

Oxidation of benzyl alcohol by cobalt(III) acetylacetonate

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The kinetics of cobalt(III) acetylacetonate oxidation of benzyl alcohol within 120–140°C was followed by measuring the decrease of oxidation agent concentration spectrophotometrically. The formation of a complex consisting of one molecule of oxidation agent and one or two benzyl alcohol molecules preceded the oxidation reaction. The equilibrium constants of complex formation as well as the rate constants of complex oxidation conversion were determined. To complete the kinetic description of the process the equilibrium constants for alcohol association had to be determined.

The oxidation of organic compounds by ions and polyvalent metal complexes has been a subject of several papers and reviews [1–4]. Relatively little attention has been, however, paid to the course of these reactions in nonpolar media. It is mainly due to the fact that most of the oxidation agents used are not soluble or sufficiently well defined in such media. Denisov *et al.* [5–7] reported on the oxidation of several organic compounds by cobalt(III) acetylacetonate. Phenol [5] and 2-propanol [6] form an associate with $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ *via* hydrogen bonding; the oxidation reaction is a monomolecular process. The oxidation of 1-butanol and cyclohexanol [7] is, on the other hand, of the first order with regard to both reactants; an associate formation has not been observed. The oxidation of benzyl alcohol by chromic acid in aqueous solution [8] is preceded by benzyl chromate formation. Vanadium(V) ions, on the other hand, oxidize benzyl alcohol directly, giving $(\text{C}_6\text{H}_5\text{CHOH})^+$ ion [9]. An equimolar amount of benzaldehyde is formed in both cases.

Experimental

Cobalt(III) acetylacetonate was prepared according to [10].

Benzyl alcohol (Lachema) was purified by double rectification and stored under a nitrogen atmosphere. Benzaldehyde was found to be present in amount of 300 p.p.m. using gas chromatography. Dichlorobenzene and nitrobenzene were purified by double rectification at 20 torr; dichlorobenzene contained only its isomers. Mesitylene was a BDH product. Other chemicals used were of anal. grade (Lachema).

Gas chromatographic measurements were carried out on a PYE 104 instrument using a 0.4×180 cm column packed with 10% polyethyleneglycoladipate on Celite 100–120 mesh at 150°C. For spectrophotometric measurements a VSU-2 (Zeiss, Jena) and a CF 4 (Optica, Milano) instruments were used.

The samples were prepared in the following way: oxidation agent and substrate solution (1 ml) in a selected solvent was transferred into a glass bulb (5–8 ml volume) fitted with

a ground joint. The bulb was attached to a vacuum line (10^{-2} – 10^{-4} torr). The reaction mixture was degassed by several times repeated freeze-pump-thaw processes, sealed off and maintained for a selected time interval in a thermostated bath. Then it was cooled and the concentration of oxidation agent in the reaction mixture was determined at 590 nm, *i.e.* in the region where only $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ absorbs ($\epsilon_{590} = 137 \text{ l mol}^{-1} \text{ cm}^{-1}$) [12].

Results and discussion

The detailed description of the oxidation reaction is complicated by association equilibria of substrate-oxidation agent. These equilibria have been studied separately.

Association of benzyl alcohol and cobalt(III) acetylacetonate

A new absorption band appears in the infrared spectra. It is ascribed to an associated –OH and is shifted towards lower frequencies [11] (Fig. 1). By measuring the absorbancy A of the band due to monomer alcohol the value of dimerization constant K_d can be determined:

$$[\text{ROH}]_0 = [\text{ROH}] + 2[(\text{ROH})_2], \quad (1)$$

$$A = \epsilon d [\text{ROH}], \quad (2)$$

$$[\text{ROH}]_0 d/A = \epsilon^{-1} + (2K_d/\epsilon^2) (A/d), \quad (3)$$

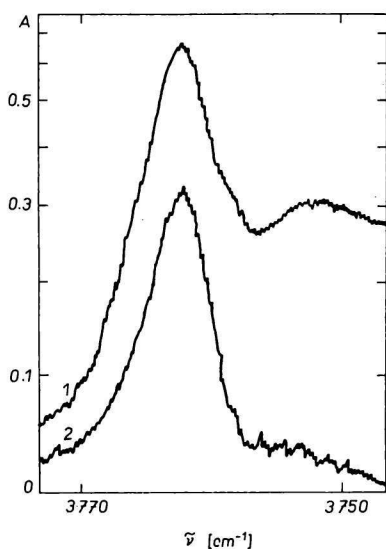


Fig. 1. Infrared spectra of benzyl alcohol –OH group in carbon tetrachloride. benzyl alcohol concentration: 1. 0.48 mol l⁻¹; 2. 0.023 mol l⁻¹. pathlength: 1. 0.210 mm; 2. 1.0506 mm.

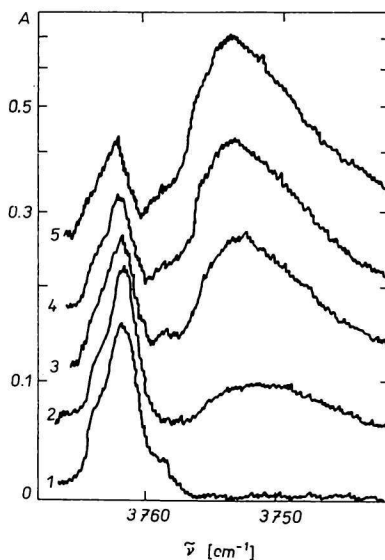


Fig. 2. Infrared spectrum of benzyl alcohol –OH group in the presence of CoL_3 taken in carbon tetrachloride medium. benzyl alcohol concentration: 2.9×10^{-3} mol l⁻¹, complex (mol l⁻¹): 1. 0; 2. 7.5×10^{-3} ; 3. 2.80×10^{-2} ; 4. 4.22×10^{-2} ; 5. 5.89×10^{-2} ; $T = 25^\circ\text{C}$.

Table 1

Dependence of function A/d $[\text{ROH}]_0$ upon benzyl alcohol concentration and temperature

T [°C]	$[\text{ROH}]_0$ [mol l ⁻¹]	A/d $[\text{ROH}]_0$ [l mol ⁻¹ cm ⁻¹]
23.7	0.0968	76.2
40.0	0.0952	74.8
65.3	0.0929	69.2
76.0	0.0918	67.8
90.0	0.0908	61.1
22.7	0.2422	68.6
23.7	0.2420	68.7
23.9	0.2420	68.7
40.0	0.2378	69.9
50.0	0.2355	68.5
50.0	0.2355	67.3
65.0	0.2232	69.4
75.0	0.2298	63.5
87.5	0.2272	62.8
22.2	0.485	57.2
23.0	0.485	56.7
27.7	0.4825	57.4
28.0	0.482	57.2
33.0	0.480	59.5
50.0	0.472	60.6
50.0	0.472	58.8
63.0	0.466	57.2
65.0	0.465	61.8
74.7	0.461	61.0
75.0	0.461	60.0
89.5	0.454	60.8

Table 2

Dependence of benzyl alcohol monomer —OH group absorbancy upon metal complex and alcohol concentration; $T = 25^\circ\text{C}$

$[\text{ROH}]_0 \cdot 10^3$ [mol l ⁻¹]	$[\text{Co}]_0 \cdot 10^2$ [mol l ⁻¹]	Absorbancy
2.9	2.805	0.122
2.9	4.22	0.103
2.9	5.89	0.100
2.9	0.75	0.164
2.9	—	0.165
9.67	8.83	0.258
9.67	—	0.560
9.67	—	0.574

where $[\text{ROH}]_0$ is the overall (analytical) concentration of alcohol,

d is the pathlength,

ϵ is the molar absorption coefficient at the maximum of absorption band due to unassociated $-\text{OH}$ group.

The value of K_d as a function of temperature was computed from eqn (3) using absorbancy values measured for various concentrations of benzyl alcohol in mesitylene within the temperature range $20-90^\circ\text{C}$ (Table 1): $K_d = 1.4 \times 10^{-3} \exp(3400/RT) \text{ l mol}^{-1}$ ($\Delta H = -3.4 \text{ kcal mol}^{-1}$, $\Delta S = -13.0 \text{ cal K}^{-1} \text{ mol}^{-1}$). The values of ΔS and ΔH found experimentally are in good agreement with those found for $-\overline{\text{O}}\text{H}\cdots\overline{\text{O}}$ bonding ([11], p. 206-209).

The hydrogen bonding of an alcohol molecule with coordinated ligand will also result in the formation of a new absorption band due to $-\text{OH}$ associated group; the band being positioned at lower frequency region (Fig. 2). Measuring the absorbancy of the unassociated $-\text{OH}$ group at various concentrations of chelate enables the evaluation of the association constant K_1 ($\text{ROH} + \text{CoL}_3 \rightleftharpoons \text{CoL}_3 \text{ROH}$).

By means of a relationship for the overall concentration of ROH and for K_1 , and using expression (2) we obtain

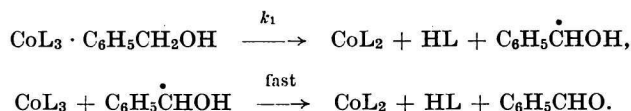
$$[\text{ROH}]_0 d/A = \epsilon^{-1} + (K_1/\epsilon) [\text{CoL}_3]_0, \quad (4)$$

where $[\text{CoL}_3]_0$ denotes the overall chelate concentration if $[\text{CoL}_3]_0 \gg [\text{ROH}]_0$.

The following values of ϵ and K_1 (25°C) were calculated from the absorbancy data corresponding to unassociated $-\text{OH}$ using eqn (4) (Table 2): $\epsilon = 58 \text{ l mol}^{-1} \text{ cm}^{-1}$, $K_1 = 13 \text{ l mol}^{-1}$. It can be assumed that at higher benzyl alcohol concentrations also higher associates can be formed such as $\text{CoL}_3 \cdot 2\text{ROH}$ and $\text{CoL}_3 \cdot 3\text{ROH}$; equilibrium constants of the formation of these complexes will, of course, be lower than K_1 .

Oxidation of benzyl alcohol

Kinetic measurements concerning the benzyl alcohol oxidation, performed at low benzyl alcohol concentrations ($0.04-0.50 \text{ mol l}^{-1}$) (Fig. 3) suggest that the formation of associate substrate-oxidation agent precedes the oxidation reaction. The associate will undergo internal redox conversion:



The stoichiometric study based on the gas chromatographic determination of benzaldehyde formed has shown that at each reaction step $2n$ moles of oxidation agent consumed correspond to n moles of benzaldehyde formed (equivalent found = 2.0; *Shanker* [9]: 1.98 equiv.). This signifies that the primary oxidation reaction is followed by the fast oxidation of the radical by another CoL_3 molecule. The measured rate of oxidation agent disappearance is twice as high as that of the rate-determining reaction. The stoichiometry also shows that the consumption of oxidation agent through the reaction with benzaldehyde formed can be — under the conditions of measurement — neglected.

We have observed, similarly as *Martemyanov* [7], also simultaneous oxidation of the solvent. The rate of this reaction was lower by an order of magnitude than that of alcohol oxidation so that our kinetic data were corrected accordingly.

When $[\text{ROH}]_0 \gg [\text{Co}]$, it holds

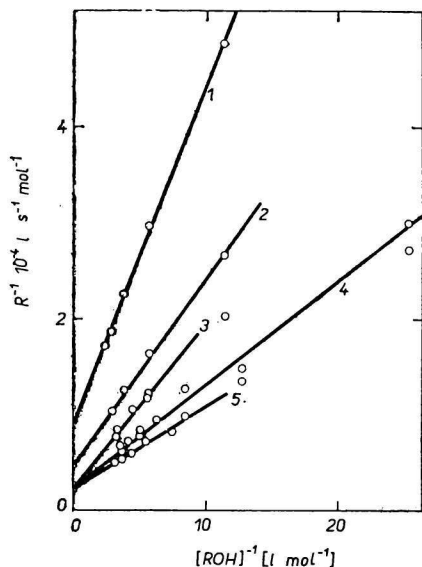


Fig. 3. Oxidation of benzyl alcohol by CoL_3 complex at low benzyl alcohol concentration.

1. 124°C; 2. 130°C; 3.–5. 138°C, mesitylene (1, 2, 4), dichlorobenzene (3), nitrobenzene (5); $[\text{CoL}_3] = 0.9\text{--}1.5 \times 10^{-2} \text{ mol l}^{-1}$.

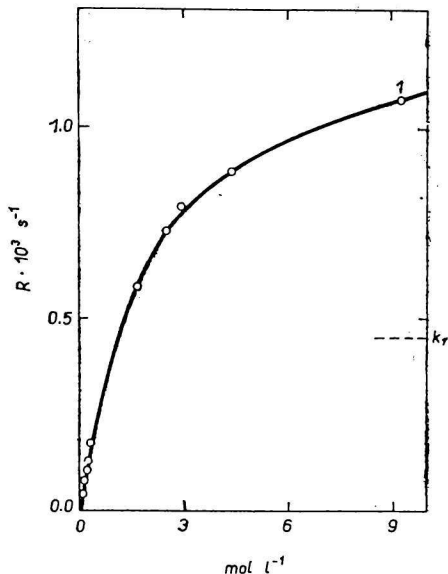


Fig. 4. Dependence of the rate function R of benzyl alcohol oxidation upon its concentration.

$[\text{CoL}_3] = 0.5\text{--}13 \times 10^{-3} \text{ mol l}^{-1}$;
 $T = 138^\circ\text{C}$.

the curve calculated according to (10), value (1) calculated from temperature dependence in pure benzyl alcohol.

$$\ln \frac{[\text{Co}]_0}{[\text{Co}]_0 - [\text{Co(II)}]} = 2k_1t \frac{K_1[\text{ROH}]_0}{1 + K_1[\text{ROH}]_0}, \quad (5)$$

where $[\text{Co}]_0$ stands for the overall (analytical) concentration of cobalt, t being time.

It thus follows that

$$\frac{1}{R} = \frac{1}{k_1} + \frac{1}{k_1K_1} \cdot \frac{1}{[\text{ROH}]_0}, \quad (6)$$

where

$$R = \frac{1}{2t} \ln \frac{[\text{Co}]_0}{[\text{Co}]_0 - [\text{Co(II)}]}. \quad (7)$$

The values of both equilibrium and rate constants according to (6) determined graphically are presented in Table 3 for various solvents and temperatures.

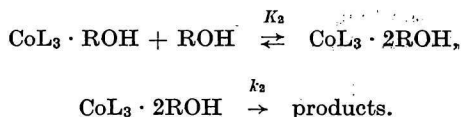
From Table 1 it will follow for the reaction proceeding in mesitylene: $k_1 = 4.6 \times 10^{13} \exp(-32\,000/RT) \text{ s}^{-1}$; $K_1 = 1.8 \times 10^{-2} \exp(3900/RT) \text{ l mol}^{-1}$. It also follows from Table 3 that the change of solvent polarity will influence the value of K_1 while the rate constant k_1 will remain unaffected. It means that at higher alcohol concentrations the

Table 3

Dependence of rate and equilibrium constants of benzyl alcohol oxidation upon the medium and temperature

Solvent	T [°C]	$k_1 \cdot 10^4 \text{ s}^{-1}$	K_1 [l mol ⁻¹]
Mesitylene	124	1.12	2.53
	130	2.18	2.34
	138	4.47	2.14
Dichlorobenzene	138	4.35	2.85
Nitrobenzene	138	4.4	1.31

function R should be approaching the value of k_1 . It reaches, however, somewhat higher values (Fig. 4). This can be accounted for by $\text{CoL}_3 \cdot 2\text{ROH}$ complex formation which decomposes at different rate



The overall reaction rate will thus be described by eqn (8) using K_1 and K_2 :

$$-\frac{d[\text{Co(III)}]}{dt} = 2k_1K_1[\text{CoL}_3][\text{ROH}] + 2k_2K_1K_2[\text{CoL}_3][\text{ROH}]^2. \quad (8)$$

From

$$[\text{Co}]_0 = [\text{CoL}_3] + [\text{CoL}_3 \cdot \text{ROH}] + [\text{CoL}_3 \cdot 2\text{ROH}] + [\text{Co(II)}] \quad (9)$$

concentration $[\text{CoL}_3]$ can be expressed using K_1 and K_2 ; substituting into (8) and by means of (7) we obtain:

$$R = \frac{k_1K_1[\text{ROH}] + k_2K_1K_2[\text{ROH}]^2}{1 + K_1[\text{ROH}] + K_1K_2[\text{ROH}]^2}, \quad (10)$$

where

$$[\text{ROH}] = \frac{\sqrt{1 + 8K_d[\text{ROH}]_0} - 1}{4K_d}. \quad (11)$$

Relationship (11) expresses the dependence of monomer alcohol concentration on the overall concentration; the presence of higher associates than dimer could be neglected.

Rearrangement of (9) and denoting

$$F = \frac{R + [\text{ROH}](RK_1 - k_1K_1)}{RK_1[\text{ROH}]^2} \quad (12)$$

gives

$$F = -K_2 + k_2K_2 \cdot 1/R. \quad (13)$$

Table 4

Dependence of rate function R and rate constant k_2 upon temperature

T [°C]	$R \cdot 10^4 \text{ s}^{-1}$	$k_2 \cdot 10^4 \text{ s}^{-1}$
175.4	3.82	6.80
128.6	5.09	9.02
131.5	6.63	11.59
134.6	8.72	15.12
138.0	11.75	20.25

It is thus possible to determine values of F (Fig. 4) from the known values of k_1K_1 and R for high alcohol concentrations. Both the rate and the equilibrium constants for $T = 138^\circ\text{C}$ were determined (according to (13)) from the values of F at various alcohol concentrations (20–100%): $k_2 = 1.80 \times 10^{-3} \text{ s}^{-1}$, $K_2 = 0.21 \text{ l mol}^{-1}$.

Table 4 shows the values of function R that were estimated for various temperatures using the kinetic data of benzyl alcohol oxidation (Fig. 5). Assuming that the value of K_2 is constant within the temperature interval studied, the values of k_2 for various temperatures can be calculated from relationship (14) obtained by rearrangement of (10)

$$k_2 = \frac{R(1 + K_1[\text{ROH}] + K_1K_2[\text{ROH}]^2) - k_1K_1[\text{ROH}]}{K_1K_2[\text{ROH}]^2} \quad (14)$$

the temperature dependence of R , K_1 , and $[\text{ROH}]$ being known. The temperature dependence of k_2 can be found using the values of k_2 calculated for different temperatures:

$$k_2 = 1.9 \times 10^{12} \exp(-28\,000/RT) \text{ s}^{-1}.$$

As it has been already shown, the thermodynamic parameters of the $\text{CoL}_3 \cdot \text{ROH}$ association equilibrium corroborate the existence of hydrogen bond in this associate.

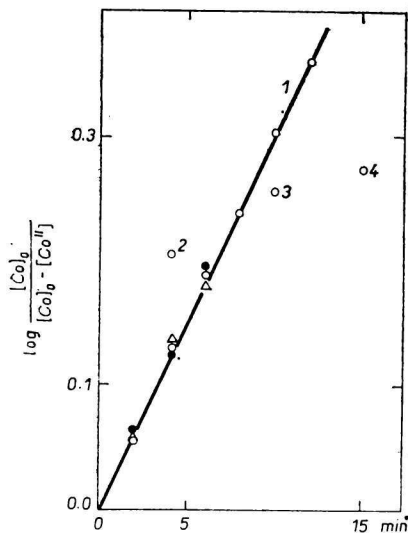
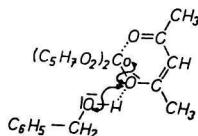


Fig. 5. Kinetics of benzyl alcohol oxidation by CoL_3 in pure benzyl alcohol. T (°C): 131.5 (1), 134.6 (2), 128.6 (3), 125.4 (4).

$[\text{CoL}_3]$ (mol l^{-1}): 5.75×10^{-4} (Δ), 9.35×10^{-4} (\bullet), 3.75×10^{-3} (\circ), 2.70×10^{-3} (2, 3, 4); points 2, 3, 4: average of four experiments.

Most of the organic compounds containing polar groups form an associate precursor or a complex [1-3] with the oxidation agent. Thus the condition of efficient donor-acceptor interaction between oxidation agent and substrate is fulfilled. The electron transfer then proceeds within this compound. The following mechanism describing the benzyl alcohol oxidation seems thus plausible:



It is assumed that the resulting radical will be converted into a more resonance stable form



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