

Oxidation of benzyl alcohol, allylbenzene, methyl benzyl ketone, and cumene by cobalt(III) complexes

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Kinetic parameters were determined for the oxidation of benzyl alcohol, allylbenzene, cumene, and methyl benzyl ketone, respectively; donor-acceptor or association equilibria accompanying these oxidations were examined.

Thermodynamic kinetic parameters of the studied reactions obey the straight-line dependence of the Leffler correlation. The Leffler correlation lines can be plotted even for organic compounds oxidations induced by other oxidation agents, the position of the correlation line being dependent upon the redox potential of the agent.

The oxidation of organic compounds by ions and complexes of polyvalent metals has been a subject of considerable interest. Most of the authors, however, focused their attention on the studies of the reaction course in water or polar solutions, the reason being that most of the oxidation agents generally used are well soluble and satisfactorily defined in the latter type of solvents. These studies have resulted in a series of monographs on the subject (see *e.g.* [1–4]).

The investigation of stabilization and degradation reactions in macromolecular chemistry requires information on the course of oxidative reactions proceeding in nonpolar media, which represent a better model of the polymer phase. For this purpose it is necessary to use electronneutral, well soluble complexes of polyvalent metals, chelates being the best choice.

A similar topic has been treated by *Volger* and *Brackman* [5–7] who studied the oxidation of carbonyl compounds by copper(II) salts in methanol; *Lewis* and *Singer* [8] on the other hand prepared a series of radical cations through the oxidation of aromatic hydrocarbons by antimony(V) chloride in dichloroethane. Moreover, some works of *Denisov's* group deal with the kinetics of oxidation of phenol and alcohols by cobalt(III) acetylacetonate in benzene, *n*-heptane, or *tert*-butyl alcohol [9–11].

In our previous communication [14] we reported on the oxidation of benzyl alcohol by cobalt(III) acetylacetonate. The formation of an associate consisting of one oxidation agent molecule combined with one or two benzyl alcohol molecules precedes the oxidation reaction. The purpose of this work is to present more data on the oxidation of benzyl alcohol by other Co(III) compounds. Moreover, other aromatic substrates have been oxidized by cobalt(III) acetylacetonate.

Experimental

Cobalt(II) and cobalt(III) acetylacetonates were prepared according to [12] and cobalt(III) 8-quinolinolate according to [13]. The preparation of cobalt(III) benzoate: benzoic acid (7.4 g) was mixed with an equivalent amount of 1 M solution of sodium

hydroxide. The solution was diluted with ethanol and mixed with a solution of cobalt dichloride hexahydrate (4.8 g) in ethanol (80 ml) into which 30% hydrogen peroxide (20 ml) was added. Dark crystals formed were washed, dried, and analyzed. Theoretical cobalt assay 13.96%, found 13.92%.

Benzyl alcohol (Lachema) was purified by double rectification. The product was then stored in an atmosphere of nitrogen. Benzaldehyde content: 300 p.p.m. Cumene (Schering—Kahlbaum A.G., Berlin), methyl benzyl ketone, and allylbenzene contained after the rectification 0.1, 2, and 0.3% of impurities. The last impurity was identified to be bromobenzene. Dichloro- and nitrobenzene were purified by a double rectification. Dichlorobenzene contained only its isomers. Mesitylene was a BDH product. Other chemicals used were of anal. grade (Lachema).

Hydroperoxides present in methyl benzyl ketone, cumene, or allylbenzene were removed on a short alumina column before use. The g.l.c. measurements were carried out on a PYE 104 instrument using the following column packings: 10% of polyethyleneglycoladipate on Celite and 15% of Silicon Oil on Chromosorb W (benzaldehyde determination at 150°C). Allylbenzene, cumene, and methyl benzyl ketone were determined at 130°C using a Beckman GC 2A instrument fitted with columns containing either 20% of Silicon Grease on Firebrick or 15% of polyethyleneglycolsuccinate on Firebrick support.

The spectrophotometric measurements were performed on a USF (Zeiss, Jena) instrument and on a CF 4 (Optica, Milano) spectrophotometer.

The method of sample preparation and the measurement procedure were described in our previous paper [14].

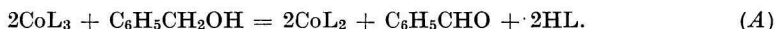
Cobalt(III) benzoate and cobalt(III) acetylacetonate concentrations were determined spectrophotometrically at 590 nm, *i.e.* at the wavelength where the analogous cobalt(II) compounds do not absorb [19]. The concentration of cobalt(III) 8-quinolinolate was determined iodometrically: the vial containing the reaction mixture was placed into an Erlenmeyer flask, then crushed in an inert atmosphere of CO₂, and the reaction mixture was dissolved in acetic acid (5 ml). After addition of saturated potassium iodide solution in methanol (5 ml), the mixture was acidified by conc. HCl (1 ml) and diluted with water. The iodine formed was titrated with 0.02 M solution of sodium thiosulfate.

The substrate concentration in the reaction mixture was determined by the g.l.c. method.

Results

The oxidation of pure benzyl alcohol by cobalt(III) 8-quinolinolate was followed at 160–180°C.

The stoichiometry of the reaction is unambiguous:



The molar ratio of oxidation agent consumed to benzaldehyde formed was found to be 2.1 (average of 4 measurements).

Kinetic measurements have revealed that in the benzyl alcohol medium the reaction rate of cobalt(III) disappearance is proportional to a square root of the Co(III) concentration (see Fig. 1). The observed reaction rate order can be accounted for by assuming the dimerization of the complex, while only the monomer form exhibits a pronounced oxidative effect. Assuming this, the following reaction scheme can be derived:



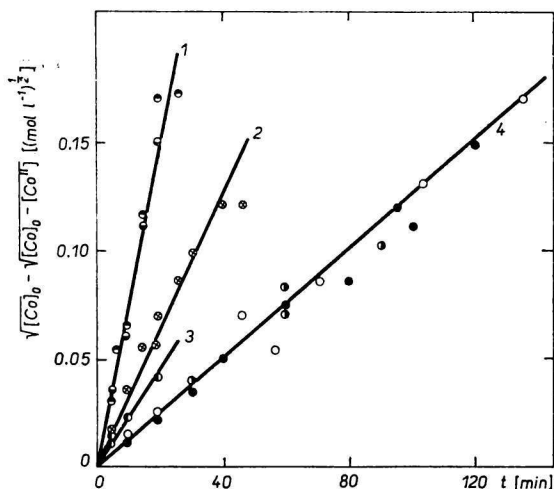
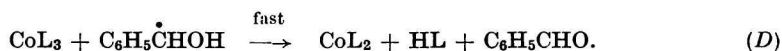
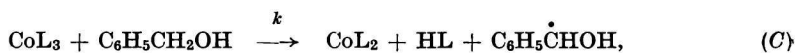


Fig. 1. Kinetics of benzyl alcohol oxidation by cobalt(III) 8-quinolinolate.

T (°C): 1. 179.2; 2. 172.8; 3. 168.0; 4. 162.4.

$[CoL_3]$ (mol l⁻¹): ● 1.07×10^{-1} ; ○ 7.99×10^{-2} ; ● 4.08×10^{-2} ; ● 8.19×10^{-2} ; ● 4.34×10^{-2} ;
 ● 8.7×10^{-2} ; ⊗ 8.89×10^{-2} .



The occurrence of a fast oxidation of the radical formed by another molecule of the oxidation agent was confirmed by benzaldehyde concentration measurements at various conversions.

The cobalt material balance is then described by the relationship

$$[Co]_0 = [CoL_3] + 2[(CoL_3)_2] + [Co(II)]. \quad (1)$$

The reaction rate can thus be expressed either in a differential

$$-\frac{d[Co(III)]}{dt} = -\frac{kK}{2} f(S) + \frac{kK}{2} f(S) \sqrt{1 + \frac{8}{K} ([Co]_0 - [Co(II)])} \quad (2)$$

or in an integral form

$$\begin{aligned} & \sqrt{1 + \frac{8}{K} ([Co] - [Co(II)])} - \sqrt{1 + \frac{8}{K} [Co]_0} - \\ & + \ln \frac{1 + \sqrt{1 + \frac{8}{K} ([Co]_0 - [Co(II)])} - 1}{\sqrt{1 + \frac{8}{K} [Co]_0} - 1} = 2k f(S) t. \end{aligned} \quad (3)$$

The substrate (benzyl alcohol) activity is described by the function $f(S)$. As it has been shown [14] the $f(S)$ is a complicated function; this is due to different activity of associates formed from the alcohol through hydrogen bonding. However, when the substrate is present in excess, the function assumes a constant value.

The analysis of experimental kinetic data has shown that relationship (3) can be further simplified

$$\sqrt{[\text{Co}]_0} - \sqrt{[\text{Co}]_0 - [\text{Co(II)}]} = \frac{k\sqrt{K}}{2} f(S) t. \quad (4)$$

This simplification follows from a considerably low value of dissociation constant K . Relationship (4) is linear over the whole range of concentrations and conversions followed.

The values of $k\sqrt{K} f(S)$ found for various temperatures are presented in Table 1.

Table 1

Temperature dependence of the product of the rate and equilibrium constants for the oxidation of benzyl alcohol by cobalt(III) 8-quinolinolate

T [°C]	$k\sqrt{K} f(S) \cdot 10^5$ [mol ^{1/2} l ^{-1/2} s ⁻¹]
162.4	3.05
168.0	5.15
172.8	8.16
179.2	17.23

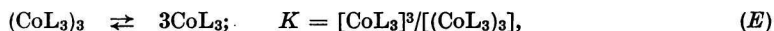
The value of

$$E_a + \frac{\Delta H_d}{2} = 40.1 \text{ kcal mol}^{-1}$$

could be determined from the tabulated data. E_a represents the activation energy of oxidation, ΔH the enthalpy change corresponding to the dissociation of the cobalt(III) 8-quinolinolate dimer.

The oxidation of benzyl alcohol by cobalt(III) benzoate was studied in pure benzyl alcohol within the temperature range 90–120°C. The stoichiometry of the reaction corresponds to eqn (A). The molar ratio of oxidation agent consumed to benzaldehyde formed was measured to be 1.90 (average of four measurements).

The initial reaction rates of oxidation were proportional to the cubic root of oxidation agent concentration; this holds both for high and for low concentrations of benzyl alcohol (Fig. 2). It is believed that the following association equilibrium was established



the oxidation activity of the trimer being negligible in comparison with that of the monomer.

On the basis of this assumption the kinetic equation can be derived both in the differential

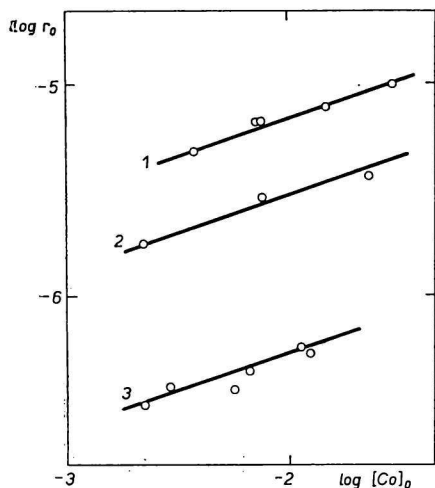


Fig. 2. Dependence of the initial reaction rate of benzyl alcohol oxidation by cobalt(III) benzoate upon the concentration of the latter.

1. 101°C, pure benzyl alcohol, determined spectrophotometrically; 2. 94.5°C, pure benzyl alcohol, determined titrimetrically; 3. 117.5°C $[S] = 0.48 \text{ mol l}^{-1}$ in mesitylene, determined spectrophotometrically.

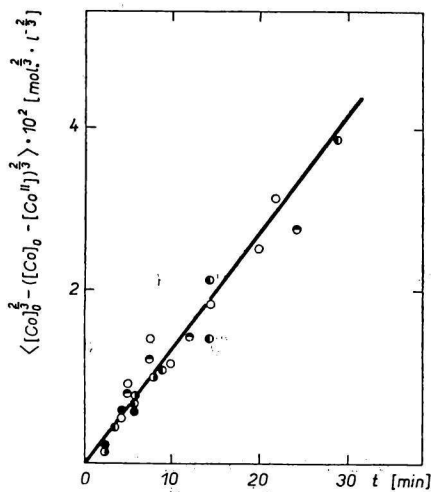


Fig. 3. Time dependence of the rate function of the oxidation of benzyl alcohol by cobalt(III) benzoate.

$T = 101^\circ\text{C}$, pure benzyl alcohol.

$[\text{CoL}_3]$: \circ 4.18×10^{-3} ; \bullet 8.58×10^{-3} ; \ominus 9.30×10^{-3} ; $\omin�$ 1.89×10^{-2} ; \circ 3.75×10^{-2} .

$$-\frac{d[\text{Co(III)}]}{dt} = 2k \sqrt[3]{\frac{K}{3}} \cdot \sqrt[3]{[\text{Co}]_0 - [\text{Co(II)}]} f(S) \quad (5)$$

and in the integral form

$$[\text{Co}]_0^{2/3} - ([\text{Co}]_0 - [\text{Co(II)}])^{2/3} = \frac{4k}{3} \sqrt[3]{\frac{K}{3}} f(S) t = 0.925 k K^{1/3} f(S) t. \quad (6)$$

The eqns (5) and (6) were derived on the assumption that $[\text{CoL}_3] \ll [(\text{CoL}_3)_3]$. The time dependence of the rate function (6) is presented in Fig. 3. The dependence of the rate function upon the benzyl alcohol concentration plotted in Fig. 4 shows that $f(S) = [S]^2$. This fact may serve as an evidence for the existence of the equilibrium $(\text{CoL}_3)_3 + 6S \rightleftharpoons 3\text{CoL}_3 \cdot 2S$.

The values of $kK^{1/3}$ for various temperatures are presented in Table 2.

The value of

$$E_a + \frac{\Delta H_t}{3} = 21 \text{ kcal mol}^{-1}$$

Table 2

Temperature dependence of the reaction rates and the product of the rate and equilibrium constants for the oxidation of benzyl alcohol by cobalt(III) benzoate in pure benzyl alcohol

T [°C]	$[\text{Co}]_0 \cdot 10^3$ [mol l ⁻¹]	$r_0 \cdot 10^6$ [mol l ⁻¹ s ⁻¹]	$kK^{1/3} \cdot 10^5$ [l ^{4/3} mol ^{-4/3} s ⁻¹]
91.0	0.926	4.06	1.023
94.5	1.012	5.07	1.39
101.0	0.8–3.8	6.3	2.16

could be determined from the tabulated data.

The oxidation of allylbenzene, cumene, and methyl benzyl ketone respectively by cobalt(III) acetylacetonate is the first order reaction with regard to both oxidation agent and substrate:

$$-\frac{d[\text{Co(III)}]}{dt} = k[\text{CoL}_3][\text{S}]. \quad (7)$$

This was found by measuring the initial reaction rates (Fig. 5).

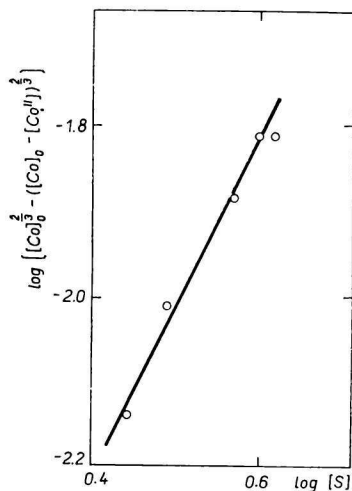


Fig. 4. Dependence of the rate function of benzyl alcohol oxidation by cobalt(III) benzoate upon the concentration of benzyl alcohol in mesitylene.

$T = 94.5^\circ\text{C}$, $[\text{CoL}_3] = 2.09 \times 10^{-2}$ mol l⁻¹,
 $t = 20$ min.

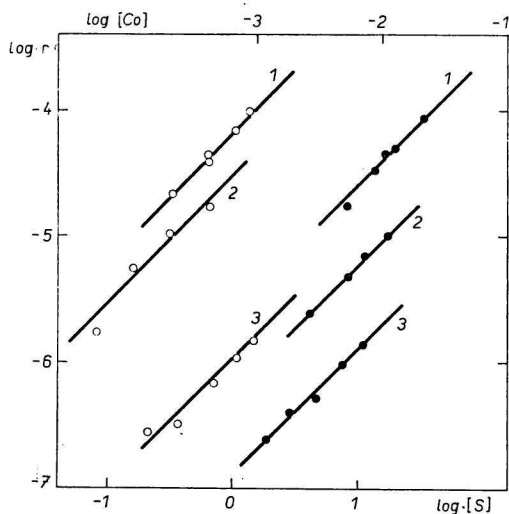


Fig. 5. Dependence of the initial reaction rate of allylbenzene, cumene, or methyl benzyl ketone oxidation upon the concentration of substrate or cobalt(III) acetylacetonate in mesitylene.

1. methyl benzyl ketone, 139.5°C ;
2. cumene, 140°C ; 3. allylbenzene, 134.5°C .
○ substrate; ● oxidation agent.

The reactions were studied in mesitylene medium within the temperature range 110–150°C, the concentration range being 2×10^{-3} – 1.2×10^{-2} mol l⁻¹ for the oxidation agent and 0.06–0.7 mol l⁻¹ for the substrate.

The results are summarized in Table 3.

Table 3

Rate constants of allylbenzene, cumene, and methyl benzyl ketone oxidation by cobalt(III) acetylacetonate

Substrate	T [°C]	$k \cdot 10^4$ [l mol ⁻¹ s ⁻¹]	log A	E_a [kcal mol ⁻¹]
Allylbenzene	121.5	0.264	17.2	41
	124.5	0.685		
	130.6	1.73		
	134.5	1.518		
	138.8	4.96		
	148.5	7.16		
Cumene	132.5	5.79	17.3	38
	135.5	7.48		
	140.0	14.00		
	143.7	18.54		
Methyl benzyl ketone	113.3	6.3	12.2	27
	116.2	6.9		
	121.5	12.0		
	130.5	23.6		
	135.0	37.4		
	139.5	63.6		

The examination of the time dependence of these reactions has shown that they do not proceed quantitatively; they are apparently inhibited by cobalt(II) acetylacetonate formed in the course of the reaction (Fig. 6). This hypothesis was further corroborated by adding the CoL_2 complex into the reaction mixture (Fig. 7). The reaction does not proceed in the presence of an excess of CoL_2 complex.

Assuming that an inactive and stable associate is formed *via* interaction of CoL_2 with CoL_3 , a general reaction scheme can be set up:

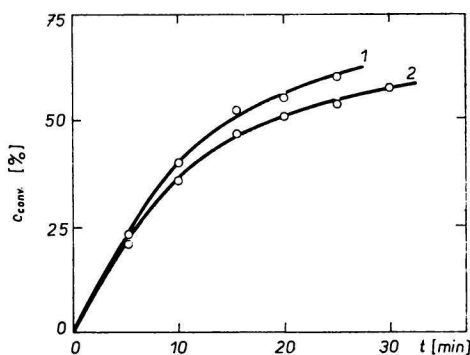


Fig. 6. Time dependence of allylbenzene oxidation by cobalt(III) acetylacetonate in mesitylene.

$T = 138.8^\circ\text{C}$, $[\text{CoL}_3] = 6.2 \times 10^{-3}$ (1),
 1.27×10^{-2} (2) mol l⁻¹.



If the concentration of A is analytically accessible then the sum Y can be expressed as

$$[A] + [AB] = Y. \quad (8)$$

The time dependence of Y is thus:

$$dY/dt = -k[A]. \quad (9)$$

If the initial concentration of A is denoted as C then the material balance is expressed by the relationship

$$C = [A] + [B] + 2[AB], \quad (10)$$

$$C - Y = [B] + [AB] = [B](1 + K[A]). \quad (11)$$

It is assumed that the rate of equilibrium (G) establishment is much greater than the rate of reaction (F).

Thus the integral form of the relationship for the reaction rate can be derived

$$\begin{aligned} & 2(KC + 1) \ln \frac{\sqrt{4Y^2 - 4CY + (C + 1/K)^2} + 2Y - (C + 1/K)}{2C} - \\ & - (2KC + 1) \ln \frac{\sqrt{4Y^2 - 4CY + (C + 1/K)^2} + 2Y - C}{2C + 1/K} + \\ & + \frac{2KC + 1}{K} \left(\frac{1}{\sqrt{4Y^2 - 4CY + (C + 1/K)^2} + 2Y - C} - \frac{1}{2C + 1/K} \right) = -2kt. \end{aligned} \quad (12)$$

The graphical expression of this equation, which represents the reaction course of the process inhibited by a reaction product, has two limits:

1. If K or $C \rightarrow \infty$ then

$$\ln(2Y - C)/C = -2kt. \quad (13)$$

The reaction proceeds only to 50% conversion.

2. If K or $C \rightarrow 0$, then

$$\ln(Y/C) = -kt. \quad (14)$$

A typical first-order reaction.

The shape of the conversion curve is dependent on the value of the product KC . The integral form of the kinetic equation is, unfortunately, too complicated to be suitable for the determination of the value of K ; it seems that none of the terms can be neglected. The value of K can, however, be determined from the slope of the conversion curve at 0 and 50%:

$$\frac{(dY/dt)_0}{(dY/dt)_{50}} = \frac{2KC}{\sqrt{1 + 2KC} - 1}. \quad (15)$$

The reaction scheme presented above is valid generally. Conversion curves calculated for various values of KC are shown in Fig. 8. Experimental points fit in well with $KC = 10$. Therefore it follows for the value of the association constant: $K > 10^2 \text{ l mol}^{-1}$.

The study of stoichiometry of allylbenzene and methyl benzyl ketone oxidation has shown that the molecules of these compounds are oxidized only by one molecule of the oxidation agent: the molar ratio of oxidation agent consumed to substrate oxidized is equal to 1.11 for allylbenzene and 0.99 for methyl benzyl ketone (determined by g.l.c. method, average of four measurements).

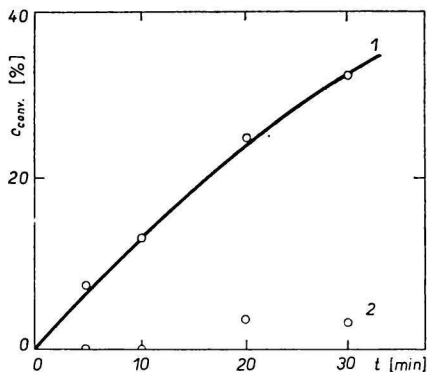


Fig. 7. Influence of CoL_2 on allylbenzene oxidation by CoL_3 in mesitylene.
 $T = 137^\circ\text{C}$, $[S] = 1.35 \text{ mol l}^{-1}$, $[\text{CoL}_3] = 2 \times 10^{-2}$ (1), (2) $[\text{CoL}_2] = 4 \times 10^{-2} \text{ mol l}^{-1}$.

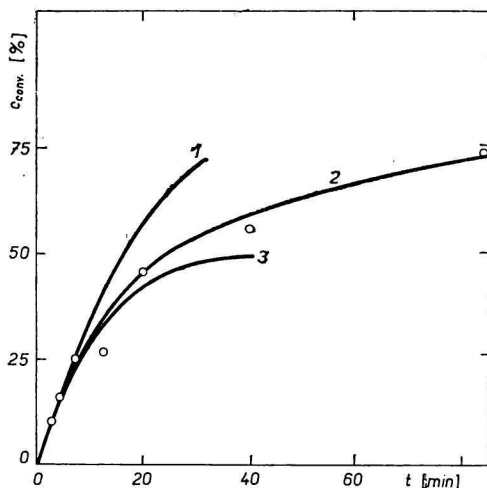


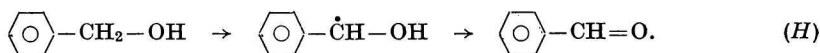
Fig. 8. Conversion curves calculated according to eqn (12):
 $KC \rightarrow \infty$ (1); $\rightarrow 10$ (2); $\rightarrow 0$ (3).
 experimental points: $T = 138.8^\circ\text{C}$,
 $[\text{CoL}_3] = 1.36 \times 10^{-2} \text{ mol l}^{-1}$
 $[S] = 1.7 \text{ mol l}^{-1}$.

The g.l.c. analysis of the reaction mixture after the oxidation of allylbenzene, cumene, and methyl benzyl ketone, respectively, has not shown any aromatic hydrocarbons $\text{C}_6\text{--C}_9$ (possible monomer oxidation products).

The infrared spectrum of the allylbenzene oxidation product contained, when compared with that of allylbenzene, an additional absorption assigned to a tertiary C—H group; the spectrum of the methyl benzyl ketone oxidation product, when compared with that of pure substrate, contained an additional peak corresponding to —C—O—C— bonding.

Discussion

According to our observation benzyl alcohol is oxidized by the used one-electron agents to benzaldehyde in a two-step process:



A simultaneous abstraction of both electron and proton takes place during each step.

In the case of allylbenzene and methyl benzyl ketone only one electron is abstracted in the process of oxidation:

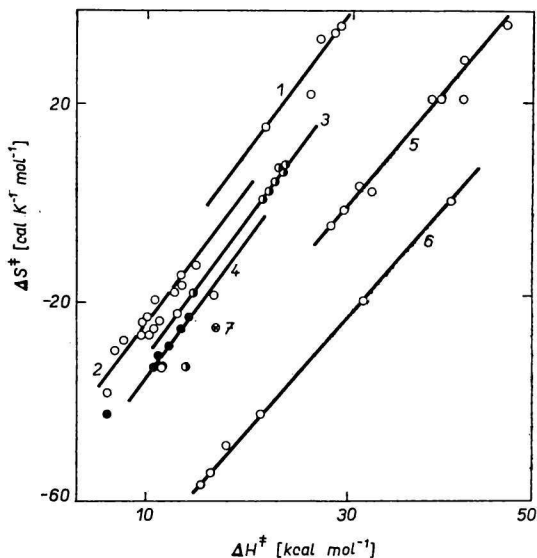
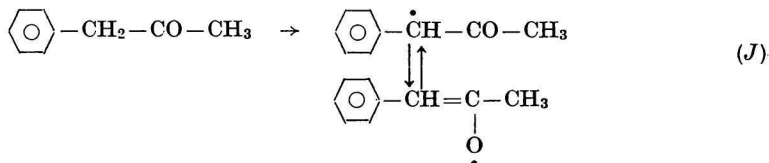
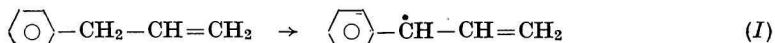


Fig. 9. Leffler correlations of thermodynamic parameters of activation plotted for oxidations of organic compounds induced by transition metal compounds.

1. Co(III), H₂O; 2. Mn(VII), H₂O; 3. V(V), H₂O; 4. Cr(VI), H₂O; 5. CoL₃, non-aqueous medium; 6. RH + O₂; 7. Co(OH) L₂, nonaqueous medium. HL — acetylacetone.

References to Fig. 9 (individual points are numbered in descending order).

Co(III): 1.—3. [25]; 4. [26]; 5., 6. [27]. Mn(VII): 1. [28]; 2. [29]; 3. [30]; 4. [31]; 5. [29]; 6. [32]; 7. [33]; 8., 9. [34]; 10.—12. [35]; 13. [36]; 14. [32]; 15. [31]; 16. [33]; 17. [37]. V(V): 1.—5. [38]; 6. [39]; 7. [40]; 8. [41]. Cr(VI): 1.—6. [42]. [CoL₃: 1., 4., 5., 7.—9. [19]; 2. [10]; 3., 6. [11]. Co(OH) L₂: [19]. RH + O₂: 1., 2. [43]; 3., 4. [44]; 5. [45]; 6. [46]. HL — acetylacetone.



The radicals formed do not undergo further oxidation. This is in accordance with the observations of *Volger et al.* [5—7] who oxidized olefinic and carboxylic compounds by Cu(II) salts. They observed only the oxidation leading to radicals which subsequently dimerized. The authors explained this phenomenon on the basis of the resonance stabilization of the radical as a consequence of the presence of a multiple bond. Also the infrared spectra of the reaction products strongly suggest that the dimerization of radicals formed in the course of allylbenzene and methyl benzyl ketone oxidation occurred. The spectrum of methyl benzyl ketone oxidation product indicates that the two forms of radical (*J*) are involved in the dimerization process; the existence of an equilibrium between the two forms of this radical has been described by *Drummond and Waters* [15].

The published values of activation thermodynamic parameters for the oxidation of organic compounds both in aqueous and in nonaqueous media (hydrocarbons, alcohols, α -hydroxy acids, ketones, *etc.*) fit well in with the linear Leffler correlation [16, 17] (Fig. 9).

The Leffler straight-line parameters are determined by the properties of the oxidation agent. The relation between the intercepts of correlation lines ($= \Delta G^*$ for hypothetical reactions when $\Delta S^* = 0$) and redox potential of the oxidation agent is presented in Fig. 10. It is obvious that the correlation is dependent upon the reversible component of the redox system *i.e.* oxidation agent. The correlations found enable us to find an approximate relationship between the free activation enthalpy of the organic molecule oxidation and the free enthalpy of the oxidation agent reduction:

$$\Delta G^* = 27 + 0.25 \Delta G (\pm 2 \text{ kcal}). \quad (16)$$

Since the slopes of correlation curves approach the value of $1/T$, the values of ΔG^* for oxidation by the same agent will be practically identical.

The data in Fig. 9 involve also parameters of several reactions of oxidation by elemental oxygen $\text{RH} + \text{O}_2$. If we take into account the experimentally found value of the redox potential of molecular oxygen [18] ($E = -0.40 \text{ V}$) then it is apparent that even this system can be satisfactorily included into this correlation. It is evident that oxygen (in the absence of H^+ ions) is a quite weak oxidation agent.

The value of free activation enthalpy of an organic compound oxidation can thus be estimated if the redox potential of the agent is known. Inversely, the value of redox potential of the agent used can be determined from the known activation thermodynamic parameters of the oxidation reaction.

In the case of oxidation of benzyl alcohol by cobalt(III) 8-quinolinolate or benzoate only the sum of activation free enthalpy of oxidation and the fraction of dimer or trimer dissociation enthalpy was found. Since no deviations from the observed reaction order were seen even at the lowest concentrations of the oxidation agent, the minimum value of the free enthalpy of the dissociation process can be estimated: let us assume that even at the

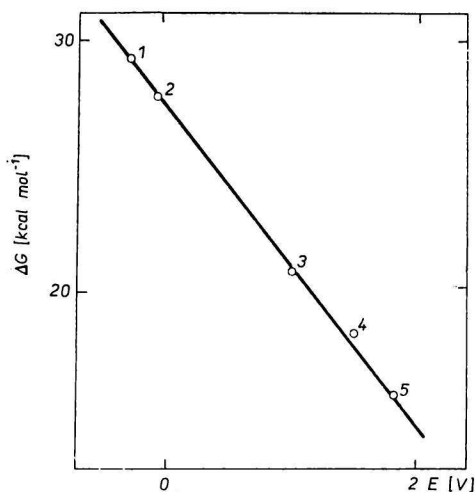


Fig. 10. Relation between activation free enthalpy of the oxidation reaction (for $\Delta S^* = 0$) and redox (or $E_{1/2}$) potential of the oxidation agent.

1. CoL_3 ; 2. $\text{Co}(\text{OH})\text{L}_2$; 3. $\text{V}(\text{V})$;
 4. $\text{Mn}(\text{VII})$; 5. $\text{Co}(\text{III})$.
- HL — acetylacetone.

lowest concentrations used at least 80% of the complex is in its associated form (deviations from the kinetic description would be evident at this or higher degrees of dissociation). Hence

$$M_n \xrightleftharpoons{K_n} nM$$

$$[M]_0 = n \underbrace{[M_n]}_{0.8 [M]_0} + \underbrace{[M]}_{0.2 [M]_0}$$

$$K_n < n [M]_0^{n-1} \cdot 2^{n-3} \cdot 10^{1-n}$$

thus

$$\Delta G > 5 \text{ kcal mol}^{-1} \quad \text{cobalt(III) 8-quinolinolate}$$

$$> 12 \text{ kcal mol}^{-1} \quad \text{cobalt(III) benzoate}$$

Relatively high values of enthalpy of the dissociation equilibrium preclude the use of relation (16) to estimate redox potential of these agents. The polycyclic form of complexes will probably have a bridge character, similarly as in the case of tetramer [20] or trimer [21] of cobalt(II) acetylacetonate or other oligomeric complexes [22–24].

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