OXIDATION OF CUMENE BY DIOXYGEN. THE EFFECT OF RADICAL INITIATORS ON THE RATE OF THE REACTION CATALYZED BY 3d-TRANSITION METAL 2,4-PENTANEDIONATES

Stanislav Luňák, Růžena Chmelíková and Pavel Lederer

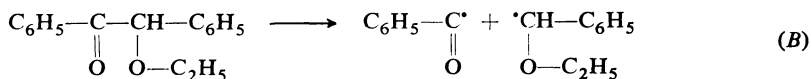*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6*

The effect of cumene hydroperoxide, benzoin ethyl ether and dibenzoyl peroxide on the oxidation of cumene by dioxygen catalyzed by VO(II), Cr(III), Mn(II), Mn(III), Fe(III), Co(II), Co(III) and Cu(II) 2,4-pentanedionates was studied. The rate of the catalyzed oxidation of cumene by dioxygen can not only be increased but also decreased by the presence of radical initiators, whereas in the absence of the catalyst the oxidation rate is always increased by the radical initiators. Which effect takes actually place is determined by the kind and oxidation state of the transition metal ion catalyst as well as by the kind of the radical initiator.

It is well known[1−3] that the oxidation of cumene by dioxygen giving rise to cumene hydroperoxide (Eq. (A)) is catalyzed by transition metal complexes.
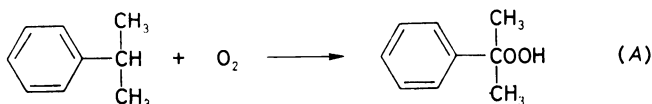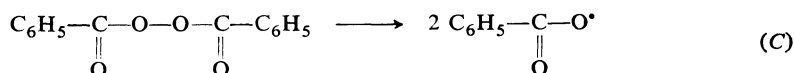

The initiating effect of free radicals produced by decomposing radical initiators is known as well[4,5]. Little attention, however, has been as yet paid to systems containing both catalyzing transition metal complexes and radical initiators. The aim of the present work was to examine the effect of addition of radical initiators on the catalytic activity of 2,4-pentanedionates of 3d-transition metals during the oxidation of cumene by dioxygen.

The radical initiators tested included cumene hydroperoxide (CHP), benzoin ethyl ether (BEE) and dibenzoyl peroxide (DBP). CHP is the primary product of cumene oxidation. BEE exhibits a high initiating activity in the thermal oxidation, although the compound is known as a photopolymerization initiator[6,7]. It is assumed that the primary step in the dissociation of BEE is formation of two free radicals according to Eq. (B).
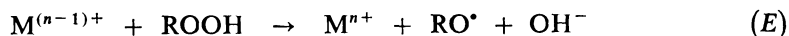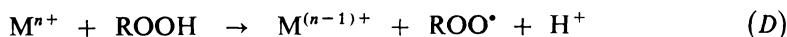
$$C_6H_5\underset{\underset{O}{\|}}{-}\overset{}{C}\underset{\underset{O-C_2H_5}{|}}{-}CH-C_6H_5 \longrightarrow C_6H_5\underset{\underset{O}{\|}}{-}\overset{}{C}{}^{\bullet} + {}^{\bullet}\underset{\underset{O-C_2H_5}{|}}{C}H-C_6H_5 \qquad (B)$$

DBP dissociates[8] according to Eq. (C).

$$C_6H_5\underset{\underset{O}{\|}}{-}C-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5 \longrightarrow 2\ C_6H_5\underset{\underset{O}{\|}}{-}C-O^{\bullet} \qquad (C)$$
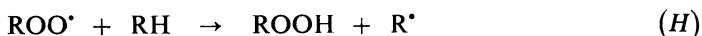
The catalytic effect of transition metals is ascribed to acceleration of the initiation due to the interaction of the metal with cumene hydroperoxide giving rise to radicals (Eqs (D), (E)) which then initiate the propagation cycle (Eqs $(F)-(H)$ (ref.[9])).

Initiation:

$$M^{n+} + ROOH \rightarrow M^{(n-1)+} + ROO^{\bullet} + H^{+} \qquad (D)$$

$$M^{(n-1)+} + ROOH \rightarrow M^{n+} + RO^{\bullet} + OH^{-} \qquad (E)$$

Propagation:

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet} \qquad (F)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (G)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (H)$$

This concept implies that the rate of the catalyzed oxidation should increase with increasing concentration of the hydroperoxide. Previously[10,11] we demonstrated that this is not the case with the oxidation of tetralin by dioxygen. In the present work, cumene was used as the object of oxidation by dioxygen.

EXPERIMENTAL

Chemicals

Particular attention was paid to the purity of cumene. The product supplied by Slovnaft (Bratislava) was freed from peroxidic substances and vacuum rectified, and stored in sealed ampoules under nitrogen. Its purity was checked by iodometric analysis for peroxidic substances[12] and by UV spectrometry using a PU 8720 instrument (Philips, Cambridge).

2,4-Pentanedionates of Mn(II), Mn(III), Fe(III) and Cu(II) (Merck, Darmstadt) and of Co(II), Co(III), Cr(III) and VO(II) (prepared according to ref.[13]) and the radical initiators: cumene hydroperoxide, benzoin ethyl ether, and dibenzoyl peroxide (all Fluka) were used without additional purification. Heptane for UV spectroscopy (Lachema, Brno) served as the solvent.

Procedure

The oxidation of cumene was conducted in a thermostatted quartz vessel connected to a thermo-statted gas burette filled with dioxygen. Effective stirring and saturation of the reaction solution with dioxygen was achieved by vigorous shaking. The reaction was monitored volumetrically, by measuring the amount of dioxygen consumed. The n-heptane solution contained cumene in a concentration of $5 \text{ mol } l^{-1}$, the concentration of the radical initiator was $0.1 \text{ mol } l^{-1}$ (CHP, BEE) or $0.01 \text{ mol } l^{-1}$ (DBP), and that of the catalyst was $1 . 10^{-4} \text{ mol } l^{-1}$. Only the initial reaction stage, during which cumene hydroperoxide is predominantly formed[4], was followed.

RESULTS AND DISCUSSION

The first task to solve was a comparison of the catalytic activity of the $3d$-transition metal 2,4-pentanedionates during the oxidation of cumene by dioxygen. Fig. 1 documents that the catalytic efficiency decreases in order $Co(II) \gg Mn(III) \gg Mn(II) \gg Co(III) \approx Cu(II) \gg Fe(III) \approx VO(II) \gg Cr(III)$; Ni(II) 2,4-pentanedio-nate exhibited no catalytic activity.

The rate of cumene oxidation by dioxygen is affected by the transition metal ion catalysts even if these are present in trace concentrations. This is demonstrated by Fig. 2, in which the cumene oxidation course is plotted for various concentrations
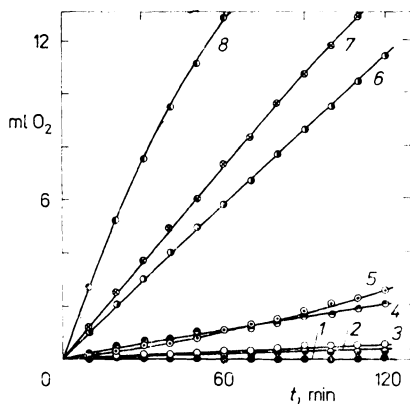

FIG. 1

Catalytic effect of 2,4-pentanedionates of $3d$-transition metals on the oxidation of cumene by dioxygen. Solution in n-heptane saturated by dioxygen, 60°C, concentrations (mol l^{-1}): cumene 5, metal 2,4-pentane-dionates $1 . 10^{-4}$. Metal: *1* Cr(III), *2* VO(II), *3* Fe(III), *4* Cu(II), *5* Co(III), *6* Mn(II), *7* Mn(III), *8* Co(II)
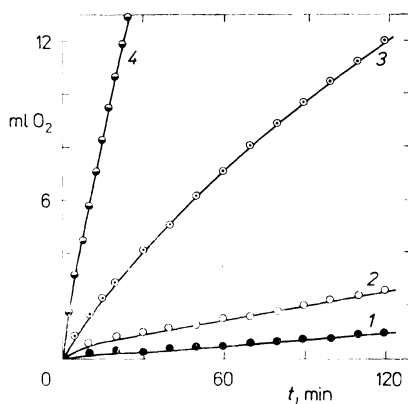
FIG. 2

Effect of concentration of Co(II) 2,4-pentane-dionate on the oxidation of cumene by di-oxygen. Solution in n-heptane saturated by dioxygen, 60°C, concentrations (mol l^{-1}): cumene 5, Co(II) 2,4-pentanedionate: *1* 0, *2* $1 . 10^{-6}$, *3* $1 . 10^{-5}$, *4* $1 . 10^{-4}$

of Co(II) 2,4-pentanedionate. In the conditions used, the oxidation rate was increased appreciably by addition of the catalyst in concentrations as low as 1 . . 10^{-6} mol l^{-1}. This indicates that during the study of the "uncatalyzed" oxidation, trace amounts of transition metals, which are inevitably present in the real reaction system, can actually exert a catalytic effect.
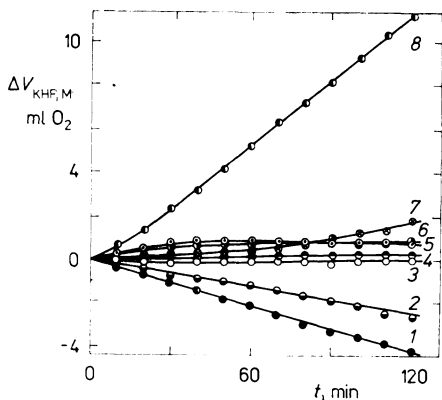

FIG. 3

Time dependence of the $\Delta V_{CHP,M}$ quantity (see text). Solution in n-heptane saturated by dioxygen, 60°C, concentrations (mol l^{-1}): cumene 5, metal 2,4-pentanedionates 1 . . 10^{-4}, CHP 0·1. Metal: *1* Co(II), *2* Mn(II), *3* Co(III), *4* Cu(II), *5* Mn(III), *6* Fe(III), *7* Cr(III), *8* VO(II)
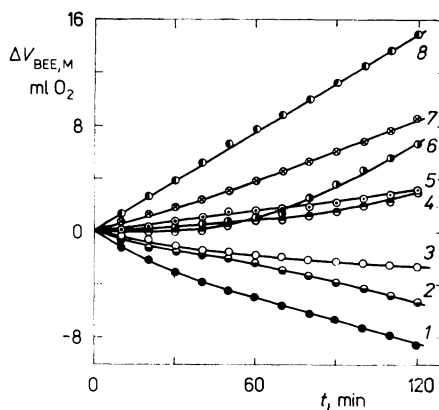
FIG. 4

Time dependence of the $\Delta V_{BEE,M}$ quantity (see text). Solution in n-heptane saturated by dioxygen, 60°C, concentrations (mol l^{-1}): cumene 5, metal 2,4-pentanedionates 1 . . 10^{-4}, BEE 0·1. Metal: *1* Mn(II), *2* Mn(III) *3* Co(II), *4* VO(II), *5* Fe(III), *6* Cr(III), *7* Cu(II), *8* Co(III)
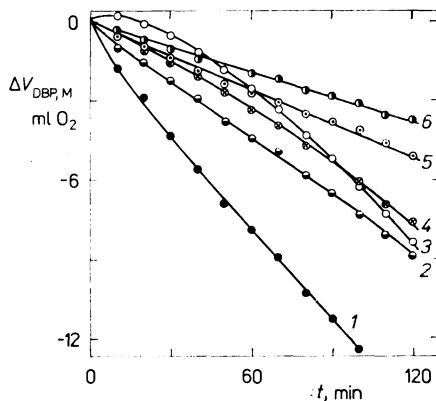

FIG. 5

Time dependence of the $\Delta V_{DBP,M}$ quantity (see text). Solution in n-heptane saturated by dioxygen, 60°C, concentrations (mol l^{-1}): cumene 5, metal 2,4-pentanedionates 1 . . 10^{-4}, DBP 0·01. Metal: *1* Mn(II), *2* Co(III), *3* Co(II), *4* Mn(III), *5* Cr(III), *6* Fe(III)

The increase in the reaction rate taking place during the oxidation is usually ascribed to the increasing concentration of the hydroperoxide, whose decomposition into radicals results in an increase in the initiation rate. The drop of the rate as observed, e.g., in the Co(II)-catalyzed reaction, can only be accounted for by a decrease in the catalytic activity of the catalyst. While studying the oxidation of tetralin by dioxygen[10,11] we were able to demonstrate that the decrease in the catalyst activity was related with the increasing concentration of tetralin hydroperoxide. This, naturally, rises the question of how cumene hydroperoxide, which prevails in the starting oxidation stage, affects the catalytic activity of the 3d-transition metal complexes. This effect is characterized in Fig. 3. In this figure, the $\Delta V_{CHP,M}$ value is plotted against time, $\Delta V_{CHP,M}$ being the difference between the volume of dioxygen taken up during the oxidation of cumene in the presence of both the catalyst, M, and cumene hydroperoxide (V_{CHP+M}) and the sum of volumes of dioxygen taken up in the presence of cumene hydroperoxide (V_{CHP}) and in the presence of the catalyst (V_M), respectively (Eq. (1)).

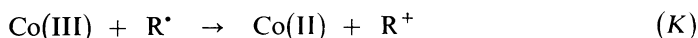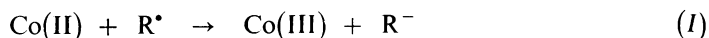$$\Delta V_{CHP,M} = V_{CHP+M} - (V_{CHP} + V_M) \qquad (1)$$

Figure 3 demonstrates that the catalytic effect of VO(II) 2,4-pentanedionate is stimulated by the presence of cumene hydroperoxide whereas that of the Co(II) and Mn(II) compounds is retarded. The catalytic activity of the remaining 2,4--pentanedionates studied, i.e. Cr(III), Fe(III), Mn(III), Cu(II) and Co(III), is only little affected by CHP.

The $\Delta V_{BEE,M}$ values, characterizing the effect of benzoin ethyl ether on the catalytic activity of the 2,4-pentanedionates, are plotted in Fig. 4. In comparison with CHP, the effect of BEE is more marked in all cases. A retarding effect is observed for Mn(II) and Co(II), which is qualitatively in accordance with the effect of CHP; in contrast to CHP, addition of BEE also retards the oxidation catalyzed by Mn(III). Stimulation of the catalytic effect by the presence of BEE is found for Co(III), Cu(II), Cr(III) and Fe(III). The autocatalytic reaction course in the presence of VO(II), i.e. increase in the catalytic activity during the oxidation, can be ascribed to the effect of the forming CHP.

Figure 5, in which the time dependence is plotted for the $\Delta V_{DBP,M}$ values, shows how the catalyzed oxidation of cumene is affected by dibenzoyl peroxide; decrease in the oxidation rate is observed for all the systems under study.

The results obtained indicate that in the oxidation of cumene by dioxygen, as in the oxidation of tetralin[10,11], the catalytic effects of the 3d-transition metal 2,4-pentanedionates cannot be explained in terms of a cycle comprising Eqs (D) and (E), the appreciable difference between the catalytic activities of Co(II) and Co(III) disagreeing with this concept. In the case of Co(II, III), the activation or deactivation of the catalyst can be ascribed to redox changes in the oxidation state

of cobalt (the catalytic activity of Co(II) can be expressed by reaction (E), which is an analogy of Fenton's reaction[14]). These redox changes can be induced by interaction of cobalt with free radicals formed by decomposition of the radical initiators. Thus, interaction of the free radical with Co(II) would result in a reduction of the catalytic activity (Eqs (I) and (J)), whereas reaction with Co(III) would result in generation of the catalyst (Eqs (K) and (L)).

$$Co(II) + R^{\bullet} \rightarrow Co(III) + R^{-} \qquad (I)$$

$$R^{-} + H^{+} \rightarrow RH \qquad (J)$$

$$Co(III) + R^{\bullet} \rightarrow Co(II) + R^{+} \qquad (K)$$

$$R^{+} + OH^{-} \rightarrow ROH \qquad (L)$$

Initiation by a cycle consisting of reactions (D) and (E) cannot be assumed for the redox pair Mn(III)–Mn(II) either, although the catalytic activity of the two oxidation states is not very different. In the case of cyclic change of the oxidation state the effect of the radical initiators on the two oxidation states should be similar, which — as Fig. 3 demonstrates — is not the case. The not very different catalytic activities of Mn(III) and Mn(II) indicate that the retarding effect cannot be explained in terms of the change in the manganese oxidation state. A possible explanation consists in a breakdown of the complex by oxidation of 2,4-pentanedione in the coordination sphere giving rise to manganese compounds containing hydroxy and acetate groups. This deactivation mechanism is also likely to play a role in oxidations catalyzed by cobalt(II) 2,4-pentanedionate[15].

Another possibility of catalyst deactivation due to the presence of a radical initiator rests in a blocking of reactant accessible coordination sites. Data of stability of complexes thus formed, however, are lacking in the literature. This mechanism is feasible for dibenzoyl peroxide, which has a retarding effect upon all of the studied catalyzed oxidations of cumene, and for which appreciable coordinating ability can be assumed.

REFERENCES

1. Hanotier J., Hanotier-Bridoux M.: J. Mol. Catal. *12*, 133 (1981).
2. Sheldon R. A., Kochi J. K.: *Metal Catalyzed Oxidations of Organic Compounds*, p. 315. Academic Press, New York 1981.
3. Pelikán P., Wurarthna S., Hronec M.: J. Mol. Catal. *19*, 17 (1983).
4. Howard J. A., Bennett J. E., Brunton G.: Can. J. Chem. *59*, 2253 (1981).
5. Emanuel N. M., Gál D.: *Modeling of Oxidation Processes*, p. 204. Akadémiai Kiadó, Budapest 1986.

6. Lewis F. D., Lauterbach R. T., Heine H. G., Hartmann W., Rudolph H.: J. Am. Chem. Soc. *97*, 1519 (1975).

7. Adams S., Guesten H., Steenken S., Schulte-Frohlinde D.: Justus Liebigs Ann. Chem. *1974*, 1831.

8. Huyser E. S.: *Free-Radical Chain Reactions*, p. 5. Wiley, New York 1970.

9. Howard J. A. in: *Free Radicals* (J. K. Kochi, Ed.), Vol. II, p. 3. Wiley, New York 1973.

10. Luňák S., Vašková M., Lederer P., Vepřek-Šiška J.: J. Mol. Catal. *34*, 321 (1986).

11. Luňák S., Vašková M., Lederer P.: Collect. Czech. Chem. Commun. *55*, 1015 (1990).

12. Swern D.: Org. Synth. *34*, 90 (1954).

13. Bryant B. E., Fernelius W. C.: Inorg. Synth. *5*, 115, 188 (1957).

14. Walling Ch.: Acc. Chem. Res. *8*, 125 (1975).

15. Vasvári G., Hajdu I. P., Gál D.: J. Chem. Soc., Dalton Trans. *1974*, 465.

Translated by P. Adámek.