

**OXIDATION OF 1,2,3,4-TETRAHYDRONAPHTHALENE BY DIOXYGEN. EFFECT OF THE FREE RADICAL INITIATORS 1,2,3,4-TETRAHYDRO-1-NAPHTHYLHYDROPEROXIDE AND 2,2'-AZOBIS(2-METHYLPROPIONITRILE) ON THE REACTION CATALYZED BY 2,4-PENTANEDIONATES OF 3d TRANSITION METALS**

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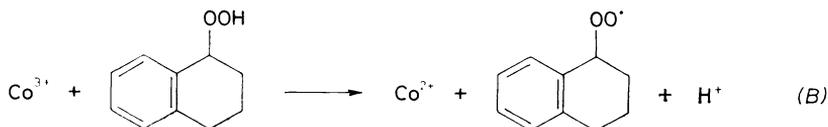
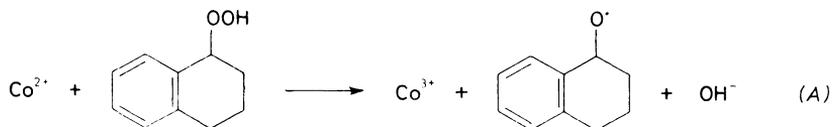
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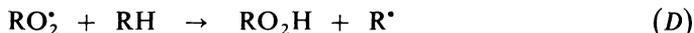
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The effect of the free radical initiators 1,2,3,4-tetrahydro-1-naphthylhydroperoxide and 2,2'-azobis(2-methylpropionitrile) on the oxidation of 1,2,3,4-tetrahydronaphthalene (tetraline) by dioxygen catalyzed by Cr(III), Mn(III), Fe(III), Co(II), Co(III) and Cu(II) 2,4-pentanedionates (acac) has been investigated. It has been found that the addition of a free radical initiator can increase the rate of catalyzed oxidation or decrease it. Which effect will operate depends on the kind of the catalyzing transition metal ion and its oxidation state. The results obtained indicate that the above free radical initiators act on the catalyzed oxidation of tetraline by affecting the catalyst activity.

In our previous studies<sup>1,2</sup> we observed a difference between the rates of the oxidation of tetraline by dioxygen catalyzed by Co(II) and Co(III) 2,4-pentanedionates. The difference was pronounced in the early stages of the reaction and gradually decreased as the reaction proceeded, but persisted up to high degrees of conversion. (The reaction rate for catalysis by Co(III) increased with increasing conversion, whereas a decrease occurred for the reaction catalyzed by Co(II).) This finding runs counter to traditional interpretation of catalyst activity<sup>3-7</sup>, which assumes that a cyclic change in the oxidation state of cobalt,  $\text{Co}^{\text{II}} \leftrightarrow \text{Co}^{\text{III}}$ , occurs in initiation reactions (A) and (B):

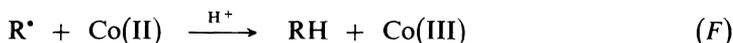


The free radicals so produced initiate a propagation cycle (Eqs (C) to (E)).



According to Eqs (A) and (B), the addition of 1,2,3,4-tetrahydro-1-naphthylhydroperoxide (THP), which is considered as a typical free radical initiator, should always increase the oxidation rate no matter which oxidation state of cobalt is present at the start of the oxidation.

Equations (A) and (B) have also been used to explain catalytic decomposition of THP. According to this concept, the catalytic effect of transition metals on the oxidation of tetraline by dioxygen is to decompose THP, thus increasing the initiation rate. No study has as yet been carried out on the reverse relationship, namely on the effect of a free radical initiator on the catalytic activity of transition metals although it has long been known that free radicals interact with ions and transition metal complexes<sup>8,9</sup>. If insertion of dioxygen into the tetraline molecule can occur within the coordination sphere of the catalyst then, instead of the usual accelerating effect, a free radical initiator could inhibit the reaction. For example, oxidation of the catalytically highly active Co(II) to the nearly inactive Co(III) (Eq. (F)) could result in a decrease in the tetraline oxidation rate.



The aim of this work was to investigate how free radical initiators affect the catalytic activity of 3d transition metal 2,4-pentanedionates for the oxidation of tetraline by dioxygen. The free radical initiators used were THP and 2,2'-azobis(2-methylpropionitrile) (AIBN). We have also studied the effect of the catalysts of tetraline oxidation on the decomposition of THP and compared the catalyst activities for the decomposition of THP and the oxidation of tetraline by dioxygen.

## EXPERIMENTAL

### Chemical

Special care was taken to ensure the purity of tetraline. The methods of purification and storage of purified tetraline have been described in our previous paper<sup>2</sup>. With the exception of ferric 2,4-pentanedionate (Merck, Darmstadt), all the 2,4-pentanedionates used were prepared as described by Lederer and co-workers<sup>10</sup>. Co(II) 2,4-pentanedionate was stored in a vacuum desiccator over dry silica gel.

### Experimental Arrangement and Procedure

The oxidation of tetraline was carried out in a quartz thermostatted vessel filled with oxygen. The reaction was followed volumetrically by measuring the quantity of consumed oxygen. In order to restrict as much as possible the contribution of consecutive reactions of THP, we followed only the initial stages of oxidation, where the total consumption of oxygen did not exceed 5% of the theoretical amount needed for complete oxidation of tetraline to THP.

The decomposition of THP was studied under conditions where the obtained results were comparable with those for the oxidation of tetraline by dioxygen. The decomposition was followed iodometrically<sup>11</sup>. Before starting the experiment, THP was dissolved in a 1 mol/l solution of tetraline in heptane to a concentration of 0.1 mol/l. The decomposition was carried out in a thermostatted vessel under an inert atmosphere of nitrogen. The reaction was started by adding a 2,4-pentanedionate catalyst.

### RESULTS AND DISCUSSION

In the first series of experiments, we compared the catalytic activities of the various catalysts for the oxidation of tetraline by dioxygen. The results are represented in Fig. 1. It is seen that the catalytic activities of the 2,4-pentanedionates investigated increase under the given experimental conditions in the order Cr(III) < Fe(III) < Co(III) < Cu(II) < Mn(III) < Co(II). While for the reactions catalyzed by Cr(III), Fe(III), Co(II) and Cu(II) the oxidation rate increased with increasing conversion, the reverse was observed for Mn(III) and Co(II). The rate increase is usually ascribed to increasing concentration of THP, which brings about an increase in the initiation rate. The marked decrease in the oxidation rate with increasing conversion at low degrees of conversion can only be due to catalyst deactivation. In order to ascertain what is the action of the THP formed, we have investigated the effect of its addition on the rate of catalyzed oxidation of tetraline. Naturally, the question arose as to what effect other (non-peroxidic) radical initiators would have on the rate of the catalyzed oxidation. To resolve this question, we have studied the effects of THP and one of the best known and most frequently used free radical initiators, AIBN, on the oxidation of tetraline by dioxygen catalyzed by 2,4-pentanedionates of 3d transition metals.

Figure 2 characterizes the effects of AIBN and THP on the oxidation of tetraline by dioxygen catalyzed by Co(II) and Co(III) 2,4-pentanedionates. As seen, the two free radical initiators show qualitatively the same behaviour: they enhance the rate of oxidation catalyzed by Co(III) and lower the rate of oxidation catalyzed by Co(II). The addition of either of the free radical initiators decreases the rate of oxidation catalyzed by Mn(III) (see Fig. 3) and increases the rates of oxidations catalyzed by Fe(III) and Cu(II) (see Figs 4 and 5). As seen from Fig. 6, the catalytic activity of Cr(III) is critically dependent on the presence of THP. AIBN exerts no pronounced effect on the catalytic activity of Cr(III). The results obtained have shown that the increase or decrease in the catalytic activity of 2,4-pentanedionates is due to THP formed during the oxidation of tetraline.

It is generally accepted<sup>6,7</sup> that the catalytic effect of transition metals on the oxidation of hydrocarbons by dioxygen is to accelerate the dissociation of hydroperoxides to free radicals which subsequently start the propagation cycle. To verify this concept, we have studied the effects of 3d transition metal 2,4-pentanedionates on the rate of THP decomposition. The results are shown in Fig. 7. The catalytic activities of 2,4-pentanedionates for THP decomposition decrease in the order Cr(III) > Co(II) > Mn(III) > Fe(III) = Co(III) = without any effect. Apparently, only the oxidation catalyzed by Cr(III) could be explained in terms of the catalytic enhancement of initiation rate, i.e., the decomposition of THP. Fe(III) and Co(III), whose catalytic activities for the oxidation are markedly enhanced by the addition of THP, have no measurable effect on the decomposition rate. On the other hand, Co(II) and Mn(III), whose catalytic activities for the oxidation decrease with increasing THP concentration, perform well in catalyzing the decomposition of THP.

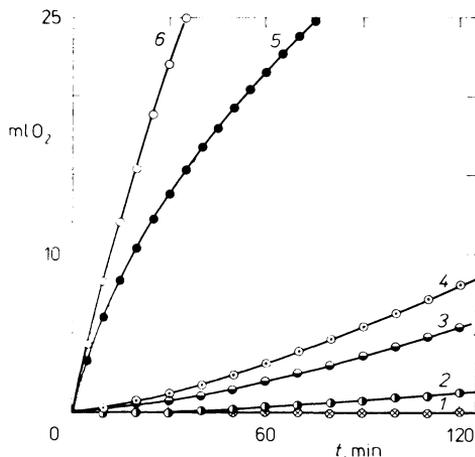


FIG. 1

Catalytic effect of 3d transition metal 2,4-pentanedionates on the oxidation of tetraline by dioxygen ( $[\text{tetraline}]_0 = 5 \text{ mol/l}$ ,  $[\text{O}_2] = \text{sat.}$ ,  $[\text{Me}(\text{acac})_n] = 1 \cdot 10^{-4} \text{ mol/l}$ , solution in heptane,  $60^\circ\text{C}$ ). 1 Cr(III), 2 Fe(III), 3 Co(III), 4 Cu(II), 5 Mn(III), 6 Co(II). When no catalyst was added, the reaction did not proceed at a measurable rate

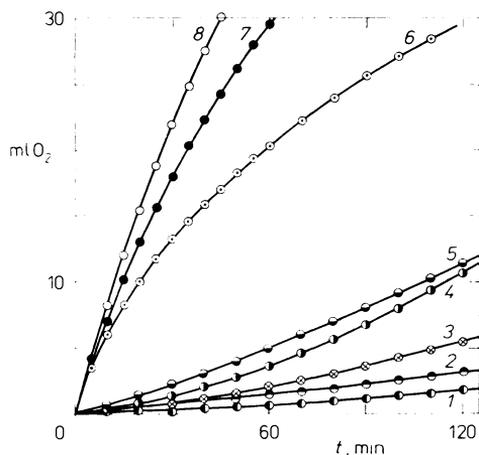


FIG. 2

Effects of THP and AIBN on the oxidation of tetraline by dioxygen catalyzed by Co(II) and Co(III) 2,4-pentanedionates ( $[\text{tetraline}]_0 = 5 \text{ mol/l}$ ,  $[\text{O}_2] = \text{sat.}$ ,  $[\text{Me}(\text{acac})_n] = 1 \cdot 10^{-4} \text{ mol/l}$ ,  $[\text{AIBN}] = 1 \cdot 10^{-3} \text{ mol/l}$ ,  $[\text{THP}] = 0.1 \text{ mol/l}$ , solution in heptane,  $60^\circ\text{C}$ ). 1 THP, 2 AIBN, 3 Co(III), 4 Co(III) + AIBN, 5 Co(III) + THP, 6 Co(II) + THP, 7 Co(II) + AIBN, 8 Co(II)

The experimental results show that the mechanistic picture used for the reaction without catalyst addition cannot be automatically invoked to account for catalyzed oxidations by ascribing the catalyst the role of a creator of initiating free radicals. The catalytic activity of Mn(III) and Co(II) is high already at the start of the reaction, where nearly no THP is present, and decreases with increasing conversion (i.e., with increasing concentration of THP) and also upon the addition of THP. It is clear that the catalytic effect of Mn(III) and Co(II) 2,4-pentanedionates on the oxidation of tetraline cannot be ascribed to acceleration of THP decomposition with the formation of free radicals which in turn start a propagation cycle. It appears that the Mn(III) and Co(II) complexes are by themselves good catalysts of the oxidation and that their catalytic effect is to promote spin-forbidden hydrocarbon oxidations by dioxygen through coordination of tetraline or dioxygen:

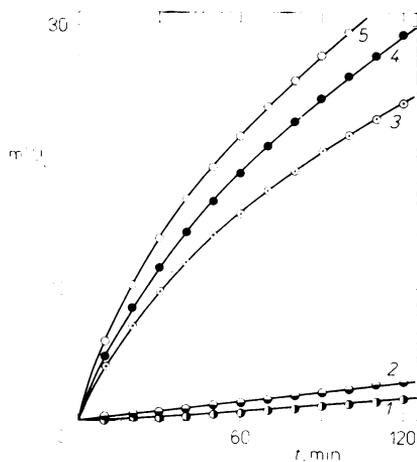
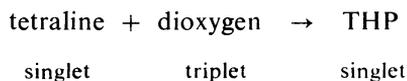


FIG. 3

Effects of THP and AIBN on the oxidation of tetraline by dioxygen catalyzed by Mn(III) 2,4-pentanedionate ( $[\text{tetraline}]_0 = 5 \text{ mol/l}$ ,  $[\text{O}_2] = \text{sat.}$ ,  $[\text{Mn}(\text{acac})_3] = 1 \cdot 10^{-4} \text{ mol/l}$ ,  $[\text{AIBN}] = 1 \cdot 10^{-3} \text{ mol/l}$ ,  $[\text{THP}] = 0.1 \text{ mol/l}$ , solution in heptane,  $60^\circ\text{C}$ ). 1 THP, 2 AIBN, 3 Mn(III) + THP, 4 Mn(III) + AIBN, 5 Mn(III)

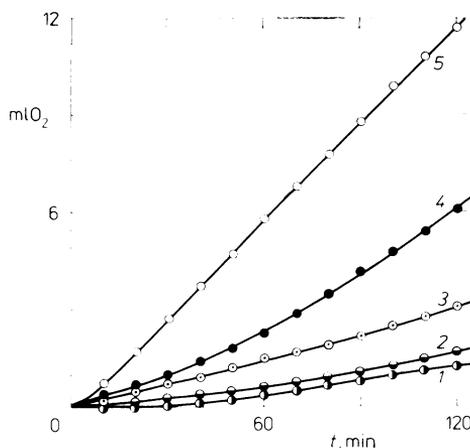


FIG. 4

Effects of THP and AIBN on the oxidation of tetraline by dioxygen catalyzed by Fe(III) 2,4-pentanedionate ( $[\text{tetraline}]_0 = 5 \text{ mol/l}$ ,  $[\text{O}_2] = \text{sat.}$ ,  $[\text{Fe}(\text{acac})_3] = 1 \cdot 10^{-4} \text{ mol/l}$ ,  $[\text{AIBN}] = 1 \cdot 10^{-3} \text{ mol/l}$ ,  $[\text{THP}] = 0.1 \text{ mol/l}$ , solution in heptane,  $60^\circ\text{C}$ ). 1 Fe(III), 2 THP, 3 AIBN, 4 Fe(III) + AIBN, 5 Fe(III) + THP

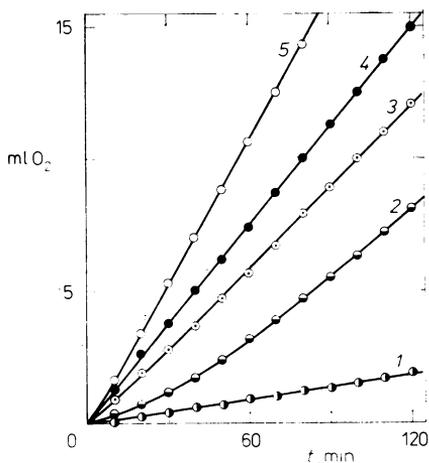


FIG. 5

Effects of THP and AIBN on the oxidation of tetraline by dioxygen catalyzed by Cu(II) 2,4-pentanedionate ( $[\text{tetraline}]_0 = 5 \text{ mol/l}$ ,  $[\text{O}_2] = \text{sat.}$ ,  $[\text{Cu}(\text{acac})_2] = 1 \cdot 10^{-4} \text{ mol/l}$ ,  $[\text{AIBN}] = 1 \cdot 10^{-2} \text{ mol/l}$ ,  $[\text{THP}] = 0.1 \text{ mol/l}$ , solution in heptane,  $60^\circ\text{C}$ ). 1 THP, 2 Cu(II), 3 AIBN, 4 Cu(II) + THP, 5 Cu(II) + AIBN

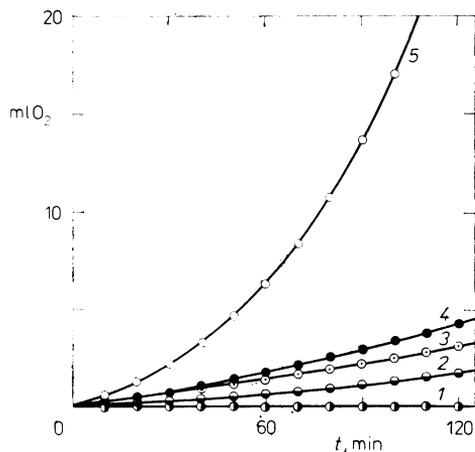


FIG. 6

Effects of THP and AIBN on the oxidation of tetraline by dioxygen catalyzed by Cr(III) 2,4-pentanedionate ( $[\text{tetraline}]_0 = 5 \text{ mol/l}$ ,  $[\text{O}_2] = \text{sat.}$ ,  $[\text{Cr}(\text{acac})_3] = 1 \cdot 10^{-4} \text{ mol/l}$ ,  $[\text{THP}] = 0.1 \text{ mol/l}$ , solution in heptane,  $60^\circ\text{C}$ ). 1 Cr(III), 2 THP, 3 AIBN, 4 Cr(III) + AIBN, 5 Cr(III) + THP

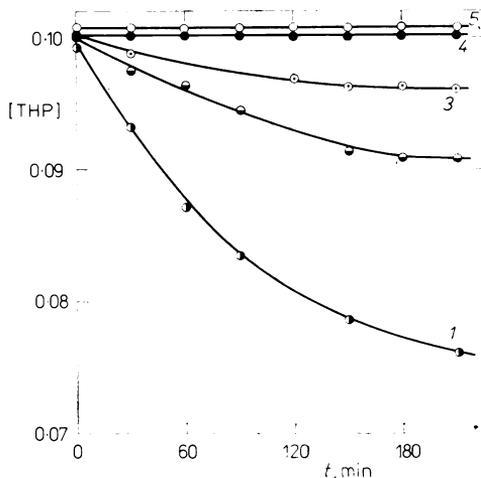


FIG. 7

Catalytic effects of 3d transition metal 2,4-pentanedionates on THP decomposition ( $[\text{THP}]_0 = 0.1 \text{ mol/l}$ ,  $[\text{tetraline}] = 1 \text{ mol/l}$ ,  $[\text{Me}(\text{acac})_n] = 1 \cdot 10^{-4} \text{ mol/l}$ , solution in heptane,  $60^\circ\text{C}$ , nitrogen atmosphere). 1 Cr(III), 2 Co(II), 3 Mn(III), 4 Co(III), 5 Fe(III)

In contrast to this, Co(III) and Fe(III), which by themselves show no pronounced catalytic activity either for tetraline oxidation or for THP decomposition, are converted by the action of THP into efficient catalysts of oxidation. Both the catalyst deactivation and precursor activation are probably associated with redox conversion of the central metal ion (Co(II), Co(III)). Several other processes contribute to the loss of catalytic activity, and may lead even to irreversible catalyst deactivation. The main processes involved are oxidative destruction of 2,4-pentanedionate in the coordination sphere and subsequent separation of the transition metal from the reaction solution in the form of an insoluble oxide.

The changeover from the catalytic to inhibiting effect of transition metals in the oxidation of tetraline by dioxygen is well-documented for both homogeneous<sup>12</sup> and heterogeneous<sup>13</sup> systems. However, the inhibiting effect of free radical initiators has not as yet been described in the literature (with the exception of our previous short communication<sup>1</sup>). This situation is apparently due to the prevalence of mechanistic concepts in which the inhibiting effect of free radical initiators is ruled out as a possibility. The results of this work show that, besides oxidations of hydrocarbons by dioxygen which occur by classical free radical chain mechanism, there are systems containing catalytically active transition metal compounds (Co(II) and Mn(III)) for which insertion of dioxygen into the hydrocarbon (tetraline) molecule situated in the coordination sphere of the catalyzing transition metal ion must be considered.

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