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THE NATURE AND IMPORTANCE OF HYDROCARBON-OXYGEN-METAL COMPLEX INTERACTION FOR C-H AND C-C BOND ACTIVATION

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<u>Abstract</u> - The understanding of the oxidation reaction mechanism of hydrocarbons, particularly the reaction initiation step, can be achieved in a model system. In a hydroperoxide-free hydrocarbon the oxidation reaction is initiated as the result of metal complex--hydrocarbon or metal complex - oxygen - hydrocarbon interaction. The reactivity of intermediate complex strongly depends on solvent properties.

## INTRODUCTION

The understanding of the oxidation reaction mechanism of hydrocarbons is essential both in problems of selective transformation to the required products and in problems of the resistance of organic materials (polymers) containing the C-H and C-C bonds accessible to the action of molecular oxygen or oxidizers as well as of other factors, such as temperature, pressure, trace amounts of metal ions and solvents of various polar and donor--acceptor properties.

The present state of knowledge makes possible satisfactory explanation of the hydrocarbon oxidation reaction mechanism catalyzed by transition metal ions in liquid phase. This mechanism is usually treated as a free-radical mechanism, analogical to that describing the high-temperature uncatalyzed oxidation reactions (Refs.1-5). The catalytic decomposition of hydroperoxides is of essential importance in this mechanism (1,2):

м <sup>п+</sup>	+	$ROOH \rightarrow (ROOH \cdots M^{n+}) \rightarrow RO' + M^{n+1} + OH^{-1}$	(1)
м <sup>n+1</sup>	+	$ROOH \longrightarrow (ROOH \cdots M^{n+1}) \longrightarrow RO_{2}^{*} + M^{n+} + H^{+}$	(2)

The formation of intermediate complexes between the catalyst and hydroperoxide which are decomposed later yielding free radicals, was confirmed by both kinetic (Refs.  $\overline{6}$ -9) and spectroscopic (Refs. 10,11) methods. A computer analysis of the model tetraline autooxidation reaction (Ref. 12) performed by assuming a possibility for the formation of a catalyst-hydroperoxide intermediate complex led to the elucidation of several important experimental facts, demonstrating thus the validity of the approved assumption. Nevertheless, it should be noted that it is not sufficient to assume only one mechanism for description of the initiation effect for the hydrocarbon oxidation reaction, since this requires the presnce of hydroperoxides in the hydrocarbon. Meanwhile it is well known that in some cases the reaction is rapidly initiated also when the hydrocarbon is very throughly purified from hydroperoxides (Refs. 13,14) or, if hydroperoxide is not formed during the autooxidation process (Refs. 15,17), or, if the catalyst does not decompose the hydroperoxide (Refs. 18-21). Under such circumstances the hydrocarbon oxidation reaction may be initiated by direct activation of the parent substances (hydrocarbon and/or molecular oxygen) by the transition metal complex acting as a catalyst. Many authors noted this type of interactions (Refs. 22-24). In the case of olefins one postulates a mechanism based upon the activation of the hydrocarbon molecule by the metal complex which facilitates the reaction with molecular oxygen leading to the formation of radical or molecular products (Refs. 25-28). For the catalyst based upon the metal complexes of high oxidation potentials

For the catalyst based upon the metal complexes of high oxidation potentials a mechanism based upon splitting of the C-H bond, formation of the RH radical and reduced catalyst form was suggested. This mechanism is particularly effective in the case of Co(III) and Mn(III) carboxylate complexes in highly polar carboxylic acids, such as CF,COOH (Refs. 30,31). For the alkylaromatic hydrocarbons the oxidation reaction is initiated as a result of  $\Im$  electron transfer from the RH molecule to the catalyst (Refs. 32,33), leading to the formation of the cationic radical "RH which, as a result of further rearrangements, yields the R radical and  $\text{H}^+$ . Such an activation mechanism of the aromatic hydrocarbon molecules of various ionization potentials was suggested on the ground of spectroscopic studies (Ref.34) which demonstrated the existence of the following equilibria (3):

existence of the following equilibria (3):  $kH + Co(III) \rightarrow \begin{bmatrix} RH - \cdots Co(III) \\ (b) \end{bmatrix} \rightarrow k + H^{\dagger} + Co(III) (3)$ (3)

ion in the complex or the hydrocarbon ionization potential do not indicate any possibility for the formation of a charge-transfer complex, the hydrocarbon oxidation reaction may be initiated by activation of the molecular oxygen. The mechanism of such a process consists of at least two important stages: i) activation of molecular oxygen by coordination to the metal complex, ii) reaction between activated oxygen and the parent substance (hydrocarbon). Typical examples of such reactions may be the autooxidation reactions of styrene (Ref. 15), ∝-methylstyrene (Ref.16), cumene (Ref.22), cyclohexene (Ref.21) and ethylbenzene (Ref. 37) to their corresponding hydroperoxides. However, activation of the molecular oxygen by the metal complex is not always essential for the autooxidation process and is very often masked by other reactions, above all, by the catalytic decomposition reaction of hydroperoxide with the same metal complex involved. The generation of free radicals as a result of the catalytic hydroperoxide decomposition reaction (reactions 1,2) proceeds as a rule with much higher rates as compared to the effects of a direct reaction between the hydrocarbon and oxygen activated by the metal complex. This fact renders difficult investigation of the catalytic systems activating the molecular oxygen and does not allow to determine explicitly both the electron structure of the coordinated oxygen and its part in the hydrocarbon oxidation reactions. Attempts to elucidate the hydrocarbon oxidation mechanism undertaken by many authors indicate on one hand how complex is the process and, on the other hand, how important is the investigation of elementary reactions involved in the process and particularly of these reactions which are essential for initiation of the oxidation process.

The low-temperature oxidation processes of hydrocarbons in the presence of transition metal complexes, or, under conditions in which the formation of hydroperoxides and their free-radical decomposition is not very probable, are of particular interest. Such conditions correspond to actual conditions under which the hydrocarbon or an organic compound in general (in the gaseous or condensed phase), containing small quantities of metal ions  $(10^{-4} - 10^{-6} \text{ M})$  is exposed to oxygen (air). In order to apprehend the stability and resistance to oxidation of certain organic compounds and unusual oxidizability of other compounds it is necessary to elucidate the nature of interactions appearing in such a systems. The nature of these interactions could not always be considered in terms of one of the generally approved concepts of the metal-oxygen, metal-hydroperoxide or metal-olefin bond and quite frequently it requires taking into consideration much weaker interactions, e.g. ion-ionic radical, ion-dipole, dipole-dipole and taking into account the function of the solvent (for processes occurring in the liquid phase). The above mentioned relationships may be investigated only in model systems, under suitable experimental conditions, such as: i) electron and molecular structure of the catalyst, ii) reactant concentration and degree of parent substance conversion, iii) type of solvent, iv) temperature. In the real system which contains the hydrocarbon, oxygen and metal complex compound (e.g. cobalt, manganese) the oxidation reaction and generation of free radicals may be initiated according to one or more, or very often to all the following reactions:

RH +	$0_{o} + Co(II)$	$\underline{\underline{\mathbf{n}}}_{\mathbf{i}},1$			(4)
RH +	C <sub>o</sub> (III)	$\underline{\mathbf{R}_{i,2}}$			(5)
ROOH	+ Co(II)/Co(III)	$-\frac{R_{i,3}}{R}$	free radicals		(6)
ROOH		<u></u>			
					(7)
RH +	°2	$\frac{R_{i,5}}{\Delta}$			(7a)
-	•• •• ••	. —		0	

Depending on the reaction conditions, the contributions of particular initiation mechanisms (4-7a) may differ considerably and their shares in the overall initiation reaction rate R<sub>1</sub> (8) may be different.  $R_i = R_{i,1} + R_{i,2} + R_{i,3} + R_{i,4} + R_{i,5}$  (8) The initiation rate affects the overall rate (R) of the hydrocarbon autooxidation reaction (9):

 $R = R_{i}^{0.5} k_{p} [RH] (2k_{t})^{-0.5}$ where: k - propagation reaction rate constant  $k_{t}^{p}$  - termination reaction rate constant (9)

During the initial period of the oxidation process carried out under mild conditions when the hydrocarbon is free from hydroperoxides, two formation mechanisms of free radicals are possible (reactions 4,5), whose contribu-tions are mainly determined by the electron structure of the catalyst. As the hydroperoxide becomes accumulated, the contribution and rate of the initiation reaction increase according to reactions (6) and (7) which might limit the maximum oxidation reaction rate (R). The rate of the non-catalyzed reaction between the hydrocarbon and molecular oxygen (7a) at low temperatures is very low in comparison to the rates of other initiation reactions (4-7) and its contribution to the overall initiation rate may be neglected.

EFFECT OF THE CATALYST ELECTRON STRUCTURE ON THE INITIATION OXIDATION REACTION OF HYDROCARBONS

The effect of the metal complex electron structure on the initiation reaction rate will be discussed on the ground of two model systems: 1) homogeneous oxidation reaction of cyclohexene by oxygen with Co(octanoate), Co(acac), (Cosalen) (OH)(OC<sub>6</sub>H<sub>0</sub>) and  $[Co(OAc)(OCH_3)_2]_x$ (Refs. 40,41) as catalysts in various solvents (S), and 2) catalytic oxidation reaction of the oleate ligand in Co(oleate)<sub>2</sub>.<sup>2</sup>H<sub>2</sub>O by oxygen at room temperature in the solid phase.

## Catalytic oxidation reaction of cyclohexene Studies of the model system

 $+ 0_2 \frac{Co(11)/Co(111); S; 20-45°C}{p_{0_2}100-620 \text{ mmHg}}$ 

where  $Co(III)-Co(octanoate)_2$ ;  $Co(acac)_2$ ;  $Co(III)-(Cosalen)_2(OH)(OC_6H_0)$ ;  $[Co(OAc)(OCH_2)_2]_2$ ; S - solvent: PhNO<sub>2</sub>; PhF, PhCl, PhBr, PhOCH<sub>2</sub>, PhOPh and PhH and cyclohexane made it possible to elucidate the effect of the cobalt catalyst electron structure, oxygen concentration and solvent structure on the oxidation reaction rate during the induction period ( $R_{ind}$ ) and on the maximum oxidation reaction rate ( $R_{max}$ ) after the induction period. The reac-tion was carried out in the equipment provided with an automatic oxygen feeding rate recorder (in 0.05 cc portions) at constant pressure accurate to  $\pm$  0.3 mm Hg (Ref. 42). The reactant concentration variation range was: cyclohexene 1-8 M, cobalt compound  $1 \times 10^{-3} - 4 \times 10^{-5}$  M (Ref. 43) in order to eliminate the effect of the limiting reaction rate and reaction inhibition by the catalyst. The data summarized in Table 1 indicate that the catalysts applied do not, in fact, participate in the termination reactions.

TABLE 1. Oxidation reaction rate for cyclohexene (4.94 M) in benzene at 45°C initiated by the cobalt catalyst ( $R_{cat}$ ), AIBN ( $R_{AIBN}$ ) and by a mixture of the catalyst and AIBN ( $R_{cat}$ , AIBN)

Catalyst	Cyclohexene <sup>R</sup> cat	$\begin{array}{c} \textbf{oxidation read} \\ \textbf{R}_{AIBN} & \times 10^{-6} \\ (\text{mol } 1^{-1} \text{ s}^{-1}) \end{array}$	etion rate <sup>R</sup> cat,AIBN
$Co(octanoate)_2$ (Cosalen) <sub>2</sub> (OH)(OC <sub>6</sub> H <sub>9</sub> )	14.5 6.1	7.0 6.9	17.1 9.2
$\left[ Co(octandate)_2 \right] - 3.7x10^{-5}M;$ [AIBN] - 9.76x10 <sup>-2</sup> M	[(Cosalen) <sub>2</sub> ((	он)(ос <sub>6</sub> н <sub>9</sub> )]- 2.	.7×10 <sup>-5</sup> м;

The effect of partial oxygen pressure on the initiation rate of the oxidation reaction of cyclohexene catalyzed by various cobalt complexes is illustrated in Table 2.

TABLE 2. Effect of the catalyst electron structure and partial oxygen pressure( $P_{0_2}$ ) on the induction period and maximum rate ( $R_{max}$ ) of the cyclohexene oxidation reaction (4.94 M) at 30°C

Catalyst	P <sub>02</sub> [mm Hg]	Induction period [min ]	R <sub>max</sub> [M s <sup>-1</sup> ]10 <sup>5</sup>	solvent
_	620	720	_	benzene
Co(octanoate) <sub>2</sub> (4.0)	620 100	15.5 28.5	2.80 2.76	11
Co(acac) (5.8)	610 125	8.5 12.0	4.25 3.70	14 11
Co salen (3.2)	625	600	-	nitrobenzene
(Cosalen)2 <sup>0</sup> 2 (3.5)	620	600	-	**
(Cosalen)(3.2)+ + ROOH (8.5)	620	48.0	1.12	H
(Cosalen) <sub>2</sub> (OH)(OR) (2.85)	615 120	72.0	0.72	benzene
[co(0Ac)(0CH <sub>3</sub> ) <sub>2</sub> ] <sub>x</sub> (1.8)	625 110	6.0 6.2	4.50 4.52	acetic acid

 $R = C_6 H_9$ ; concentrations in brackets [M]x 10<sup>4</sup>

The Co(II) complexes Co(octanoate), and Co(acac), of a d<sup>7</sup> electron configuration exhibit an increase in catalytic activity with the increasing partial oxygen pressure which is manifested by shorter induction periods. This is evidence of a considerable contribution of the Co(II) - molecular oxygen interaction in the initiation of the oxidation reaction during the induction period (reaction 4). For (Cosalen) and its oxidized modification (Cosalen).<sup>0</sup> the induction period is very long (more than 600 min ) which may be explaided as due to irreversibility of the oxygen bonding process (Cosalen), i.e. elimination of the catalyst from the reacting system. The inert salen complex may be activated by adding small amounts of cyclohexene hydroperoxide (C<sub>6</sub>H<sub>0</sub>O0H) which leads to the formation of the active form (Co(III) salen)<sub>2</sub>(OH)(OC<sub>6</sub>H<sub>9</sub>).

The Co(III) complexes of a d<sup>6</sup> electron configuration (Cosalen)<sub>2</sub>(OH)(OC<sub>6</sub>H<sub>9</sub>) and  $[Co(OAc)(OCH_3)_2]$  initiate very effectively the oxidation reaction although they do not exhibit any changes in catalytic activities at various partial oxygen pressures. This leads to a conclusion that for the Co(III) complexes the oxidation reaction is initiated as a result of the Co(III)-RH interaction according to the scheme (3).

# Effect of partial oxygen pressure

The induction period of the cyclohexene oxidation reaction catalyzed by the Co(II) complexes depends to a high degree on partial oxygen pressure (Table 2) which indicates that in the initial oxidation period reaction (4) is predominant. Taking into account equations (8) and (9) one can assume that during the induction period and a very low degree of hydrocarbon conversion (below 0.02% M) the contribution of other reactions is insignificant and constant for a given system (10).  $R_{i,1} > R_{i,2} + R_{i,3} + R_{i,4} + R_{i,5}$  (10) Under such circumstances the oxidation reaction rate during the induction

kT ln k' = f ( $\epsilon$ ,  $\mu_i$ ,  $q_i$ ,  $\alpha_i$ ,  $r_i$ ) +  $\sum \mathcal{Y}_i$  + const. (12)where: k and T are the Boltzmann constant and temperature, respectively, k' is the reaction rate constant in a given solvent. The first term of the relationship (12) describes the unspecific contribution of solvation interactions whose magnitudes depend on the dielectric constant of a solvent  $\in$ and also on the dipole moments  $\mu$ , quadrupole moments q, polarizability  $\alpha$  and molecular radii r of the reacting molecules and intermediate complex. On the other hand, the second term describes the contribution of specific interactions consisting in the formation of complexes with the hydrogen bonds or EDA complexes. Sometimes, particularly for the reactions of non--polar reactants and intermediate complex, one should also consider the effect of internal solvent pressure (Ref. 47). The formation of complexes with the hydrogen bonds in aprotic solvents may be neglected. Then the expression  $\sum \varphi_i$  in equation (12) may be interpreted as a sum of energies between the donor solvent molecules and reactants as well as the intermediate complex. The effect of the solvent dielectric constant on the autooxidation reaction rate of hydrocarbons (without catalysts) was investigated by several authors (Refs. 44-46). These studies demonstrated that both the autooxidation reaction rate (R) and constant k  $(2k_{\perp})^{-0.5}$  increase with the increasing  $\in$  of the solvent. This applies particularly to solvents of high dielectric constants in which polar structure of the intermediate complex may contribute considerably to the chain prolongation reaction (13).

Effect of solvent The effect of solvent on the rate of oxidation reaction taking place in solution may be described by the following general relationship:

rate for cyclohexene (4.94 M) during the induction period (for 0.02% M degree of conversion). The reactions were carried out at  $30^{\circ}$ C in benzene with Co(octanoate)<sub>2</sub> -  $3.8 \times 10^{-1}$  M as catalyst.



period  $(R_{ind})$  and for a very low degree of conversion will depend mainly on the rate of trimolecular initiation reaction (4) and may be expressed

by equation (11):

3. Effect of solvent dielectric constant  $\boldsymbol{\varepsilon}$  on the (4.94 M) during the induction period -  $R_{max}$  (for 0.02% degree of conversion) and after the induction period  $R_{max}$  and on the  $k_p(2k_t)^{-0.5}$  constant at 30°C. TABLE

	Co(octanoate	e)2	(Cosalen) <sub>2</sub> (OH	()(oc <sub>6</sub> II <sub>9</sub> )	$k_{\rm p}(2k_{\rm t})^{-0.5}$	· · · · · · · · · · · · · · · · · · ·
Solvent	Rind Ms-1	]10 <sup>6</sup> Rmax	Rind [M s-	1]10 <sup>6</sup> max	[ <sub>M</sub> -0.5 s-0.5] 10 <sup>3</sup>	ω
PhNO2	4.9 (1.1)	48.5 (11)	4.2 (1,1)	18.7 (4.4)	4.3	34.7
PhF	4.0 (1.2)	32.0 (9.7)	2.1 (0.6)	8.6 (2.6)	3.3	5.4
НЧА	6.5 (1.9)	27.5 (8.1)	1.7 (0.5)	7.2 (2.1)	3.4	2.3
с <sub>6</sub> н <sub>12</sub>	5.1 (1.9)	16.0 (6.0)			2.65	2.02
[Co(octan values R	loate)2]- 3.8 1 1nd/kp(2kt)-0.	10 <sup>-4</sup> M, [[Cosal. 5 and N <sub>max</sub> /k	L еп) <sub>2</sub> (ОН)(ОС <sub>6</sub> Н <sub>р</sub> (2k <sub>t</sub> ) <sup>-0.5</sup> 10	1 19]-2.85 10 13 are given	) <sup>-4</sup> M; in brackets th respectively.	

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<sup>k</sup>p

A similar relation between the reaction rate and dielectric constant appears in the reaction catalyzed by Co(octanoate)<sub>2</sub> after the induction period (R<sub>max</sub>) and (Cosalen)<sub>2</sub>(OH)(OC<sub>6</sub>H<sub>9</sub>) in both reaction periods (R<sub>ind</sub> and R<sub>max</sub>), (see Table 3).

R' + ROOH

R:H

δ+ κ• •00R

1 бн:оок

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RH + ROO"

(13)

Effect of solvent ionization potential $\rm I_D$ on the catalytic oxidation reaction rate of cyclohexene (4.94 M) during the induction period - $\rm R_{ind}$ (for 0.02% degree of conversion) and after the induction period - $\rm R_{max}$ and on the $\rm k_p^{-0.5}$ constant at 30°C
<b>.</b>
TABLE

	Co(octanos	ate) <sub>2</sub>	(Cosalen) <sub>2</sub> (OF	(00 <sup>6H</sup> 9)	$k_{p}(2k_{t})$ -0.5	u <sup>I</sup>
Solvent	Rind [M s <sup>-1</sup> ]	и <sup>в</sup> тах 10 <sup>6</sup>	Rind M s-1-	R <sub>max</sub> ]10 <sup>6</sup>	$[M^{-0.5} = -0.5] 10^3$	eV
PhC1	4.2 (1.3)	31.8 (9.9)	2.2 (0.7)	8.55 (2.7)	3.2	9.09
PhBr	4.3 (1.4)	31.0 (10)	2.0 (0.7)	8.10 (2.7)	3.0	8.89
PhOMe	5.8 (2.8)	30.5 (14.5)	1.9 (0.9)	8.25 (3.9)	2.1	8.22
рори	5.5 (3.0)	28.5 (16)	1.8 (1.0)	8.06 (4.5)	1.8	8.10
		-			-	

Catalyst concentrations and symbols applied are given in a legend under TABLE 3.

Variations of the reaction rate in particular solvent are even larger than it might result from relatively small changes of the k  $(2k_{\perp})^{-0.5}$  constant. The values of the k  $(2k_{\perp})^{-0.5}$  constants in particular Solvents were deter-mined by the Ingold method (Ref.48) using AIBN as initiator and  $\beta$ -naphtol as inhibitor, taking advantage of extrapolation of the relationship log k  $(2k_{\perp})^{-0.5} = f(1/T)$  down to 30°C. For instance, for the Co(octanoate) catalyst R in nitrobenzene and cyclohexane is 48.5 and 16.0x10<sup>-0</sup> M respectively, whereas the k  $(2k_{\perp})^{-0.5}$  constants differ to a lesser extent and are 4.3 and 2.65x10<sup>-3</sup> M<sup>p-0.5</sup> s<sup>-0.5</sup>, respectively. This effect may be explained as due to an increase in the initiation reaction rate in polar solvents as indicated by an increase in R/k  $(2k_{\perp})^{-0.5}$ , proportional to the initiation reaction rate  $(R_{\perp})^{0.5}$ . The values of R/k  $_{p}(2k_{\perp})^{-0.5}$  are given in brackets. brackets.

The results summarized in Tables 3 and 4 indicate that polar structures in the intermediate complexes are very essential for initiation of the oxidation process according to mechanisms (5) and (6):

$$RH + Co(III) \longrightarrow \begin{bmatrix} {}^{\text{(H)}} \\ R \\ R \\ R \\ H^{\text{+}}, H^{\text{+}}, Co(II) \end{bmatrix} \xrightarrow{R_{12}} R^{\text{+}} H^{\text{+}} + Co(II) \qquad (14)$$

$$ROOH + Co(II) \longrightarrow \begin{bmatrix} ROOH \cdots - Co(II) \\ ROOH \\ ROOH \\ RO^{\text{+}}, OH^{\text{-}}, Co(III) \end{bmatrix} \xrightarrow{R_{13}} RO^{\text{+}} + Co(III)OH \qquad (15)$$

On the other hand, in the case of Co(octanoate), the effect of solvent on the reaction rate during the induction period  $(R_{ind})$  is positively different. In solvents of higher dielectric constants both the rate in the induction period  $(R_{ind})$  and the value of  $(R_{ind})/k(2k_{\perp})^{-0.5}$  are lower than their cor-responding values in solvents of lower dielectric constants, for instance in nitrobenzene and benzene. This is indicative of a different reaction initiation mechanism during the induction period. This effect may be explained as due to stronger solvation of the parent substances by the polar solvent than solvation of the intermediate complex in the initiation reaction (16).

$$RH + 0_{2} + Co(II) \longrightarrow \begin{bmatrix} RH \cdots 0_{2} \cdots Co(II) \\ R, H0_{2}^{\bullet}, Co(II) \end{bmatrix} \xrightarrow{R_{11}} R^{\bullet} + H0_{2}^{\bullet} + Co(II) \quad (16)$$

For the solvents of low and similar dielectric constants  $\in$  and dipole moments  $\mu$  one could find out the contribution of specific solvent interactions (second term of equation 12). This effect results from electron donor properties of the solvent (whose measure is the ionization potential  $I_D$ ) and from the free-radical nature of the initiation reaction. This is evidenced by substantial differences between the relationship of the reaction rate R and also the values of R  $_{max}/k_{p}(2k_{t})^{-0.5}$  versus the ionization potentials of the solvent and that found for the  $k_{p}(2k_{t})^{-0.5}$  constants.

<u>Catalytic oxidation reaction of ligand in  $Co(oleate)_2$ </u> Co(II) oleate may be considered a model compound for investigating interactions in the Co(II) - olefin - oxygen system (reaction 4) in solid phase. The olefin fragment in the CH<sub>3</sub>-(CH<sub>2</sub>)<sub>2</sub>CH=CH-(CH<sub>2</sub>)<sub>2</sub>COO<sup>-</sup> ligand causes that within the Co(II)(oleate)<sub>2</sub> molecule under oxygen favourable conditions for the formation of a ternary intermediate complex may be created (Fig. 2). The Co(II) ion in Co(oleate)<sub>2</sub>  $\cdot$  nH<sub>2</sub>0, (n  $\leq$  4) has its ligand environment typical of the homogeneous oxidation catalyst. The reaction between Co(II)oleate<sub>2</sub> and oxygen is fairly slow in the solid phase which makes possible following of particular reaction stages and particularly the initiation reaction. However, this process is very complex as indicated by changes in weight of the sample during reaction with oxygen (Fig. 3). Co(oleate), 3H,0 prepared under argon is stable but under oxygen it reacts without any induction period. This reaction is accompanied by changes in the electron spectrum (in CHCl<sub>3</sub> or in Nujol) indicating a change in the ligand field symmetry from octahedral to tetrahedral (Table 5). At the same time a new band appears at about 36800 cm<sup>-1</sup>, which may be assigned to the  $[Co(II)-0_2]$  charge-transfer









Fig. 3. Changes in weight of Co(II) oleate during reaction with oxygen

This band disappears after more than ten hours and a new band appears at about 16000 cm<sup>-1</sup> which is typical of Co(III) in the octahedral oxygen ligand environment. It is highly probable that a  $[Co_2(III)Co(II)0(oleate)_{0}]$  complex is formed as one of the stable forms of the active intermediate complex. <sup>1</sup>H nmr studies of Co(oleate)<sub>2</sub>·2H<sub>2</sub>O before the reaction and after 48 hours of reacting with oxygen suggest that an olefin (ally1) group participates in the active complex. This is indicated by a change in the band intensity ratio for the olefin (5.24 ppm) and methyl (0.86 ppm) protons after 48 h reaction from 0.63 to 0.012. These data suggest that the reaction is initiated as a result of synergetic interaction of oxygen with the olefin group and the Co(II) ion without participation of the hydroperoxide and its decomposition products. In the later period this reaction is very complex, mainly because it involves the intermediates of the oleinic ligand oxidation products (Table 6). This process is known and utilized in autooxidative polymerisation and drying of paints (38).

	Band position*)	(cm <sup>-1</sup> ); £ (1 M <sup>-</sup>	.1 cm <sup>-1</sup> ) and assign	lement	
Co(II) oleate sample		${}^{4}\mathbf{T}_{2g}^{(\mathrm{F})} - {}^{4}\mathbf{T}_{1g}^{(\mathrm{F})}$	$^{4}T_{1}(P) \xrightarrow{4} A_{2}$ (Td)	<sup>4</sup> T <sub>1</sub> (F) - <sup>4</sup> A <sub>2</sub> (Td)	c.T. [co(II)-02]
crude moisture compound in CHCl <sub>3</sub> solution	19200 (16.8)	8350 (3.1)	17600 (sh)	7100 (sh)	I
dried in Ar atmosphere, in CHCl <sub>3</sub> solution	19200 (24.5)	8350 (5.1)	17700 (24)	7100 (5.0)	
after 3 h exposure in oxygen and dissolution in $CHCl_3$ or in Nujol film	19200 (32.6)	8300 (5.2)	17700 (32.9)	7100 (5.0)	36800 (90.0)
after 20 days exposure in oxygen in Nujol film	1 <sub>726</sub> 1 <sub>8</sub>	(° <sup>u</sup> )	<sup>1</sup> T <sub>16</sub>	$A_{1g}$ (0 <sub>h</sub> )	c.T.
	28600 (s)		1.6400	(m)	42000 (vs)
<pre>[eo2 (III)co(II)0(0Ac)6(H0Ac)3]</pre>	29240 (2880)		16390 (;	358)	42700 (3 10 <sup>4</sup> )

 $n \twoheadrightarrow \mathfrak{N}^{\bigstar}$  transitions in carbonyl group omitted

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TABLE 5. Electronic absorption spectra of cobalt(II) oleate and products of its reaction with oxygen

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TABLE 6. GIC analysis of the oxidation reaction products of oleate ligands in Co(II) oleate

Sample	Fracti	on of C - chain [%]	
	c <sub>6</sub> - c <sub>10</sub>	$c_{11} - c_{18}$	> c <sub>18</sub>
oleic acid	traces	palmitic acid	l
(TIRG TIRGIN		oleic acid (90)	
after 30 h exposure in O <sub>2</sub>	50	palmitic acid (10)	traces
	3	oleic acid (50) others (20)	
after 60 h exposure in O <sub>2</sub>	38	palmitic acid (5) oleic acid (15)	15
		others (27)	

Hydrocarbon-oxygen-metal complex interaction

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- The following kinetic results for oxidation reaction of cyclohene in 43. benzene were found: a)  $0.46 \pm 0.03$  order reaction with respect to benzene were found: a) 0.46  $\pm$  0.05 order reaction with respect to Co(octanoate), 1.18  $\pm$  0.1 with respect to cyclohexene and total activa-tion energy  $E_a^2 = 14.9 \pm 1.2$  Kcal mole<sup>-1</sup> and b) 0.42  $\pm$  0.03 order reaction with respect to (Cosalen)<sub>2</sub>(OH)(OC<sub>6</sub>H<sub>0</sub>), 1.35  $\pm$  0.1 with respect to cyclo-hexene, and  $E_a = 19.3 \pm 1.2$  Kcal mole<sup>-1</sup> D.G.Hendry and G.A.Russel, J.Am.Chem.Soc., 86, 2368 (1964) D.E.Van Sickle, F.R.May and R.M.Arluck, J.Am.Chem.Soc., 87, 4824 (1965) G.E.Zaikov and Z.K.Maizus, <u>Dokl.Akad.Nauk SSSR</u>, <u>150</u>, 116 (1963) B.C. Neuman J. Org. Chem. 37, 495 (1972)
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