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EFFECT OF THE METAL ATOM OF ACETYLACETONATES ON THE AUTOXIDATION OF CUMENE

S. K. Ivanov and Chr. Karshalykov

Institute of Organic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria

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The oxidation of cumene and a cumene-nitrobenzene (1:2) mixture at 60 °C in the presence of AIBN and acetylacetonates of Co(II), Cu(II), Fe(II), Fe(III), V(III), Cr(III), Mn(III) and MoO_2^{2+} has been investigated.

Было исследовано окисление кумола и смеси кумола с нитробензолом (1 : 2) при 60 °С и в присутствии АИБН и ацетил-ацетонатов Co(II), Cu(II), Fe(II), Fe(III), V(III), Cr(III), Mn(III) и MoO_2^{+2} .

The literature on the catalytic activity of acetylacetonates and the influence of the medium was surveyed in previous papers /1, 2/.

The aim of the present work was to study the effect of different metal ions in their complexes with acetylacetone on the rate of oxidation of cumene and the influence of nitrobenzene in the presence of AIBN as initiator. The rate of oxygen absorption was measured by a manometric apparatus.

As Fig. 1a shows, the kinetic curves have a linear character from the beginning (with the exception of Cr and V acetylacetonates) and induction periods are practically absent.

Initiation by cumyl hydroperoxide (CHP), present as an impurity at the initial moment, or by CHP formed in the process of oxidation was found to be negligible. From experiments on the decomposition of CHP in benzene, it can be seen that some catalysts (Fe^{2+}, Fe^{3+} and Cu^{2+} acac) do not decompose CHP at all. But these catalysts along with others are active in the oxidation of cumene.

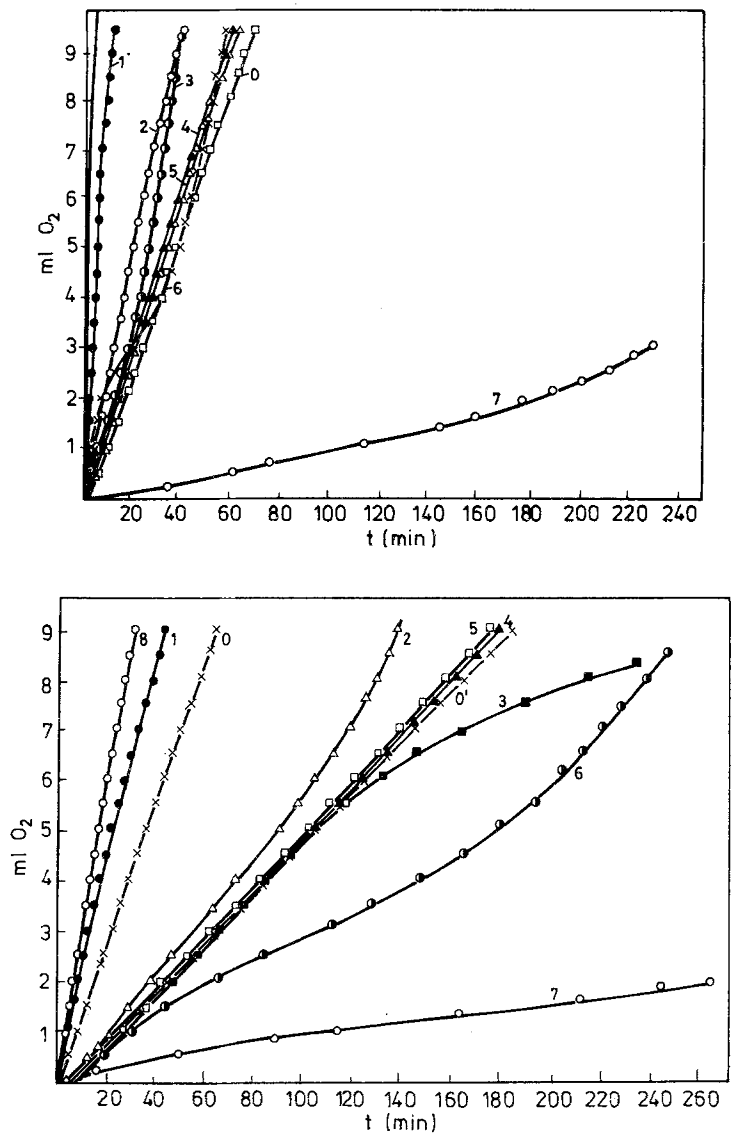

Fig. 1. Oxidation at 60 °C in the presence of AIBN (5x10^{-2} mol/l) and acetylacetonate complexes (4 x 10^{-3} mol/l) of (1) Co(II); (2) Cu(II); (3) Cr(III); (4) Fe(III); (5) Fe(II); (6) V(III); (7) MoO_2^{2+}; (8) Mn(III). (a) cumene, (b) cumene-nitrobenzene (1 : 2). With AIBN only (O) cumene, (O') cumene-nitrobenzene

The experimental results indicate an acceleration of oxidation in the simultaneous presence of AIBN and the catalysts (with the exception of $MoO_2(acac)_2$), relative to oxidation in the presence of sole AIBN (Fig. 1, curves 0 and 0'). These data show that the increase of the rate of oxidation is due to the ability of these catalysts to form complexes with the oxygen molecule and thus to activate oxygen and its interaction with the hydrocarbon according to the scheme:

$$Me^{n+}(acac)_n + O_2 \overset{K_p}{\rightleftarrows} Me^{n+}(acac)_n \ldots O_2 \qquad (1)$$

$$Me^{n+}(acac)_n \ldots O_2 + RH \xrightarrow{k_{i2}} Me^{n+}(acac)_n \ldots \dot{O}_2H + \dot{R} \qquad (2)$$

$$Me^{n+}(acac)_n \ldots \dot{O}_2H + O_2 \xrightarrow{k_{i3}} Me^{n+}(acac)_n \ldots O_2 + H\dot{C}_2 \qquad (3)$$

The solution of the acetylacetonates in cumene change their color very quickly (within 1-2 min) for the color of the higher valency. This fact supports the following equilibrium:

$$\underset{(I)}{Co^{2+}(acac)_2 \ldots O_2} \rightleftarrows Co^{3+}(acac)_2 \ldots O_2^-$$

If we accept this mechanism, which corresponds to Michaelis-Menten kinetics (Fig. 2), the constants of interaction of complex (I) with the hydrocarbon as well as equilibrium constant K_p can be calculated. If $[Me^{n+}(acac)_n] > [O_2]_{sol}$, i.e. when the total oxygen in the system is bound to the catalyst (part of the catalyst is not dissolved at the begining of the process) the following expression

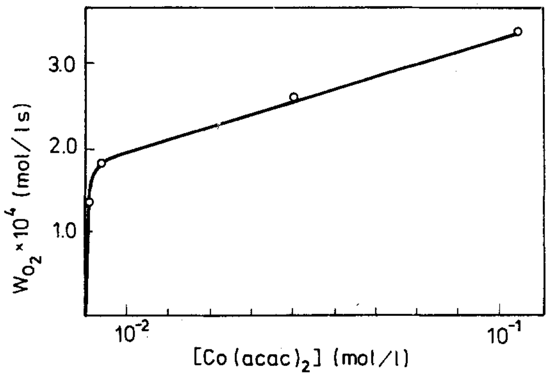

Fig. 2. Dependence of the oxidation rate on the initial concentration of Co(acac)2 in the oxidation of cumene at 60°C, [AIBN] = 5×10^{-2} mol/l

can be written for W_i:

$$W_i = \frac{k_i K_p [Me(acac)_n] [O_2]_s [RH]}{1 + K_p [Me(acac)_n]} \tag{4}$$

where $k_i = k_{i2} + k_{i3}$ is the overall rate constant for reactions (2) and (3); K_p is an equilibrium constant. If $K_p[Me(acac)_n] \gg 1$ we have $W_i = k_i [O_2]_s [RH]$.

Carrying out two experiments with $Co(acac)_2$ for which (a) $[Co(acac)_2] \gg [O_2]_{sol.}$ and (b) $[Co(acac)_2] \sim [O_2]_{sol.}$ we were able to determine separately the values of k_i and K_p (Table 1). The data show the appreciable influence of the metal ion of the catalyst on the oxidation rate.

If the rate constants for the interaction of complex (I) with cumene, and that of cumylperoxy radicals with cumene are compared, it can be seen that the rate constant of chain propagation $RO_2^{\bullet} + RH \longrightarrow$ at 65° is 0.56 /5/, which is greater by two orders of magnitude than the value of k_i determined by us for the reaction:

$$Co(acac)_2 \ldots O_2 + RH \xrightarrow{k_i} HO_2^{\bullet} + R^{\bullet} + Co(acac)_2 \tag{5}$$

Table 1

Maximum oxidation rate W_o and rate of initiation ΔW_i. Oxidation of cumene and a mixture cumene with nitrobenzene at 60 °C in the presence of $4x10^{-3}$ mol/1 acetylacetonate and $5x10^{-2}$ mol/I AIBN

	Cumene				Cumene/nitrobenzene(1:2)			
Acac complex	$W_o x10^5$ (mol/l s)	$\Delta W_i x10^6$ (mol/l s)	$k_i x10^3$ (l/mol s)	K_p (l/mol)	$W_o x10^5$ (mol/l s)	$\Delta W_i x10^6$ (mol/l s)	$k_i x10^3$ (l/mol s)	K_p (l/mol)
MoO_2	0.4	0.0	-	-	0.1	0.0	-	-
V^{3+}	4.8	3.2	-	-	0.8	0.1	-	-
Cr^{3+}	7.4	8.9	-	-	0.8	0.1	-	-
Mn^{3+}	24.6	105.9	-	-	4.9	13.2	-	-
Fe^{3+}	2.5	0.2	-	-	0.8	0.1	-	-
Fe^{2+}	2.5	0.2	-	-	0.8	0.1	-	-
Co^{2+}	18.6	39.4	1.1	115	3.0	10.3	0.7	134
			1.1[a]	151[a]				
Cu^{2+}	4.3	2.3	-	-	1.8	1.5	-	-
AIBN	2.2	$W_i = 0.8$	-	-	0.8	$W_i = 0.2$		

[a] Calculated by our method from the data of Ref. /3/; $\Delta W_i = W_i^{cat., AIBN} - W_i^{AIBN}$;

$W_i^{cat., AIBN}$ -rate of initiation in the presence of both catalyst and AIBN.

W_i^{AIBN} -rate of initiation in the presence of AIBN only

Cumylperoxy radicals, due to the positive induction effect of the alkyl group on the oxygen atoms, will be significantly more active in the formation of the activated complex with cumene and thus the abstraction of the H-atom from the latter will be facilitated. On the other hand, because of the formation of a $\delta - \pi$ bond, the electron density on the oxygen molecule in complex (I) will be shifted towards the metal ion and thus reaction (5) will proceed more slowly. This explains the insignificant decrease of k_i under the action of a polar solvent such as nitrobenzene. K_p has a somewhat greater value in the cumene-nitrobenzene mixture and the peculiar green color of Co^{3+} appears significantly faster than in cumene. It is obvious that in this case the increase of the dielectric constant facilitates both electron transfer to the oxygen molecule and the polarization of complex (I), which explains the decrease of the oxidation rate.

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