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Catalysis by Metal Acetylacetonates in the Autoxidation of Hydrocarbons

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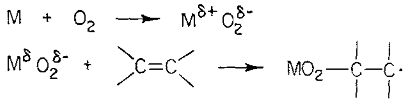
The rate of oxidation of α-methylstyrene catalyzed by cobaltous or manganous acetylacetonates was much higher than that catalyzed by cobaltous decanoate or cobalt phthalocyanine, and the reactions have shown excellent half order relations with respect to metal acetylacetonates over wide range of concentration and a first order dependence on α-methylstyrene concentration. The effect of metal acetylacetonates was remarkably suppressed in the basic solvents pyridine or ethanol. It was concluded that cobaltous and manganous acetylacetonates initiate the chain of autoxidation of α-methylstyrene by activating the oxygen molecule, although they are also effective decomposers of hydroperoxide and so are effective catalysts in the autoxidation of cumene. When 50% of cobaltous acetylacetonate was replaced by manganous acetylacetonate, the metals showed a strong antagonistic effect and the rate of oxidation coincided with the rate catalyzed by cobaltous decanoate.

INTRODUCTION

Catalysis of autoxidation by metal-complexes (*1*, *2*, *3*) has recently received considerable attention. A metal complex is expected to initiate the chain of autoxidation due to activation of the oxygen molecule, but it also decomposes hydroperoxide concurrently. Therefore, it is difficult to distinguish the effect due to the activation of oxygen molecule from the effect due to hydroperoxide decomposition by a metal complex, when the autoxidation of hydrocarbon proceeds by hydrogen abstraction mechanism as in the case of cumene. However, Kropf (*1*), Betts and Uri (*2*) preferred to interpret their results on autoxidation of tertiary hydrocarbons on the basis of the activation of the oxygen molecule.

It has been confirmed that α-copper phthalocyanine (*4*), which is quite inactive for the decomposition of hydroperoxide and for the autoxidation of cumene, initiates remarkably the chain of autoxidation of α-methylstyrene by the addition mechanism. The following initiation reaction due to a metal complex can be suggested.



In this connection, it should be mentioned that the catalysis by a metal complex such as copper phthalocyanine is quite different from that by a metal-oxygen complex (*5*) such as salicylaldehyde ethylene diimine cobalt, because there exists a great difference in the concentration and also in the reactivity between the active species. Although it has been reported on the basis of ESR work (*6*) that salicylaldehyde ethylene diimine cobalt activates the oxygen molecule, and salcomines (*5a*, *5b*) as well as Vaska's complex (*6*) work as very characteristic catalysts in the autoxidation reaction, they are not such effective initiators in the autoxidation of α-methylstyrene (*7*) as cobalt acetylacetonate, which apparently does not form appreciable amounts of metal-oxygen complex.

A metal acetylacetonate is an appropriate metal complex for investigating the effect of activation of molecular oxygen, because it seems to be as good an electron donor as copper phthalocyanine and is quite soluble in aromatic hydrocarbons.

In this paper, the effect of metal acetylacetonates on the rate of oxidation of α-methylstyrene with reactive double bond and of cumene was studied kinetically in order to draw out the two autoxidation mechanisms, that is, addition and hydrogen abstraction. It was concluded that cobaltous and manganous acetylacetonates effectively initiate the autoxidation chain of α-methylstyrene due to the activation of the oxygen molecule.

EXPERIMENTAL

The oxidation technique has been described previously (*9*). All experiments were carried out at 60°C except otherwise stated. Diffusion of oxygen did not affect the rate of oxidation at the reaction conditions. The catalysts used are cobaltous and manganous decanoates and the cobaltous, manganous, nickelous, cupric and cobaltic acetylacetonates along with cobalt phthalocyanine. Metal acetylacetonates were purified by recrystallization from chlorobenzene.

The visible spectra were determined after sampling of the oxidized solution by using a Hitachi-124 spectrometer.

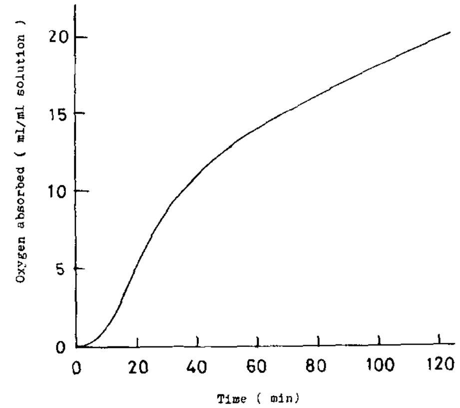


FIG. 1. Oxygen absorption curve of α-methylstyrene catalyzed by 0.02 M cobaltous acety acetonate.

RESULTS AND DISCUSSION

Autoxidation of α-Methylstyrene

A typical oxygen absorption curve, as given in Fig. 1, shows that the steady state of oxidation is observed after an induction period of several minutes and the rate of oxidation starts to decrease after the reagents have absorbed a considerable amount of oxygen.

In Fig. 2, the log of the rate of oxidation is plotted against the concentration of the metal acetylacetonates. As is clear from Fig. 2, the rate of oxidation of α-methyl-

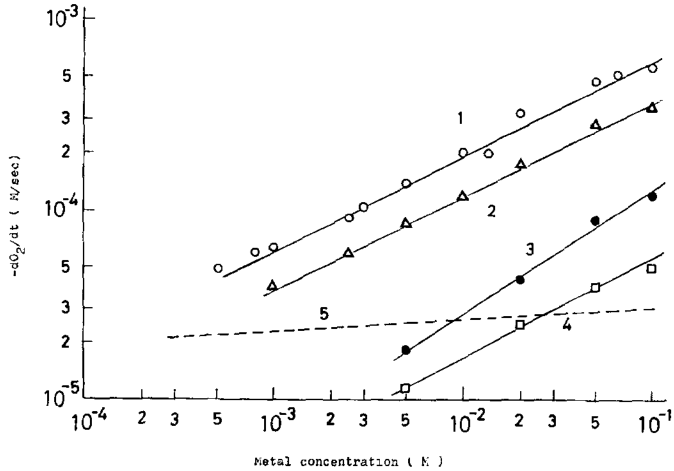


FIG. 2. The rate of oxidation of α-methylstyrene catalyzed by various metal acetylacetonates as a function of metal concentration. 1: cobaltous acetylacetonate, 2: manganous acetylacetonate, 3: cobaltic acetylacetonate, 4: nickelous acetylacetonate, 5: cobalt decanoate and cobalt phthalocyanine.

styrene is exactly half order with respect to cobaltous, manganous and nickelous acetylacetonates, i.e., the rate of chain initiation is first order with respect to catalyst concentration.

Cobaltous acetylacetonate (CoA_2) is so active that its rate of initiation is about four times as fast as α-copper phthalocyanine (*5*).

When a very active decomposer of hydroperoxide, such as cobaltous decanote or cobalt phthalocyanine, is used, the steady rate of oxidation can not exceed a limiting value of 3.2×10^{-5} M/sec as shown previously (*8*).

It was reported that the autoxidation of α-methylstyrene proceeds entirely by the addition mechanism (*10*). However, if 0.07% of the propagation step proceeds by hydrogen abstraction mechanism, the limiting rate of oxidation catalyzed by metal salts will be 3×10^{-5} M/sec, since the value of $k_p^2(RH)^2/2k_t$ can be calculated to be 4.5×10^{-2} M/sec at 60°C according to k_p and k_t given by Howard and Ingold (*11*).

The difference in the rates of oxidation between cobaltous decanoate and cobaltous acetylacetonate can be attributed to the direct chain initiation due to the activated oxygen molecule, which is one thousand times as fast as hydroperoxide decomposition at 0.05 M of cobalt.

Although CoA_2 and MnA_2 were found to be very active catalysts, cupric acetylacetonate has shown very low rates of oxidation, i.e., 1.6×10^{-6} M/sec at 0.01 M and 4×10^{-6} M/sec at 0.1 M in contrast to the case of metal phthalocyanines.

Autoxidation of Cumene

The effect of catalyst concentration on the rate of oxidation of cumene is shown in Fig. 3. CoA_2 reaches a limiting rate of oxidation of 3.2×10^{-4} M/sec which is the same as cobaltous decanoate ($CoDe_2$) and manganous decanoate ($MnDe_2$) at concentrations above 0.01 M. It is seen that CoA_2 is as active a catalyst for the decomposition of hydroperoxide as are $CoDe_2$ and $MnDe_2$, since at low catalyst concentrations the rate of oxidation is half order with respect to the rate of hydroperoxide decomposition. MnA_2 has a little lower activity than CoA_2.

It should be mentioned that CoA_2 is deactivated faster than $CoDe_2$ in the autoxidation of cumene, i.e., the oxygen absorption curve with CoA_2 starts to fall below the steady state curve after absorbing 2.5 to 4 ml of oxygen per 1 ml of cumene as compared with 6 to 10 ml in the case of $CoDe_2$. This result seems to suggest that CoA_2 is relatively unstable and that it is converted to an inactive form in the course of hydroperoxide decomposition.

The Effect of Solvent

The rate of oxidation of a mixture of α-methylstyrene and solvent (1:1 by volume) is shown in Table 1. The values should be compared with half the rate of

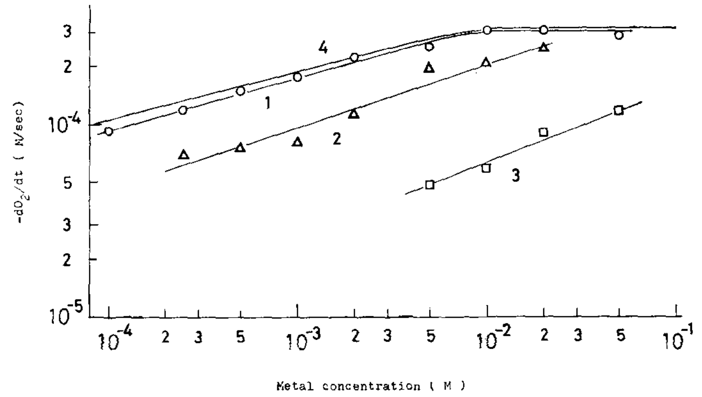


FIG. 3. The rate of oxidation of cumene catalyzed by various metal acetylacetonates as a function of metal concentration. 1: cobaltous acetylacetonate, 2: manganous acetylacetonate, 3: nickelous acetylacetonate, 4: cobalt and manganese decanoates.

TABLE 1

EFFECT OF SOLVENT ON THE RATE OF OXIDATION OF α-METHYLSTYRENE (CATALYST 0.02 M, 60°C)

Catalyst / Solvent		$-dO_2/dt \times 10^4$ (M/sec)		
		CoA_2	MnA_2	CoA_3
None		3.20	1.7	0.45
Chlorobenzene	(1:1 by volume)	1.62	0.90	0.20
Acetic acid	(1:1 by volume)	1.65	0.32	0.78
Ethanol	(1:1 by volume)	0.40	0.32	0.15
Pyridine	(1:1 by volume)	0.33	—	—
Acetonitrile	(1:1 by volume)	1.90	—	—

oxidation of neat α-methylstyrene, since the rate of the initiated autoxidation is exactly first order with respect to the concentration of reactant. Chlorobenzene shows only the effect of dilution, but ethanol and pyridine strongly inhibit the autoxidation. A basic solvent probably solvates metal acetylacetonate and retards the activation of the oxygen molecule by the metal complex. The increase in the rate can be attributed to the dielectric effect of the solvent in the case of acetonitrile. The rate of oxidation catalyzed by CoA_2 in acetic acid is entirely first order with respect to α-methylstyrene as shown in Fig. 4. This result supports the hypothesis that CoA_2 is working not as a hydroperoxide decomposer but an initiator in the autoxidation, because the autoxidation of tetralin and cumene catalyzed by metal salt is exactly second order with respect to hydrocarbon concentration. The effect of acetic acid seems to be complicated, because there is no inhibition effect in the case of CoA_2, contrary to the case of MnA_2, and the rate of oxidation by cobaltic acetylacetonate (CoA_3) increased by a factor of three and it retained its activity for a longer time than it did in a neutral solvent.

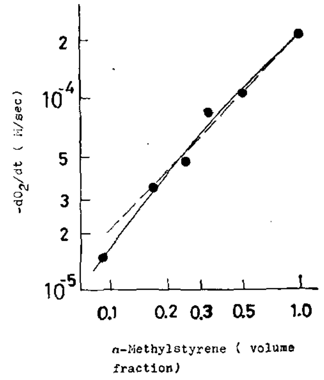


FIG. 4. The rate of oxidation of α-methylstyrene catalyzed by 0.01 M cobaltous acetylacetonate as a function of α-methylstyrene concentration when diluted by acetic acid. Broken line represents a first order correlation.

In acetic acid CoA_3 will be converted to cobaltic acetate to some extent and this will initiate effectively the chain of autoxidation as shown later.

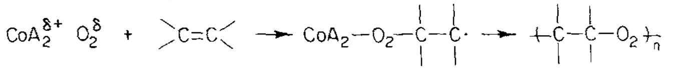
Moreover, there was neither an induction period nor deactivation of the catalyst even in alcohol solution in the case of CoA_3, suggesting that the effect of CoA_3 is quite different from that of the cobaltous salt.

Reaction Mechanism

Although cobaltous acetylacetonate has shown itself to be a very active catalyst for the autoxidation of cumene as well as cobaltous decanoate, it has also exhibited much higher activity in the autoxidation of α-methylstyrene than cobaltous decanoate, showing an excellent half order correlation (Fig. 2). The result in Fig. 2 strongly suggests that the following initiation reaction, which is first order with respect to CoA_2, is taking place in the case of α-methylstyrene.

The fact that cobaltic acetylacetonate was relatively inactive in the autoxidation in neutral solvents and was deactivated as time proceeds seems to support the theory that the metal-complex is activating the oxygen molecule, because the reaction *(1)* will be unfavorable in the case of cobaltic ion.

$$CoA_2 + O_2 \rightleftharpoons CoA_2^{\delta+} O_2^{\delta-} \qquad (1)$$



$$CoA_2^{\delta+} O_2^{\delta} + \rangle C{=}C\langle \longrightarrow CoA_2{-}O_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot \longrightarrow \left(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}O_2\right)_n \qquad (2)$$

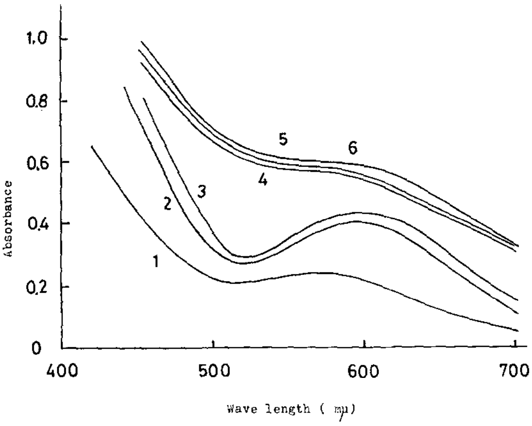


FIG. 5. Visible spectra of 0.02 M cobaltous acetylacetonate in the oxidation of a mixture of α-methylstyrene and chlorobenzene 1:1 by volume. Absorbance after 1: 15 min, 2: 30 min, 3: 60 min, 4: 120 min, 5: 180 min, 6: 240 min.

The reason why the activation of oxygen by cobaltous acetylacetonates is not effective in the direct initiation of cumene but very effective in the case of α-methylstyrene is attributable to the difference in the rate constant of propagation step and chain length.

The rate of oxidation of α-methylstyrene catalyzed by 0.02 M CoA_2 is 3×10^{-4} M/sec, which corresponds to the rate of initiation of 1.5×10^{-6} M/sec. In the presence of 5×10^{-3} M 2,6-di-tert-butyl-*p*-cresol and 0.02 M cobaltous acetylacetonate the induction period in the oxidation of α-methylstyrene was determined to be 7,000 sec, which corresponds to the initiation rate of 1.4×10^{-6} M/sec, showing excellent agreement with the initiation rate at the steady state.

However, even if the initiation reaction by CoA_2 and O_2 is also effective in the autoxidation of cumene, the increased rate of oxidation in addition to that due to hydroperoxide decomposition (3.2×10^{-4} M/sec) will be undetectable, since the chain length in the autoxidation of cumene catalyzed by a high concentration of CoA_2 is nearly unity.

The over-all activation energy in the autoxidation of α-methylstyrene catalyzed by CoA_2 at temperatures from 40 to 70°C was determined to be 16.2 ± 0.5 kcal/mole. According to Howard and Ingold (*11*), activation energies for propagation and termination are 8.07 and 3.7 kcal/mole respectively.

Therefore, the activation energy for the activation of the oxygen molecule by CoA_2 can be calculated to be 20 kcal/mole, which is considerably higher than the values of 10 to 15 kcal/mole for the metal-oxygen complex formation (*12*).

As soon as the oxidation starts, the color of cobaltous acetylacetonate solution (Fig. 5) changes from pink to green and the absorbance at 580 mμ increases markedly and remains constant after 120 min. The absorption spectrum after 120 min corresponds to a ratio of cobaltic to total cobalt ions of 0.55, when cobaltic acetylacetonate is taken as a standard spectrum of cobaltic ion. In contrast, the rate of oxidation reaches a maximum value after 10 min and starts to decrease after 25 min, that is, an inverse relation can be observed between the absorbance at 580 mμ and the rate of oxidation. These results and the low reactivity of CoA_3 suggest that cobaltic compounds formed in the course of oxidation may play only a very small part in the autoxidation of α-methylstyrene. The autoxidation of α-methylstyrene in acetic acid by 0.02 M CoA_2 shows only a small change in the absorbance at 580 mμ, for example from 0.13 to 0.16 even after 60 min reaction, but gives a quite high rate of oxidation (see Table 1). The visible spectra of 0.02 M CoA_2 in chlorobenzene at 60°C in the presence of oxygen (Fig. 6) vary very little even after 60 min, and the small deviation probably due to cobaltic ion did not disappear after evacuation of oxygen.

Although cobaltic acetylacetonate is inactive in the autoxidation in neutral solvents, its activity increases considerably in acetic acid due to the formation of an ac-

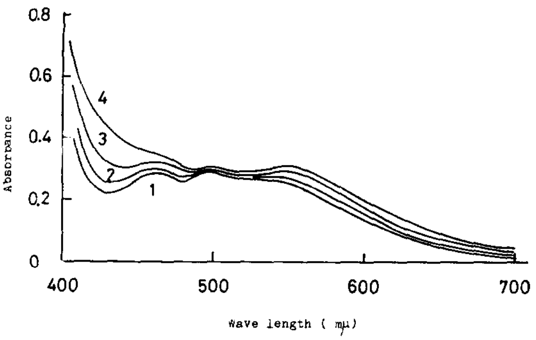


FIG. 6. Visible spectra of 0.02 M cobaltous acetylacetonate in chlorobenzene in the presence of oxygen at 60°C. Absorbance after 1: 30 min, 2: 60 min, 3: 120 min, 4: 240 min.

tive cobaltic salt, that is, cobaltic acetate. It is not surprising to find that the autoxidation of a mixture of acetic acid and α-methylstyrene (1:1 by volume) with 0.01 M cobalt acetate (90% cobaltic ion) gives a rate of 3×10^{-4} M/sec. It is well known that olefins are easily oxidized by cobaltic salts such as cobaltic sulfate and cobaltic perchlorate. However, the rate of oxidation by cobaltic acetate is second order in cobaltic ion and inversely first order in cobaltous ion in the case of methyl benzenes (*14*) and stilbene. Thus, the oxidation of α-methylstyrene in acetic acid with low ratio of Co(III)/Co(II) will be very slow and may be negligible as compared with the effect due to CoA_2 and the oxygen molecule.

According to the results described above, it is concluded that rather than cobaltic ion formed in the autoxidation, CoA_2–O_2 complex is responsible for the chain initiation reaction especially in neutral solvent.

When 0.01 M of CoA_2 in chlorobenzene is treated with oxygen in the presence of 0.03 M AIBN at 60°C, the absorption at 580 mμ increases as time proceeds, showing that cobaltic compounds are formed by the reaction of the peroxy radical with cobaltous acetylacetonate. In order to separate the cobalt catalyst after an oxidation, the oxidation product of α-methylstyrene with CoA_2 was repeatedly treated with methanol and the resultant green solution was evaporated to dryness under vacuum. Elementary analysis showed that the carbon content of CoA_2 increases from 46.1% to 59.5% and hydrogen from 5.4% to 7.0%. These results probably indicate that a large molecule of an oxidation product such as $(C_9H_8O_2)_2$, the dimer of styrenyl peroxide, may be complexed with CoA_2, as suggested by Betts and Uri (*2*).

Addition of 0.1 M free acetyl acetone to 0.02 M cobalt decanoate increased the rate of oxidation of α-methylstyrene from 2.5×10^{-5} to 4.4×10^{-4} M/sec. Similar profound effects were observed in the autoxidation catalyzed by cobaltous acetate and so on. Since the stabilization constants (*15*) of cobaltous acetylacetonate from cobaltous ion and acetylacetone are relatively large, the rate-enhancing effect by free acetylacetone should be mainly due to chelate formation, but chain initiation resulting from the oxidation of free acetylacetone appears to be taking part to some extent.

The Mixing Effect of Metal Complex

When 50% of CoA_2 was replaced by MnA_2, the rate of oxidation of α-methylstyrene decreased by a factor of thirteen showing that the metals are strongly antagonistic. The minimum value of 2.5×10^{-5} M/sec in Fig. 7 coincides well with the rate of oxidation catalyzed by cobaltous decanoate.

Therefore, at the minimum point metal acetylacetonates may be working only as

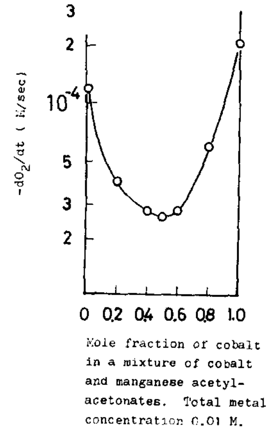


FIG. 7. The mixing effect of cobaltous and manganous acetylacetonates with total concentration of 0.01 M on the rate of oxidation of α-methylstyrene.

the hydroperoxide decomposer, since no antagonistic effect was observed in the autoxidation of cumene catalyzed by CoA_2 and MnA_2. Manganous acetylacetonate cannot inhibit the autoxidation of α-methylstyrene by reacting with polystyrenyl peroxy radical, because it is an effective catalyst as well as CoA_2.

Deactivation of the metal-oxygen complex by the other metal may be an explanation for the antagonistic effect.

$$CoA_2^{\delta+}O_2^{\delta-} + MnA_2 \rightarrow CoA_2 + MnA_2 + O_2$$

If the chain initiation effect by CoA_2 is due to the formation of radicals by the oxidation of CoA_2 or decomposition of hydroperoxide or formation of a trivalent metal salt, such a remarkable antagonistic effect should not be observed.

Incidentally, when α-copper phthalocyanine and cobaltous acetylacetonate are used as catalysts, an additivity in the initiation reaction is observed, since the rate of oxidation of α-methylstyrene is 1.1×10^{-4} M/sec with 0.01 M α-CuPc, 2.0×10^{-4} M/sec with 0.01 M CoA_2, and 2.3×10^{-4} M/sec with 0.01 M α-CuPc and 0.01 M CoA_2, respectively.

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