With a large excess of substrate, the rate of the oxidation of hydrobenzoin did not obey the first-order law found for the oxidation of cycloalkanediols and the first-order rate decreased with reaction time. The rate was first order with respect to the concentration of cobalt(III) acetate and inverse first order with respect to that of cobalt(II) acetate, equation (2).

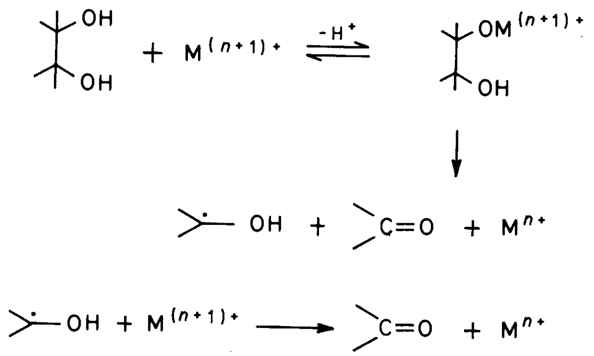
$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = k'[\mathrm{Co^{III}}]/[\mathrm{Co^{II}}] \qquad (2)$$

The rate constant was not varied on changing the initial concentrations of cobalt(III) acetate or by the addition of anhydrous cobalt(II) acetate. The rate constants are listed in Table 1. At constant concentration of cobalt(III) acetate, a plot of k' against the concentration of diol gave a straight line through the origin, *i.e.* equation (3) holds. First-order rate constants are summarized in the last column in Table 1.

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = k[\mathrm{Diol}][\mathrm{Co^{III}}]/[\mathrm{Co^{II}}] \qquad (3)$$

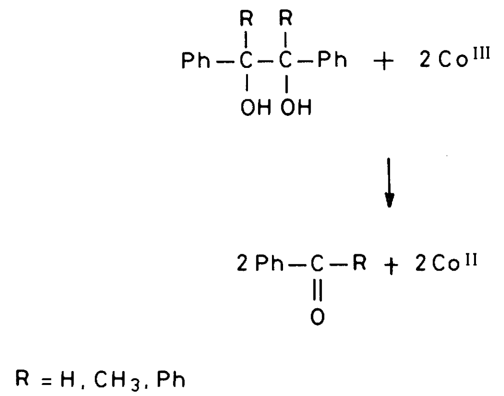


Scheme 1



Scheme 2

The retardation by cobalt(II) ion in the present reaction is in contrast to the fact that the oxidations of cycloalkanediols were not retarded by this ion. However, similar retardation has been observed in the oxidation of alkylaromatic compounds by the oxidant [4] and the reaction is considered to proceed through a one-electron abstraction from the substrate to generate a radical cation. There remained, therefore, doubt that the oxidative cleavage of hydrobenzoin with this oxidant proceeds by a different mechanism from that of cycloalkanediols, *i.e.* a hydrogen abstraction mechanism or a monodentate complex mechanism. In order to clarify this the rate of oxidation of DL-hydrobenzoin was compared with that of the *meso*-isomer, as the DL-isomer is reported to be more rapidly oxidized in a bidentate complex mechanism. DL-Hydrobenzoin reacted with the oxidant 4.5 times faster than the *meso*-isomer as shown in Table 1. This indicates that the two hydroxy-groups required to make a bidentate complex are necessary for the fast reaction and the mechanism of the present reaction is the same as that suggested for cycloalkanediols. Trahanovsky and his co-workers [5] reported that the k_{DL}/k_{meso} ratio for the oxidation of hydrobenzoins was 8.29 for lead(IV) acetate, 5.16 for iodate, and 0.90 for cerium(IV) ion and they considered this to be evidence that the first two oxidations proceed through a bidentate complex and the



$$\mathrm{Ph{-}C(R)(OH){-}C(R)(OH){-}Ph + 2\,Co^{III} \longrightarrow 2\,Ph{-}C({=}O){-}R + 2\,Co^{II}} \quad (1)$$

$R = H, CH_3, Ph$

Table 1. Rate constants for the oxidation of hydrobenzoin with cobalt(III) acetate in acetic acid at 35 °C

[Diol]/M	10^3[Co^{III}]/ M	10^3[Co^{II}]/ M	10^6 k'/ l mol^{-1} s^{-1}	10^5 k/s^{-1}
meso-Isomer				
7.53×10^{-2}	1.63	0	10.7	14.2
	3.21	0	7.09	9.42
	4.74	0	8.11	10.8
	6.22	0	8.21	10.9
	1.08	0.55	8.70	11.6
	2.37	2.37	8.86	11.8
	3.11	3.11	9.08	12.1
	3.21	0	6.88	9.14
9.03	3.21	0	8.44	9.35
10.5	3.21	0	9.79	9.32
DL-Isomer				
7.59	3.45	0	32.3	42.6
10.1	3.45	0	41.4	41.0

third through a monodentate complex. Our result is close to that for the iodate oxidation.

We have already suggested a bidentate complex formed from cobalt(III) dimer and diols for the oxidation of cycloalkanediols. On the bases of the above discussion, the present reaction is also considered to proceed by the same bidentate complex mechanism. Although the complex is a seven-membered ring, the O–C–C–O moiety is almost planar since the distance between two Co ions in cobalt(III) dimer and thus in the intermediate complex is considered to be fixed and the two Co–O bonds are essentially parallel to each other. Therefore, the difference in rate between the DL- and *meso*-isomers may be due to different degrees of eclipsing of the phenyl groups.

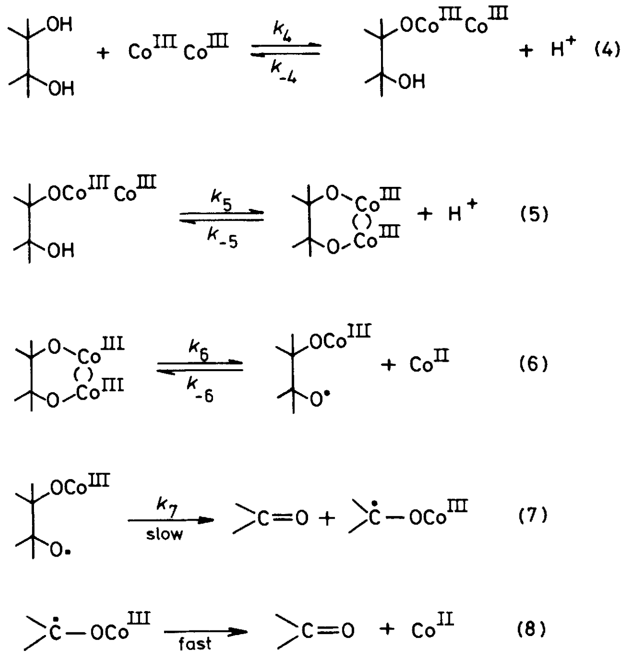
For the explanation of these results, the mechanism in Scheme 3 can be suggested.

Assuming stationary states for monodentate and bidentate complexes and alkoxyl radicals, reactions (4)—(8) give the rate expression (9). When equilibria (4)—(6) are reached, $k_{-4}k_{-5}k_{-6}[\mathrm{Co^{II}}] \gg k_{-4}k_{-5}k_7 + k_{-4}k_6k_7 + k_5k_6k_7$. Then equation (9) leads to (10) where K_4—K_6 are equilibrium constants

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = \frac{k_4k_5k_6k_7[\mathrm{Diol}][\mathrm{Co^{III}\ dimer}]}{k_{-4}k_{-5}k_{-6}[\mathrm{Co^{II}}] + k_{-4}k_{-5}k_7 + k_{-4}k_6k_7 + k_5k_6k_7} \quad (9)$$

$$-\mathrm{d}[\mathrm{Co^{III}}]/\mathrm{d}t = \frac{k_4k_5k_6}{k_{-4}k_{-5}k_{-6}}\,k_7\,\frac{[\mathrm{Diol}][\mathrm{Co^{III}dimer}]}{[\mathrm{Co^{II}}]} = K_4K_5K_6k_7\,\frac{[\mathrm{Diol}][\mathrm{Co^{III}dimer}]}{[\mathrm{Co^{II}}]} \quad (10)$$

for reactions (4)—(6), respectively, *i.e.* $K_4 = k_4/k_{-4}$, $K_5 = k_5/k_{-5}$, and $K_6 = k_6/k_{-6}$. The rate law (10) is the same as the observed rate law (3), when $k = \frac{1}{2}K_4K_5K_6k_7$.



Scheme 3

Equilibrium (6) was assumed for the explanation of the retardation by cobalt(II) ion and is fairly speculative since the reverse reaction involves trapping the alkoxyl radical by the ion and this reaction is considered to be thermodynamically unfavourable. Alkoxyl radicals have been reported to be trapped by some metallic ions such as Cr^{II}, V^{IV}, Fe^{II}, *etc.* when present in large excess.[6] It is unlikely that Co^{II} ion can trap the alkoxyl radical because of its high oxidation–reduction potential (1.81 V) in water. However, the potential may be reduced in acetic acid because of the co-ordination of acetate ions.* A reduction in the potential may allow trapping of the alkoxyl radical with Co^{II} ion in acetic acid.

In order to clarify the reverse reaction of (6) or retardation by cobalt(II) ion, the effects of added cobalt(II) acetate on the rate of oxidation of *trans*-cyclohexane-1,2-diol were examined. The rate of the oxidation of cycloalkanediols was first order in both cobalt(III) acetate and substrate and the retardation of the rate by cobalt(II) ion was not found. If the oxidation of cycloalkanediols proceeds by the mechanism described above, the rate-determining step should be reaction (6) and then no retardation by cobalt(II) ion should occur. Since reaction (6) is an equilibrium, however, the addition of a large amount of cobalt(II) ion to the reaction mixture should lower the concentration of the alkoxyl radical and thus decrease the reaction rate.

The effects of added cobalt(II) acetate on the rates of oxidation of *trans*-cyclohexane-1,2-diol are summarized in Table 2. The addition did not affect the rate at low concentrations but high concentrations retard the rate considerably.

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* This is expected from the fact that oxidation of organic compounds by Co^{III} ion is much slower in acetic acid than in water.[7]

Table 2. Effect of the concentration of added cobalt(II) acetate on the rate of oxidation of hydrobenzoin with cobalt(III) acetate in acetic acid at 50 °C

$10^2[\mathrm{Diol}]_0$/ M	$10^3[\mathrm{Co^{III}}]_0$/ M	$10^3[\mathrm{Co^{II}}]_0$/ M	$10^2\,k'$/ l mol^{-1} s^{-1}	k/s^{-1}
4.21	3.24	0	4.97	1.18
4.08	3.24	1.76	4.91	1.20
4.08	3.24	3.68	4.67	1.19
4.13	3.24	7.88	2.61	0.63
4.05	3.24	15.7	1.22	0.31

$$\begin{tikzcd}\mathrm{Co^{III}-Co^{III}} + 2\,\mathrm{Co^{II}}\ (\text{or }\mathrm{Co^{II}-Co^{II}}) \arrow[d, shift left] \\ 2\,\mathrm{Co^{III}-Co^{II}} \arrow[u, shift left]\end{tikzcd} \qquad (11)$$

Thus it is concluded that the oxidation of cycloalkanediols proceeds with the mechanism in Scheme 3.

Another possible explanation for the retardation by cobalt(II) ion is the formation of $\mathrm{Co^{III}}$–$\mathrm{Co^{II}}$ dimers which are ineffective as oxidants.[8] In this case, direct decomposition of the cyclic intermediate follows after reactions (4) and (5) to give two carbonyl groups and two cobalt(II) ions. If the equilibrium (11) favours $\mathrm{Co^{III}}$–$\mathrm{Co^{II}}$, $\mathrm{Co^{II}}$ ion can retard the reaction rate. In this circumstance, half the $\mathrm{Co^{III}}$ ion can oxidize the substrate and thus four molecules of $\mathrm{Co^{III}}$ ion should be consumed for each molecule of substrate. This does not agree with the equation (1). In addition, the rate of the oxidation of cycloalkanediols should obey equation (3) since the conditions do not change drastically. As shown above, the oxidation rate of *trans*-cyclohexane-1,2-diol is first order in both cobalt(III) acetate and substrate and the rate was retarded only in the presence of a large excess of cobalt(II) ion. Thus, the retardation by the formation of $\mathrm{Co^{III}}$–$\mathrm{Co^{II}}$ dimer may be excluded.

Experimental

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

Starting Materials.—*meso*, m.p. 137.3—137.5 °C,[9] and DL-hydrobenzoin, m.p. 118.5—119.5 °C,[9] 2,3-diphenylbutane-1,2-diol, m.p. 86—88 °C,[10] and 1,1,2,2-tetraphenylethane-1,2-diol, m.p. 184—186 °C,[11] were prepared by reported methods. Cobalt(III) acetate were made by the oxidation of cobalt(II) acetate tetrahydrate with ozone in the presence of acetic anhydride.

Product Study.—In a flask, *meso*-hydrobenzoin was mixed with cobalt(III) acetate in acetic acid. The flask was then flushed with dry nitrogen gas, sealed with a silicone rubber stopper, and kept at a constant temperature in a thermostat. After diphenyl (internal standard) was added, the mixture was poured into water and the products were extracted with ether. The extract was washed with aqueous sodium carbonate and water, and then dried (Na_2SO_4). Evaporation of the solvent left a yellow oil which was analysed by g.l.c. The data are summarized in Table 3.

Table 3. Yields of aldehydes in the oxidation of diols with cobalt(III) acetate in acetic acid at 50 °C

$\mathrm{Co^{III}}$ (mmole)	Substrate (mmole)	t/h	Product (mmole)
Hydrobenzoin			
4.24	4.25	1.5	4.32
4.17	2.16	1.5	4.01
4.31	4.33	3	4.43
4.24	2.24	3	4.15
2,3-Diphenylbutane-2,3-diol			
0.132	0.135	40	0.142
0.132	0.0654	40	0.117
Benzpinacol			
0.192	0.194	70	0.210
0.192	0.0960	70	0.200

Kinetic Measurements.—The 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. Then, cobalt(III) acetate solution in acetic acid (0.1—0.5 ml) was added through a hypodermic syringe under a gentle nitrogen flow and the reaction was started. The reaction was traced with the decrease of the absorption of cobalt(III) acetate at 610 nm. The molar absorption of cobalt(III) acetate in acetic acid at the 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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Received 16*th April* 1982; *Paper* 2/638